CHEM 440: STRUCTURE DETERMINATION



Lafayette College

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CHEM 440 Structure Determination

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Glossary

Detailed Licensing

Licensing

*A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.*

CHAPTER OVERVIEW

1: Mass Spectrometry

Mass spectrometry is an analytic method that employs ionization and mass analysis of compounds in order to determine the mass, formula and structure of the compound being analyzed. A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output.

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Thumbnail: SIMS mass spectrometer, model IMS 3f. (GNU Free Documentation Licenses; CAMECA Archives).

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1.1: How the Mass Spectrometer Works

This page describes how a mass spectrum is produced using a mass spectrometer.

How a mass spectrometer works

If something is moving and you subject it to a sideways force, instead of moving in a straight line, it will move in a curve - deflected out of its original path by the sideways force. Suppose you had a cannonball traveling past you and you wanted to deflect it as it went by you. All you've got is a jet of water from a hose that you can squirt at it. Frankly, its not going to make a lot of difference! Because the cannonball is so heavy, it will hardly be deflected at all from its original course. But suppose instead, you tried to deflect a ping-pong ball traveling at the same speed as the cannonball using the same jet of water. Because this ball is so light, you will get a huge deflection.

The amount of deflection you will get for a given sideways force depends on the mass of the ball. If you knew the speed of the ball and the size of the force, you could calculate the mass of the ball if you knew what sort of curved path it was deflected through. The less the deflection, the heavier the ball. You can apply exactly the same principle to atomic sized particles.

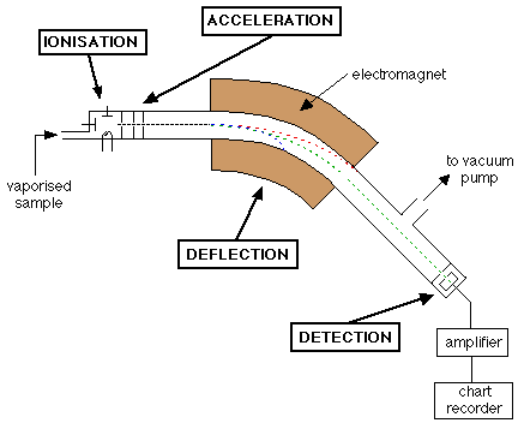
An outline of what happens in a mass spectrometer

Atoms can be deflected by magnetic fields - provided the atom is first turned into an ion. Electrically charged particles are affected by a magnetic field although electrically neutral ones aren't.

The sequence is :

- **Stage 1: Ionization**: The atom is ionized by knocking one or more electrons off to give a positive ion. This is true even for things which you would normally expect to form negative ions (chlorine, for example) or never form ions at all (argon, for example). Mass spectrometers always work with positive ions.
- **Stage 2: Acceleration:** The ions are accelerated so that they all have the same kinetic energy.
- **Stage 3: Deflection:** The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected. The amount of deflection also depends on the number of positive charges on the ion - in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.
- **Stage 4: Detection**: The beam of ions passing through the instrument is detected electrically.

A full diagram of a mass spectrometer



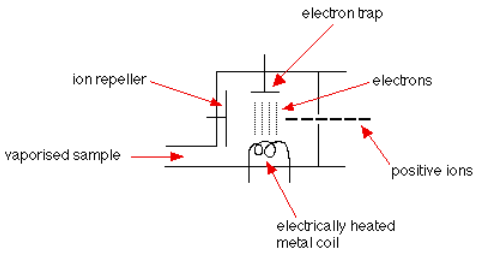
Understanding what's going on

The need for a vacuum

It's important that the ions produced in the ionization chamber have a free run through the instrument without hitting air molecules.

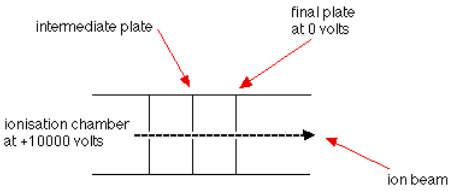
Ionization

The vaporized sample passes into the ionization chamber. The electrically heated metal coil gives off electrons which are attracted to the electron trap which is a positively charged plate.



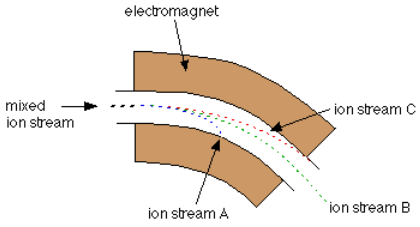
The particles in the sample (atoms or molecules) are therefore bombarded with a stream of electrons, and some of the collisions are energetic enough to knock one or more electrons out of the sample particles to make positive ions. Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion. These positive ions are persuaded out into the rest of the instrument by the ion repeller which is another metal plate carrying a slight positive charge.

Acceleration



The positive ions are repelled away from the very positive ionization chamber and pass through three slits, the final one of which is at 0 volts. The middle slit carries some intermediate voltage. All the ions are accelerated into a finely focused beam.

Deflection



Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:

- the mass of the ion. Lighter ions are deflected more than heavier ones.
- the charge on the ion. Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.

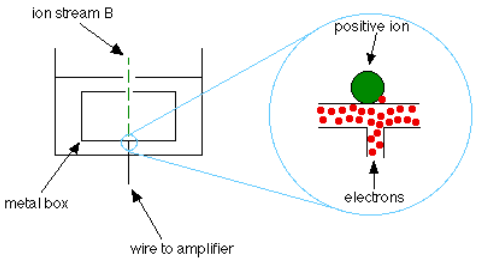
These two factors are combined into the mass/charge ratio. Mass/charge ratio is given the symbol m/z (or sometimes m/e). For example, if an ion had a mass of 28 and a charge of 1+, its mass/charge ratio would be 28. An ion with a mass of 56 and a charge of 2+ would also have a mass/charge ratio of 28.

In the last diagram, ion stream A is most deflected - it will contain ions with the smallest mass/charge ratio. Ion stream C is the least deflected - it contains ions with the greatest mass/charge ratio.

It makes it simpler to talk about this if we assume that the charge on all the ions is 1+. Most of the ions passing through the mass spectrometer will have a charge of 1+, so that the mass/charge ratio will be the same as the mass of the ion. Assuming 1+ ions, stream A has the lightest ions, stream B the next lightest and stream C the heaviest. Lighter ions are going to be more deflected than heavy ones.

Detection

Only ion stream B makes it right through the instrument to the ion detector. The other ions collide with the walls where they will pick up electrons and be neutralized. Eventually, they get removed from the mass spectrometer by the vacuum pump.



When an ion hits the metal box, its charge is neutralized by an electron jumping from the metal on to the ion (right hand diagram). That leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it. A flow of electrons in the wire is detected as an electric current which can be amplified and recorded. The more ions arriving, the greater the current.

Detecting the other ions

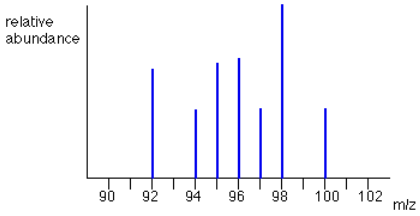
How might the other ions be detected - those in streams A and C which have been lost in the instrument?

Remember that stream A was most deflected - it has the smallest value of m/z (the lightest ions if the charge is 1+). To bring them on to the detector, you would need to deflect them less - by using a smaller magnetic field (a smaller sideways force). To bring those with a larger m/z value (the heavier ions if the charge is +1) on to the detector you would have to deflect them more by using a larger magnetic field.

If you vary the magnetic field, you can bring each ion stream in turn on to the detector to produce a current which is proportional to the number of ions arriving. The mass of each ion being detected is related to the size of the magnetic field used to bring it on to the detector. The instrument can be calibrated to record current (which is a measure of the number of ions) against m/z directly. The mass is measured on the ^{12}C scale.

What the mass spectrometer output looks like

The output from the chart recorder is usually simplified into a "stick diagram". This shows the relative current produced by ions of varying mass/charge ratio. The stick diagram for molybdenum looks like this:



You may find diagrams in which the vertical axis is labeled as either "relative abundance" or "relative intensity". Whichever is used, it means the same thing. The vertical scale is related to the current received by the chart recorder - and so to the number of ions arriving at the detector: the greater the current, the more abundant the ion.

As you will see from the diagram, the commonest ion has a mass/charge ratio of 98. Other ions have mass/charge ratios of 92, 94, 95, 96, 97 and 100. That means that molybdenum consists of 7 different isotopes. Assuming that the ions all have a charge of 1+, that means that the masses of the 7 isotopes on the carbon-12 scale are 92, 94, 95, 96, 97, 98 and 100.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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1.2: Mass Spectrometers (Instrumentation)

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1.2.1: Electrospray Ionization Mass Spectrometry

Electrospray ionization is a soft ionization technique that is typically used to determine the molecular weights of proteins, peptides, and other biological macromolecules. Soft ionization is a useful technique when considering biological molecules of large molecular mass, such as the aformetioned, because this process does not fragment the macromolecules into smaller charged particles, rather it turns the macromolecule being ionized into small droplets. These droplets will then be further desolvated into even smaller droplets, which creates molecules with attached protons. These protonated and desolvated molecular ions will then be passed through the mass analyzer to the detector, and the mass of the sample can be determined.

Introduction

Electrospray ionization mass spectrometry is a desorption ionization method. Desorption ionization methods can be performed on solid or liquid samples, and allows for the sample to be nonvolatile or thermally unstable. This means that ionization of samples such as proteins, peptides, olgiopeptides, and some inorganic molecules can be performed. Electrospray ionization mass spectrometry requires that a molecule be of a fairly large mass. The instrument has a small mass range that it is able to detect, so therefore the mass of the unknown injected sample can easily be determined; as it must be in the range of the instrument. This quantitative analysis is done by considering the mass to charge ratios of the various peaks in the spectrum (Figure 1). The spectrum is shown with the mass-to-charge (m/z) ratio on the x-axis, and the relative intensity (%) of each peak shown on the y-axis. Calculations to determine the unknown mass, M_r, from the spectral data can then be performed using

$$p = \frac{m}{z} \tag{1.2.1.1}$$

$$p_1 = \frac{M_r + z_1}{z_1} \tag{1.2.1.2}$$

$$p_2 = \frac{M_r + (z_1 - 1)}{z_1 - 1} \tag{1.2.1.3}$$

where p_1 and p_2 are adjacent peaks. Peak p_1 comes before peak p_2 in the spectrum, and has a lower m/z value. The z_1 value represents the charge of peak one. It should be noted that as the m/z value increases, the number of protons attached to the molecular ion decreases. Figure 1 below illustrates these concepts. Electrospray ionization mass spectrometry research was pioneered by the analytical chemistry professor John Bennet Fenn, who shared the Nobel Prize in Chemistry with Koichi Tanaka in 2002 for his work on the subject.

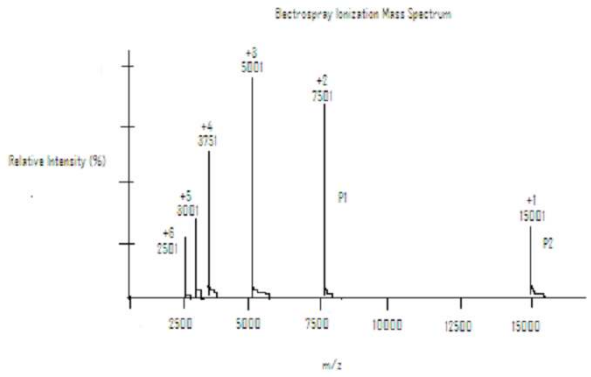


Figure 1. Mass Spectrum Example

Calculations for m/z in spectrum

$[M + 6H]^{6+}$ $[M + 5H]^{5+}$ $[M + 4H]^{4+}$

m/z = 15006/6 = 2501 m/z = 15005/5 = 3001 m/z = 15004/4 = 3751

$$[M + 3H]^{3+}\ [M + 2H]^{2+}\ [M + H]^{1+}$$

$$m/z = 15003/3 = 5001\ m/z = 15002/2 = 7501\ m/z = 15001/1 = 15001$$

Sample Preparation

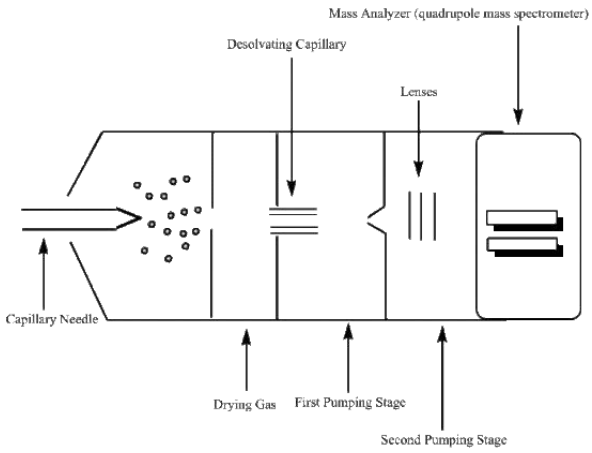
Samples for injection into the electrospray ionization mass spectrometer work the best if they are first purified. The reason purity in a sample is important is because this technique does not work well when mixtures are used as the analyte. For this reason a means of purification is often employed to inject a homogeneous sample into the capillary needle. High performance liquid chromatography, Capillary Electrophoresis, and Liquid-Solid Column Chromatography are methods of choice for this purpose. The chosen purification method is then attached to the capillary needle, and the sample can be introduced directly.

Advantages and Disadvantages

There are some clear advantages to using electrospray ionization mass spectrometry as an analytical method. One advantage is its ability to handle samples that have large masses. Another advantage is that this ionization method is one of the softest ionization methods available, therefore it has the ability to analyze biological samples that are defined by non-covalent interactions. A quadrupole mass analyzer can also be used for this method, which means that a sample's structure can be determined fairly easily. The m/z ratio range of the quadrupole instrument is fairly small, which means that the mass of the sample can be determined to with a high amount of accuracy. Finally, the sensitivity for this instrument is impressive and therefore can be useful in accurate quantitative and qualitative measurements.

Some disadvantages to electrospray ionization mass spectrometry are present as well. A major disadvantage is that this technique cannot analyze mixtures very well, and when forced to do so, the results are unreliable. The apparatus is also very difficult to clean and has a tendency to become overly contaminated with residues from previous experiments. Finally, the multiple charges that are attached to the molecular ions can make for confusing spectral data. This confusion is further fueled by use of a mixed sample, which is yet another reason why mixtures should be avoided when using an electrospray ionization mass spectrometer.

Apparatus



Capillary Needle

The capillary needle is the inlet into the apparatus for the liquid sample. Once in the capillary needle, the liquid sample is nebulized and charged. There is a large amount of pressure being applied to the capillary needle, which in effect nebulizes the liquid sample forming a mist. The stainless steel capillary needle is also surrounded by an electrode that retains a steady voltage of around 4000 volts. This applied voltage will place a charge on the droplets. Therefore, the mist that is ejected from the needle will be comprised of charged molecular ions.

Desolvating Capillary

The molecular ions are oxidized upon entering the desolvating capillary, and a continual voltage is applied to the gas chamber in which this capillary is located. Here the desolvation process begins, through the use of a dry gas or heat, and the desolvation process continues through various pumping stages as the molecular ion travels towards the mass analyzer. An example of a dry gas

would be an N_2 gas that has been dehydrated. The gas or heat then provides means of evaporation, or desolvation, for the ionized droplets. As the droplets become smaller in size, their electric field densities become more concentrated. The increase in electric field density causes the like charges to repel one another, which induces an increase in surface tension. The point where the droplet can no longer support this increase in surface tension is known as the Rayleigh limit. At this point, the droplet divides into smaller droplets of either positive or negative chrage. This process is refered to as either a coulombic explosion or the ions are described as exiting the droplet through the "Taylor cone". Once the molecular ions have reached the entrance to the mass analyzer, they have been effectively reduced through protonation.

Mass Analyzer

Mass Analyzers (Mass Spectrometry) are used to determine the mass-to-charge ratio (m/z), this ratio is used to differentiate between molecular ions that were formed in the desolvating capillary. In order for a mass-to-charge ratio to be determined, the mass analyzer must be able to separate even the smallest masses. The ability of the analyzer to resolve the mass peaks can be defined with the following equation;

$$R = \frac{m}{\Delta m} \tag{1.2.1.4}$$

This equation represents the mass of the first peak (m), divided by the difference between the neighboring peaks Δm. The better the resolution, the more useful the data. The mass analyzer must also be able to measure the ion currents produced by the multiply charged particles that are created in this process.

Mass analyzers use electrostatic lenses to direct the beam of molecular ions to the analyzer. A vacuum system is used to maintain a low pressure environment in order to prevent unwanted interactions between the molecular ions and any components that may be present in the atmosphere. These atmospheric components can effect the determined mass-to-charge ratio, so it is best to keep them to a minimum. The mass-to-charge ratio is then used to determine quantitative and qualitative properties of the liquid sample.

The mass analyzer used for electrospray ionization is a quadrupole mass spectrometer. A quadrupole mass spectrometer uses four charged rods, two negatively charged and two positively charged, that have alternating AC and DC currents. The rods are connected to both the positive terminal of the DC voltage and the negative terminal. Each pair of rods contains a negatively charged rod and a positively charged rod. The molecular ions are then sped through the chamber between these pairs of oppositely charged rods making use of a potential difference to do so. To maintain charge, and ultimately be readable by the detector, the molecular ions must travel through the quadrupole chamber without touching any of the four charged rods. If a molecular ion does run into one of the rods it will deem it neutral and undetectable.

Detector

The molecular ions pass through the mass analyzer to the detector. The detector most commonly used in conjunction with the quadrupole mass analyzer is a high energy dynode (HED), which is a electron multiplier with some slight variations. In an HED detector, the electrons are passed through the system at a high voltage and the electrons are measured at the end of the funnel shaped apparatus; otherwise known as the anode. A HED detector differs from the electron multiplier in that it operates at a much higher sensitivity for samples with a large mass than does the electron multiplier detector. Once the analog signal of the mass-to-charge ratio is recorded, it is then converted to a digital signal and a spectrum representing the data run can be analyzed.

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1. Skoog, D.A.; Holler, F.J.; Crouch, S.R. Principles of Instrumental Analysis. Sixth Edition, Thomson Brooks/Cole, USA (2007).
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3. Chapman, J.R. Mass Spectrometry of Proteins and Peptides. Methods in Molecular Biology volume 146,Humana Press, Totowa, NJ (2000).
4. Snyder, A. P. Biochemical and Biotechnological Applications of Electrospray Ionization Mass Spectrometry. American Chemical Society, Washington, DC (1996).

Problems

Using the above spectrum, calculate the mass of the protein. For p_1, shown in spectrum, the m/z is 7501 and for p_2 the m/z is 15001. (Hint: Use the above equations, and the charge of p_1 for z_1)

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1.2.2: Injection Stage

The principle components of a mass spectrometer are an inlet, ion source, mass analyzer, detector, and data analysis. The function of an inlet system is to introduce a small amount of sample into the ion source with minimal loss of vacuum. However, many mass spectrometers contain more than one inlet system to accommodate a variety of samples. These include batch inlets, direct probe inlets, and chromatographic and capillary electrophoretic inlet systems.

Batch Inlets

The batch inlet system is considered the most common and simplest inlet system. Normally, the inside of the system is lined with glass to elude losses of polar analytes by adsorption. This system externally volatizes the sample which leaks into an empty ionization region. Boiling points up to 500 degrees C of gaseous and liquid samples can be used on typical systems. The system's vacuum contains a sample pressure of 10^{-4} to 10^{-5} Torr. Liquids are introduced using a microliter syringe into a reservoir; gases are enclosed in a metering area that is confined between two valves before being expanded into a reservoir container. Liquids that have boiling points lower than 500 degrees C can not be used in the system because the reservoir and tubing need to be kept at high temperatures by ovens and heating tapes. This is to ensure that the liquid samples are transformed to the gaseous phase and then leaked through a metal or glass diaphragm containing pinholes to the ionization area.

Direct Probe Inlets

A direct probe inlet is for small quantities of sample, solids, and nonvolatile liquids. Solids and nonvolatile liquids are injected through a probe, or sample holder. The probe is inserted through a vacuum lock which is designed to limit the volume of air needed to pump from the system after the probe has been inserted into the ionization section. Unlike the batch inlet, the sample will need to be cooled and/or heated on the probe. The probe is placed extremely close (a few millimeters) to the ionization source, where the slit leads to the spectrometer, and the sample is held in place on the surface of a glass or aluminum capillary tube or a small cup. This position makes it possible for thermally unstable compounds to be analyzed before decomposition because of the low pressure in the ionization area which is in close proximity to the sample. Do to the probe, nonvolatile samples such as carbohydrates, steroids, and metal-organic species can be studied because the low pressures lead to increased concentrations of the nonvolatile samples. The principle sample requirement is attainment of an analyte partial pressure of at least 10^{-8} torr before the onset of decomposition.[1]

Chromatographic and Capillary Electrophoretic Inlets

Chromatographic systems and Capillary Electrophoretic units are often coupled with mass spectrometers in order to allow separation and identification of the components in the sample. If these systems and units are linked with a mass spectrometer, then other specialized inlets, electrokinetic and pressure injection, are required. Electrokinetic and pressure injection controls the amount of volume injected by the duration of the injection, which typically range between 5 to 50 nL.

Electrokinetic Injection

The electrokinetic injection method involves one end of the capillary and electrode in a small cup removed from the buffer. Ionic migration and electroosmotic flow of the sample in the capillary are a result of a voltage applied for a recorded time. After this voltage is applied, the capillary end and electrode are placed back into the regular buffer solution for the remainder of the separation. The electrokinetic Injection technique injects larger quantities of the mobile ions versus the slower moving ions.

Pressure Injection

The pressure injection method is similar to the electrokinetic injection because the capillary end and electrode are removed from the buffer and placed into a small cup. However, instead of a voltage being applied, a pressure difference drives the sample into the capillary. A vacuum is applied at the detector end which produces the potential difference by pressurizing the sample or elevating the sample end. Pressure injection does not discriminate because of ion mobility, but it cannot be used in gel-filled capillaries.[1]

References

1. Skoog, D., Holler, J., Crouch, S. Principles of Instrumental Analysis, 6th Ed.; Thomson Brooks/Cole: Belmont, 2007

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1.2.3: Mass Analyzers (Mass Spectrometry)

Mass spectrometry is an analytic method that employs ionization and mass analysis of compounds to determine the mass, formula and structure of the compound being analyzed. A mass analyzer is the component of the mass spectrometer that takes ionized masses and separates them based on charge to mass ratios and outputs them to the detector where they are detected and later converted to a digital output.

Introduction

There are six general types of mass analyzers that can be used for the separation of ions in a mass spectrometry.

1. Quadrupole Mass Analyzer
2. Time of Flight Mass Analyzer
3. Magnetic Sector Mass Analyzer
4. Electrostatic Sector Mass Analyzer
5. Quadrupole Ion Trap Mass Analyzers
6. Ion Cyclotron Resonance

Quadrupole Mass Analyzer

The DC bias will cause all the charged molecules to accelerate and move away from the center line, the rate being proportional to their charge to mass ratio. If their course goes off too far they will hit the metal rods or the sides of the container and be absorbed. So the DC bias acts like the magnetic field B of the mass spec and can be tuned to specific charge to mass ratios hitting the detector.

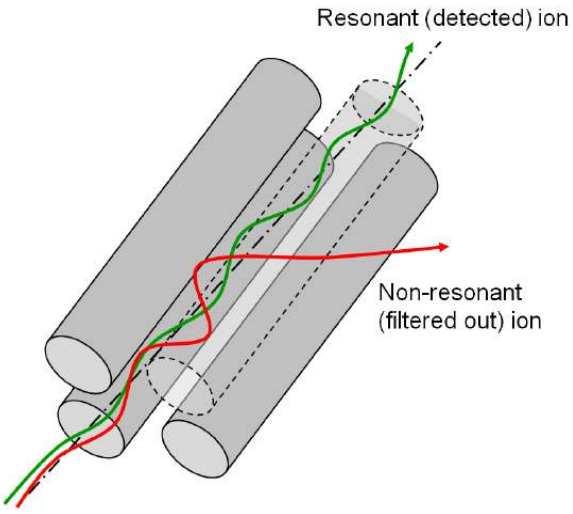


Figure **1.2.3.1**: A quadrupole

The two sinusoidal electric fields at 90 orientation and 90 degrees degrees phase shift will cause an electric field which oscillates as a circle over time. So as the charged particles fly down toward the detector, they will be traveling in a spiral, the diameter of the spiral being determined by the charge to mass ratio of the molecule and the frequency and strength of the electric field. The combination of the DC bias and the circularly rotating electric field will be the charge particles will travel in a spiral which is curved. So by timing the peak of the curved spiral to coincide with the position of the detector at the end of the quadrupole, a great deal of selectivity to molecules charge to mass ratio can be obtained.

TOF (Time of Flight) Mass Analyzer

TOF Analyzers separate ions by time without the use of an electric or magnetic field. In a crude sense, TOF is similar to chromatography, except there is no stationary/ mobile phase, instead the separation is based on the kinetic energy and velocity of the ions.

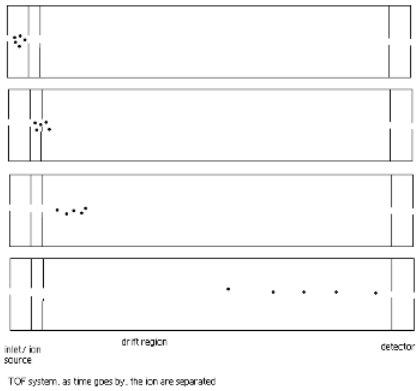


Figure **1.2.3.2**: A TOF system. As time evolves, the ions (formed at the source) are separated.

Ions of the same charges have equal kinetic energies; kinetic energy of the ion in the flight tube is equal to the kinetic energy of the ion as it leaves the ion source:

$$KE = \frac{mv^2}{2} = zV \tag{1.2.3.1}$$

The time of flight, or time it takes for the ion to travel the length of the flight tube is:

$$T_f = \frac{L}{v} \tag{1.2.3.2}$$

- with L is the length of tube and
- v is the velocity of the ion

Substituting Equation 1 for kinetic energy in Equation 2 for time of flight:

$$T_f = L\sqrt{\frac{m}{z}}\sqrt{\frac{1}{2V}} \propto \sqrt{\frac{m}{z}} \tag{1.2.3.3}$$

During the analysis, L, length of tube, the Voltage from the ion source V are held constant, which can be used to say that time of flight is directly proportional to the root of the mass to charge ratio.

Unfortunately, at higher masses, resolution is difficult because flight time is longer. Also at high masses, not all of the ions of the same m/z values reach their ideal TOF velocities. To fix this problem, often a **reflectron** is added to the analyzer. The reflectron consists of a series of ring electrodes of very high voltage placed at the end of the flight tube. When an ion travels into the reflectron, it is reflected in the opposite direction due to the high voltage. The reflectron increases resolution by narrowing the broadband range of flight times for a single m/z value. Faster ions travel further into the reflectrons, and slower ions travel less into the reflector. This way both slow and fast ions, of the same m/z value, reach the detector at the same time rather then at different times, narrowing the bandwidth for the output signal.

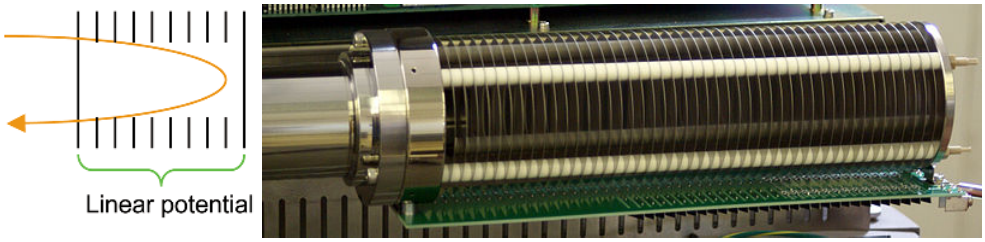


Figure **1.2.3.3**: (left) A reflection. from Wikipedia. (right) 4. A photo of a reflectron. An ion mirror (right) attached to a flight tube (left) of the reflectron. Voltages applied to a stack of metal plates create the electric field reflecting the ions back to the flight tube. In this particular design, gaps between the mirror electrodes are too large. This can lead to a distortion of the field inside the mirror caused by a proximity of metal surface of the enveloping vacuum tube. from Wikipedia.

Magnetic Sector Mass Analyzer

Similar to time of flight (TOF) analyzer mentioned earlier,in magnetic sector analyzers ions are accelerated through a flight tube, where the ions are separated by charge to mass ratios. The difference between magnetic sector and TOF is that a magnetic field is used to separate the ions. As moving charges enter a magnetic field, the charge is deflected to a circular motion of a unique radius in a direction perpendicular to the applied magnetic field. Ions in the magnetic field experience two equal forces; force due to the magnetic field and centripetal force.

$$F_B = zvB = F_c = \frac{mv^2}{r} \tag{1.2.3.4}$$

The above equation can then be rearranged to give:

$$v = \frac{Bzr}{m} \tag{1.2.3.5}$$

If this equation is substituted into the kinetic energy equation:

$$KE = zV = \frac{mv^2}{2} \tag{1.2.3.6}$$

$$\frac{m}{z} = \frac{B^2r^2}{2V} \tag{1.2.3.7}$$

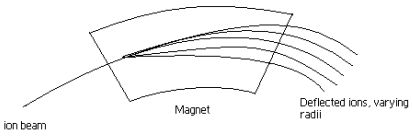


Figure 1.2.3.4: A magnetic sector separator.

Basically the ions of a certain m/z value will have a unique path radius which can be determined if both magnetic field magnitude B, and voltage difference V for region of acceleration are held constant. when similar ions pass through the magnetic field, they all will be deflected to the same degree and will all follow the same trajectory path. Those ions which are not selected by V and B values, will collide with either side of the flight tube wall or will not pass through the slit to the detector. Magnetic sector analyzers are used for mass focusing, they focus angular dispersions.

Electrostatic Sector Mass Analyzer

Is similar to time of flight analyzer in that it separates the ions while in flight, but it separates using an electric field. Electrostatic sector analyzer consists of two curved plates of equal and opposite potential. As the ion travels through the electric field, it is deflected and the force on the ion due to the electric field is equal to the centripetal force on the ion. Here the ions of the same kinetic energy are focused, and ions of different kinetic energies are dispersed.

$$KE = zV = \frac{mv^2}{2} \tag{1.2.3.8}$$

$$F_E = zE = F_c = \frac{mv^2}{R} \tag{1.2.3.9}$$

Electrostatic sector analyzers are energy focusers, where an ion beam is focused for energy. Electrostatic and magnetic sector analyzers when employed individually are single focusing instruments. However when both techniques are used together, it is called a double focusing instrument., because in this instrument both the energies and the angular dispersions are focused.

Quadrupole Ion Trap Mass Analyzers

This analyzer employs similar principles as the quadrupole analyzer mentioned above, it uses an electric field for the separation of the ions by mass to charge ratios. The analyzer is made with a ring electrode of a specific voltage and grounded end cap electrodes. The ions enter the area between the electrodes through one of the end caps. After entry, the electric field in the cavity due to the electrodes causes the ions of certain m/z values to orbit in the space. As the radio frequency voltage increases, heavier mass ion

orbits become more stabilized and the light mass ions become less stabilized, causing them to collide with the wall, and eliminating the possibility of traveling to and being detected by the detector.

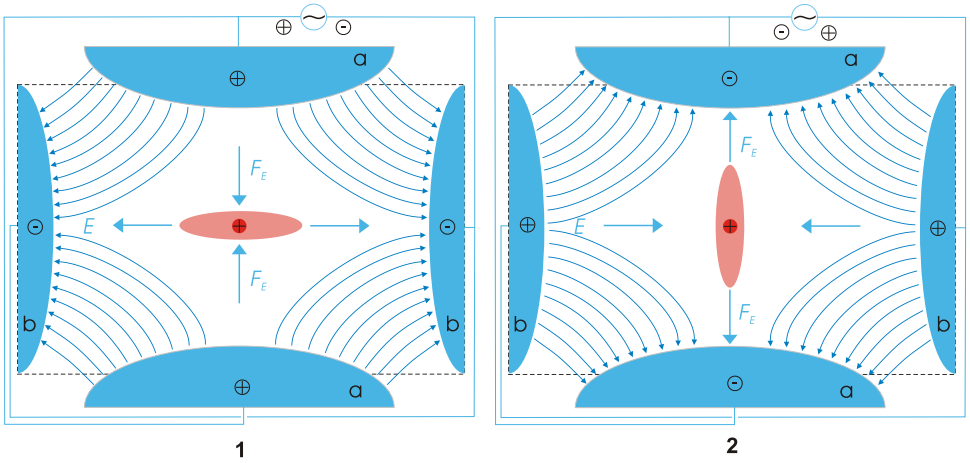


Figure 1.2.3.5: Scheme of a Quadrupole ion trap of classical setup with a particle of positive charge (dark red), surrounded by a cloud of similarly charged particles (light red). The electric field E (blue) is generated by a quadrupole of endcaps (a, positive) and a ring electrode (b). Picture 1 and 2 show two states during an AC cycle. (CC BY 2.5; Arian Kriesch Akriesch via Wikipedia).

The quadrupole ion trap usually runs a mass selective ejection, where selectively it ejects the trapped ions in order of in creasing mass by gradually increasing the applied radio frequency voltage.

Ion Cyclotron Resonance (ICR)

ICR is an ion trap that uses a magnetic field in order to trap ions into an orbit inside of it. In this analyzer there is no separation that occurs rather all the ions of a particular range are trapped inside, and an applied external electric field helps to generate a signal. As mentioned earlier, when a moving charge enters a magnetic field, it experiences a centripetal force making the ion orbit. Again the force on the ion due to the magnetic field is equal to the centripetal force on the ion.

$$zvB = \frac{mv^2}{r} \tag{1.2.3.10}$$

Angular velocity of the ion perpendicular to the magnetic field can be substituted here $w_c = v/r$

$$zB = mw_c \tag{1.2.3.11}$$

$$w_c = \frac{zB}{m} \tag{1.2.3.12}$$

Frequency of the orbit depends on the charge and mass of the ions, not the velocity. If the magnetic field is held constant, the charge to mass ratio of each ion can be determined by measuring the angular velocity ω_c. The relationship is that, at high w_c, there is low m/z value, and at low ω_c, there is a high m/z value. Charges of opposite signs have the same angular velocity, the only difference is that they orbit in the opposite direction.

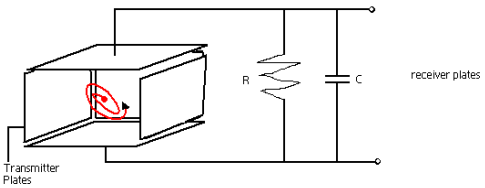


Figure 1.2.3.6: An ICR trap.

To generate an electric signal from the trapped ions, a vary electric field is applied to the ion trap

$$E = E_o \cos(\omega_c t) \tag{1.2.3.13}$$

When the ω_c in the electric field matches the ω_c of a certain ion, the ion absorbs energy making the velocity and orbiting radius of the ion increase. In this high energy orbit, as the ion oscillates between two plates, electrons accumulate at one of the plates over the other inducing an oscillating current, or current image. The current is directly proportional to the number of ions in the cell at a certain frequency.

In a Fourier Transform ICR, all of the ions within the cell are excited simultaneously so that the current image is coupled with the image of all of the individual ion frequencies. A Fourier transform is used to differential the summed signals to produce the desired results.

References

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1.3: Mass Spectrometry additional details

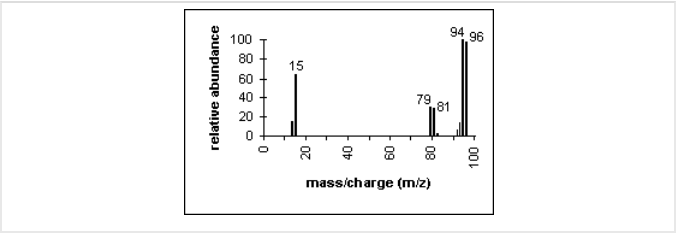
Terms for mass spectra interpretation

- **Molecular ion ($M^{\cdot+}$)**: If the molecular ion appears, it will be the highest mass in an EI spectrum (except for isotope peaks discussed below). This peak will represent the molecular weight of the compound. Its appearance depends on the stability of the compound. Double bonds, cyclic structures and aromatic rings stabilize the molecular ion and increase the probability of its appearance.
- **Reference Spectra**: Mass spectral patterns are reproducible. The mass spectra of many compounds have been published and may be used to identify unknowns. Instrument computers generally contain spectral libraries which can be searched for matches.
- **Fragmentation**: General rules of fragmentation exist and are helpful to predict or interpret the fragmentation pattern produced by a compound. Functional groups and overall structure determine how some portions of molecules will resist fragmenting, while other portions will fragment easily. A detailed discussion of those rules is beyond the scope of this introduction, and further information may be found in your organic textbook or in mass spectrometry reference books. A few brief examples by functional group are described (see Fragmentation Patterns).
- **Isotopes**: Isotopes occur in compounds analyzed by mass spectrometry in the same abundances that they occur in nature. A few of the isotopes commonly encountered in the analyses of organic compounds are below along with an example of how they can aid in peak identification.

Relative Isotope Abundance of Common Elements

Element	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.20
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.40
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98.0

Methyl Bromide: An example of how isotopes can aid in peak identification.



The ratio of peaks containing ^{79}Br and its isotope ^{81}Br (100/98) confirms the presence of bromine in the compound.

Other ionization methods

An array of ionization methods and mass analyzers are available to meet the needs of many types of chemical analysis. A few are listed here with a highlight of their usefulness.

Sample introduction/ionization methods

Ionization method	Typical Analytes	Sample Introduction	Mass Range	Method Highlights
Electron Impact (EI)	Relatively small volatile	GC or liquid/solid probe	to 1,000 Daltons	Hard method versatile provides structure info
Chemical Ionization (CI)	Relatively small volatile	GC or liquid/solid probe	to 1,000 Daltons	Soft method molecular ion peak $[M+H]^+$
Electrospray (ESI)	Peptides Proteins nonvolatile	Liquid Chromatography or syringe	to 200,000 Daltons	Soft method ions often multiply charged
Fast Atom Bombardment (FAB)	Carbohydrates Organometallics Peptides nonvolatile	Sample mixed in viscous matrix	to 6,000 Daltons	Soft method but harder than ESI or MALDI
Matrix Assisted Laser Desorption (MALDI)	Peptides Proteins Nucleotides	Sample mixed in solid matrix	to 500,000 Daltons	Soft method very high mass

Outside Links

- A library of spectra can be found in the NIST WebBook, a data collection of the National Institute of Standards and Technology.
- Useful tools such as an exact mass calculator and a spectrum generator can be found in the MS Tools section of Scientific Instrument Services webpage.
- The JEOL Mass Spectrometry website contains tutorials, reference data and links to other sites.
- More general information and tutorials can be found in Scimedia, an educational resource.
- At the University of Arizona, the Wysocki Research Group studies surface-induced dissociation (SID) tandem mass spectrometry.
- Many more interesting and useful links can be found by following the site links in the above references.

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1.4: High Resolution vs Low Resolution

Two common categories of mass spectrometry are high resolution mass spectrometry (HRMS) and low resolution mass spectrometry (LRMS). Not all mass spectrometers simply measure molecular weights as whole numbers. High resolution mass spectrometers can measure mass so accurately that they can detect the minute differences in mass between two compounds that, on a regular low-resolution instrument, would appear to be identical.

The reason is because atomic masses are not exact multiples of the mass of a proton, as we might usually think.

- An atom of ^{12}C weighs 12.00000 amu.
- An atom of ^{16}O weighs 15.9949 amu.
- An atom of ^{14}N weighs 14.0031 amu.
- An atom of ^{1}H weighs 1.00783 amu.

As a result, on a high resolution mass spectrometer, 2-octanone, $C_8H_{16}O$, has a molecular weight of 128.12018 instead of 128. Naphthalene, $C_{10}H_8$, has a molecular weight of 128.06264. Thus a high resolution mass spectrometer can supply an exact molecular formula for a compound because of the unique combination of masses that result.

- In LRMS, the molecular weight is determined to the nearest amu. The type of instrument used here is more common because it is less expensive and easier to maintain.
- In HRMS, the molecular weight in amu is determined to several decimal places. That precision allows the molecular formula to be narrowed down to only a few possibilities.

HRMS relies on the fact that the mass of an individual atom does not correspond to an integral number of atomic mass units.

Problem MS7.

Calculate the high-resolution molecular weights for the following formulae.

1. $C_{12}H_{20}O$ and $C_{11}H_{16}O_2$
2. $C_6H_{13}N$ and $C_5H_{11}N_2$

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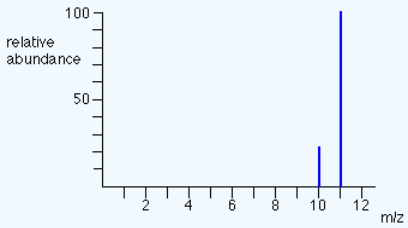
1.5: The Mass Spectra of Elements

This page looks at the information you can get from the mass spectrum of an element. It shows how you can find out the masses and relative abundances of the various isotopes of the element and use that information to calculate the relative atomic mass of the element. It also looks at the problems thrown up by elements with diatomic molecules - like chlorine, Cl_2.

The mass spectrum of monatomic elements

Monatomic elements include all those except for things like chlorine, Cl_2, with molecules containing more than one atom.

Example 1.5.1: The Mass Spectrum of Boron



The number of isotopes: The two peaks in the mass spectrum shows that there are 2 isotopes of boron - with relative isotopic masses of 10 and 11 on the ^{12}C scale.

The abundance of the isotopes: The relative sizes of the peaks gives you a direct measure of the relative abundances of the isotopes. The tallest peak is often given an arbitrary height of 100 - but you may find all sorts of other scales used. It doesn't matter in the least. You can find the relative abundances by measuring the lines on the stick diagram. In this case, the two isotopes (with their relative abundances) are:

boron-10		23
boron-11		100

Working out the relative atomic mass

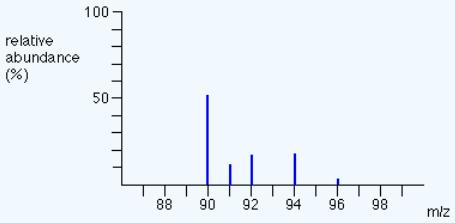
The relative atomic mass (RAM) of an element is given the symbol $\mathbf{A_r}$ and is defined as:

The relative atomic mass of an element is the weighted average of the masses of the isotopes on a scale on which a carbon-12 atom has a mass of exactly 12 units A "weighted average" allows for the fact that there won't be equal amounts of the various isotopes. The example coming up should make that clear.

> Suppose you had 123 typical atoms of boron. 23 of these would be ^{10}B and 100 would be ^{11}B.
>
> The total mass of these would be (23 x 10) + (100 x 11) = 1330
>
> The average mass of these 123 atoms would be 1330 / 123 = 10.8 (to 3 significant figures).
>
> 10.8 is the relative atomic mass of boron.

Notice the effect of the "weighted" average. A simple average of 10 and 11 is, of course, 10.5. Our answer of 10.8 allows for the fact that there are a lot more of the heavier isotope of boron - and so the "weighted" average ought to be closer to that.

Example 1.5.2: The Mass Spectrum of Zirconium



The number of isotopes: The 5 peaks in the mass spectrum shows that there are 5 isotopes of zirconium - with relative isotopic masses of 90, 91, 92, 94 and 96 on the ^{12}C scale.

The abundance of the isotopes: This time, the relative abundances are given as percentages. Again you can find these relative abundances by measuring the lines on the stick diagram. In this case, the 5 isotopes (with their relative percentage abundances) are:

zirconium-90		51.5
zirconium-91		11.2
zirconium-92		17.1
zirconium-94		17.4
zirconium-96		2.8

Working out the relative atomic mass

Suppose you had 100 typical atoms of zirconium. 51.5 of these would be ^{90}Zr, 11.2 would be ^{91}Zr and so on.

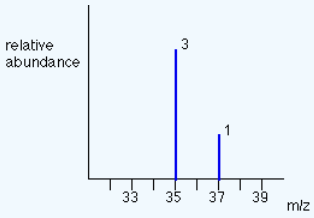
The total mass of these 100 typical atoms would be

$$(51.5 \times 90) + (11.2 \times 91) + (17.1 \times 92) + (17.4 \times 94) + (2.8 \times 96) = 9131.8$$

The average mass of these 100 atoms would be 9131.8 / 100 = 91.3 (to 3 significant figures). 91.3 is the relative atomic mass of zirconium.

Example 1.5.3: The Mass Spectrum of Chlorine

Chlorine is taken as typical of elements with more than one atom per molecule. We'll look at its mass spectrum to show the sort of problems involved. Chlorine has two isotopes, ^{35}Cl and ^{37}Cl, in the approximate ratio of 3 atoms of ^{35}Cl to 1 atom of ^{37}Cl. You might suppose that the mass spectrum would look like this:



You would be wrong! The problem is that chlorine consists of molecules, not individual atoms. When chlorine is passed into the ionization chamber, an electron is knocked off the molecule to give a molecular ion, Cl_2^+. These ions won't be particularly stable, and some will fall apart to give a chlorine atom and a Cl^+ ion. The term for this is fragmentation.

$$Cl_2^+ \rightarrow Cl + Cl^+$$

If the Cl atom formed is not then ionized in the ionization chamber, it simply gets lost in the machine - neither accelerated nor deflected.

The Cl^+ ions will pass through the machine and will give lines at 35 and 37, depending on the isotope and you would get exactly the pattern in the last diagram. The problem is that you will also record lines for the unfragmented Cl_2^+ ions.

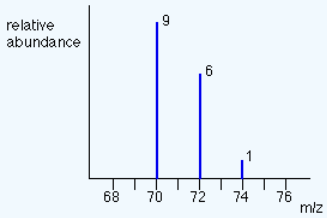
Think about the possible combinations of chlorine-35 and chlorine-37 atoms in a Cl_2^+ ion. Both atoms could be ^{35}Cl, both atoms could be ^{37}Cl, or you could have one of each sort. That would give you total masses of the Cl_2^+ ion of:

35 + 35 = 70

35 + 37 = 72

37 + 37 = 74

That means that you would get a set of lines in the m/z = 70 region looking like this:

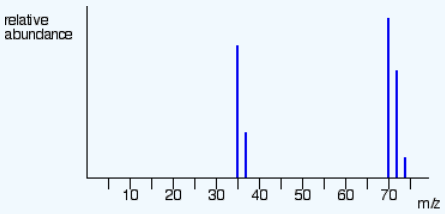


These lines would be in addition to the lines at 35 and 37.

The relative heights of the 70, 72 and 74 lines are in the ratio 9:6:1. If you know the right bit of math, it's very easy to show this. If not, don't worry. Just remember that the ratio is 9:6:1.

What you can't do is make any predictions about the relative heights of the lines at 35/37 compared with those at 70/72/74. That depends on what proportion of the molecular ions break up into fragments. That's why you've got the chlorine mass spectrum in two separate bits so far. You must realise that the vertical scale in the diagrams of the two parts of the spectrum isn't the same.

The overall mass spectrum looks like this:



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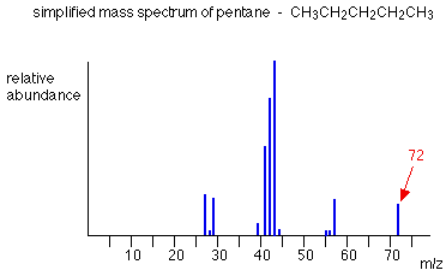
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1.5.1: The Molecular Ion (M^+) Peak

This page explains how to find the relative formula mass (relative molecular mass) of an organic compound from its mass spectrum. It also shows how high resolution mass spectra can be used to find the molecular formula for a compound.

When the vaporised organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the molecular ion. The molecular ion is often given the symbol M^+ or $M^{\cdot+}$ - the dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process. The molecular ions tend to be unstable and some of them break into smaller fragments. These fragments produce the familiar stick diagram. Fragmentation is irrelevant to what we are talking about on this page - all we're interested in is the molecular ion.

In the mass spectrum, the heaviest ion (the one with the greatest m/z value) is likely to be the molecular ion. A few compounds have mass spectra which don't contain a molecular ion peak, because all the molecular ions break into fragments. For example, in the mass spectrum of pentane, the heaviest ion has an m/z value of 72.



Because the largest m/z value is 72, that represents the largest ion going through the mass spectrometer - and you can reasonably assume that this is the molecular ion. The relative formula mass of the compound is therefore 72.

Finding the relative formula mass (relative molecular mass) from a mass spectrum is therefore trivial. Look for the peak with the highest value for m/z, and that value is the relative formula mass of the compound. There are, however, complications which arise because of the possibility of different isotopes (either of carbon or of chlorine or bromine) in the molecular ion. These cases are dealt with on separate pages.

Using a mass spectrum to find a molecular formula

So far we've been looking at m/z values in a mass spectrum as whole numbers, but it's possible to get far more accurate results using a high resolution mass spectrometer. You can use that more accurate information about the mass of the molecular ion to work out the molecular formula of the compound.

For normal calculation purposes, you tend to use rounded-off relative isotopic masses. For example, you are familiar with the atomic mass numbers (Z). To 4 decimal places, however, these are the relative isotopic masses.

Isotope	Z	Mass
^{1}H	1	1.0078
^{12}C	12	12.0000
^{14}N	14	14.0031
^{16}O	16	15.9949

The carbon value is 12.0000, of course, because all the other masses are measured on the carbon-12 scale which is based on the carbon-12 isotope having a mass of exactly 12.

Using these accurate values to find a molecular formula

Two simple organic compounds have a relative formula mass of 44 - propane, C_3H_8, and ethanal, CH_3CHO. Using a high resolution mass spectrometer, you could easily decide which of these you had. On a high resolution mass spectrometer, the molecular ion peaks for the two compounds give the following m/z values:

C_3H_8		44.0624
CH_3CHO		44.0261

You can easily check that by adding up numbers from the table of accurate relative isotopic masses above.

Example 1.5.1.1:

A gas was known to contain only elements from the following list:

^{1}H		1.0078
^{12}C		12.0000
^{14}N		14.0031
^{16}O		15.9949

The gas had a molecular ion peak at m/z = 28.0312 in a high resolution mass spectrometer. What was the gas?

Solution

After a bit of playing around, you might reasonably come up with 3 gases which had relative formula masses of approximately 28 and which contained the elements from the list. They are N_2, CO and C_2H_4. Working out their accurate relative formula masses gives:

N_2		28.0062
CO		27.9949
C_2H_4		28.0312

The gas is obviously C_2H_4.

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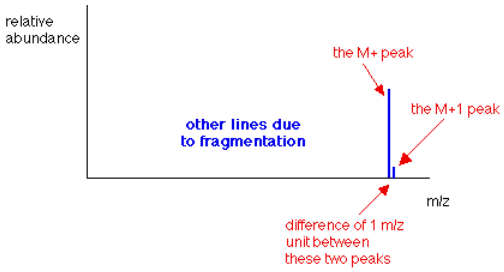
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1.5.2: The M+1 Peak

This page explains how the M+1 peak in a mass spectrum can be used to estimate the number of carbon atoms in an organic compound.

What causes the M+1 peak?

If you had a complete (rather than a simplified) mass spectrum, you will find a small line 1 m/z unit to the right of the main molecular ion peak. This small peak is called the M+1 peak.

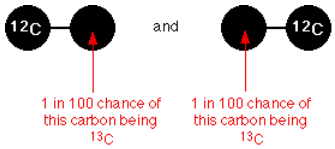


The carbon-13 isotope

The M+1 peak is caused by the presence of the ^{13}C isotope in the molecule. ^{13}C is a stable isotope of carbon - don't confuse it with the ^{14}C isotope which is radioactive. Carbon-13 makes up 1.11% of all carbon atoms. If you had a simple compound like methane, CH_4, approximately 1 in every 100 of these molecules will contain carbon-13 rather than the more common carbon-12. That means that 1 in every 100 of the molecules will have a mass of 17 (13 + 4) rather than 16 (12 + 4). The mass spectrum will therefore have a line corresponding to the molecular ion $[^{13}CH_4]^+$ as well as $[^{12}CH_4]^+$. The line at m/z = 17 will be much smaller than the line at m/z = 16 because the carbon-13 isotope is much less common. Statistically you will have a ratio of approximately 1 of the heavier ions to every 99 of the lighter ones. That's why the M+1 peak is much smaller than the M+ peak.

Using the M+1 peak

Imagine a compound containing 2 carbon atoms. Either of them has an approximately 1 in 100 chance of being ^{13}C.



There's therefore a 2 in 100 chance of the molecule as a whole containing one ^{13}C atom rather than a ^{12}C atom - which leaves a 98 in 100 chance of both atoms being ^{12}C. That means that the ratio of the height of the M+1 peak to the M+ peak will be approximately 2 : 98. That's pretty close to having an M+1 peak approximately 2% of the height of the M+ peak.

Using the relative peak heights to predict the number of carbon atoms

If you measure the peak height of the M+1 peak as a percentage of the peak height of the M+ peak, that gives you the number of carbon atoms in the compound. We've just seen that a compound with 2 carbons will have an M+1 peak approximately 2% of the height of the M+ peak. Similarly, you could show that a compound with 3 carbons will have the M+1 peak at about 3% of the height of the M+ peak. The approximations we are making won't hold with more than 2 or 3 carbons. The proportion of carbon atoms which are ^{13}C isn't 1% - it's 1.11%. And the approximation that a ratio of 2 : 98 is about 2% doesn't hold as the small number increases.

Consider a molecule with 5 carbons in it. You could work out that 5.55 (5 x 1.11) molecules will contain 1 ^{13}C to every 94.45 (100 - 5.55) which contain only ^{12}C atoms. If you convert that to how tall the M+1 peak is as a percentage of the M+ peak, you get an answer of 5.9% (5.55/94.45 x 100). That's close enough to 6% that you might assume wrongly that there are 6 carbon atoms. Above 3 carbon atoms, then, you shouldn't really be making the approximation that the height of the M+1 peak as a percentage of the height of the M+ peak tells you the number of carbons - you will need to do some fiddly sums!

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1.5.3: Isotopes- 13C

Isotopomers or isotopic isomers are isomers with isotopic atoms, having the same number of each isotope of each element but differing in their positions.

Isotopomers

If you look closely at the mass spectrum of an organic compound, 2-butanone, you see a line at m/z 72, which corresponds to 4 carbons, an oxygen and 8 hydrogens.

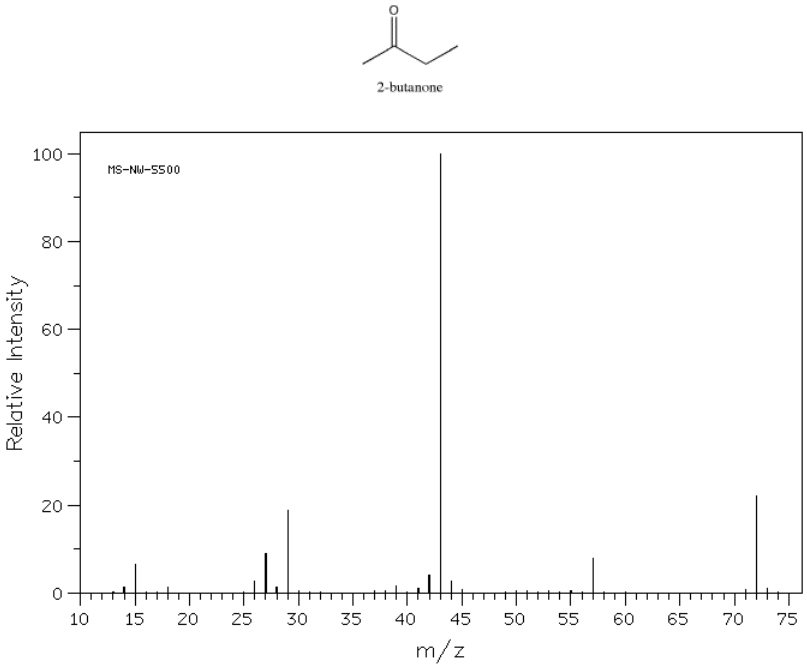


Figure MS3. Mass spectrum of 2-butanone. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 22 August 2008)

- Usually, whole numbers are used for molecular weights in mass spectrometry.
- The atomic masses in the periodic table, out to 4 decimal places, are the average masses including different possible isotopes.
- Because mass spectrometry examines individual molecules, individual atomic masses are needed, not average ones. Usually that means using a whole number.

In addition, there are a number of other lines at lower values of m/z; these correspond to the masses of smaller pieces of those 2-butanone molecules that fall apart during the experiment. We won't look too closely at how those arise until we get to radical reactions later in the course. However, we will look at some factors that make cations stable later in this chapter.

If you look closely at the mass spectrum of 2-butanone, you'll also see another little peak at m/z 73. This is referred to as the M+1 peak (one greater than the molecular ion), and it arises because of ^{13}C. This compound is referred to as an isotopomer; that means the same compound with a different isotope.

- ^{12}C is about 99% abundant; 99% of carbon atoms have a mass of 12 amu.
- ^{13}C is about 1% abundant; 1% of carbon atoms have a mass of 13 amu.
- Compounds that contain a ^{13}C atom have a mass one larger than expected.

The chance that a molecule in a sample contains a ^{13}C atom is related to the number of carbons present. If there is just one carbon atom in the molecule, it has a 1% chance of being a ^{13}C. That means the M+1 peak would be only 1/100th as tall as M+, the peak for the molecular ion.

- The M+1 peak from a ^{13}C atom is very small.
- The more carbons there are in a molecule, the bigger the M+1 peak.

- If there are 10 carbon atoms in the molecule, there is a 10% chance of a ^{13}C atom being present. The M+1 peak is about 1/10th the size of the M+ peak.
- If there are 100 carbons in the molecule, there is a very good chance that a ^{13}C atom is present. At that point, the M+1 peak is actually much larger than the M+. peak

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1.5.4: Isotopes- Br and Cl



bromoethane

Figure MS5. Mass spectrum of chlorobenzene.

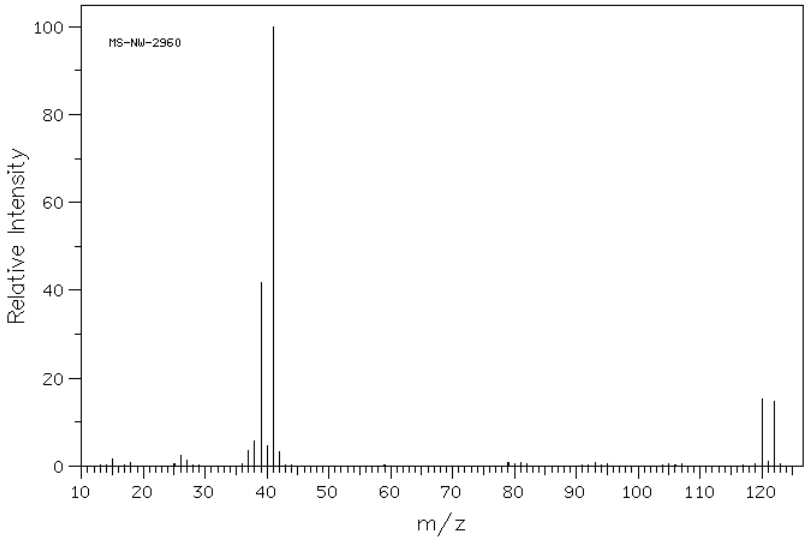
Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 22 August 2008)

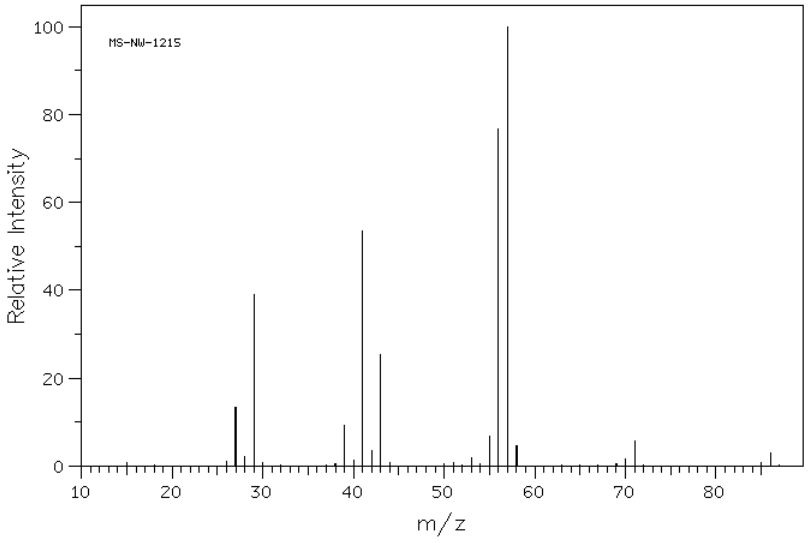
- Chlorinated compounds show an M+2 peak that is 1/3 as large as the M+ peak.

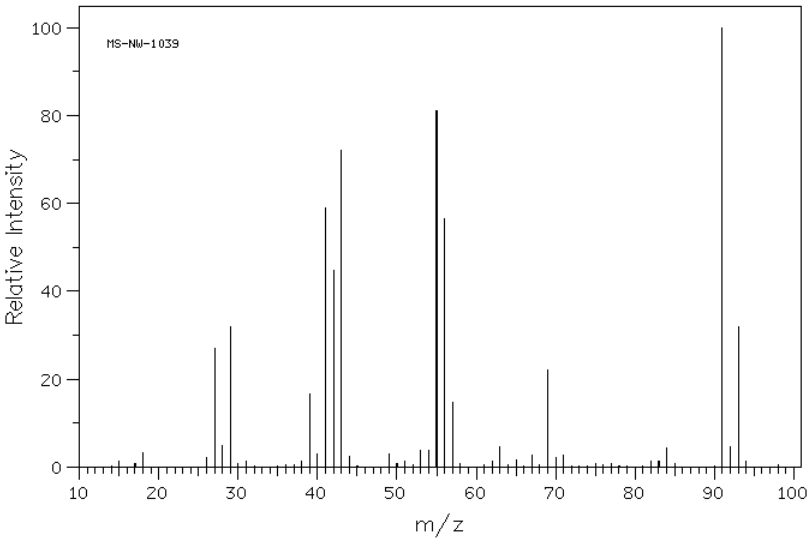
Note also that halogens are easily lost during mass spectrometry. If you subtract the mass of the halogen from the molecular ion mass, you will often find a peak that corresponds to the remainder of the structure.

Problem MS4.

Draw one possible structure for the compound in each of the following mass spectra.





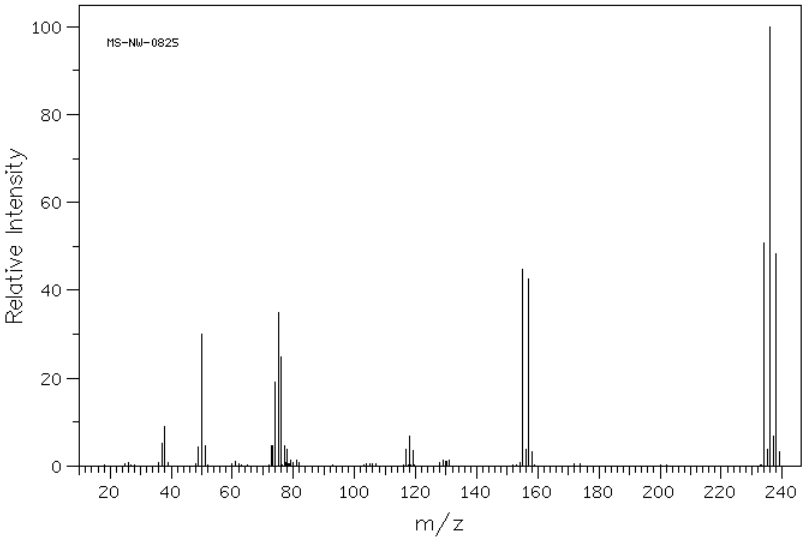


Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 25 August 2008)

Problem MS5.

In the following mass spectrum, more than one halogen atom is present.

1. What is a possible structure of the compound?
2. Show why this pattern of molecular ions is observed.



Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 25 August 2008)

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1.5.5: Measuring the Molecular Mass of Organic Compounds- Mass Spectrometry

Objectives

After completing this section, you should be able to

1. describe, briefly, how a mass spectrometer works.
2. sketch a simple diagram to show the essential features of a mass spectrometer.
3. identify peaks in a simple mass spectrum, and explain how they arise.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- base peak
- parent peak (molecular ion peak)
- cation radical
- relative abundance
- mass spectrometer
- mass spectroscopy
- mass spectrum
- molecular ion ($M^{+\cdot}$)
- mass-to-charge ratio (*m/z*)

Study Notes

You may remember from general first-year chemistry how mass spectroscopy has been used to establish the atomic mass and abundance of isotopes.

Mass spectrometers are large and expensive, and usually operated only by fully trained personnel, so you may not have the opportunity to use such an instrument as part of this course. Research chemists often rely quite heavily on mass spectra to assist them in the identification of compounds, and you will be required to interpret simple mass spectra both in assignments and on examinations. Note that in most attempts to identify an unknown compound, chemists do not rely exclusively on the results obtained from a single spectroscopic technique. A combination of chemical and physical properties and spectral evidence is usually employed.

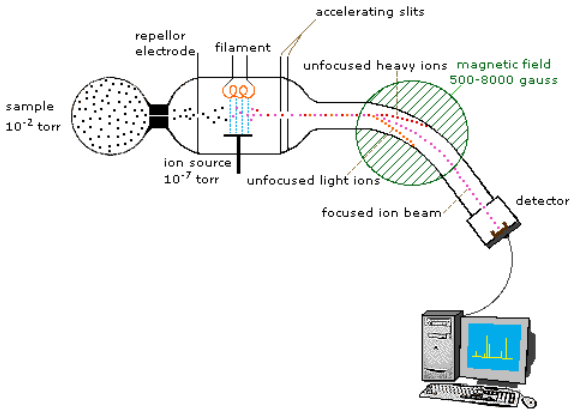
The Mass Spectrometer

In order to measure the characteristics of individual molecules, a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of a mass spectrometer, and the associated components, are:

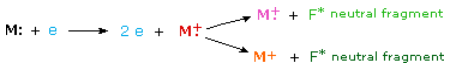
1. A small sample is ionized, usually to cations by loss of an electron. **The Ion Source**
2. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**
3. The separated ions are then measured, and the results displayed on a chart. **The Detector**

Because ions are very reactive and short-lived, their formation and manipulation must be conducted in a vacuum. Atmospheric pressure is around 760 torr (mm of mercury). The pressure under which ions may be handled is roughly 10^{-5} to 10^{-8} torr (less than a billionth of an atmosphere). Each of the three tasks listed above may be accomplished in different ways. In one common procedure, ionization is effected by a high energy beam of electrons, and ion separation is achieved by accelerating and focusing the ions in a beam, which is then bent by an external magnetic field. The ions are then detected electronically and the resulting information is stored and analyzed in a computer. A mass spectrometer operating in this fashion is outlined in the following diagram. The heart of the spectrometer is the **ion source**. Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament. This is called an **EI** (electron-ionization) source. Gases and volatile liquid samples are allowed to leak into

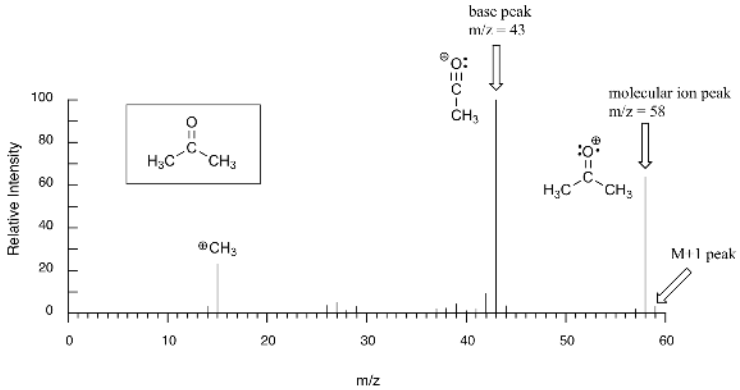
the ion source from a reservoir (as shown). Non-volatile solids and liquids may be introduced directly. Cations formed by the electron bombardment (red dots) are pushed away by a charged repellor plate (anions are attracted to it), and accelerated toward other electrodes, having slits through which the ions pass as a beam. Some of these ions fragment into smaller cations and neutral fragments. A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion. Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field, ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).



When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.



Below is typical output for an electron-ionization MS experiment (MS data below is derived from the Spectral Database for Organic Compounds, a free, web-based service provided by AIST in Japan.



The sample is acetone. On the horizontal axis is the value for m/z, which is the mass to charge ratio (as we stated above, the charge z is almost always +1, so in practice this is the same as mass). On the vertical axis is the relative abundance of each ion detected. On this scale, the most abundant ion, called the **base peak**, is set to 100%, and all other peaks are recorded relative to this value. For acetone, the base peak corresponds to a fragment with m/z = 43 - . The molecular weight of acetone is 58, so we can identify the peak at m/z = 58 as that corresponding to the **molecular ion peak**, or **parent peak**. Notice that there is a small peak at m/z =

59: this is referred to as the **M+1 peak**. How can there be an ion that has a greater mass than the molecular ion? Simple: a small fraction - about 1.1% - of all carbon atoms in nature are actually the ^{13}C rather than the ^{12}C isotope. The ^{13}C isotope is, of course, heavier than ^{12}C by 1 mass unit. In addition, about 0.015% of all hydrogen atoms are actually deuterium, the ^{2}H isotope. So the M+1 peak represents those few acetone molecules in the sample which contained either a ^{13}C or ^{2}H.

1.5.5: Measuring the Molecular Mass of Organic Compounds- Mass Spectrometry is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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1.6: GC/MS Combination- Shockwave

GC MS Combination: Shockwave

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1.7: Interpreting a Mass Spectrum

Here are a list of steps to follow when interpreting a mass spectrum. This simplified list will help you to interpret many spectra, however there are other mechanisms of fragmentation which cannot be covered in this brief tutorial.

Steps to interpret a mass spectrum

1. Look for the molecular ion peak.

- This peak (if it appears) will be the highest mass peak in the spectrum, except for isotope peaks.
- Nominal MW (meaning=rounded off) will be an even number for compounds containing only C, H, O, S, Si.
- Nominal MW will be an odd number if the compound also contains an odd number of N (1,3,...).

2. Try to calculate the molecular formula:

- The isotope peaks can be very useful, and are best explained with an example.
  - Carbon 12 has an isotope, carbon 13. Their abundances are ^{12}C=100%, ^{13}C=1.1%. This means that for every 100 $^{(12)}C$ atoms there are 1.1 $^{(13)}C$ atoms.
  - If a compound contains 6 carbons, then each atom has a 1.1% abundance of $^{(13)}C$.
  - Therefore, if the molecular ion peak is 100%, then the isotope peak (1 mass unit higher) would be 6x1.1%=6.6%.
  - If the molecular ion peak is not 100% then you can calculate the relative abundance of the isotope peak to the ion peak. For example, if the molecular ion peak were 34% and the isotope peak 2.3%: (2.3/34)x100 = 6.8%. 6.8% is the relative abundance of the isotope peak to the ion peak. Next, divide the relative abundance by the isotope abundance: 6.8/1.1=6 carbons.
- Follow this order when looking for information provided by isotopes: (A simplified table of isotopes is provided in the introduction, more detailed tables can be found in chemistry texts.)
  - Look for A+2 elements: O, Si, S, Cl, Br
  - Look for A+1 elements: C, N
  - "A" elements: H, F, P, I

3. Calculate the total number of rings plus double bonds:

- For the molecular formula: $C_xH_yN_zO_n$
  - rings + double bonds = x - (1/2)y + (1/2)z + 1

4. Postulate the molecular structure consistent with abundance and m/z of fragments.

- More information on specific fragmentation can be found in the quiz for each functional group.

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1.7.1: Degree of Unsaturation- Another Aid to Identifying Molecular Structure

Objectives

After completing this section, you should be able to

- determine the degree of unsaturation of an organic compound, given its molecular formula, and hence determine the number of double bonds, triple bonds and rings present in the compound.
- draw all the possible isomers that correspond to a given molecular formula containing only carbon (up to a maximum of six atoms) and hydrogen.
- draw a specified number of isomers that correspond to a given molecular formula containing carbon, hydrogen, and possibly other elements, such as oxygen, nitrogen and the halogens.

Key Terms

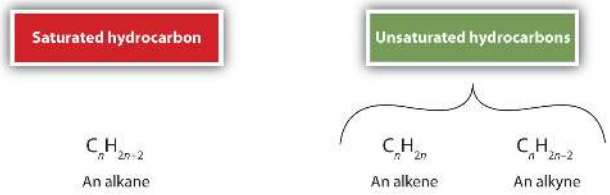
Make certain that you can define, and use in context, the key terms below.

- degree of unsaturation
- saturated
- unsaturated

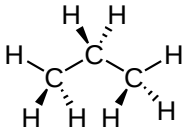
There are many ways one can go about determining the structure of an unknown organic molecule. Although, nuclear magnetic resonance (NMR) and infrared radiation (IR) are the primary ways of determining molecular structures, calculating the degrees of unsaturation is useful information because it easily provides information about molecular structure.

Saturated and Unsaturated Molecules

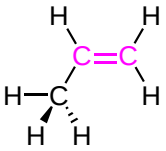
Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**. The presence of a double bond causes alkenes to have less hydrogens than an alkane with the same number of carbons. Likewise, compounds containing a carbon-to-carbon triple bonds (R–C≡C–R) called alkynes (**Discussed in Chapter 9**), also have fewer hydrogens than the corresponding alkane. Collectively, compounds which have fewer hydrogen atoms than an alkane with the same number of carbon atoms are called **unsaturated hydrocarbons**. The relationship between the number of carbons (n) and hydrogens in the molecular formula for alkanes, alkenes, and alkynes are listed below.



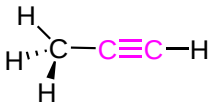
For example, the three carbon alkane, propane has the molecular formula of C_3H_8. While the unsaturated compounds propene (C_3H_6) and propyne (C_3H_4) both have fewer hydrogens. Also, it is important to note that cycloalkanes with one ring have a general molecular formula of C_nH_{2n} just like alkenes. Because they also have fewer than maximum number of hydrogens possible, cyclic compounds are also considered unsaturated.



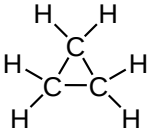
Propane
(C_3H_8)
Saturated



Propene
(C_3H_6)
Unaturated



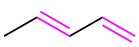
Propyne
(C_3H_4)
Unaturated



Cyclopropane
(C_3H_6)
Unaturated

Identifying Degrees of Unsaturation

Every ring or pi bond in a compound is said to represent one degree of unsaturation. Being able to determine the degrees of unsaturation in a given compound is an important skill. Each of the following compounds are isomers of C_5H_7 and contain two degrees of unsaturation.



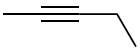
1,3-Pentadiene
(Two double bonds)



Cyclopentene
(One double bond and one ring)



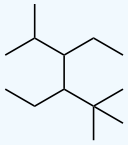
Bycyclo[2.1.0]pentane
(Two rings)



2-Pentyne
(One triple bond)

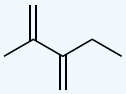
? Exercise 1.7.1.1

How many degrees of unsaturation do the following compounds have?

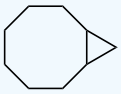
a) 

b) $CH_3CH_2CH{=}CHCF_3$

c) 

d) 

e) 3-chloro-5-octyne

f) 

Answer

a) 0

b) 1

c) 1

d) 2

e) 2

f) 2

Calculating the Degree of Unsaturation (DoU)

As noted above, every degree of unsaturation causes the loss of two hydrogens from a compound's molecular formula when compared to an alkane with the same number of carbons. Understanding this relationship allows for the degrees of unsaturation of a compound to be calculated from its molecular formula. First, the maximum number of hydrogens possible for a given compound **(2C + 2)** is calculated and then the actual number of hydrogens present in the compound **(H)** is subtracted**.** If this difference is then divided by 2 the answer will be equal to the degrees of unsaturation for the compound.

For a compound which only contains carbon and hydrogen:

$$DoU = (2C + 2) - H / 2$$

As an example, for the molecular formula C_3H_4 the number of actual hydrogens needed for the compound to be saturated is 8 **[2C+2=(2x3)+2=8]**. Because the compound only has 4 hydrogens in its molecular formula, it would have to gain 4 more hydrogens in order to be fully saturated **(8-4 = 4)**. Degrees of unsaturation is equal to half the number of hydrogens the molecule needs to be fully saturated. This compound has 2 degrees of unsaturation **(4/2 = 2)**.

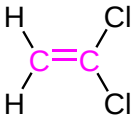
The DoU of compounds containing elements other than carbon and hydrogen can also be calculated in a similar fashion. However, different elements can affect the formula used to calculate DoU.

For a compound which contains elements other than carbon and hydrogen:

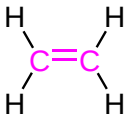
$$DoU = \frac{2C + 2 + N - X - H}{2} \quad (7.2.1)$$

- C is the number of carbons
- N is the number of nitrogens
- X is the number of halogens (F, Cl, Br, I)
- H is the number of hydrogens

A halogen (X) replaces a hydrogen in a compound because both form one single bond. Therefore the DoU formula subtracts the number of halogens (X) present in a compound. For instance, 1,1-dichloroethene ($C_2H_2Cl_2$) has two fewer hydrogens than ethene (C_2H_4) yet they both have one degree of unsaturation.



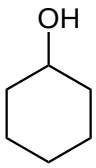
1,1-Dichloroethene ($C_2H_2Cl_2$)



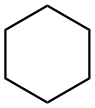
Ethene (C_2H_4)

One Degree of Unsaturation

Oxygen and sulfur are not included in the DoU formula because saturation is unaffected by these elements. The inclusion of an alcohol or sulfur in a compound does not change the number of hydrogens to obtain saturation. As seen in alcohols, the number of hydrogens in cyclohexanol ($C_6H_{12}O$) matches the number of hydrogens in cyclohexane (C_6H_{12}) and they both have one degree of unsaturation.



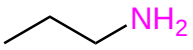
Cyclohexanol ($C_6H_{12}O$)



Cyclohexane (C_6H_{12})

One Degree of Unsaturation

When a nitrogen is present in a compound one more hydrogen is required to reach saturation. Therefore, we add the number of nitrogens (N). Propyl amine (C_3H_9N) has one more hydrogen compared to propane (C_3H_8) both of which are saturated compounds with 0 DoU.





Propyl Amine
(C_3H_9N)

Propane
(C_3H_8)

Zero Degrees of Unsaturation

With the degrees of unsaturation comes information about the possible number of rings and multiple bonds in a given compound. Remember, the degrees of unsaturation only gives the sum of pi bonds and/or rings.

- One degree of unsaturation is equivalent to 1 ring or 1 double bond (1 π bond).
- Two degrees of unsaturation is equivalent to 2 double bonds, 1 ring and 1 double bond, 2 rings, or 1 triple bond (2 π bonds).

Example 7.3.1: Benzene

What is the Degree of Unsaturation for Benzene?

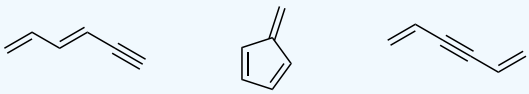
Solution

The molecular formula for benzene is C_6H_6. Thus,

DoU= 4, where C=6, N=0,X=0, and H=6. 1 DoB can equal 1 ring or 1 double bond. This corresponds to benzene containing 1 ring and 3 double bonds.

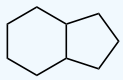


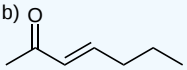
However, when given the molecular formula C_6H_6, benzene is only one of many possible structures (isomers). The following structures all have DoB of 4 and have the same molecular formula as benzene.

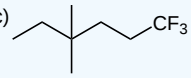


Exercise 1.7.1.2

Determine whether the following molecules are saturated or unsaturated.

a) 

b) 

c) 

d) $C_{10}H_6N_4$

e) $C_5H_{10}O$

f) $C_6H_{12}F_2$

Answer

a) **unsaturated** (E*ven though the rings only contain single bonds, rings are considered unsaturated.)*

b) **unsaturated**

c) **saturated**

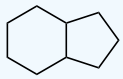
d) **unsaturated**

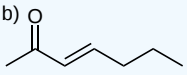
e) **unsaturated**

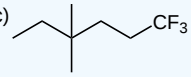
f) **saturated**

Exercise 1.7.1.3

Determine the degrees of unsaturation for each of the following compounds.

a) 

b) 

c) 

d) $C_{10}H_6N_4$ e) $C_5H_{10}O$ f) $C_6H_{12}F_2$

Answer

If the molecular structure is given, the easiest way to solve is to count the number of double bonds, triple bonds and/or rings. However, you can also determine the molecular formula and solve for the degrees of unsaturation by using the formula.

a) **2** (2 rings)

b) **2** *(one double bond and the double bond from the carbonyl)*

c) **0** (no double bonds or rings)

d) **10 (2(10) + 2 + 4 - 0 - 6)/2 = 10**

e) **1 (2(5) + 2 + 0 - 0 - 10)/2 = 1**

f) **0 (2(6) + 2 + 0 - 2 - 12)/2 = 0**

Exercise 1.7.1.4

Calculate the degrees of unsaturation for the following molecular formulas:

a) C_9H_{20} b) C_7H_8 c) C_5H_7Cl d) $C_9H_9NO_4$

Answer

Use the formula to solve (O not involved in the formula)

(a.) **0 (2(9) + 2 - 20)/2 = 0**

(b.) **4 (2(7) + 2 - 8)/2 = 4**

(c.) **2 (2(5) + 2 - 1 -7)/2 = 2**

(d.) **6 (2(9) + 1 - 7)/2 = 6**

References

1. Vollhardt, K. P.C. & Shore, N. (2007). *Organic Chemistry* (5thEd.). New York: W. H. Freeman. (473-474)
2. Shore, N. (2007). *Study Guide and Solutions Manual for Organic Chemistry* (5th Ed.). New York: W.H. Freeman. (201)

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1.7.2: Fragmentation Patterns of Organic Molecules

Objectives

After completing this section, you should be able to

1. suggest possible molecular formulas for a compound, given the *m/z* value for the molecular ion, or a mass spectrum from which this value can be obtained.
2. predict the relative heights of the M+·, (M + 1)+·, etc., peaks in the mass spectrum of a compound, given the natural abundance of the isotopes of carbon and the other elements present in the compound.
3. interpret the fragmentation pattern of the mass spectrum of a relatively simple, known compound (e.g., hexane).
4. use the fragmentation pattern in a given mass spectrum to assist in the identification of a relatively simple, unknown compound (e.g., an unknown alkane).

Study Notes

When interpreting fragmentation patterns, you may find it helpful to know that, as you might expect, the weakest carbon-carbon bonds are the ones most likely to break. You might wish to refer to the table of bond dissociation energies when attempting problems involving the interpretation of mass spectra.

This page looks at how fragmentation patterns are formed when organic molecules are fed into a mass spectrometer, and how you can get information from the mass spectrum.

The Origin of Fragmentation Patterns

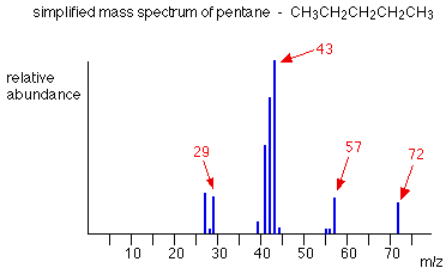
When the vaporized organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the **molecular ion - or sometimes the parent ion** and is often given the symbol M^+ or $M^{+\bullet}$. The dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process.

The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.



The uncharged free radical will **not** produce a line on the mass spectrum. Only charged particles will be accelerated, deflected and detected by the mass spectrometer. These uncharged particles will simply get lost in the machine - eventually, they get removed by the vacuum pump.

The ion, X^+, will travel through the mass spectrometer just like any other positive ion - and will produce a line on the stick diagram. All sorts of fragmentations of the original molecular ion are possible - and that means that you will get a whole host of lines in the mass spectrum. For example, the mass spectrum of pentane looks like this:



Note

The pattern of lines in the mass spectrum of an *organic compound* tells you something quite different from the pattern of lines in the mass spectrum of an *element*. With an element, each line represents a different isotope of that element. With a compound, each line represents a different fragment produced when the molecular ion breaks up.

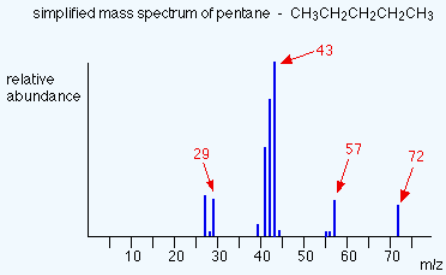
In the stick diagram showing the mass spectrum of pentane, the line produced by the heaviest ion passing through the machine (at m/z = 72) is due to the molecular ion. The tallest line in the stick diagram (in this case at m/z = 43) is called the **base peak**. This is usually given an arbitrary height of 100, and the height of everything else is measured relative to this. The base peak is the tallest peak because it represents the commonest fragment ion to be formed - either because there are several ways in which it could be produced during fragmentation of the parent ion, or because it is a particularly stable ion.

Using Fragmentation Patterns

This section will ignore the information you can get from the molecular ion (or ions). That is covered in three other pages which you can get at via the mass spectrometry menu. You will find a link at the bottom of the page.

Example 12.2.1: Pentane

Let's have another look at the mass spectrum for pentane:



What causes the line at m/z = 57?

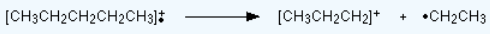
How many carbon atoms are there in this ion? There cannot be 5 because 5 x 12 = 60. What about 4? 4 x 12 = 48. That leaves 9 to make up a total of 57. How about $C_4H_9^+$ then?

$C_4H_9^+$ would be $[CH_3CH_2CH_2CH_2]^+$, and this would be produced by the following fragmentation:

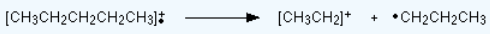


The methyl radical produced will simply get lost in the machine.

The line at m/z = 43 can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:



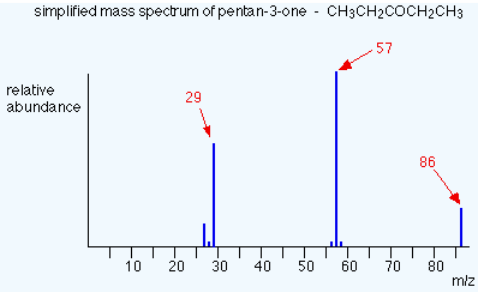
The line at m/z = 29 is typical of an ethyl ion, $[CH_3CH_2]^+$:



The other lines in the mass spectrum are more difficult to explain. For example, lines with m/z values 1 or 2 less than one of the easy lines are often due to loss of one or more hydrogen atoms during the fragmentation process.

Example 12.2.2: Pentan-3-one

This time the base peak (the tallest peak - and so the commonest fragment ion) is at m/z = 57. But this is not produced by the same ion as the same m/z value peak in pentane.

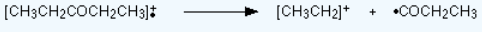


If you remember, the m/z = 57 peak in pentane was produced by $[CH_3CH_2CH_2CH_2]^+$. If you look at the structure of pentan-3-one, it's impossible to get that particular fragment from it.

Work along the molecule mentally chopping bits off until you come up with something that adds up to 57. With a small amount of patience, you'll eventually find $[CH_3CH_2CO]^+$ - which is produced by this fragmentation:



You would get exactly the same products whichever side of the CO group you split the molecular ion. The m/z = 29 peak is produced by the ethyl ion - which once again could be formed by splitting the molecular ion either side of the CO group.



Peak Heights and Stability

The more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. We'll look at two common examples of this.

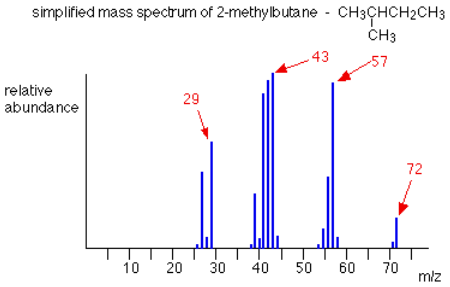
Carbocations (carbonium ions)

Summarizing the most important conclusion from the page on carbocations:

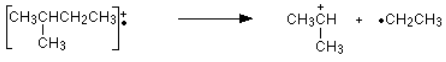
Order of stability of carbocations

primary < secondary < tertiary

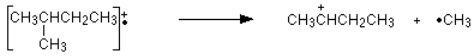
Applying the logic of this to fragmentation patterns, it means that a split which produces a secondary carbocation is going to be more successful than one producing a primary one. A split producing a tertiary carbocation will be more successful still. Let's look at the mass spectrum of 2-methylbutane. 2-methylbutane is an isomer of pentane - isomers are molecules with the same molecular formula, but a different spatial arrangement of the atoms.



Look first at the very strong peak at m/z = 43. This is caused by a different ion than the corresponding peak in the pentane mass spectrum. This peak in 2-methylbutane is caused by:



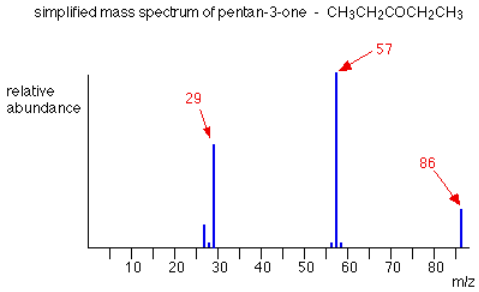
The ion formed is a secondary carbocation - it has two alkyl groups attached to the carbon with the positive charge. As such, it is relatively stable. The peak at m/z = 57 is much taller than the corresponding line in pentane. Again a secondary carbocation is formed - this time, by:



You would get the same ion, of course, if the left-hand CH_3 group broke off instead of the bottom one as we've drawn it. In these two spectra, this is probably the most dramatic example of the extra stability of a secondary carbocation.

Acylium ions, $[RCO]^+$

Ions with the positive charge on the carbon of a carbonyl group, C=O, are also relatively stable. This is fairly clearly seen in the mass spectra of ketones like pentan-3-one.



The base peak, at m/z=57, is due to the $[CH_3CH_2CO]^+$ ion. We've already discussed the fragmentation that produces this.

Note

The more stable an ion is, the more likely it is to form. The more of a particular ion that is formed, the higher will be its peak height.

Using mass spectra to distinguish between compounds

Suppose you had to suggest a way of distinguishing between pentan-2-one and pentan-3-one using their mass spectra.

pentan-2-one		$CH_3COCH_2CH_2CH_3$
pentan-3-one		$CH_3CH_2COCH_2CH_3$

Each of these is likely to split to produce ions with a positive charge on the CO group. In the pentan-2-one case, there are two different ions like this:

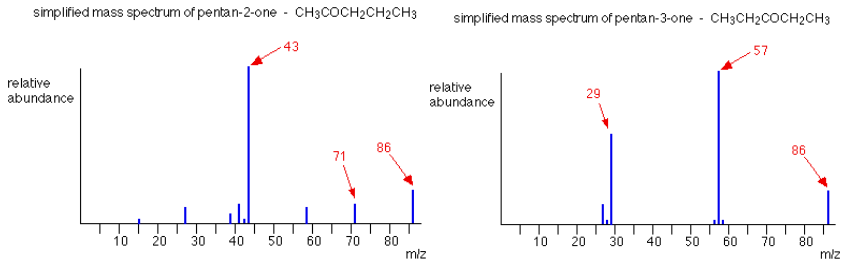
- $[CH_3CO]^+$
- $[COCH_2CH_2CH_3]^+$

That would give you strong lines at m/z = 43 and 71. With pentan-3-one, you would only get one ion of this kind:

- $[CH_3CH_2CO]^+$

In that case, you would get a strong line at 57. You don't need to worry about the other lines in the spectra - the 43, 57 and 71 lines give you plenty of difference between the two. The 43 and 71 lines are missing from the pentan-3-one spectrum, and the 57 line is missing from the pentan-2-one one.

The two mass spectra look like this:



As you've seen, the mass spectrum of even very similar organic compounds will be quite different because of the different fragmentation patterns that can occur. Provided you have a computer data base of mass spectra, any unknown spectrum can be computer analyzed and simply matched against the data base.

Exercises

Questions

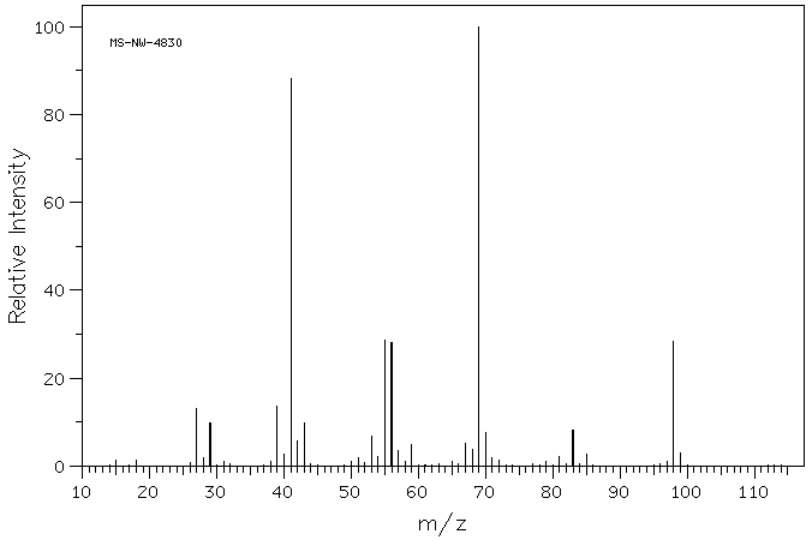
Q12.2.1

Caffeine has a mass of 194.19 amu, determined by mass spectrometry, and contains C, N, H, O. What is a molecular formula for this molecule?

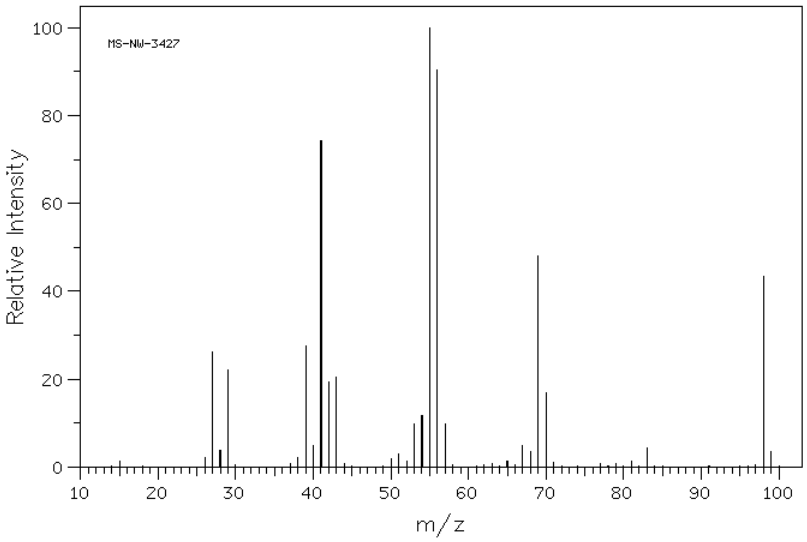
Q12.2.2

The following are the spectra for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A:



B:



Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

Solutions

S12.2.1

$C_8H_{10}N_4O_2$

C = 12 × 8 = 96

N = 14 × 4 = 56

H = 1 × 10 = 10

O = 2 × 16 = 32

96+56+10+32 = 194 g/mol

S12.2.2

The (A) spectrum is 2-methyl-2-hexene and the (B) spectrum is 2-heptene. Looking at (A) the peak at 68 *m/z* is the fractioned molecule with just the tri-substituted alkene present. While (B) has a strong peak around the 56 *m/z*, which in this case is the di-substituted alkene left behind from the linear heptene.

Objective

After completing this section, you should be able to predict the expected fragmentation for common functional groups, such as alcohols, amines, and carbonyl compounds.

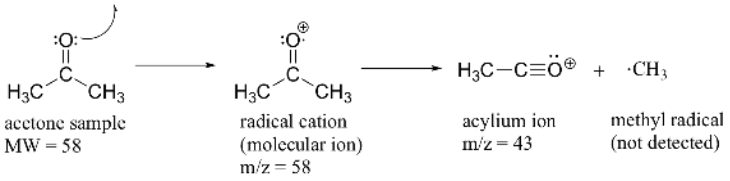
Key Terms

Make certain that you can define, and use in context, the key terms below.

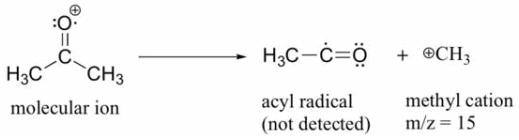
- alpha (α) cleavage
- McLafferty rearrangement

Much of the utility in electron-ionization MS comes from the fact that the radical cations generated in the electron-bombardment process tend to fragment in predictable ways. Detailed analysis of the typical fragmentation patterns of different functional groups is beyond the scope of this text, but it is worthwhile to see a few representative examples, even if we don't attempt to understand the exact process by which the fragmentation occurs. We saw, for example, that the base peak in the mass spectrum of acetone is m/z = 43. This is the result of cleavage at the 'alpha' position - in other words, at the carbon-carbon bond adjacent to the carbonyl.

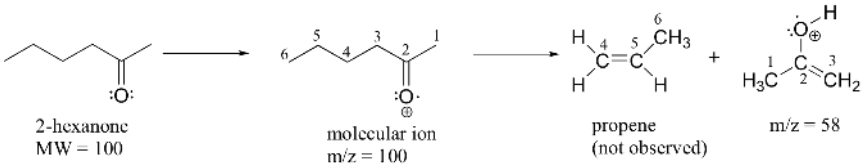
Alpha cleavage results in the formation of an acylium ion (which accounts for the base peak at m/z = 43) and a methyl radical, which is neutral and therefore not detected.



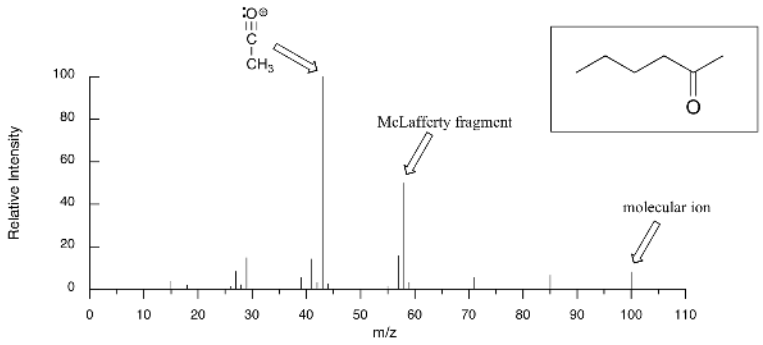
After the parent peak and the base peak, the next largest peak, at a relative abundance of 23%, is at m/z = 15. This, as you might expect, is the result of formation of a methyl cation, in addition to an acyl radical (which is neutral and not detected).



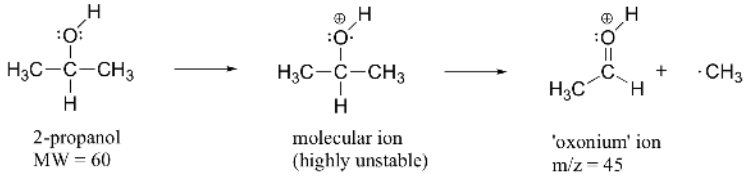
A common fragmentation pattern for larger carbonyl compounds is called the **McLafferty rearrangement**:

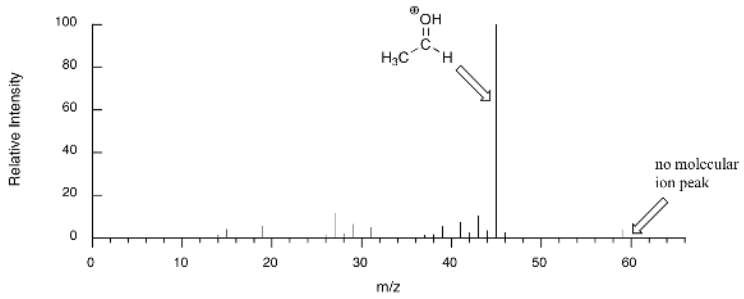


The mass spectrum of 2-hexanone shows a 'McLafferty fragment' at m/z = 58, while the propene fragment is not observed because it is a neutral species (remember, only cationic fragments are observed in MS). The base peak in this spectrum is again an acylium ion.



When alcohols are subjected to electron ionization MS, the molecular ion is highly unstable and thus a parent peak is often not detected. Often the base peak is from an ‘oxonium’ ion.





Other functional groups have predictable fragmentation patterns as well. By carefully analyzing the fragmentation information that a mass spectrum provides, a knowledgeable spectrometrist can often 'put the puzzle together' and make some very confident predictions about the structure of the starting sample.

Click here for examples of compounds listed by functional group, which demonstrate patterns which can be seen in mass spectra of compounds ionized by electron impact ionization.

Example 12.3.1

The mass spectrum of an aldehyde gives prominent peaks at *m/z* = 59 (12%, highest value of *m/z* in the spectrum), 58 (85%), and 29 (100%), as well as others. Propose a structure, and identify the three species whose *m/z* values were listed.

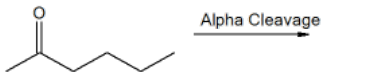
Solution

Exercises

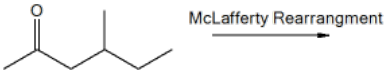
Questions

Q12.3.1

What are the masses of all the components in the following fragmentations?

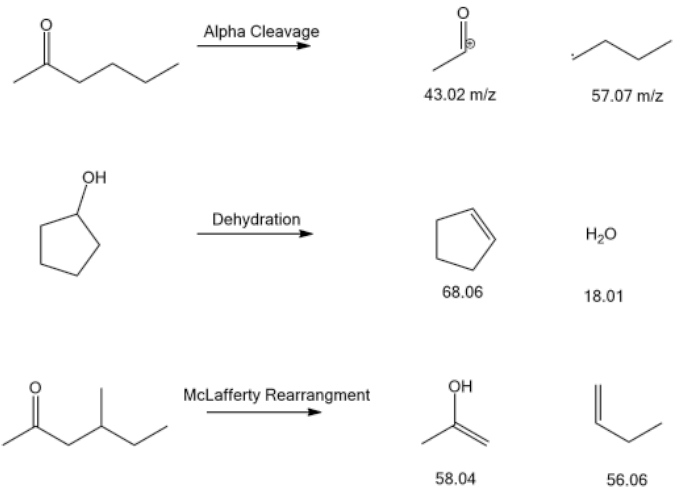






Solutions

S12.3.1



1.7.2: Fragmentation Patterns of Organic Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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- **12.3: Mass Spectrometry of Some Common Functional Groups** by Dietmar Kennepohl, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

1.7.3: Fragmentation Patterns in Mass Spectra

This page looks at how fragmentation patterns are formed when organic molecules are fed into a mass spectrometer, and how you can get information from the mass spectrum.

The formation of molecular ions

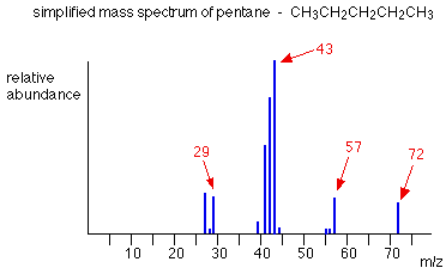
When the vaporized organic sample passes into the ionization chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the **molecular ion - or sometimes the parent ion.** The molecular ion is often given the symbol $\mathbf{M}^+$ or $\mathbf{M}^{\cdot+}$- the dot in this second version represents the fact that somewhere in the ion there will be a single unpaired electron. That's one half of what was originally a pair of electrons - the other half is the electron which was removed in the ionization process.

Fragmentation

The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.

$$M^{\cdot+} \rightarrow X^+ + Y^{\cdot}$$

The uncharged free radical won't produce a line on the mass spectrum. Only charged particles will be accelerated, deflected and detected by the mass spectrometer. These uncharged particles will simply get lost in the machine - eventually, they get removed by the vacuum pump. The ion, X^+, will travel through the mass spectrometer just like any other positive ion - and will produce a line on the stick diagram. All sorts of fragmentations of the original molecular ion are possible - and that means that you will get a whole host of lines in the mass spectrum. For example, the mass spectrum of pentane looks like this:



It's important to realize that the pattern of lines in the mass spectrum of an organic compound tells you something quite different from the pattern of lines in the mass spectrum of an element. With an element, each line represents a different isotope of that element. With a compound, each line represents a different fragment produced when the molecular ion breaks up.

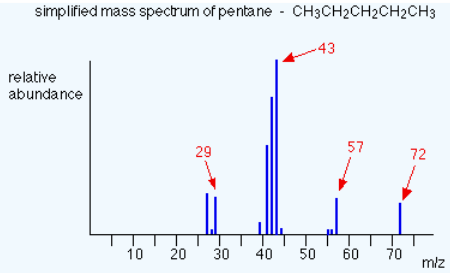
In the stick diagram showing the mass spectrum of pentane, the line produced by the heaviest ion passing through the machine (at m/z = 72) is due to the molecular ion. The tallest line in the stick diagram (in this case at m/z = 43) is called the **base peak**. This is usually given an arbitrary height of 100, and the height of everything else is measured relative to this. The base peak is the tallest peak because it represents the commonest fragment ion to be formed - either because there are several ways in which it could be produced during fragmentation of the parent ion, or because it is a particularly stable ion.

Using fragmentation patterns

This section will ignore the information you can get from the molecular ion (or ions). That is covered in three other pages which you can get at via the mass spectrometry menu. You will find a link at the bottom of the page.

Example 1.7.3.1: Mass Spectrum of Pentane

Let's have another look at the mass spectrum for pentane:

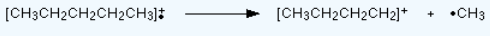


What causes the line at m/z = 57?

Solution

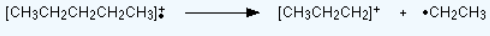
How many carbon atoms are there in this ion? There can't be 5 because 5 x 12 = 60. What about 4? 4 x 12 = 48. That leaves 9 to make up a total of 57. How about $C_4H_9^+$ then?

$C_4H_9^+$ would be $[CH_3CH_2CH_2CH_2]^+$, and this would be produced by the following fragmentation:

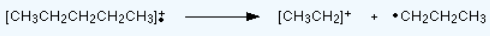


The methyl radical produced will simply get lost in the machine.

The line at m/z = 43 can be worked out similarly. If you play around with the numbers, you will find that this corresponds to a break producing a 3-carbon ion:



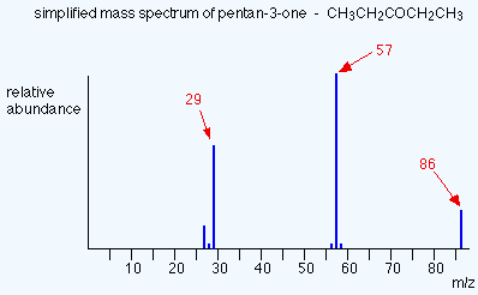
The line at m/z = 29 is typical of an ethyl ion, $[CH_3CH_2]^+$:



The other lines in the mass spectrum are more difficult to explain. For example, lines with m/z values 1 or 2 less than one of the easy lines are often due to loss of one or more hydrogen atoms during the fragmentation process.

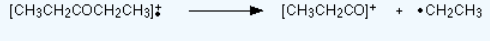
Example 1.7.3.2: Pentan-3-one

This time the base peak (the tallest peak - and so the commonest fragment ion) is at m/z = 57. But this isn't produced by the same ion as the same m/z value peak in pentane.

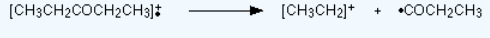


If you remember, the m/z = 57 peak in pentane was produced by $[CH_3CH_2CH_2CH_2]^+$. If you look at the structure of pentan-3-one, it's impossible to get that particular fragment from it.

Work along the molecule mentally chopping bits off until you come up with something that adds up to 57. With a small amount of patience, you'll eventually find $[CH_3CH_2CO]^+$ - which is produced by this fragmentation:



You would get exactly the same products whichever side of the CO group you split the molecular ion. The m/z = 29 peak is produced by the ethyl ion - which once again could be formed by splitting the molecular ion either side of the CO group.



Peak heights and the stability of ions

The more stable an ion is, the more likely it is to form. The more of a particular sort of ion that's formed, the higher its peak height will be. We'll look at two common examples of this.

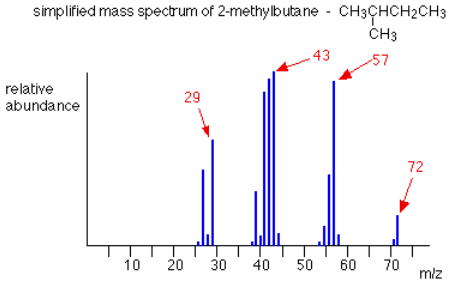
Examples involving carbocations (carbonium ions)

Summarizing the most important conclusion from the page on carbocations:

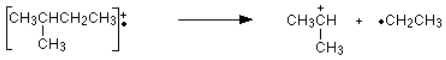
Order of stability of carbocations

primary < secondary < tertiary

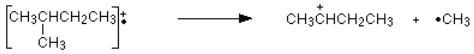
Applying the logic of this to fragmentation patterns, it means that a split which produces a secondary carbocation is going to be more successful than one producing a primary one. A split producing a tertiary carbocation will be more successful still. Let's look at the mass spectrum of 2-methylbutane. 2-methylbutane is an isomer of pentane - isomers are molecules with the same molecular formula, but a different spatial arrangement of the atoms.



Look first at the very strong peak at m/z = 43. This is caused by a different ion than the corresponding peak in the pentane mass spectrum. This peak in 2-methylbutane is caused by:



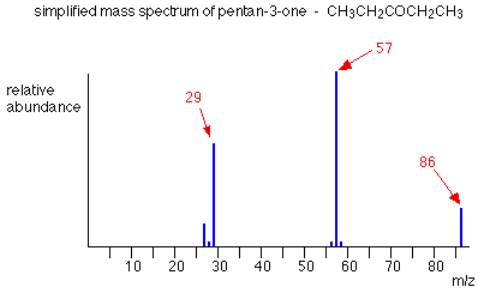
The ion formed is a secondary carbocation - it has two alkyl groups attached to the carbon with the positive charge. As such, it is relatively stable. The peak at m/z = 57 is much taller than the corresponding line in pentane. Again a secondary carbocation is formed - this time, by:



You would get the same ion, of course, if the left-hand CH_3 group broke off instead of the bottom one as we've drawn it. In these two spectra, this is probably the most dramatic example of the extra stability of a secondary carbocation.

Examples involving acylium ions, $[RCO]^+$

Ions with the positive charge on the carbon of a carbonyl group, C=O, are also relatively stable. This is fairly clearly seen in the mass spectra of ketones like pentan-3-one.



The base peak, at m/z=57, is due to the $[CH_3CH_2CO]^+$ ion. We've already discussed the fragmentation that produces this.

Using mass spectra to distinguish between compounds

Suppose you had to suggest a way of distinguishing between pentan-2-one and pentan-3-one using their mass spectra.

pentan-2-one		$CH_3COCH_2CH_2CH_3$
pentan-3-one		$CH_3CH_2COCH_2CH_3$

Each of these is likely to split to produce ions with a positive charge on the CO group. In the pentan-2-one case, there are two different ions like this:

- $[CH_3CO]^+$
- $[COCH_2CH_2CH_3]^+$

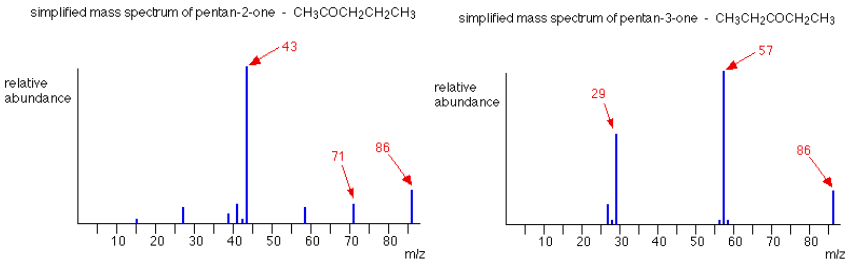
That would give you strong lines at m/z = 43 and 71.

With pentan-3-one, you would only get one ion of this kind:

- $[CH_3CH_2CO]^+$

In that case, you would get a strong line at 57. You don't need to worry about the other lines in the spectra - the 43, 57 and 71 lines give you plenty of difference between the two. The 43 and 71 lines are missing from the pentan-3-one spectrum, and the 57 line is missing from the pentan-2-one one.

The two mass spectra look like this:



Computer matching of mass spectra

As you've seen, the mass spectrum of even very similar organic compounds will be quite different because of the different fragmentations that can occur. Provided you have a computer data base of mass spectra, any unknown spectrum can be computer analysed and simply matched against the data base.

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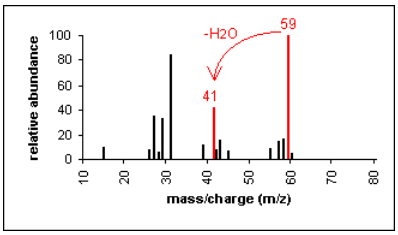
1.7.4: Mass Spectrometry - Fragmentation Patterns

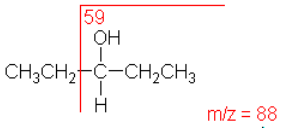
Following are examples of compounds listed by functional group, which demonstrate patterns which can be seen in mass spectra of compounds ionized by electron impact ionization. These examples do not provide information about the fragmentation mechanisms that cause these patterns. Additional information can be found in mass spectrometry reference books.

Alcohol

An alcohol's molecular ion is small or non-existent. Cleavage of the C-C bond next to the oxygen usually occurs. A loss of H_2O may occur as in the spectra below.

3-Pentanol ($C_5H_{12}O$) with MW = 88.15

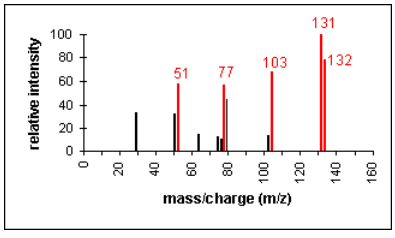


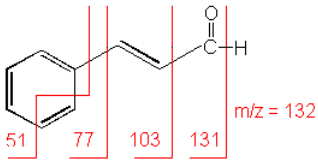


Aldehyde

Cleavage of bonds next to the carboxyl group results in the loss of hydrogen (molecular ion less 1) or the loss of CHO (molecular ion less 29).

3-Phenyl-2-propenal (C_9H_8O) with MW = 132.16

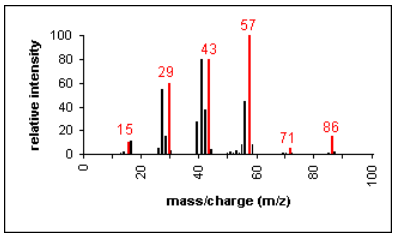


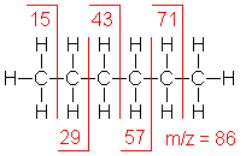


Alkane

Molecular ion peaks are present, possibly with low intensity. The fragmentation pattern contains clusters of peaks 14 mass units apart (which represent loss of (CH2)nCH3).

Hexane (C6H14) with MW = 86.18

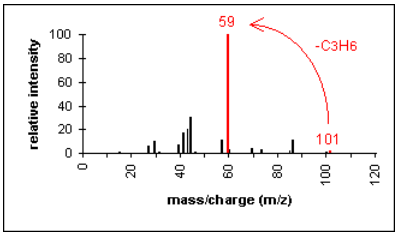


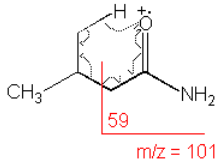


Amide

Primary amides show a base peak due to the McLafferty rearrangement.

3-Methylbutyramide ($C_5H_{11}NO$) with MW = 101.15

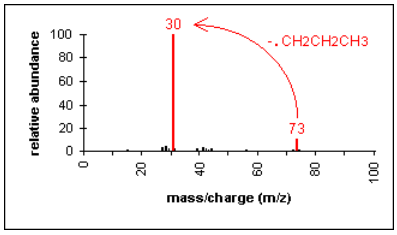


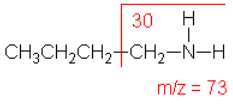


Amine

Molecular ion peak is an odd number. Alpha-cleavage dominates aliphatic amines.

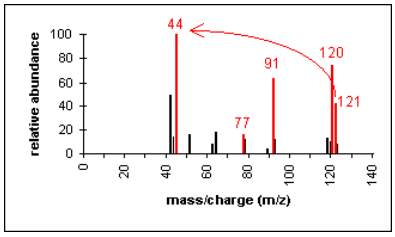
n-Butylamine (C4H11N) with MW = 73.13

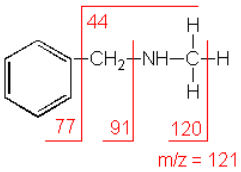




Another example is a secondary amine shown below. Again, the molecular ion peak is an odd number. The base peak is from the C-C cleavage adjacent to the C-N bond.

n-Methylbenzylamine ($C_8H_{11}N$) with MW = 121.18

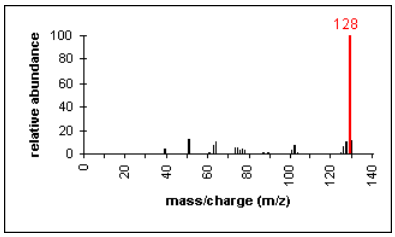


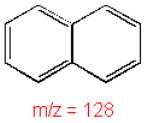


Aromatic

Molecular ion peaks are strong due to the stable structure.

Naphthalene ($C_{10}H_8$) with MW = 128.17

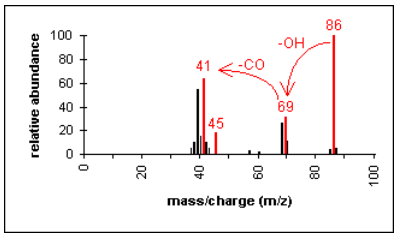


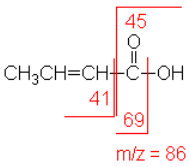


Carboxylic Acid

In short chain acids, peaks due to the loss of OH (molecular ion less 17) and COOH (molecular ion less 45) are prominent due to cleavage of bonds next to C=O.

2-Butenoic acid ($C_4H_6O_2$) with MW = 86.09

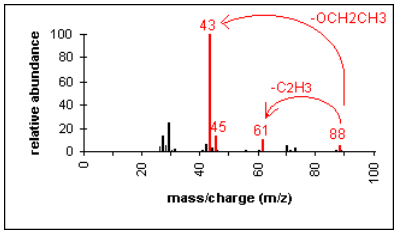


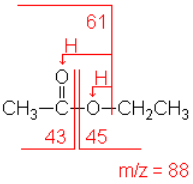


Ester

Fragments appear due to bond cleavage next to C=O (alkoxy group loss, -OR) and hydrogen rearrangements.

Ethyl acetate ($C_4H_8O_2$) with MW = 88.11

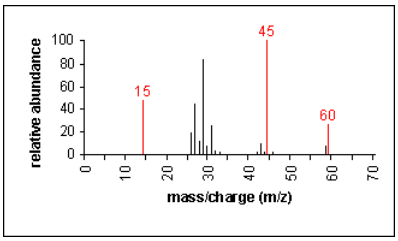


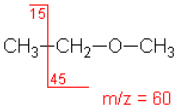


Ether

Fragmentation tends to occur alpha to the oxygen atom (C-C bond next to the oxygen).

Ethyl methyl ether (C_3H_8O) with MW = 60.10

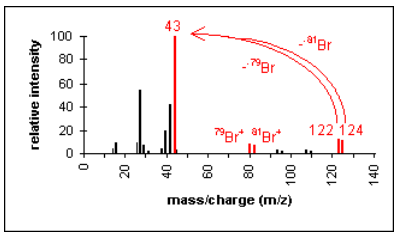


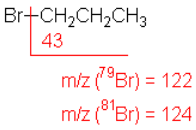


Halide

The presence of chlorine or bromine atoms is usually recognizable from isotopic peaks.

1-Bromopropane (C_3H_7Br) with MW = 123.00

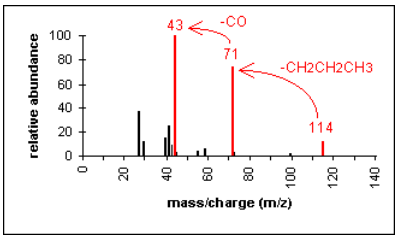


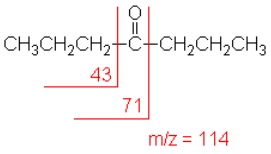


Ketone

Major fragmentation peaks result from cleavage of the C-C bonds adjacent to the carbonyl.

4-Heptanone ($C_7H_{14}O$) with MW = 114.19





Contributors and Attributions

Dr. Linda Breci, Associate Director Arizona Proteomics Consortium University of Arizona

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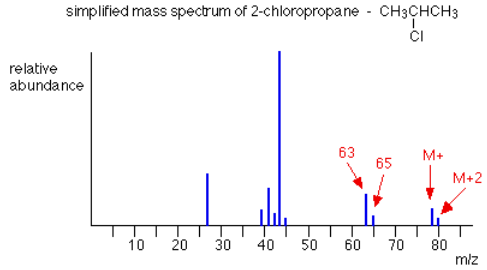
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1.7.5: Organic Compounds Containing Halogen Atoms

This page explains how the M+2 peak in a mass spectrum arises from the presence of chlorine or bromine atoms in an organic compound. It also deals briefly with the origin of the M+4 peak in compounds containing two chlorine atoms.

One chlorine atom in a compound



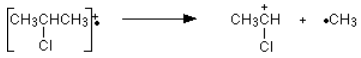
The molecular ion peaks (M+ and M+2) each contain one chlorine atom - but the chlorine can be either of the two chlorine isotopes, ^{35}Cl and ^{37}Cl.

The molecular ion containing the ^{35}Cl isotope has a relative formula mass of 78. The one containing ^{37}Cl has a relative formula mass of 80 - hence the two lines at m/z = 78 and m/z = 80.

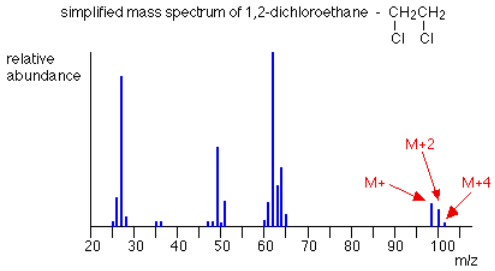
Notice that the peak heights are in the ratio of 3 : 1. That reflects the fact that chlorine contains 3 times as much of the ^{35}Cl isotope as the ^{37}Cl one. That means that there will be 3 times more molecules containing the lighter isotope than the heavier one.

So . . . if you look at the molecular ion region, and find two peaks separated by 2 m/z units and with a ratio of 3 : 1 in the peak heights, that tells you that the molecule contains 1 chlorine atom.

You might also have noticed the same pattern at m/z = 63 and m/z = 65 in the mass spectrum above. That pattern is due to fragment ions also containing one chlorine atom - which could either be ^{35}Cl or ^{37}Cl. The fragmentation that produced those ions was:



Two chlorine atoms in a compound



The lines in the molecular ion region (at m/z values of 98, 100 ands 102) arise because of the various combinations of chlorine isotopes that are possible. The carbons and hydrogens add up to 28 - so the various possible molecular ions could be:

$$28 + 35 + 35 = 98$$

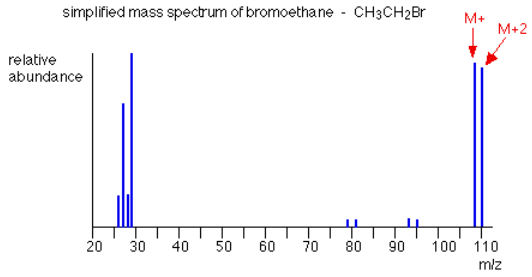
$$28 + 35 + 37 = 100$$

$$28 + 37 + 37 = 102$$

If you have the necessary math, you could show that the chances of these arrangements occurring are in the ratio of 9:6:1 - and this is the ratio of the peak heights. If you don't know the right bit of math, just learn this ratio! So . . . if you have 3 lines in the molecular ion region (M+, M+2 and M+4) with gaps of 2 m/z units between them, and with peak heights in the ratio of 9:6:1, the compound contains 2 chlorine atoms.

Compounds containing bromine atoms

Bromine has two isotopes, ^{79}Br and ^{81}Br in an approximately 1:1 ratio (50.5 : 49.5 if you want to be fussy!). That means that a compound containing 1 bromine atom will have two peaks in the molecular ion region, depending on which bromine isotope the molecular ion contains. Unlike compounds containing chlorine, though, the two peaks will be very similar in height.



The carbons and hydrogens add up to 29. The M+ and M+2 peaks are therefore at m/z values given by:

$$29 + 79 = 108$$

$$29 + 81 = 110$$

Hence, if two lines in the molecular ion region are observed with a gap of 2 m/z units between them and with almost equal heights, this suggests the presence of a bromine atom in the molecule.

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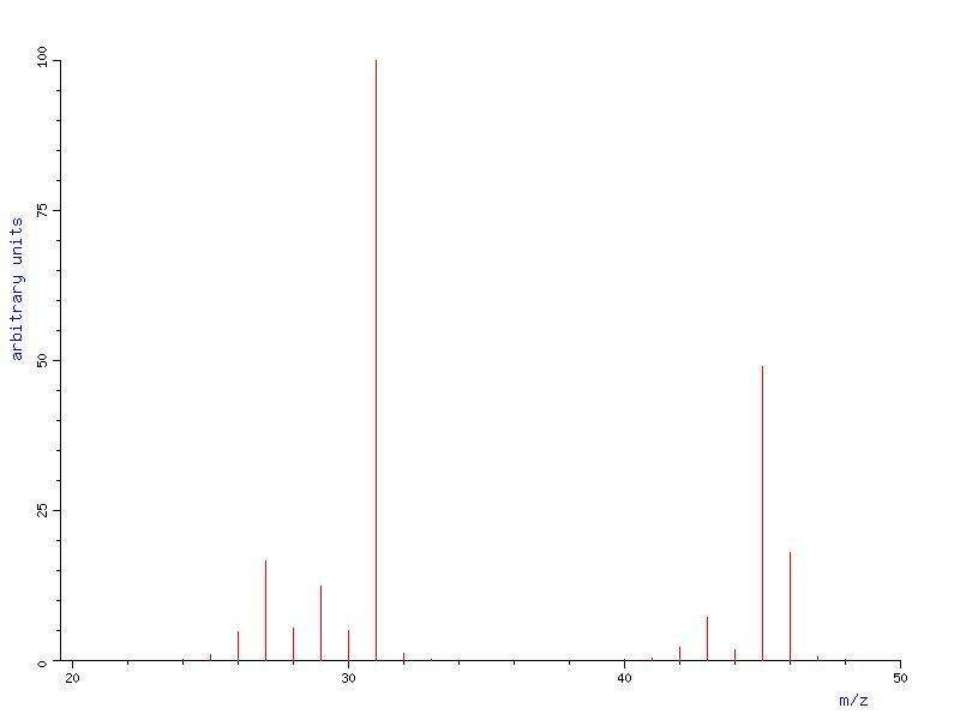
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1.7.6: Mass Spectrometry- Problems

Exercise 1.7.6.1

What is the m/z of the molecular ion in this mass spectrum?



Hint

Some compounds can lose a hydrogen easily, for example CH₃OH (methanol) will lose an H to form CH₂=OH⁺. In deciding whether 45 or 46 is the MW of this compound, ask whether the isotope ratio of peaks 45/46 makes sense? How about peaks 46/47?

Answer

The molecular ion peak has a m/z of 46.

Exercise 1.7.6.2

The mass spectrum of which of the following compounds is in Exercise **1.7.6.1**?

1. formic acid (aka methanoic acid)
2. 1-propanol
3. ethanol
4. methanol
5. 2-propanol

Hint

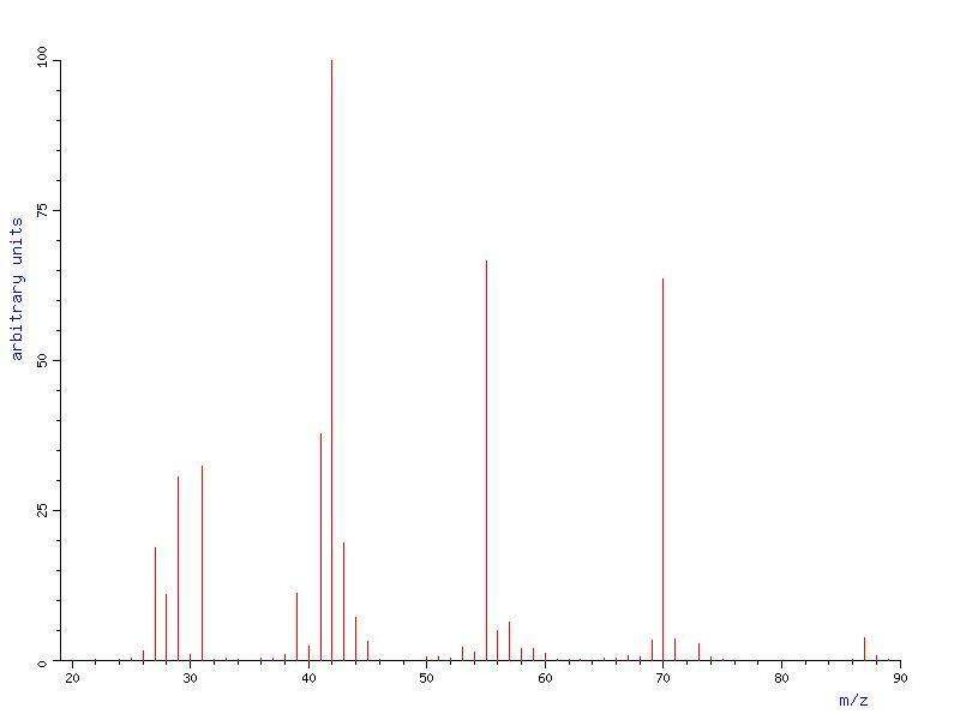
Alpha cleavage (the C-C bond next to the oxygen) occurs in alcohols. The fragment at 31 does not contain just carbon and hydrogen; it is part of a series (31, 45, 59) that indicates the presence of oxygen.

Answer

ethanol

Exercise 1.7.6.3

Identify the molecular ion in the mass spectrum shown below.



Hint

Addition of an alcohol group to a saturated alkane reduces the intensity of the molecular ion (in fact, it may not be observed!).

Answer

88

Exercise 1.7.6.4

An alkyl ion series is a pattern formed by alkyl groups. Identify the m/z values in Exercise **1.7.6.3** for peaks corresponding to an alkyl ion.

Hint

Alkyl ion series will follow a pattern formed by CH₃(CH₂)_n where n = 0, 1, 2, 3, ...

Answer

15 (not shown and quite small), 29, 43, 57

Exercise 1.7.6.5

The loss of an alkyl group also forms a distinct pattern. Identify the m/z values in Exercise **1.7.6.3** for peaks corresponding to loss of an alkyl ion.

Hint

Alkyl ion series will follow a pattern formed by CH₃(CH₂)_n where n = 0, 1, 2, 3, ... so there loss whould follow a pattern of mass loss from the molecular ion.

Answer

73, 59, 45, 31

Exercise 1.7.6.6

Which of the following compounds is most likely the compound in Exercise 1.7.6.3?

2-methyl-2-propanol

1-butanol

2-butanol

1-pentanol

2-methyl-1-propanol

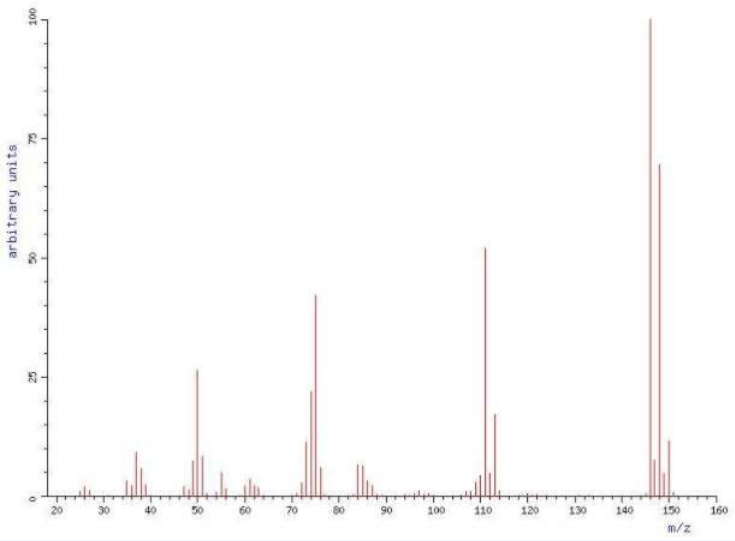
Answer

1-pentanol

Although this could be deduced solely on the molar mass, it is the only compound that would likely see any loss of a butyl group.

Exercise 1.7.6.7

The compound below has a degree of unsaturation of 4 and contains two halogen atoms. Identify the molecular ion in the mass spectrum shown below.



Hint

You may want to think about the mass of halogen atoms and the relative ratios of the isotopes to help narrow down the formula. Remember, there are two halogen atoms which will impact the expected distribution of the peaks.

Answer

146

Exercise 1.7.6.8

Which compound is most likely present in Exercise **1.7.6.7**?

difluorobenzene

dichlorbenzene

dibromobenzene

diiodobenzene

Answer

dichlorobenzene

Exercise 1.7.6.9

Does the group of peaks around m/z = 100 in in Exercise **1.7.6.7** still contain a halogen atom? Why or why not?

Hint

Think about the halogen that is present and the distribution of the isotopes.

Answer

Yes, the 3:1 ratio common for chlorine is still present. One could also consider the mass of the fragment.

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CHAPTER OVERVIEW

2: Infrared Spectroscopy

Infrared Spectroscopy is the analysis of infrared light interacting with a molecule. This can be analyzed in three ways by measuring absorption, emission and reflection. The main use of this technique is in organic and inorganic chemistry. It is used by chemists to determine functional groups in molecules. IR Spectroscopy measures the vibrations of atoms, and based on this it is possible to determine the functional groups.5 Generally, stronger bonds and light atoms will vibrate at a high stretching frequency (wavenumber).

2.1: Infrared Spectroscopy - Background
2.2: How an FTIR Spectrometer Operates
2.3: IR Spectroscopy - Theory
2.4: IR Spectroscopy - Interpretation
2.4.1: Carbon Nitrogen Bonds
2.4.2: IR10. More Practice with IR Spectra
2.4.3: IR11. Appendix- IR Table of Organic Compounds
2.4.4: IR2. Hydrocarbon Spectra
2.4.5: IR3. Subtle Points of IR Spectroscopy
2.4.6: IR4. Carbon Carbon Multiple Bonds
2.4.7: IR5. Carbon Oxygen Single Bonds
2.4.8: IR6. Carbon Oxygen Double Bonds
2.4.9: IR8. More Complicated IR Spectra
2.4.10: IR9. Misleading Peaks
2.4.11: What Does an IR Spectrum Look Like?

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2.1: Infrared Spectroscopy - Background

Infrared spectroscopy, an analytical technique that takes advantage of the vibrational transitions of a molecule, has been of great significance to scientific researchers in many fields such as protein characterization, nanoscale semiconductor analysis and space exploration.

Introduction

Infrared spectroscopy is the study of interaction of infrared light with matter, which can be used to identify unknown materials, examine the quality of a sample or determine the amount of components in a mixture. Infrared light refers to electromagnetic radiation with wavenumber ranging from 13000 – 10 cm^{-1} (corresponding wavelength from 0.78 – 1000 μm). Infrared region is further divided into three subregions: near-infrared (13000 – 4000 cm^{-1} or 0.78 – 2.5 μm), mid-infrared (4000 – 400 cm^{-1} or 2.5 – 25 μm) and far-infrared (400 – 10 cm^{-1} or 25 – 1000 μm). The most commonly used is the middle infrared region, since molecules can absorb radiations in this region to induce the vibrational excitation of functional groups. Recently, applications of near infrared spectroscopy have also been developed.

By passing infrared light through a sample and measuring the absorption or transmittance of light at each frequency, an infrared spectrum is obtained, with peaks corresponding to the frequency of absorbed radiation. Since all groups have their characteristic vibrational frequencies, information regarding molecular structure can be gained from the spectrum. Infrared spectroscopy is capable of analyzing samples in almost any phase (liquid, solid, or gas), and can be used alone or in combination with other instruments following different sampling procedures. Besides fundamental vibrational modes, other factors such as overtone and combination bands, Fermi resonance, coupling and vibration-rotational bands also appear in the spectrum. Due to the high information content of its spectrum, infrared spectroscopy has been a very common and useful tool for structure elucidation and substance identification.

Instrumentation

Most commonly used instruments in infrared spectroscopy are dispersive infrared spectrometer and Fourier transform infrared spectrometer.

Dispersive infrared spectrometer

A dispersive infrared spectrometer is mainly composed of radiation source, monochromator and detector. For mid-infrared region, Globar (silicon carbide), Nernst glower (oxides of zirconium, yttrium and erbium) and metallic helices (chromium-nickel alloy or tungsten) are frequently used as radiation sources. Tungsten-halogen lamps and metallic conductors coated with ceramic are utilized as sources for near-infrared region. A mercury high-pressure lamp is suitable for far-infrared region.

Monochromator in conjunction with slits, mirrors and filters separates the wavelengths of light emitted. The dispersive elements within monochromator are prisms or gratings. Gratings have gradually replaced prisms due to their comparatively low cost and good quality. As shown in **Figure 1**, radiation passes through both a sample and a reference path. Then the beams are directed to a diffraction grating (splitter), which disperses the light into component frequencies and directs each wavelength through a slit to the detector. The detector produces an electrical signal and results in a recorder response.

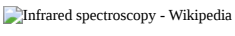


Figure 1. Schematic illustration of dispersive infrared spectrometer. Figure from Wikipedia.

Two types of detectors are employed in dispersive infrared spectrometer, namely, thermal detectors and photon detectors. Thermal detectors include thermocouples, thermistors, and pneumatic devices, which measure the heating effect generated by infrared radiation. Photon detectors are semiconductor-based. Radiation is able to promote electrons in photon detectors from valence band to conduction band, generating a small current. Photon detectors have faster response and higher sensitivity than do thermal detectors but are more susceptible to thermal noise.

Fourier transform infrared spectrometer

Dispersive infrared spectrometer has many limitations because it examines component frequencies individually, resulting in slow speed and low sensitivity. Fourier transform infrared (FTIR) spectrometer is preferred over dispersive spectrometer, since it is

capable of handling all frequencies simultaneously with high throughput, reducing the time required for analysis. The radiation sources used in dispersive infrared spectrometer can also be used in FTIR spectrometer.

In contrast with the monochromator in dispersive spectrometer, FTIR spectrometer as shown in **Figure 2** employs an interferometer. The beamsplitter within the interferometer splits the incoming infrared beam into two beams, one of which is reflected by a fixed mirror, while the other one reflected by a moving mirror perpendicular to the fixed one. The length of path one beam travels is fixed and that of the other one is changing as the mirror moves, generating an optical path difference between the two beams. After meeting back at the beamsplitter, the two beams recombine, interfere with each other, and yield an interferogram. The interferogram produces inference signal as a function of optical path difference. It is converted to a spectrum of absorbance or transmittance versus wavenumber or frequency by Fourier transform.



Figure 2. Schematic representation of Fourier transform infrared spectrometer. Figure from Wikipedia.

Detectors used in FTIR spectrometers are mainly pyroelectric and photoconductive detectors. The former are constructed of crystalline materials (such as deuterated triglycine sulfate) whose electric polarization rely on temperature. The change in temperature leads to change in charge distribution of the detector and electric signal is produced. The latter (such as mercury cadmium telluride) provide better sensitivity and faster speed than do pyroelectric detectors over a broad spectral range. However, liquid nitrogen is needed for cooling of photoconductive detectors.

Application

Since different molecules with different combination of atoms produce their unique spectra, infrared spectroscopy can be used to qualitatively identify substances. In addition, the intensity of the peaks in the spectrum is proportional to the amount of substance present, enabling its application for quantitative analysis.

Qualitative analysis

For qualitative identification purposes, the spectrum is commonly presented as transmittance versus wavenumber. Functional groups have their characteristic fundamental vibrations which give rise to absorption at certain frequency range in the spectrum (**Figure 3**).

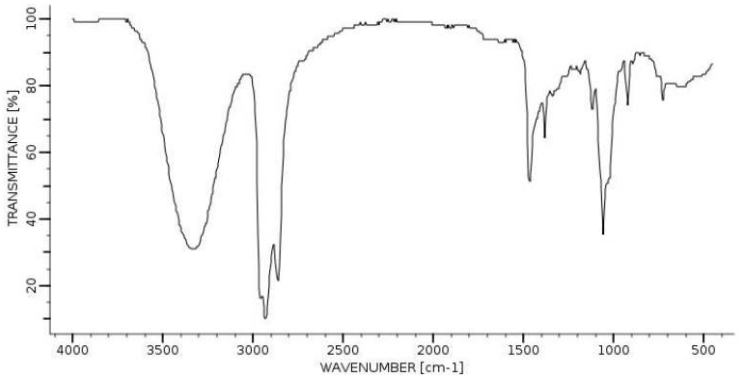


Figure 3. Infrared spectrum of 1-hexanol.

Each band in a spectrum can be attributed to stretching or bending mode of a bond. Almost all the fundamental vibrations appear in the mid-infrared region. For instance, 4000 – 2500 cm^{-1} region usually can be assigned to stretching modes of O-H, N-H or C-H. Triple-bond stretching modes appear in the region of 2500 – 2000 cm^{-1}. C=C and C=O stretching bands fall in the 2000 – 1500 cm^{-1} region. Hence, characterization of functional groups in substances according to the frequencies and intensities of absorption peaks is feasible, and also structures of molecules can be proposed. This method is applicable to organic molecules, inorganic molecules, polymers, etc. A detailed frequency list of functional groups is shown in **Figure 4**. Note that several functional groups may absorb at the same frequency range, and a functional group may have multiple-characteristic absorption peaks, especially for 1500 – 650 cm^{-1}, which is called the fingerprint region.

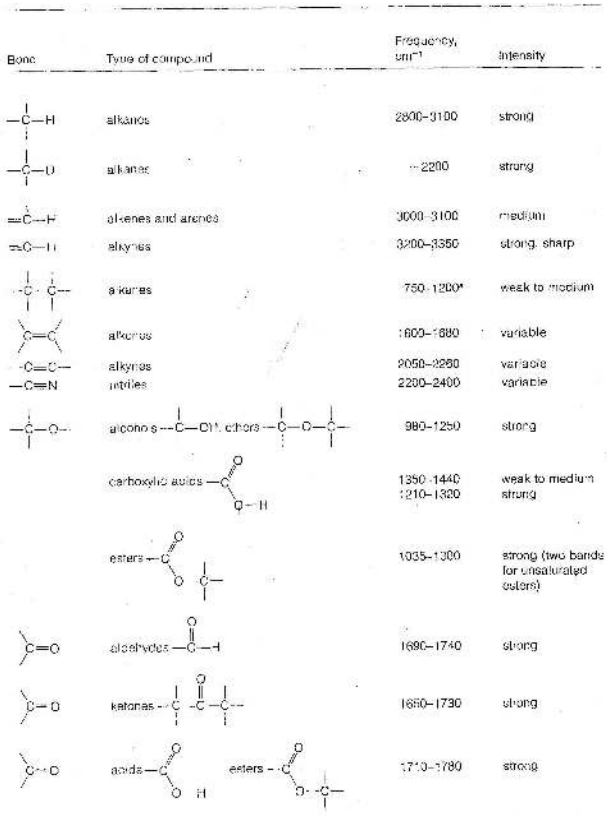


Figure 4. Characteristic infrared absorption frequencies.

Bands in the near-infrared region are overtones or combination bands. They are weak in intensity and overlapped, making them not as useful for qualitative analysis as those in mid-infrared region. However, absorptions in this region are helpful in exploiting information related to vibrations of molecules containing heavy atoms, molecular skeleton vibrations, molecular torsions and crystal lattice vibrations.

Besides structural elucidation, another qualitative application of infrared spectroscopy is the identification of a compound with a reference infrared spectrum. If all the peaks of the unknown match those of the reference, the compound can be identified. Additional reference spectra are available online at databases such as NIST Chemistry WebBook.

Quantitative analysis

Absorbance is used for quantitative analysis due to its linear dependence on concentration. Given by Beer-Lambert law, absorbance is directly proportional to the concentration and pathlength of sample:

$$A = \epsilon c l \tag{2.1.1}$$

where A is absorbance, ε the molar extinction coefficient or molar absorptivity which is characteristic for a specific substance, c the concentration and l the pathlength (or the thickness) of sample. The conversion from transmittance to absorbance is given by

$$A = -\log T \tag{2.1.2}$$

where T is transmittance.

For quantitative analysis of liquid samples, usually an isolated peak with high molar absorptivity that appears in the spectrum of the compound is chosen. A calibration curve of absorbance at the chosen frequency against concentration of the compound is acquired by measuring the absorbance of a series of standard compound solution with known concentrations. These data are then graphed to get a linear plot, from which the concentration of the unknown can be calculated after measuring its absorbance at the same frequency. The number of functional groups can also be calculated in this way, since the molar absorptivity of the band is proportional to the number of functional groups that are present in the compound.

For solid samples, an internal standard with a constant known amount is added to the unknown sample and the standards. Then similar procedures as those with liquid samples are carried out except that the calibration curve is a graph of the ratio of absorbance of analyte to that of the internal standard versus concentration of the analyte.

A multi-component analysis of the mixture is also feasible since different components have different values of molar absorptivity at the same frequency.

However, infrared spectroscopy may be more susceptible to deviation from Beer's law than is UV-Vis spectroscopy because of its narrow bands, complex spectra, weak incident beam, low transducer sensitivity and solvent absorption.

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Outside Links

- NIST Chemistry WebBook: http://webbook.nist.gov/
- Wikipedia: http://en.Wikipedia.org/wiki/Infrared_spectroscopy

Contributor

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2.2: How an FTIR Spectrometer Operates

FTIR spectrometers (Fourier Transform Infrared Spectrometer) are widely used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis. In addition, since FTIR spectrometers can be hyphenated to chromatography, the mechanism of chemical reactions and the detection of unstable substances can be investigated with such instruments.

Introduction

The range of Infrared region is 12800 ~ 10 cm^{-1} and can be divided into near-infrared region (12800 ~ 4000 cm^{-1}), mid-infrared region (4000 ~ 200 cm^{-1}) and far-infrared region (50 ~ 1000 cm^{-1}). The discovery of infrared light can be dated back to the 19th century. Since then, scientists have established various ways to utilize infrared light. Infrared absorption spectroscopy is the method which scientists use to determine the structures of molecules with the molecules' characteristic absorption of infrared radiation. Infrared spectrum is molecular vibrational spectrum. When exposed to infrared radiation, sample molecules selectively absorb radiation of specific wavelengths which causes the change of dipole moment of sample molecules. Consequently, the vibrational energy levels of sample molecules transfer from ground state to excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The number of absorption peaks is related to the number of vibrational freedom of the molecule. The intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels. Therefore, by analyzing the infrared spectrum, one can readily obtain abundant structure information of a molecule. Most molecules are infrared active except for several homonuclear diatomic molecules such as O_2, N_2 and Cl_2 due to the zero dipole change in the vibration and rotation of these molecules. What makes infrared absorption spectroscopy even more useful is the fact that it is capable to analyze all gas, liquid and solid samples. The common used region for infrared absorption spectroscopy is 4000 ~ 400 cm^{-1} because the absorption radiation of most organic compounds and inorganic ions is within this region.

FTIR spectrometers are the third generation infrared spectrometer. FTIR spectrometers have several prominent advantages: (1) The signal-to-noise ratio of spectrum is significantly higher than the previous generation infrared spectrometers. (2) The accuracy of wavenumber is high. The error is within the range of ± 0.01 cm^{-1}. (3) The scan time of all frequencies is short (approximately 1 s). (4) The resolution is extremely high (0.1 ~ 0.005 cm^{-1}). (5) The scan range is wide (1000 ~ 10 cm^{-1}). (6) The interference from stray light is reduced. Due to these advantages, FTIR Spectrometers have replaced dispersive IR spectrometers.

Development of IR Spectrometers

Up till FTIR spectrometers, there have been three generations of IR spectrometers.

1. The first generation IR spectrometer was invented in late 1950s. It utilizes prism optical splitting system. The prisms are made of NaCl. The requirement of the sample's water content and particle size is extremely strict. Further more, the scan range is narrow. Additionally, the repeatability is fairly poor. As a result, the first generation IR spectrometer is no longer in use.
2. The second generation IR spectrometer was introduced to the world in 1960s. It utilizes gratings as the monochrometer. The performance of the second generation IR spectrometer is much better compared with IR spectrometers with prism monochrometer, But there are still several prominent weaknesses such as low sensitivity, low scan speed and poor wavelength accuracy which rendered it out of date after the invention of the third generation IR spectrometer.
3. The invention of the third generation IR spectrometer, Fourier transform infrared spectrometer, marked the abdication of monochrometer and the prosperity of interferometer. With this replacement, IR spectrometers became exceptionally powerful. Consequently, various applications of IR spectrometer have been realized.

Dispersive IR Spectrometers

To understand the powerfulness and usefulness of FTIR spectrometer, it is essential to have some background information of dispersive IR Spectrometer. The basic components of a dispersive IR spectrometer include a radiation source, monochromator, and detector. The common IR radiation sources are inert solids that are heated electrically to promote thermal emission of radiation in the infrared region of the electromagnetic spectrum. The monochromator is a device used to disperse or separate a broad spectrum of IR radiation into individual narrow IR frequencies.

Generally, dispersive spectrometers have a double-beam design with two equivalent beams from the same source passing through the sample and reference chambers as independent beams. These reference and sample beams are alternately focused on the

detector by making use of an optical chopper, such as, a sector mirror. One beam will proceed, traveling through the sample, while the other beam will pass through a reference species for analytical comparison of transmitted photon wavefront information.

After the incident radiation travels through the sample species, the emitted wavefront of radiation is dispersed by a monochromator (gratings and slits) into its component frequencies. A combination of prisms or gratings with variable-slit mechanisms, mirrors, and filters comprise the dispersive system. Narrower slits gives better resolution by distinguishing more closely spaced frequencies of radiation and wider slits allow more light to reach the detector and provide better system sensitivity. The emitted wavefront beam (analog spectral output) hits the detector and generates an electrical signal as a response.

Detectors are devices that convert the analog spectral output into an electrical signal. These electrical signals are further processed by the computer using mathematical algorithm to arrive at the final spectrum. The detectors used in IR spectrometers can be classified as either photon/quantum detectors or thermal detectors.

It is the absorption of IR radiation by the sample, producing a change of IR radiation intensity, which gets detected as an off-null signal (e.g. different from reference signal). This change is translated into the recorder response through the actions of synchronous motors. Each frequency that passes through the sample is measured individually by the detector which consequently slows the process of scanning the entire IR region. A block diagram of a classic dispersive IR spectrometer is shown in Figure **2.2.1**.

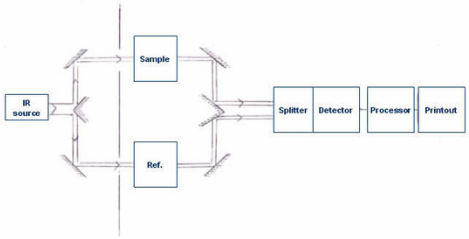


Figure **2.2.1**. Simplified representation of a dispersive IR spectrometer.

FTIR Spectrometers

The Components of FTIR Spectrometers

A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer. The source generates radiation which passes the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal by the amplifier and analog-to-digital converter, respectively. Eventually, the signal is transferred to a computer in which Fourier transform is carried out. Figure **2.2.2** is a block diagram of an FTIR spectrometer.

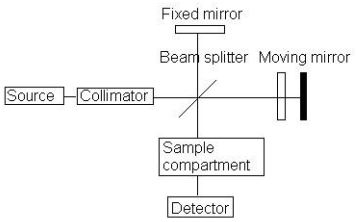


Figure **2.2.2**. Block diagram of an FTIR spectrometer

The major difference between an FTIR spectrometer and a dispersive IR spectrometer is the Michelson interferometer.

Michelson Interferometer

The Michelson interferometer, which is the core of FTIR spectrometers, is used to split one beam of light into two so that the paths of the two beams are different. Then the Michelson interferometer recombines the two beams and conducts them into the detector where the difference of the intensity of these two beams are measured as a function of the difference of the paths. Figure **2.2.3** is a schematic of the Michelson Interferometer.

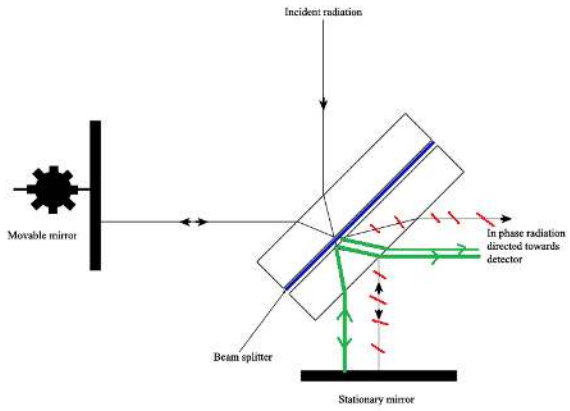


Figure **2.2.3**. Schematic of the Michelson interferometer

A typical Michelson interferometer consists of two perpendicular mirrors and a beamsplitter. One of the mirror is a stationary mirror and another one is a movable mirror. The beamsplitter is designed to transmit half of the light and reflect half of the light. Subsequently, the transmitted light and the reflected light strike the stationary mirror and the movable mirror, respectively. When reflected back by the mirrors, two beams of light recombine with each other at the beamsplitter.

If the distances travelled by two beams are the same which means the distances between two mirrors and the beamsplitter are the same, the situation is defined as zero path difference (ZPD). But imagine if the movable mirror moves away from the beamsplitter, the light beam which strikes the movable mirror will travel a longer distance than the light beam which strikes the stationary mirror. The distance which the movable mirror is away from the ZPD is defined as the mirror displacement and is represented by Δ. It is obvious that the extra distance travelled by the light which strikes the movable mirror is 2Δ. The extra distance is defined as the optical path difference (OPD) and is represented by delta. Therefore,

$$\delta = 2\Delta \tag{2.2.1}$$

It is well established that when OPD is the multiples of the wavelength, constructive interference occurs because crests overlap with crests, troughs with troughs. As a result, a maximum intensity signal is observed by the detector. This situation can be described by the following equation:

$$\delta = n\lambda \tag{2.2.2}$$

with n = 0,1,2,3...

In contrast, when OPD is the half wavelength or half wavelength add multiples of wavelength, destructive interference occurs because crests overlap with troughs. Consequently, a minimum intensity signal is observed by the detector. This situation can be described by the following equation:

$$\delta = (n + \frac{1}{2})\lambda \tag{2.2.3}$$

with n = 0,1,2,3...

These two situations are two extreme situations. If the OPD is neither n-fold wavelengths nor (n+1/2)-fold wavelengths, the interference should be between constructive and destructive. So the intensity of the signal should be between maximum and minimum. Since the mirror moves back and forth, the intensity of the signal increases and decreases which gives rise to a cosine wave. The plot is defined as an interferogram. When detecting the radiation of a broad band source rather than a single-wavelength source, a peak at ZPD is found in the interferogram. At the other distance scanned, the signal decays quickly since the mirror moves back and forth. Figure **2.2.4**(a) shows an interferogram of a broad band source.

Fourier Transform of Interferogram to Spectrum

The interferogram is a function of time and the values outputted by this function of time are said to make up the time domain. The time domain is Fourier transformed to get a frequency domain, which is deconvolved to product a spectrum. Figure **2.2.4** shows the Fast Fourier transform from an interferogram of polychromatic light to its spectrum.

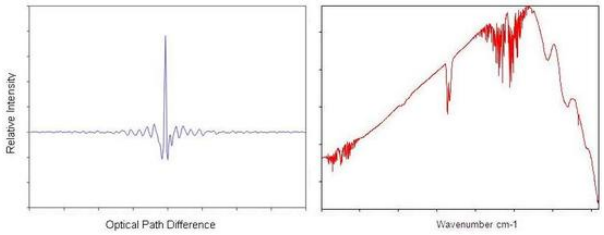


Figure **2.2.4.** (a) Interferogram of a monochromatic light; (b) its spectrum

The Fourier Transform

The first one who found that a spectrum and its interferogram are related via a Fourier transform was Lord Rayleigh. He made the discover in 1892. But the first one who successfully converted an interferogram to its spectrum was Fellgett who made the accomplishment after more than half a century. Fast Fourier transform method on which the modern FTIR spectrometer based was introduced to the world by Cooley and Turkey in 1965. It has been applied widely to analytical methods such as infrared spectrometry, nuclear magnetic resonance and mass spectrometry due to several prominent advantages which are listed in **Table 2.2.1**.

feature	improvement factor	applicable to
speed	10,000	IR, NMR, MS
signal-to-noise	100	IR, NMR, MS
automation		IR, NMR, MS
double resonance	no. coupled spins or ions	NMR, MS
resolution	10,000	MS
upper mass limit	30	MS

Table 2.2.1. Advantages of Fourier Transform over Continuous-Wave Spectrometry

Fourier transform, named after the French mathematician and physicist Jean Baptiste Joseph Fourier, is a mathematical method to transform a function into a new function. The following equation is a common form of the Fourier transform with unitary normalization constants:

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt \tag{2.2.4}$$

in which t is time, i is the square root of -1.

The following equation is another form of the Fourier transform(cosine transform) which applies to real, even functions:

$$F(\nu) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) \cos(2\pi\nu t) dt \tag{2.2.5}$$

The following equation shows how f(t) is related to F(v) via a Fourier transform:

$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\nu) \cos(2\pi\nu t) d\nu \tag{2.2.6}$$

An Alternative Explanation of the Fourier Transform in FTIR Spectrometers

The math description of the Fourier transform can be tedious and confusing. An alternative explanation of the Fourier transform in FTIR spectrometers is provided here before we jump into the math description to give you a rough impression which may help you understand the math description.

The interferogram obtained is a plot of the intensity of signal versus OPD. A Fourier transform can be viewed as the inversion of the independent variable of a function. Thus, Fourier transform of the interferogram can be viewed as the inversion of OPD. The unit of OPD is centimeter, so the inversion of OPD has a unit of inverse centimeters, cm^{-1}. Inverse centimeters are also known as

wavenumbers. After the Fourier transform, a plot of intensity of signal versus wavenumber is produced. Such a plot is an IR spectrum. Although this explanation is easy to understand, it is not perfectly rigorous.

Simplified Math Description of the Fourier Transform in FTIR

The wave functions of the reflected and transmitted beams may be represented by the general form of:

$$E_1 = rtcE_m \times \cos(\nu t - 2\pi kx) \tag{2.2.7}$$

and

$$E_1 = rtcE_m \times \cos[\nu t - 2\pi k(\nu x + \Delta d)] \tag{2.2.8}$$

where

- Δd is the path difference,
- r is the reflectance (amplitude) of the beam splitter,
- t is the transmittance, and
- c is the polarization constant.

The resultant wave function of their superposition at the detector is represented as:

$$E = E_1 + E_2 = 2(r \times t \times c \times E_m) \times \cos(\nu t - 2\pi kx)\cos(\pi k\Delta d) \tag{2.2.9}$$

where E_m, ν, and k are the amplitude, frequency and wave number of the IR radiation source.

The intensity (I) detected is the time average of E_2 and is written as

$$I = 4r^2t^2c^2E_m^2 cos^2(\nu t - 2\pi kx)\cos^2(\pi k\Delta d) \tag{2.2.10}$$

Since the time average of the first cosine term is just ½, then

$$I = 2I(k)\cos^2(\pi k\Delta d) \tag{2.2.11}$$

and

$$I(\Delta d) = I(k)[1 + \cos(2\pi k\Delta d)] \tag{2.2.12}$$

where $I(k)$ is a constant that depends only upon k and $I(\Delta d)$ is the **interferogram**.

From $I(\Delta d)$ we can get $I(k)$ using Fourier transform as follows:

$$I(\Delta d) - I(\infty) = \int_0^{k_m} I(k)\cos(2\Pi k\Delta d)dk \tag{2.2.13}$$

Letting $K_m \rightarrow \infty$, we can write

$$I(k) = \int_0^{\infty} [I(\Delta d) - I(\infty)]\cos(2\Pi k\Delta d)d\Delta d \tag{2.2.14}$$

The physically measured information recorded at the detector produces an interferogram, which provides information about a response change over time within the mirror scan distance. Therefore, the interferogram obtained at the detector is a time domain spectrum. This procedure involves sampling each position, which can take a long time if the signal is small and the number of frequencies being sampled is large.

In terms of ordinary frequency, ν, the Fourier transform of this is given by (angular frequency $\omega = s\pi\nu$):

$$f(\nu) = \int_{-\infty}^{\infty} f(t)e^{-i2\Pi\nu t}dt \tag{2.2.15}$$

The inverse Fourier transform is given by:

$$f(\nu) = \int_{-\infty}^{\infty} f(t)e^{+i2\pi\nu t}dt \tag{2.2.16}$$

The interferogram is transformed into IR absorption spectrum (Figure **2.2.5**) that is commonly recognizable with absorption intensity or % transmittance plotted against the wavelength or wavenumber. The ratio of radiant power transmitted by the sample (I) relative to the radiant power of incident light on the sample (I_0) results in quantity of Transmittance, (T). Absorbance (A) is the logarithm to the base 10 of the reciprocal of the transmittance (T):

$$A = log_{10}\frac{1}{T} = -log_{10}T = -log_{10}\frac{I}{I_0} \tag{2.2.17}$$

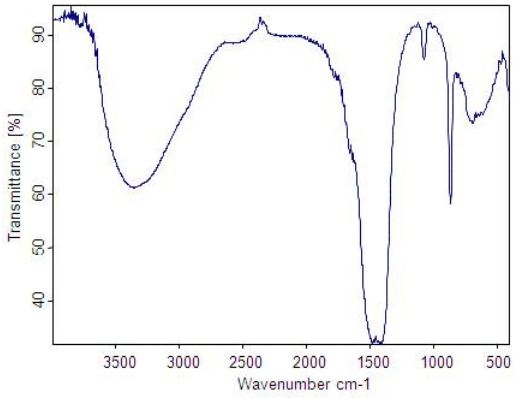


Figure **2.2.5**. IR spectrum of a sample

Hands-on Operation of an FTIR Spectrometer

Step 1: The first step is sample preparation. The standard method to prepare solid sample for FTIR spectrometer is to use KBr. About 2 mg of sample and 200 mg KBr are dried and ground. The particle size should be unified and less than two micrometers. Then, the mixture is squeezed to form transparent pellets which can be measured directly. For liquids with high boiling point or viscous solution, it can be added in between two NaCl pellets. Then the sample is fixed in the cell by skews and measured. For volatile liquid sample, it is dissolved in CS_2 or CCl_4 to form 10% solution. Then the solution is injected into a liquid cell for measurement. Gas sample needs to be measured in a gas cell with two KBr windows on each side. The gas cell should first be vacuumed. Then the sample can be introduced to the gas cell for measurement.

Step 2: The second step is getting a background spectrum by collecting an interferogram and its subsequent conversion to frequency data by inverse Fourier transform. We obtain the background spectrum because the solvent in which we place our sample will have traces of dissolved gases as well as solvent molecules that contribute information that are not our sample. The background spectrum will contain information about the species of gases and solvent molecules, which may then be subtracted away from our sample spectrum in order to gain information about just the sample. Figure **2.2.6** shows an example of an FTIR background spectrum.

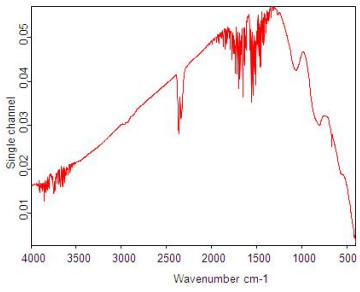


Figure **2.2.6**. Background IR spectrum

The background spectrum also takes into account several other factors related to the instrument performance, which includes information about the source, interferometer, detector, and the contribution of ambient water (note the two irregular groups of lines at about 3600 cm^{-1} and about 1600 cm^{-1} in Figure **2.2.6**) and carbon dioxide (note the doublet at 2360 cm^{-1} and sharp spike at 667 cm^{-1} in Figure **2.2.6**) present in the optical bench.

Step 3: Next, we collect a single-beam spectrum of the sample, which will contain absorption bands from the sample as well as the background (gaseous or solvent).

Step 4: The ratio between the single-beam sample spectrum and the single beam background spectrum gives the spectrum of the sample (Figure **2.2.7**).

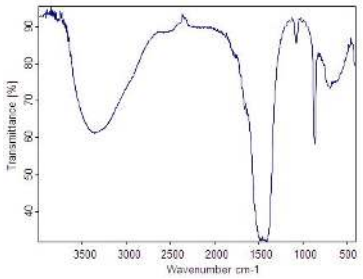


Figure **2.2.7**. Sample IR spectrum

Step 5: Data analysis is done by assigning the observed absorption frequency bands in the sample spectrum to appropriate normal modes of vibrations in the molecules.

Portable FTIR Spectrometers

Despite of the powerfulness of traditional FTIR spectrometers, they are not suitable for real-time monitoring or field use. So various portable FTIR spectrometers have been developed. Below are two examples.

Ahonen *et al* developed a portable, real-time FTIR spectrometer as a gas analyzer for industrial hygiene use. The instrument consists of an operational keyboard, a control panel, signal and control processing electronics, an interferometer, a heatable sample cell and a detector. All the components were packed into a cart. To minimize the size of the instrument, the resolution of FTIR spectrometer was sacraficed. But it is good enough for the use of industrial hygiene. The correlation coefficient of hygienic effect between the analyzer and adsorption tubes is about 1 mg/m^3.

Korb *et al* developed a portable FTIR spectrometer which only weighs about 12.5 kg so that it can be held by hand. Moreover, the energy source of the instrument is battery so that the mobility is significantly enhanced. Besides, the instrument can function well within the temperature range of 0 to 45 ^oC and the humidity range of 0 to 100%. Additionally, this instrument resists vibration. It works well in an operating helicopter. Consequently, this instrument is excellent for the analysis of radiation from the surface and atmosphere of the Earth. The instrument is also very stable. After a three-year operation, it did not lose optical alignment. The reduction of size was implemented by a creative design of optical system and accessory components. Two KBr prisms were used to constitute the interferometer cavity. Optical coatings replaced the mirrors and beam splitter in the interferometer. The optical path is shortened with a much more compact packaging of components. A small, low energy consuming interferometer drive was designed. It is also mass balanced to resist vibration. The common He-Ne tube was replaced by a smaller laser diode.

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2.3: IR Spectroscopy - Theory

This page describes what an infra-red spectrum is and how it arises from bond vibrations within organic molecules.

How an infra-red spectrum is produced

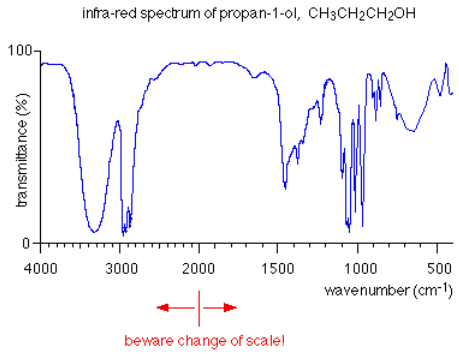
You probably know that visible light is made up of a continuous range of different electromagnetic frequencies - each frequency can be seen as a different color. Infra-red radiation also consists of a continuous range of frequencies - it so happens that our eyes can't detect them.

If you shine a range of infra-red frequencies one at a time through a sample of an organic compound, you find that some frequencies get absorbed by the compound. A detector on the other side of the compound would show that some frequencies pass through the compound with almost no loss, but other frequencies are strongly absorbed.

How much of a particular frequency gets through the compound is measured as percentage transmittance. A percentage transmittance of 100 would mean that all of that frequency passed straight through the compound without any being absorbed. In practice, that never happens - there is always some small loss, giving a transmittance of perhaps 95% as the best you can achieve. A transmittance of only 5% would mean that nearly all of that particular frequency is absorbed by the compound. A very high absorption of this sort tells you important things about the bonds in the compound.

What an infra-red spectrum looks like

A graph is produced showing how the percentage transmittance varies with the frequency of the infra-red radiation.



Notice that an unusual measure of frequency is used on the horizontal axis. Wavenumber is defined like this:

$$\text{wavenumber} = \frac{1}{\text{wavelength in cm}} \quad cm^{-1}$$

Similarly, don't worry about the change of scale half-way across the horizontal axis. You will find infra-red spectra where the scale is consistent all the way across, infra-red spectra where the scale changes at around 2000 cm^{-1}, and very occasionally where the scale changes again at around 1000 cm^{-1}. As you will see when we look at how to interpret infra-red spectra, this does not cause any problems - you simply need to be careful reading the horizontal scale.

What causes some frequencies to be absorbed?

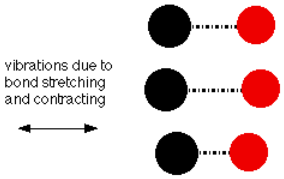
Each frequency of light (including infra-red) has a certain energy. If a particular frequency is being absorbed as it passes through the compound being investigated, it must mean that its energy is being transferred to the compound.

Energies in infra-red radiation correspond to the energies involved in bond vibrations.

Bond stretching

In covalent bonds, atoms aren't joined by rigid links - the two atoms are held together because both nuclei are attracted to the same pair of electrons. The two nuclei can vibrate backwards and forwards - towards and away from each other - around an average position.

The diagram shows the stretching that happens in a carbon-oxygen single bond. There will, of course, be other atoms attached to both the carbon and the oxygen. For example, it could be the carbon-oxygen bond in methanol, CH_3OH.

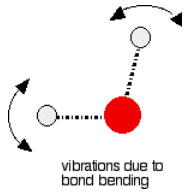


The energy involved in this vibration depends on things like the length of the bond and the mass of the atoms at either end. That means that each different bond will vibrate in a different way, involving different amounts of energy.

Bonds are vibrating all the time, but if you shine exactly the right amount of energy on a bond, you can kick it into a higher state of vibration. The amount of energy it needs to do this will vary from bond to bond, and so each different bond will absorb a different frequency (and hence energy) of infra-red radiation.

Bond bending

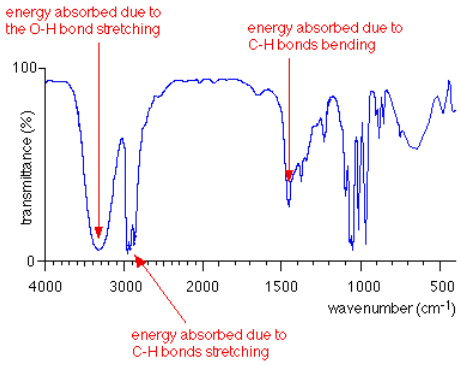
As well as stretching, bonds can also bend. The diagram shows the bending of the bonds in a water molecule. The effect of this, of course, is that the bond angle between the two hydrogen-oxygen bonds fluctuates slightly around its average value. Imagine a lab model of a water molecule where the atoms are joined together with springs. These bending vibrations are what you would see if you shook the model gently.



Again, bonds will be vibrating like this all the time and, again, if you shine exactly the right amount of energy on the bond, you can kick it into a higher state of vibration. Since the energies involved with the bending will be different for each kind of bond, each different bond will absorb a different frequency of infra-red radiation in order to make this jump from one state to a higher one.

Tying all this together

Look again at the infra-red spectrum of propan-1-ol, $CH_3CH_2CH_2OH$:



In the diagram, three sample absorptions are picked out to show you the bond vibrations which produced them. Notice that bond stretching and bending produce different troughs in the spectrum.

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SECTION OVERVIEW

2.4: IR Spectroscopy - Interpretation

This chapter will focus on infrared (IR) spectroscopy. The wavelengths found in infrared radiation are a little longer than those found in visible light. IR spectroscopy is useful for finding out what kinds of bonds are present in a molecule, and knowing what kinds of bonds are present is a good start towards knowing what the structure could be.

Topic hierarchy

2.4.1: Carbon Nitrogen Bonds

2.4.2: IR10. More Practice with IR Spectra

2.4.3: IR11. Appendix- IR Table of Organic Compounds

2.4.4: IR2. Hydrocarbon Spectra

2.4.5: IR3. Subtle Points of IR Spectroscopy

2.4.6: IR4. Carbon Carbon Multiple Bonds

2.4.7: IR5. Carbon Oxygen Single Bonds

2.4.8: IR6. Carbon Oxygen Double Bonds

2.4.9: IR8. More Complicated IR Spectra

2.4.10: IR9. Misleading Peaks

2.4.11: What Does an IR Spectrum Look Like?

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2.4.1: Carbon Nitrogen Bonds

The IR spectra of nitrogen-containing compounds can be messier than the ones you have seen so far. N-H bends and C-N stretches tend to be broader and weaker than peaks involving oxygen atoms. However, some peaks in nitrogen compounds are useful. The problems in this section will guide you through some of these features.

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2.4.2: IR10. More Practice with IR Spectra

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2.4.3: IR11. Appendix- IR Table of Organic Compounds

Table of IR Absorptions Common. Note: strong, medium, weak refers to the length of the peak (in the y axis direction). Note: spectra taken by ATR method (used at CSB/SJU) have weaker peaks between 4000-2500 cm^{-1} compared to reference spectra taken by transmittance methods (typical on SDBS and other sites).

Approximate Frequency (cm^{-1})	Description	Bond Vibration	Notes
3500 - 3200	broad, round	O-H	much broader, lower frequency (3200-2500) if next to C=O
3400-3300	weak, triangular	N-H	stronger if next to C=O
3300	medium-strong	=C-H (sp C-H)	
3100-3000	weak-medium	=C-H (sp2 C-H)	can get bigger if lots of bonds present
3000-2900	weak-medium	-C-H (sp3 C-H)	can get bigger if lots of bonds present
2800 and 2700	medium	C-H in O=C-H	two peaks; "alligator jaws"
2250	medium	C=N	
2250-2100	weak-medium	C=C	stronger if near electronegative atoms
1800-1600	strong	C=O	lower frequency (1650-1550) if attached to O or N middle frequency if attached to C, H higher frequency (1800) if attached to Cl
1650-1450	weak-medium	C=C	lower frequency (1600-1450) if conjugated (i.e. C=C-C=C) often several if benzene present
1450	weak-medium	H-C-H bend	
1300 - 1000	medium-strong	C-O	higher frequency (1200-1300) if conjugated (i.e. O=C-O or C=C-O)
1250-1000	medium	C-N	
1000-650	strong	C=C-H bend	often several if benzene present

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2.4.4: IR2. Hydrocarbon Spectra

All organic and biological compounds contain carbon and hydrogen, usually with various other elements as well. Hydrocarbons are compounds containing only carbon and hydrogen, but no other types of atoms. Since all organic compounds contain carbon and hydrogen, looking at hydrocarbon spectra will tell us what peaks are due to the basic C&H part of these molecules. It is sometimes useful to think of the C&H part of a molecule as the basic skeleton or scaffolding used to construct the molecule. The other atoms often form more interesting and active features, like the doors, windows and lights on a building.

The simplest hydrocarbons contain only single bonds between their carbons, and no double or triple bonds. These hydrocarbons are variously referred to as saturated hydrocarbons, paraffins or alkanes. Examples of alkanes include hexane and nonane. (You can take a look at the Glossary to see what these names tell you about the structure.)



hexane

Look at the IR spectrum of hexane. You should see:

- Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

  If you look at an IR spectrum of any other alkane, you will also see peaks at about 2900 and 1500 cm^{-1}. The IR spectra of many organic compounds will show these peaks because the compound may contain paraffinic parts in addition to parts with other elements in them.

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2.4.5: IR3. Subtle Points of IR Spectroscopy

Alkanes show two sets of peaks in the IR spectrum. Alkanes contain two kinds of bonds: C-C bonds and C-H bonds. However, these two facts are not related. The reasons are explained through bond polarity and molecular vibrations.

Bond polarity can play a role in IR spectroscopy.

- Molecular vibrations play a major role in IR spectroscopy.
  - The factors that govern what bonds (and what vibrations) show up at what frequencies are easily handled by computational chemistry software. In fact, prediction of absorption frequencies in IR spectra can be done using 17^{th} century classical mechanics, specifically Hooke's Law (devised to explain the vibrational frequencies of springs). Computation is not the focus of this chapter but it may help you keep track of what kinds of vibrations absorb at what frequencies.

    Hooke's Law states:

    - IR light is absorbed if it is in resonance with a vibrating bond; that means the light's frequency is the same as the frequency of the bond vibration, or else an exact multiple of it (2x, 3x, 4x...). It's a little like pushing a child on a swing: unless you are pushing at the same frequency that the swing is swinging, you will not be able to transfer your energy to the swing.

      Hooke's Law in IR spectroscopy means:

      - Remember, there are two factors here, so you won't be able to make predictions knowing only one factor. Some strong bonds may not absorb at high frequency because they are between heavy atoms. The information is presented mostly to help you organize what bonds absorb at what general frequencies after you have learned about them.

        The reasons explaining why C-H bending vibrations are at lower frequency than C-H stretching vibrations are also related to Hooke's Law. An H-C-H bending vibration involves three atoms, not just two, so the mass involved is greater than in a C-H stretch. That means lower frequency. Also, it turns out that the "stiffness" of a bond angle (analogous to the strength of a spring) is less than the "stiffness" of a bond length; the angle has a little more latitude to change than does the length. Both factors lead to a lower bending frequency.

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2.4.6: IR4. Carbon Carbon Multiple Bonds

Unsaturated hydrocarbons contain only carbon and hydrogen, but also have some multiple bonds between carbons. One type of unsaturated hydrocarbon is an olefin, also known as an alkene. Alkenes contain double bonds between carbons. One example of an alkene is 1-heptene. It looks similar to hexane, except for the double bond from the first carbon to the second.

1-heptene

Look at the IR spectrum of 1-heptene. You should see:

- Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

  So far, these peaks are the same as the ones seen for hexane. We can assign them as the C-H stretching and bending frequencies, respectively.

  Looking further, you will also see:

  - The peak at 3100 cm^{-1} hardly seems different from the C-H stretch seen before. It is also a C-H stretch, but from a different type of carbon. This stretch involves the sp^2 or trigonal planar carbon of the double bond, whereas the peak at 2900 involves an sp^3 or tetrahedral carbon.

    The peak at 1650 cm^{-1} can be identified via computational methods as arising from a carbon-carbon double bond stretch. It is a weak stretch because this bond is not very polar. Sometimes it is obscured by other, larger peaks.

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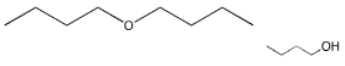
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2.4.7: IR5. Carbon Oxygen Single Bonds

These bonds are pretty polar, so they show up strongly in IR spectroscopy. IR spectroscopy is therefore a good way to determine what heteroatom-containing functional groups are present in a molecule.

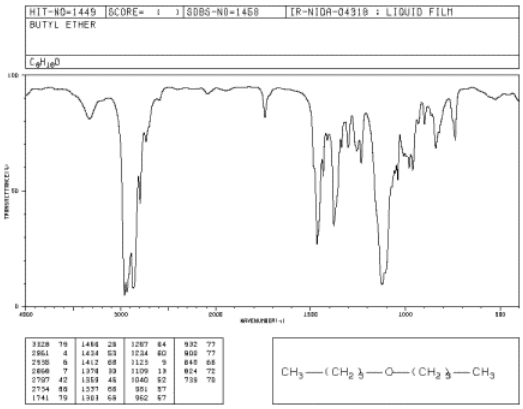
Compounds Containing C-O Single Bonds

Oxygen forms two bonds. An oxygen atom could be found in between two carbons, as in dibutyl ether, or between a carbon and a hydrogen as in 1-butanol. Dibutyl ether is an example of an ether and 1-butanol is an example of an alcohol.



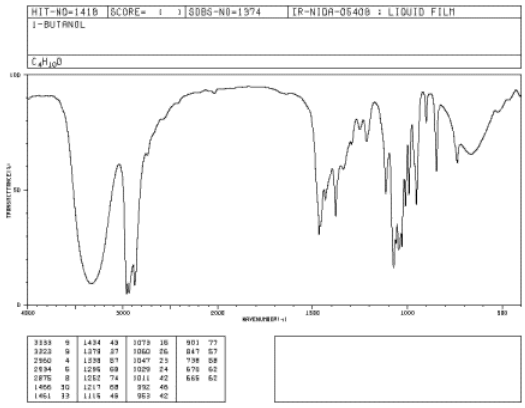
dibutyl ether or butyl ether 1-butanol

If you look at an IR spectrum of dibutyl ether, you will see:



Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

If you look at an IR spectrum of 1-butanol, you will see:



Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

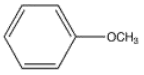
Peak shapes are sometimes very useful in recognizing what kind of bond is present. The rounded shape of most O-H stretching modes occurs because of hydrogen bonding between different hydroxy groups. Because protons are shared to varying extent with neighboring oxygens, the covalent O-H bonds in a sample of alcohol all vibrate at slightly different frequencies and show up at slightly different positions in the IR spectrum. Instead of seeing one sharp peak, you see a whole lot of them all smeared out into one broad blob. Since C-H bonds don't hydrogen bond very well, you don't see that phenomenon in an ether, and an O-H peak is very easy to distinguish in the IR spectrum.

Problem IR.7.

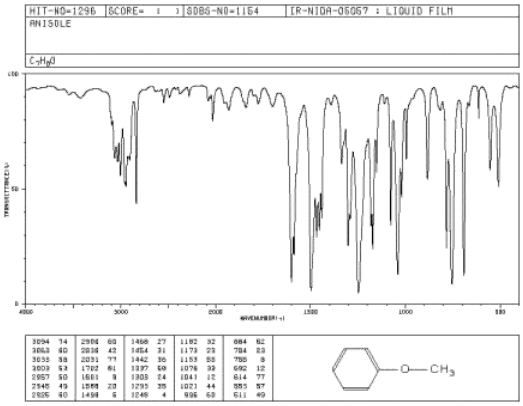
Even though there are only two C-O bonds in dibutyl ether, the C-O stretching mode is even stronger than the peak at 2900 cm^{-1} arising from 10 different C-H bonds. Explain why.

Problem IR.8.

The IR spectrum of methyl phenyl ether (aka anisole) has strong peaks at 1050 and 1250 cm^{-1}.



methoxybenzene

1. 

Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

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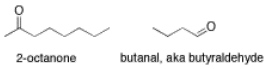
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2.4.8: IR6. Carbon Oxygen Double Bonds

The largest class of oxygen-containing molecules is carbonyl compounds, which contain C=O bonds. A C=O stretch is normally easy to find in an IR spectrum, because it is very strong and shows up in a part of the spectrum that is not cluttered with other peaks. Examples of carbonyl compounds include 2-octanone, a ketone, and butanal, an aldehyde. In an aldehyde, the carbonyl is at the end of a chain, with a hydrogen attached to the carbonyl carbon.



If you look at the IR spectrum of 2-octanone:

- Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

  Even though there is just one C=O bond, the carbonyl stretch is often the strongest peak in the spectrum. That makes carbonyl compounds easy to identify by IR spectroscopy.

  If you look at the IR spectrum of butanal:

  - Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

    The aldehyde C-H bond absorbs at two frequencies because it can vibrate in phase with the C=O bond (a symmetric stretch) and out of phase with the C=O bond (an asymmetric stretch), and these vibrations are of different energies. The probability of the symmetric stretch and the asymmetric stretch are about equal, so the two peaks are always about the same size. This unusual C-H peak can often be used to distinguish between an aldehyde and a ketone.

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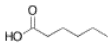
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2.4.9: IR8. More Complicated IR Spectra

Sometimes more complicated heteroatomic functional groups, containing bonds to more than one heteroatom, have slightly different spectra. Carboxylic acids feature a hydroxyl group bonded to a carbonyl. Hexanoic acid, a carboxylic acid in a six-atom chain, is one example.



hexanoic acid

If you look at the IR spectrum of hexanoic acid:

- Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

  At first, the O-H peak appears to be absent. The C-H stretch appears to be very broad. The wide peak between 3000 and 2600 cm^{-1} is really the usual C-H stretch with a broad O-H stretch superimposed on it. The low frequency vibration of this O-H bond is related to the partial dissociation of protons due to strong hydrogen bonding.

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2.4.10: IR9. Misleading Peaks

There are some practical problems that can make IR interpretation in real life more difficult. Being aware of these problems may make you double-check your suspicions:

- In addition, there are complications that you may run into based on the instrument or technique used to obtain the spectrum.
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2.4.11: What Does an IR Spectrum Look Like?

A spectrum is a graph in which the amount of light absorbed is plotted on the y-axis and frequency is plotted on the x-axis. An example is shown below. You can run your finger along the graph and see whether any light of a particular frequency is absorbed; if so, you will see a "peak" at that frequency. If not, you will see "the baseline" at that frequency.

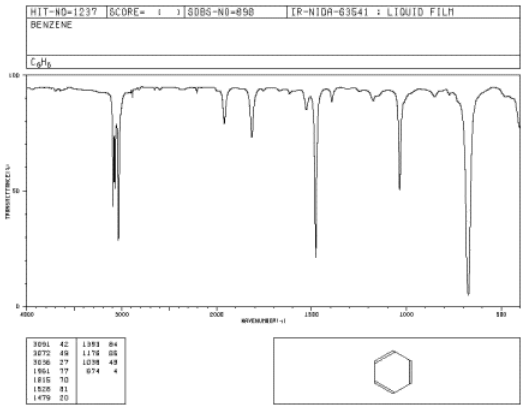


Figure IR1. IR spectrum of benzene. The x-axis labels are, from right to left, 500, 1000, 1500, 2000, 3000 and 4000 cm-1.

Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 14 July 2008)

In IR spectra (spectra = plural of spectrum):

- As you run your finger from left to right across an IR spectrum, you can see whether or not light is absorbed at particular frequencies. When the curve dips down, less light is transmitted. That means light is absorbed. The dip in the graph is called a peak. Different bonds absorb different frequencies of light, so the peaks tell you what kinds of bonds are present.

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CHAPTER OVERVIEW

3: Nuclear Magnetic Resonance Spectroscopy

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Thumbnail: A diagram of an aromatic ring current. $\boldsymbol{B_0}$ is the applied magnetic field, the red arrow indicating its direction. The orange ring shows the direction of the ring current, and the purple rings show the direction of the induced magnetic field. (Public Domain; Benjah-bmm27).

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3.1: Introduction

Magnetic resonance imaging is a medical diagnostic technique that uses radio waves to learn about the environment of hydrogen atoms in your body. As it happens, the hydrogen atoms do not respond to the radio waves unless there is a strong magnetic field present. Looking at the hydrogen atoms in your body gives the technician and the doctor information on any of the soft tissues of the body, since they are largely composed of water and contain lots of hydrogen atoms.

Nuclear magnetic resonance (NMR) is a technique that is very closely related to magnetic resonance imaging. The term "nuclear" refers to the fact that the radio waves interact with the nucleus of the hydrogen atom, or other atoms that you might be interested in studying. NMR spectroscopy is probably the most important tool available for determining the structure of organic compounds because it tells you what atoms are present and how they are connected to each other.

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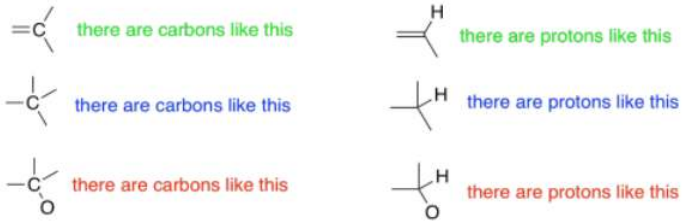
3.2: ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy is used more often than ^{13}C NMR, partly because proton spectra are much easier to obtain than carbon spectra. The ^{13}C isotope is only present in about 1% of carbon atoms, and that makes it difficult to detect. The ^{1}H isotope is almost 99% abundant, which helps make it easier to observe. Another advantage is that ^{1}H NMR spectroscopy gives more information than ^{13}C NMR, as you will find out later.

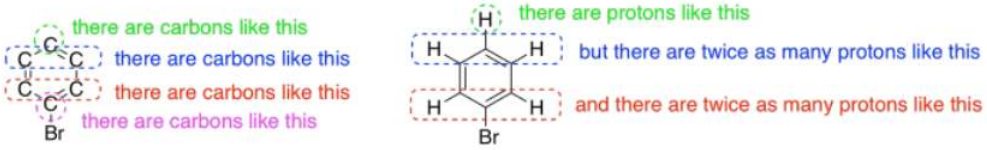
Note that in this discussion, the word "proton" is used for "hydrogen atom", because it is the proton in the nucleus of the ^{1}H isotope that is observed in these experiments. Although ^{2}H (deuterium) and ^{3}H (tritium) are also NMR-active, they absorb at frequencies that are different from the ones used in ^{1}H NMR. The ^{1}H isotope is also much more common than the other two, so ^{1}H NMR spectroscopy is more conveniently done than ^{2}H NMR spectroscopy.

^{1}H NMR spectroscopy provides more kinds of information than a typical ^{13}C NMR approach. In ^{13}C NMR spectroscopy, we get information about the environment of each unique carbon atom in a molecule. We can tell the geometry of the carbon atom by its shift, and we can also tell a little about what other atoms are nearby.

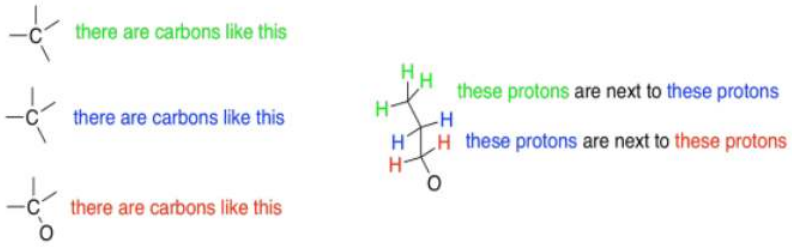
That kind of information is revealed by the chemical shift of the carbon atom -- where the peak corresponding to that carbon shows up along the x-axis of the spectrum. ^{1}H spectroscopy also gives chemical shift information, and it is very closely analogous to shift in ^{13}C spectroscopy. If you understand shift in carbon, you will understand shift in proton.



^{1}H NMR spectroscopy can be quantitative. Not only can you tell what kinds of protons are in a compound, but you can also tell how many of each you have. The spectrum might tell you that you have one proton of one kind and two identical protons of another kind. Remember in a ^{13}C spectrum, we might see two carbons that looked identical to each other because the molecule is symmetric. We might have another carbon that is different from those two. All a ^{13}C spectrum would tell you is that there were two different kinds of carbons. We would get no indication that there were actually three carbons: two of one kind and one of another. However, a ^{1}H spectrum will give that sort of detail.



^{1}H NMR spectroscopy gives us information about connectivity. In ^{13}C spectroscopy, we just know we have a bunch of different carbons in some different environments. There might be a number of different ways that those carbons could be connected together. With ^{1}H spectroscopy, it is usually much more obvious which protons go in which order throughout the molecule.



The next few sections will look at these different aspects of ^{1}H NMR spectroscopy, one at a time.

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3.3: Chemical Shift in Proton Spectra

The trends here are exactly the same as in carbon spectra. Wherever the carbon goes, it takes the proton with it. Proton spectra are only around 10 ppm wide, compared to the 200 ppm of carbon spectra, so by analogy with carbon spectra,

- hydrogens on sp^3 carbons usually show up in the upfield half of the spectrum, about 0 to 5 ppm.
- hydrogens on sp^2 carbons usually show up in the downfield half of the spectrum, about 5 to 10 ppm.
- within these two halves of the spectrum, electronegative atoms attached to the same carbon as a proton will draw that proton downfield.

So, in the spectrum of hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) all of the hydrogens are on sp^3 or tetrahedral carbons. They all show up below 5 ppm. There are no electronegative atoms around, so they are even further upfield, at 1 ppm.

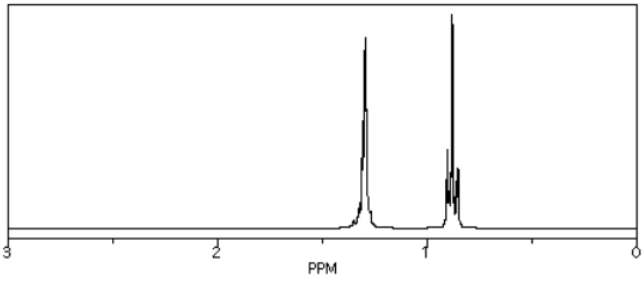
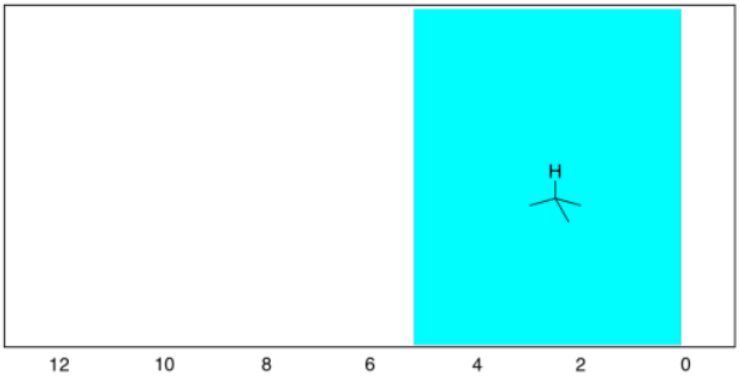


Figure **3.3.1**: ^1H NMR spectrum of hexane.

Source: Simulated spectrum.

Those peaks fall well within the expected window.



If we look at 1-hexene (CH_2=$CHCH_2CH_2CH_2CH_3$), we see a similar spectrum, but two of the peaks show up above 5 ppm. These hydrogens are on sp^2 or trigonal planar carbons. There are other, more subtle changes, but that is the main one.

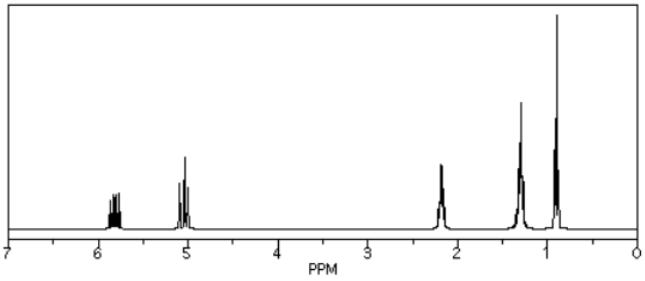
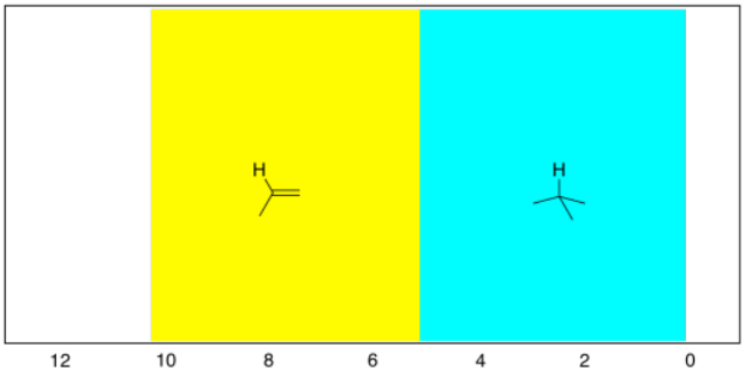


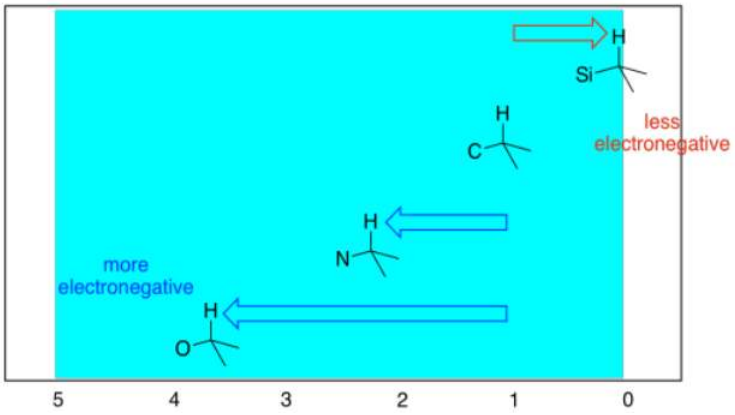
Figure **3.3.2**: ^1H NMR spectrum of 1-hexene.

Source: Simulated spectrum.

Again, the new peaks fall right around where we would expect them.

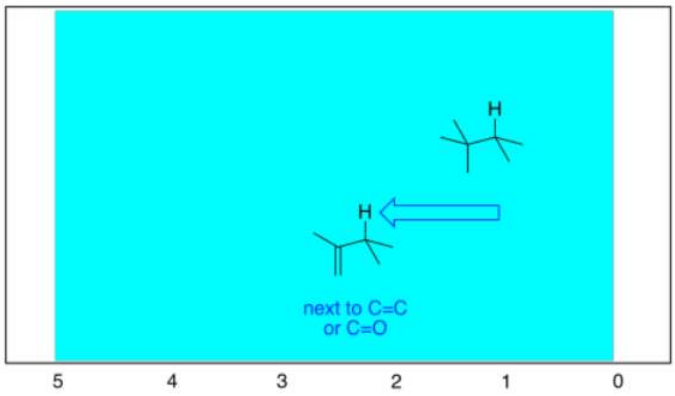


The electronegativity shifts that we saw earlier of 13C NMR spectra hold true for 1H spectra as well. The more electronegative the neighbour of the carbon on which the proton is sitting, the further the proton will be shifted to the left in the spectrum.



It can be useful to think of 1 ppm as the default position for a proton on a tetrahedral carbon, and to think of the effects of other groups as moving the peak a certain distance away from that starting point. For example, a neighbouring oxygen atom moves the peak 2.5 ppm to the left. Thinking of it that way helps you predict what will be the effect of two different attached groups. For example, if there were two oxygens attached to the carbon on which the proton is sitting, it would move 5 ppm, and end up at 6 ppm overall.

Just as in 13C NMR spectroscopy, there are more subtle effects of having sp^2 carbon neighbors nearby. Once again, that's because of the effect that the magnetic field has on the electrons in the double bond.



We see similar trends in the left-hand, sp^2 region. If we look at butanal ($CH_3CH_2CH_2CHO$), we also have several hydrogen on sp^3 carbons and one on an sp^2 carbon. The former show up below 5 ppm and the latter above 5 ppm. This time, that peak is way downfield at 10 ppm. That hydrogen is on a carbonyl carbon; being double bonded to an oxygen deshields the carbon, and its partner hydrogen a lot.

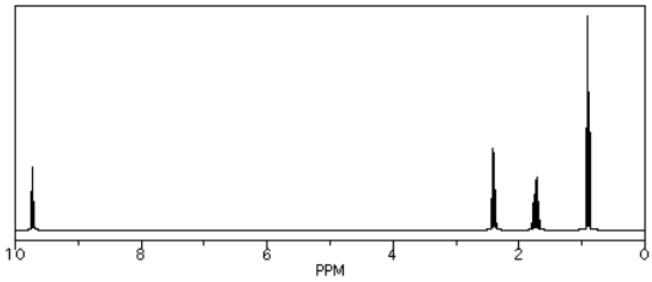
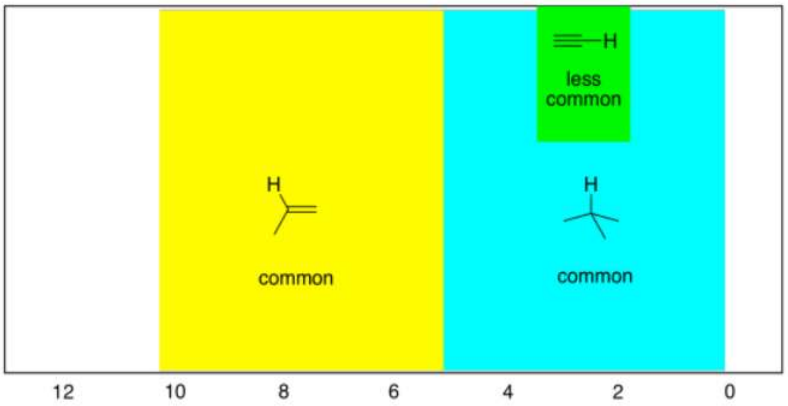


Figure **3.3.3**: ^{1}H NMR spectrum of butanal.

Source: Simulated spectrum.

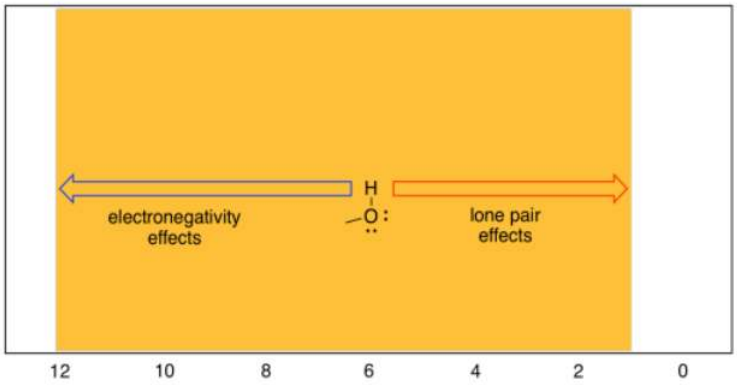
As before, there are also hydrogens on linear or sp carbons, although they are much less common than tetrahedral or trigonal carbons.

- hydrogens on sp carbons show up between 2 and 6 ppm, and most often between 2 and 3 ppm.



Remember, these are general rules that you should know. The proton in chloroform shows up at 7 ppm although it is attached to a tetrahedral carbon, because it has three different, electronegative chlorines pulling it to the left. (World-record shifts occur for hydrogens attached to transition metals: "late" metals like ruthenium or rhodium can move hydrogen peaks all the way up to -20 ppm, but "early" metals like tantalum can move them down as far as 25 ppm.)

One word of caution: students often catch on to the electronegativity rule and immediately make assumptions about OH groups that turn out not to be true. The obvious conclusion so far is that OH groups should always show up at the left hand of the spectrum, because the hydrogen is directly attached to that very electronegative oxygen. That can sometimes be true: the proton in a carboxylic acid, if it can be seen in the spectrum at all, generally shows up around 12 ppm. However, the proton in water is usually around 1.5 ppm. In fact, protons on OH groups in slightly different situations cover the entire range of the proton spectrum.



The reason for this wide range has to do with the fact that, although oxygen is very electronegative (so its neighbouring hydrogen should be electron-poor) it also posesses lone pairs. Those lone pairs have the effect of shielding the hydrogen from the magnetic

field. Thus, there are two competing effects in OH protons, and different situations tilt the balance one way or another.

Exercise 3.3.1

Indicate whether each of the following peaks in the ^{1}H NMR spectrum probably represents a hydrogen on a tetrahedral carbon (H-$C_{sp}3$) or a hydrogen on a trigonal planar carbon (H-$C_{sp}2$).

a) 1.1 ppm b) 3.4 ppm c) 7.8 ppm d) 4.2 ppm e) 5.7 ppm f) 9.9 ppm g) 2.3 ppm

Answer

a) H-$C_{sp}3$ b) H-$C_{sp}3$ c) H-$C_{sp}2$ d) H-$C_{sp}3$ e) H-$C_{sp}2$ f) H-$C_{sp}2$ g) H-$C_{sp}3$

Exercise 3.3.2

The following peaks in the ^{1}H NMR spectrum represent hydrogen atoms on tetrahedral carbons (H-$C_{sp}3$). Indicate whether that carbon is probably attached to another tetrahedral carbon, an oxygen, or a nitrogen.

a) 1.1 ppm b) 1.9 ppm c) 2.5 ppm d) 4.2 ppm e) 1.8 ppm f) 3.6 ppm g) 2.7 ppm

Answer

a) carbon b) carbon c) nitrogen d) oxygen e) carbon f) oxygen g) nitrogen

Exercise 3.3.3

Although aromatic C-H and alkene C-H are both bound to sp2 carbons the following peaks in the ^{1}H NMR spectrum probably represent hydrogen atoms on alkene carbons or aromatic carbons.

a) 7.3 ppm b) 8.3 ppm c) 5.1 ppm d) 6.2 ppm e) 5.4 ppm f) 7.8 ppm

Answer

a) aromatic b) aromatic c) alkene d) alkene e) alkene f) aromatic

Exercise 3.3.4

The following peaks in the ^{1}H NMR spectrum represent hydrogen atoms on trigonal planar carbons (H-$C_{sp}2$). Indicate whether that carbon is probably attached to another trigonal planar carbon in an aromatic ring, is single-bonded to a nitrogen in an aromatic ring, or is double-bonded to an oxygen.

a) 7.1 ppm b) 6.9 ppm c) 8.5 ppm d) 10.2 ppm e) 9.8 ppm f) 8.2 ppm g) 7.9 ppm

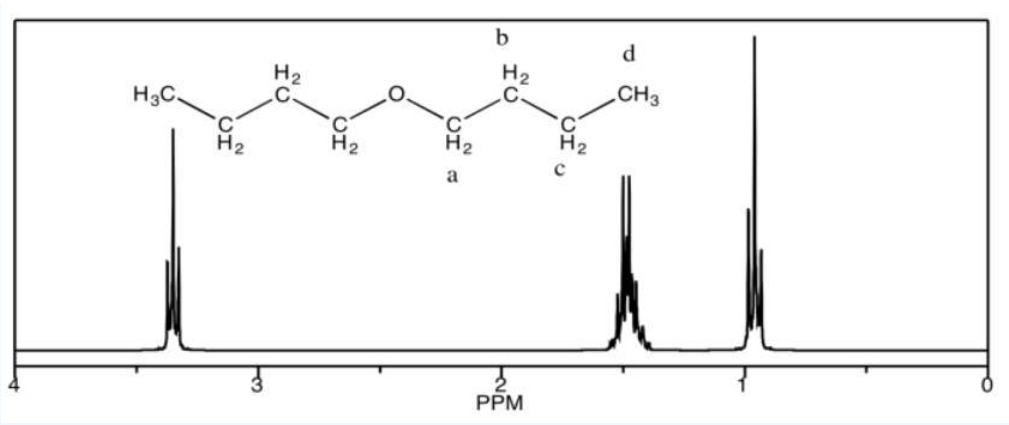
Answer

a) H-C_{Ar}-C b) H-C_{Ar}-C c) H-C_{Ar}-N d) C=O e) C=O f) H-C_{Ar}-N g) H-C_{Ar}-N

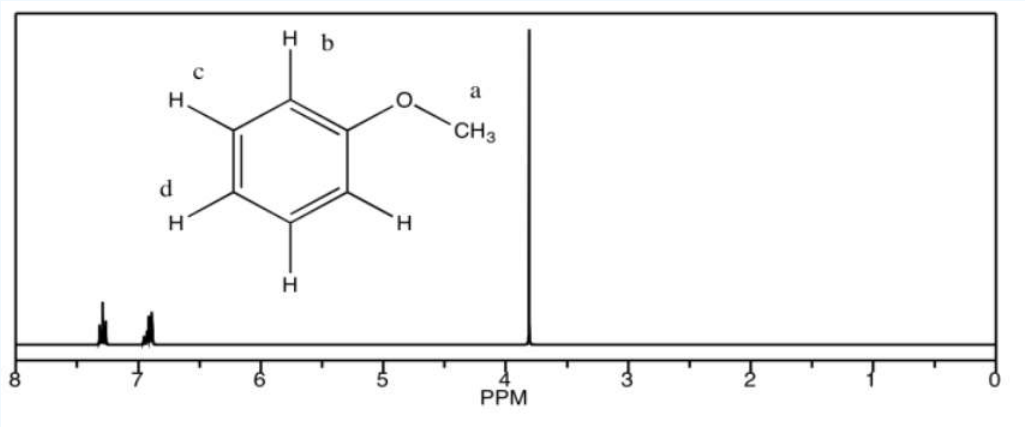
Exercise 3.3.5

Looking at the ^{1}H NMR spectra of the following compounds, indicate which peak belongs to which proton.

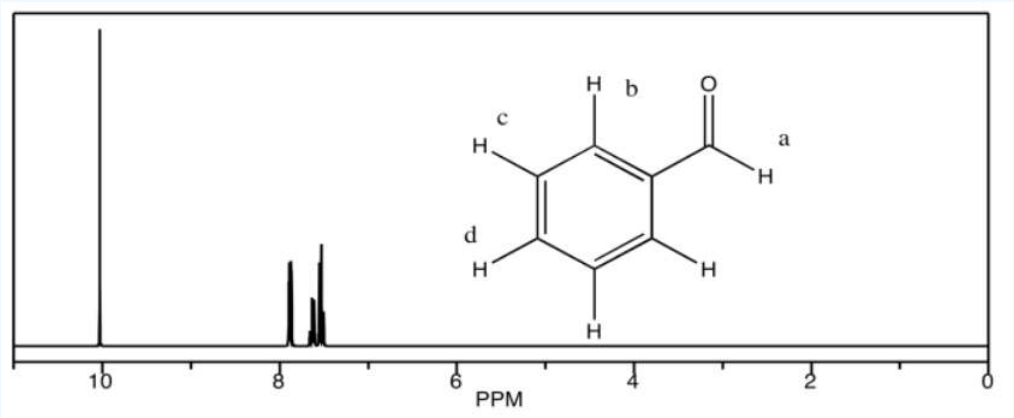
a) dibutyl ether



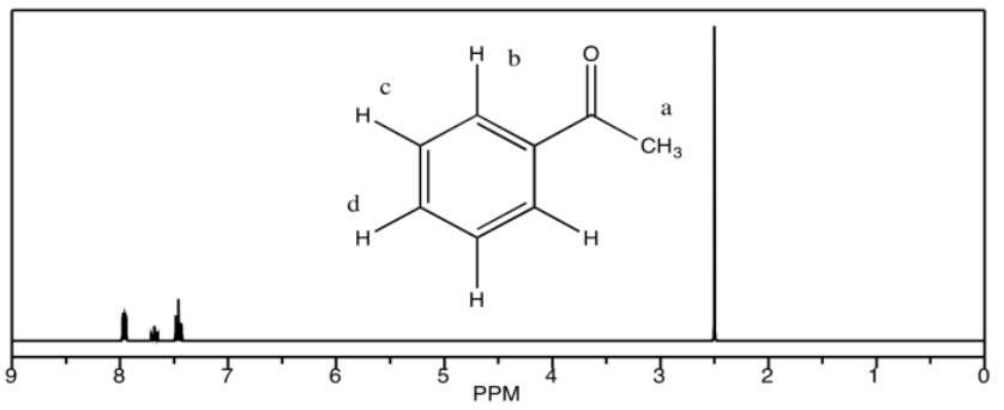
b) methyl phenyl ether



c) benzaldehyde



d) acetophenone



Answer

a) 3.4 ppm: H_a 1.5 ppm: H_b, H_c 0.9 ppm: H_d

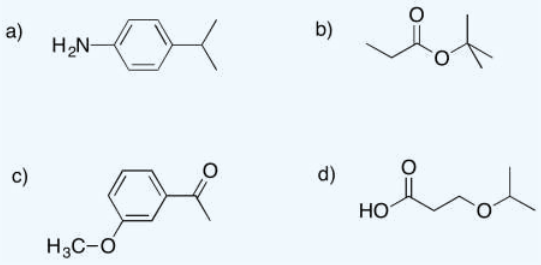
b) 7.4 ppm: H_d 6.9 ppm: H_b, H_c 3.7 ppm: H_a

c) 10.1 ppm: H_a 7.9 ppm: H_b 7.6 ppm: H_d 7.5 ppm: H_c

d) 7.9 ppm: H_b 7.6 ppm: H_d 7.4 ppm: H_c 2.5 ppm: H_a

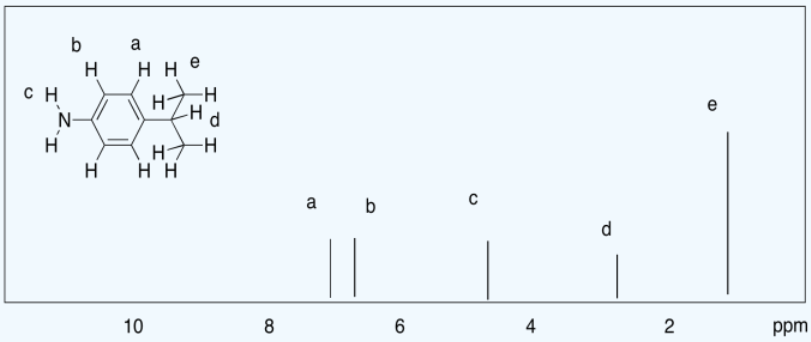
Exercise 3.3.6

Sketch a ^1H NMR spectrum for each of the following compounds, showing a simple line corresponding to the expected shift for each of the different hydrogens.

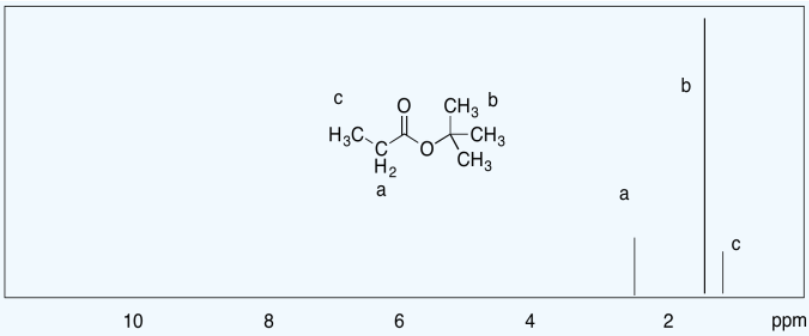


Answer

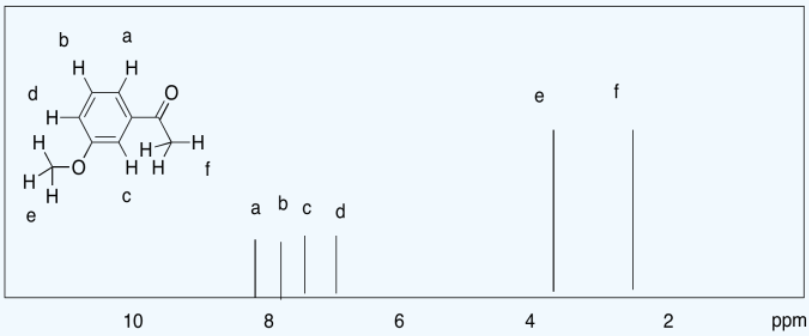
a)



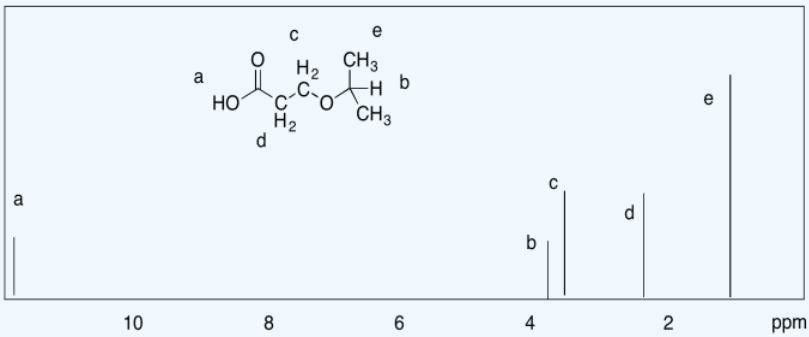
b)



c)



d)



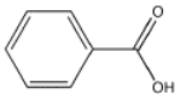
Notice that a major difference from ^{13}C NMR is that a carbon spectrum is spread out over 200 ppm, while a typical proton spectrum is compressed into about 10 ppm. There is a consequence of that difference, and it can be frustrating. It is usually easy to distinguish two different ^{13}C peaks, whereas two peaks in the ^{1}H spectrum could easily be so close together that they overlap. For example, the aliphatic hydrocarbons hexane and nonane display only two distinct peaks in the ^{1}H spectrum, one for the methyl hydrogens and one for the methylene hydrogens, because the latter are all too similar to tell apart given the limited amount of resolution in the spectrum.

- coincidental overlap of peaks in the ^{1}H spectrum is common.

There is another complication in the chemical shifts seen in ^{1}H spectroscopy, and that is the behavior of protons attached directly to heteroatoms such as oxygen and nitrogen. Oxygen is very electronegative, and hydrogen is not, so it stands to reason that an OH proton would absorb at very low field, say 10 ppm. That's completely wrong. OH protons in aliphatic alcohols show up between 2 and 6 ppm, phenolic OH protons between 5 and 9 ppm, and carboxylic acid OH protons between 11 and 12 ppm. Water shows up around 1.6 ppm when dissolved in chloroform, but if the water is present in high concentrations it can show up further downfield. Thus:

- a proton attached to oxygen shows up between 1 and 12 ppm.
- hydroxy proton shifts can vary depending on factors such as hydrogen bonding with the solvent and other molecules.

- except for carboxylic acid protons, which occur beyond the normal range of other peaks, a peak showing up at a particular shift is not strong evidence for the presence of an OH proton.



benzoic acid

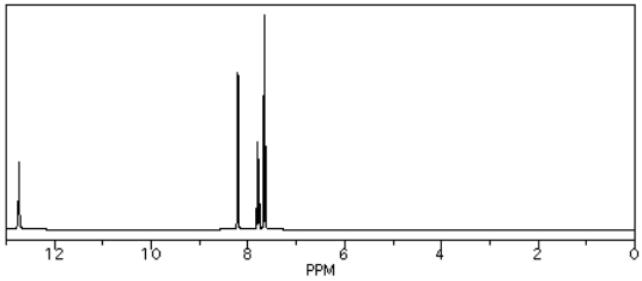


Figure **3.3.4**: ^{1}H NMR spectrum of benzoic acid.

Source: Simulated spectrum.



ethanol

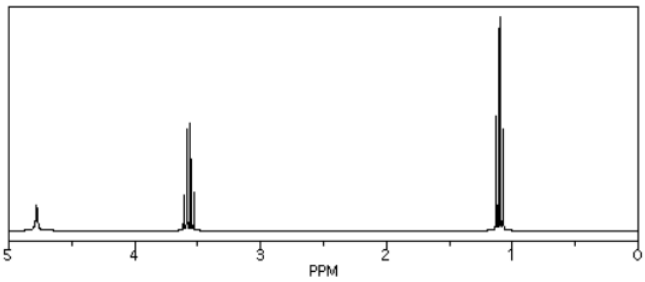


Figure **3.3.5**: ^{1}H NMR spectrum of ethanol.

Source: Simulated spectrum.

Although oxygen is very electronegative, it also has two lone pairs of electrons; those lone pairs on oxygen are often crucial in understanding chemistry. The oxygen atom does pull electron density away from the hydrogen through the sigma bond between them, but the lone pairs also bathe the nearby hydrogen in the shielding effects of their electron density. Depending on how these two factors balance out, OH and NH protons don't absorb nearly as far downfield as expected.

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3.4: Integration

There is additional information obtained from ^{1}H NMR spectroscopy that is not typically available from ^{13}C NMR spectroscopy. Chemical shift can show how many different types of hydrogens are found in a molecule; integration reveals the number of hydrogens of each type.

Looking at the spectrum of ethanol, you can see that there are three different kinds of hydrogens in the molecule. You can also see by integration that there are three hydrogens of one type, two of the second type, and one of the third type -- corresponding to the CH_3 or methyl group, the CH_2 or methylene group and the OH or hydroxyl group. That information helps narrow down the number of possible structures of the sample, and so it makes structure elucidation of an unknown sample much easier.

- integration reveals the ratio of one type of hydrogen to another within a molecule.

Integral data can be given in different forms. You should be aware of all of them. In raw form, an integral is a horizontal line running across the spectrum from left to right. Where the line crosses the frequency of a peak, the area of the peak is measured. This measurement is shown as a jump or step upward in the integral line; the vertical distance that the line rises is proportional to the area of the peak. The area is related to the amount of radio waves absorbed at that frequency, and the amount of radio waves absorbed is proportional to the number of hydrogen atoms absorbing the radio waves.

The following spectrum was recorded with a sample of ethanol in deuterochloroform ($CDCl_3$). Ethanol has the condensed formula CH_3CH_2OH. Its ^{1}H NMR spectrum should reflect a 3:2:1 ratio of hydrogens.

Those ratios are shown by the height that the blue integral line "hops" or "steps" as it passes each peak. There are three peaks in ethanol: a sharp peak near 4 ppm, a little blob near 1.5 ppm and another sharp peak near 1 ppm. The first step in the integral line, near 4 ppm, is pretty big. The second step, near 1.5 ppm, is only about half as big as the first one. The third step, near 1 ppm, looks a little bigger than the first. Without getting out a ruler, it's hard to judge exactly how big, but maybe it's 1.5 times bigger than the first.

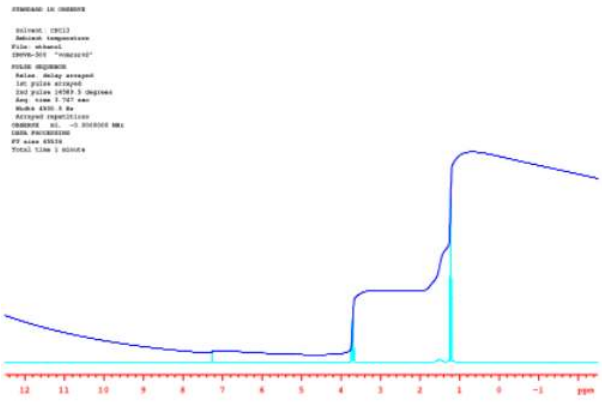


Figure 3.4.1: ^{1}H NMR spectrum of ethanol with solid integral line.

Source: Spectrum taken in $CDCl_3$ on a Varian Gemini 2000 Spectrometer with 300 MHz Oxford magnet.

That means the ratio of these peaks is 1:0.5:1.5. That's the same thing as a 2:1:3 ratio. We are probably looking at, from left to right, the CH_2, the OH and the CH_3 in the ethanol.

We'll get back to looking at that ratio within ethanol in a moment. Meanwhile, it's worth noting that there is an additional, small peak in the spectrum near 7.25 ppm. That's a little bit of regular chloroform, $CHCl_3$, in the $CDCl_3$ solvent used for the NMR spectrum. You might imagine that it's pretty difficult to separate two compounds that differ from each other only by the presence or absence of one neutron. Consequently, there is always a tiny amount of $CHCl_3$ in a bottle of $CDCl_3$. But why is that peak so tiny? nd why does the integral line barely budge upwards as it passes over the peak? If there is one H in $CHCl_3$, should its integral match the 1H in ethanol?

Let's get back to the ethanol spectrum and look at some different ways in which we can view the integration. Sometimes, the integral line is cut into separate integrals for each peak so that they can be compared to each other more easily.

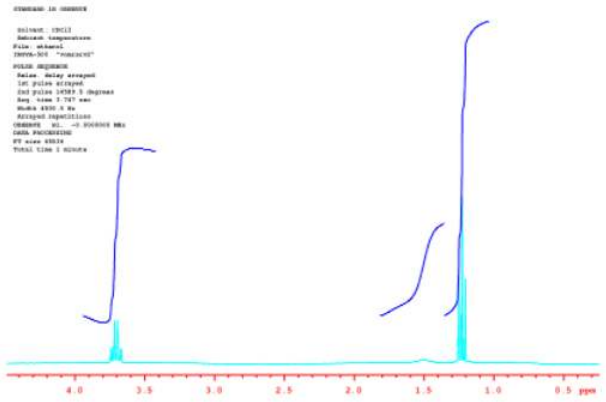


Figure **3.4.2**: ^{1}H NMR spectrum of ethanol with broken integral line.

Source: Spectrum taken in $CDCl_3$ on a Varian Gemini 2000 Spectrometer with 300 MHz Oxford magnet.

In the picture above, it's easier to see the 2:1:3 ratio between the peaks.

Often, instead of displaying raw data, the integrals are measured and their heights are displayed on the spectrum.

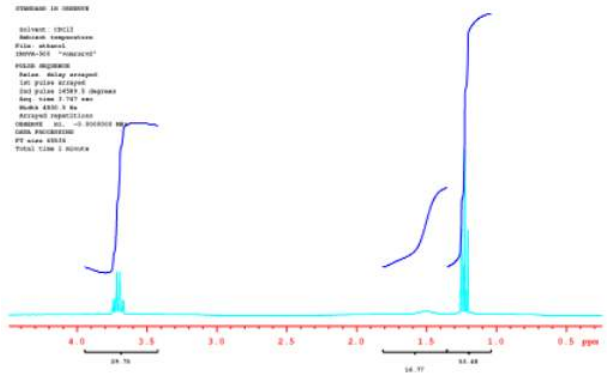


Figure **3.4.3**: ^{1}H NMR spectrum of ethanol with numerical integrals.

Source: Spectrum taken in $CDCl_3$ on a Varian Gemini 2000 Spectrometer with 300 MHz Oxford magnet.

The numbers under the spectrum read, from left to right, 29.76, then 14.99 and finally 53.48. Roughly, these numbers are 30:15:54. That's close to a 2:1:3 ratio, although 30:15:45 would be an even better fit. Note that the numerical printout we get does not exactly match the ratio we expect; in fact, it seems a little worse than the ratio we roughly estimated by eye. That's because it really is worse than the ratio we roughly measured by eye.

When you compared the integrals by eye, you were looking at an entire blue integral line and comparing it to another entire blue integral line. You were performing what is called "mulivariable analysis". Each integral line is composed of dozens or hundreds of data points. Your brain takes in all of that information and weighs it carefully to come up with an idea of how high the integral steps as it passes a peak.

It's hard to find NMR software that will perform this analysis as well as you can. It may come up with much more precise numbers than you can, but it's numbers are less trustworthy than yours. That's because the computer is just doing a two-data-point analysis; it measures the change in y coordinate from the beginning of the blue line to the end of the blue line. It's still useful, but keep in mind that it won't be dead on, especially if the ends of the integral line are tilted.

Sometimes the heights are "normalized". They are reduced to a lowest common factor so that their ratios are easier to compare. These numbers could correspond to numbers of hydrogens, or simply to their lowest common factors. Two peaks in a ratio of 1H:2H could correspond to one and two hydrogens, or they could correspond to two and four hydrogens, etc.

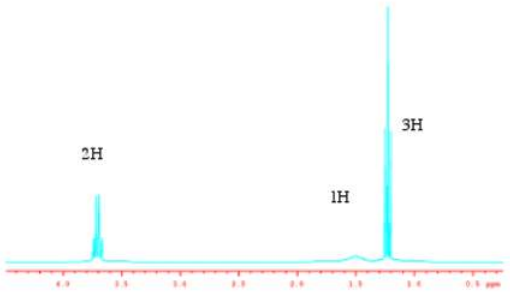


Figure **3.4.4**: ^{1}H NMR spectrum of ethanol with normalized integral numbers.

Source: Spectrum taken in $CDCl_3$ on a Varian Gemini 2000 Spectrometer with 300 MHz Oxford magnet.

Note that the ratio is nothing like a comparison of the heights of the peaks. If we were to just estimate the heights of the peaks, we might come up with something like 1:0.1:3 or 10:1:30. The integrals are measuring the total area of the peak, so the width of the peak matters as well as its height.

? Exercise 3.4.1

Because the 1H NMR spectrum has relatively low resolution, the spectra of saturated, straight-chain hydrocarbons are all similar: a peak for the methyl hydrogens at 0.9 ppm and a peak for the methylene (CH_2) hydrogens at 1.0 ppm. However, different hydrocarbons can be identified by their integration values.

Predict the integrations for the following compounds:

a) pentane b) octane c) decane d) heptane e) hexane

Answer

a) 0.9 ppm, 6H; 1.0 ppm, 6H (1:1 ratio)

b) 0.9 ppm, 6H; 1.0 ppm, 12H (1:2 ratio)

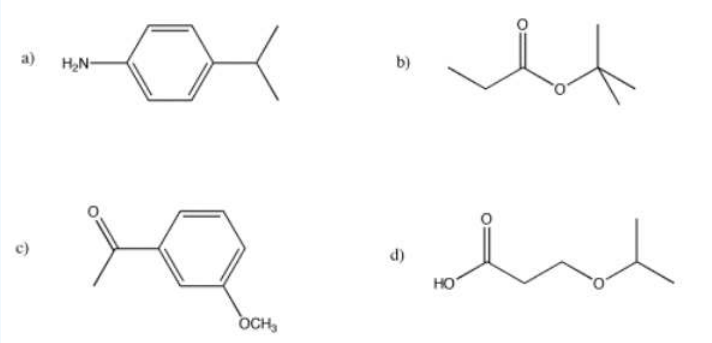
c) 0.9 ppm, 6H; 1.0 ppm, 16H (3:8 ratio)

d) 0.9 ppm, 6H; 1.0 ppm, 10H (3:5 ratio)

e) 0.9 ppm, 6H; 1.0 ppm, 8H (3:4 ratio)

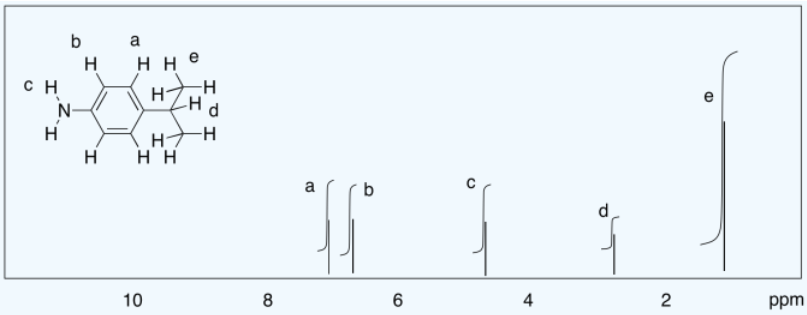
? Exercise 3.4.2

Sketch a predicted NMR spectrum for each of the following compounds, with an integral line over each peak.

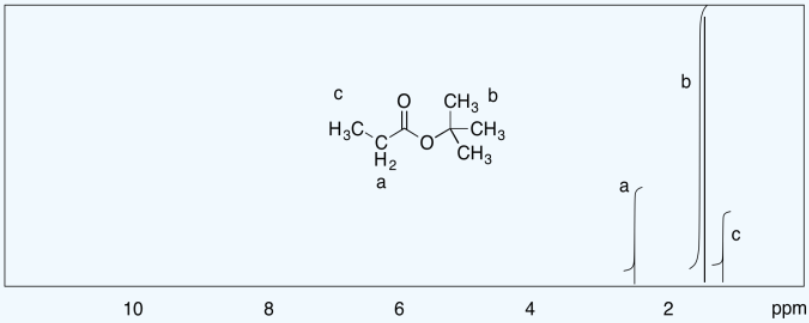


Answer

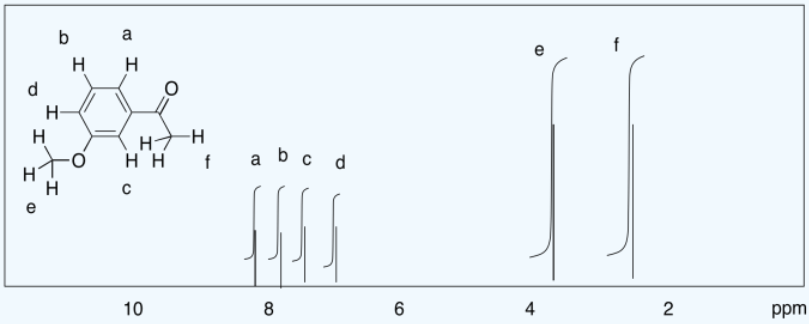
a)



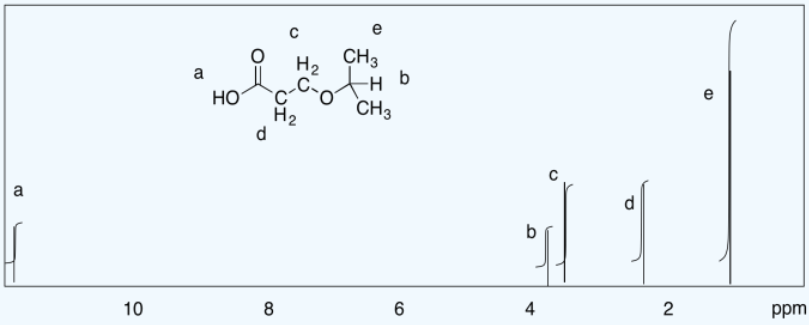
b)



c)

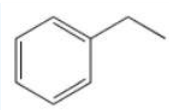


d)

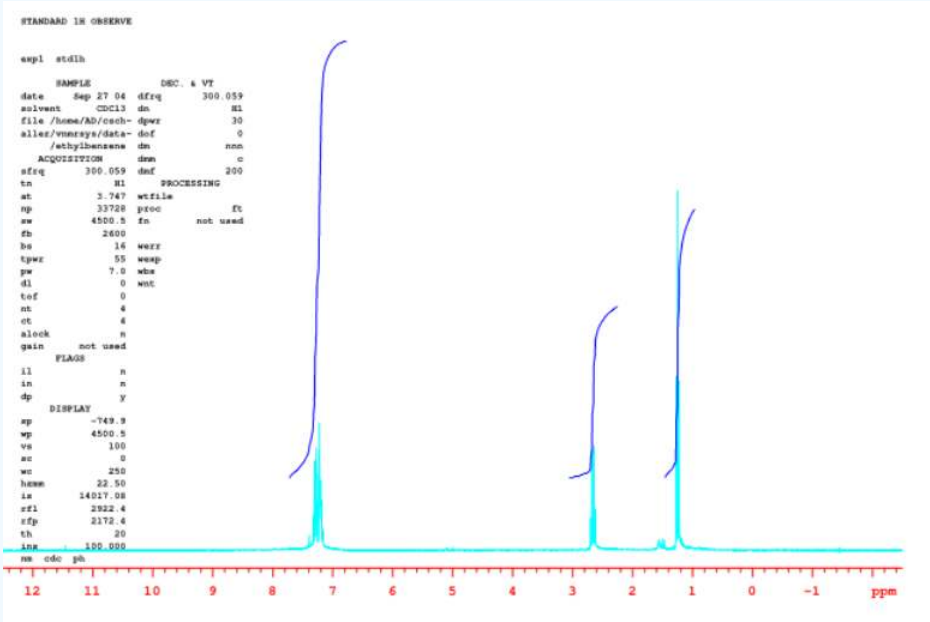


? Exercise 3.4.3

Measure the integrals in the following compounds. Given the integral ratios and chemical shifts, can you match each peak to a set of protons?



ethylbenzene



Answer

a) 5:2:3

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3.5: Multiplicity

Another type of additional data available from ^{1}H NMR spectroscopy is called multiplicity or coupling. Coupling is useful because it reveals how many hydrogens are on the *next* carbon in the structure. That information helps to put an entire structure together piece by piece.

In ethanol, CH_3CH_2OH, the methyl group is attached to a methylene group. The ^{1}H spectrum of ethanol shows this relationship through the shape of the peaks. The peak near 3.5 ppm is the methylene group with an integral of 2H.

- This peak is split into four smaller peaks, evenly spaced, with taller peaks in the middle and shorter on the outside.
- This pattern is called a multiplet, and specifically a quartet. A quartet means that these hydrogens have three neighbouring hydrogens on adjacent carbons.

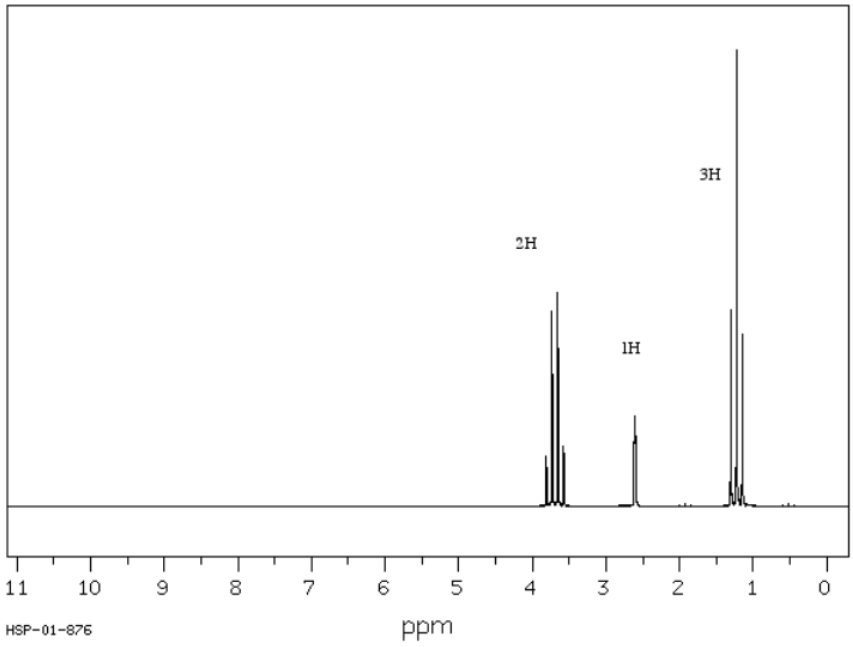


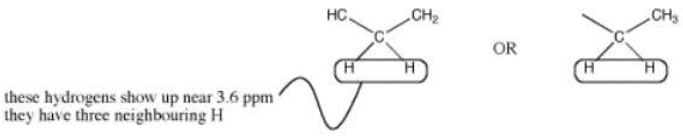
Figure **3.5.1**: .^{1}H NMR spectrum of ethanol.

Source: Modified from SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

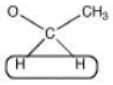
The integral of 2H means that this group is a methylene, so it has two hydrogens. The carbon bearing these two hydrogens can have two other bonds.



There could be two hydrogens on one neighbouring carbon and one on another. Otherwise, all three hydrogens could be on one neighbouring carbon.



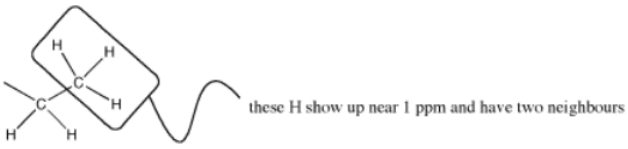
However, the shift of 3.5 ppm means that this carbon is attached to an oxygen. Mutliplicity usually only works with hydrogens on neighbouring *carbons*. If there is an oxygen on one side of the methylene, all three neighbouring hydrogens must be on a carbon on the other side.



Alternatively, look at the spectrum the other way around. The peak at 1 ppm is the methyl group with an integral of 3H.

- The peak is split into three smaller ones, evenly spaced, with a taller one in the middle and shorter ones on the outside.
- This pattern is called a triplet. A triplet means that these hydrogens have two neighbouring hydrogens on adjacent carbons.

The neighbouring H could be on two different neighbouring carbons or both on the same one.



But this group is a methyl; the carbon already has three bonds, so it can have only one neighbouring carbon. It is next to a methylene group.

The number of lines in a peak is always one more than the number of hydrogens on the neighboring carbon. The triplet for the methyl peak means that there are two neighbors on the next carbon (3 - 1 = 2H); the quartet for the methylene peak indicates that there are three hydrogens on the next carbon (4 - 1 = 3H). Table NMR 1 summarizes coupling patterns that arise when protons have different numbers of neighbors.

# of lines	ratio of lines	term for peak	# of neighbors
1	-	singlet	0
2	1:1	doublet	1
3	1:2:1	triplet	2
4	1:3:3:1	quartet	3
5	1:4:6:4:1	quintet	4
6	1:5:10:10:5:1	sextet	5
7	1:6:15:20:15:6:1	septet	6
8	1:7:21:35:35:21:7:1	octet	7
9	1:8:28:56:70:56:28:8:1	nonet	8

The third peak in the ethanol spectrum is usually a "broad singlet". This is the peak due to the OH. You would expect it to be a triplet because it is next to a methylene. Under very specific circumstances, it does appear that way. However, coupling is almost always lost on hydrogens bound to heteroatoms (OH and NH). The lack of communication between an OH or NH and its neighbors is related to rapid proton transfer, in which that proton can trade places with another OH or NH in solution. This exchange happens quite easily if there are even tiny traces of water in the sample.

In summary, multiplicity or coupling is what we call the appearance of a group of symmetric peaks representing one hydrogen in NMR spectroscopy.

- A proton can absorb at different frequencies because of the influence of neighbouring hydrogens.
- Protons on one carbon atom are affected by different protons on the next carbon atom, provided those two carbons are directly attached to each other.
- Stated another way, these neighboring hydrogens must be three bonds away (and so this phenomenon is sometimes called "three-bond coupling").

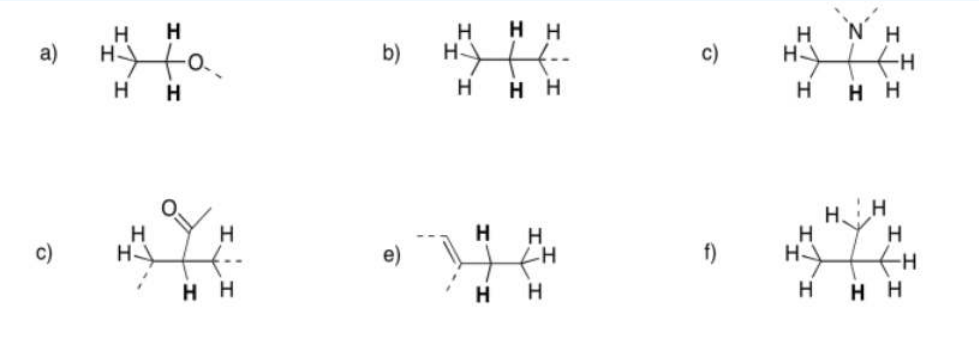
- When a proton is coupled, the number of neighbouring hydrogens is one less than the number of peaks in the multiplet.

There are limitations on coupling:

- coupling does not occur between hydrogens of the same type ("equivalent hydrogens"). In the proton spectrum of ethane, CH_3-CH_3, you would only observe one singlet.
- coupling often does not occur across heteroatoms such as oxygen and nitrogen. The OH peak in ethanol may be a singlet instead of a triplet, although there are two hydrogens on the neighboring carbon. The methylene peak in ethanol may be a quartet instead of a quintet, even though there are actually four neighboring hydrogens: three on the attached methyl and one on the attached hydroxyl

Exercise 3.5.1

Predict the shift, integration, and multiplicity for the **bold** hydrogen in each case.



Answer

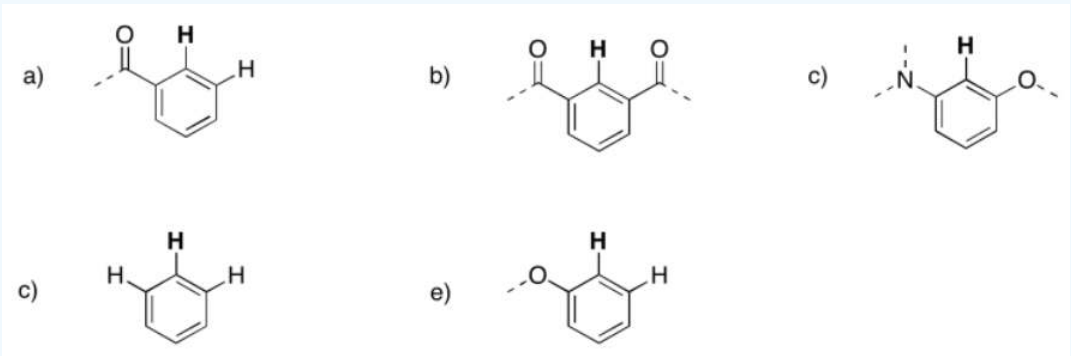
(There will be some variation in the shift depending on the rest of the structure; this is just an estimate.)

a) 3.5 ppm, quartet, 2H b) 1.5 ppm, sextet, 2H c) 2.6 ppm, septet, 1H

d) 2.3 ppm, quintet, 1H e) 2.2 ppm, quartet, 2H f) 1.7 ppm, nonet, 1H

Exercise 3.5.2

Predict the shift, integration, and multiplicity for the **bold** hydrogen in each case.



Answer

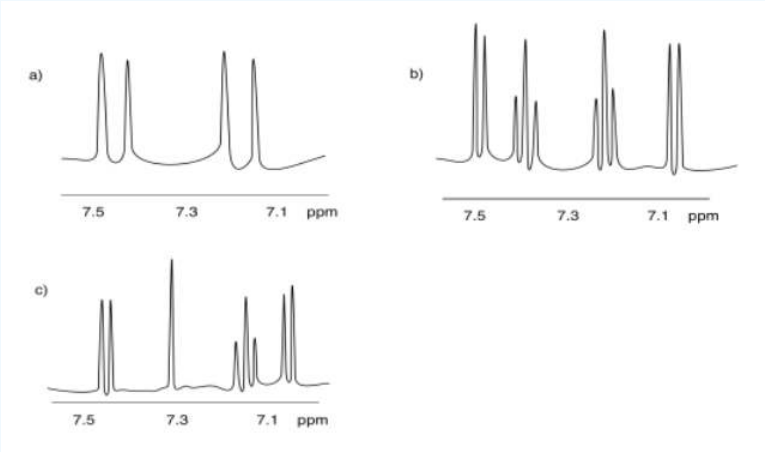
(There will be some variation in the shift depending on the rest of the structure; this is just an estimate.)

a) 7.8 ppm, doublet, 1H b) 8.4 ppm, singlet, 1H c) 6.7 ppm, singlet, 1H

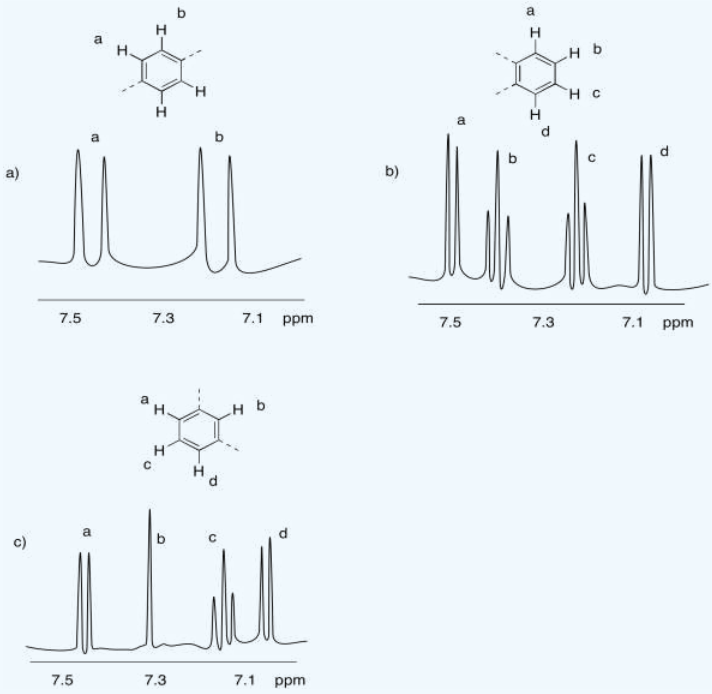
d) 7.2 ppm, troplet, 1H e) 6.9 ppm, doublet, 1H

Exercise 3.5.3

The following patterns indicate particular substitution patterns in disubstituted benzenes: 1,2-C_6H_4XY; 1,3-C_6H_4XY; or 1,4-C_6H_4XY. Match each pattern to the correct structure.

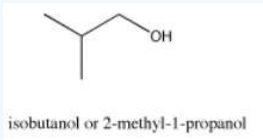


Answer

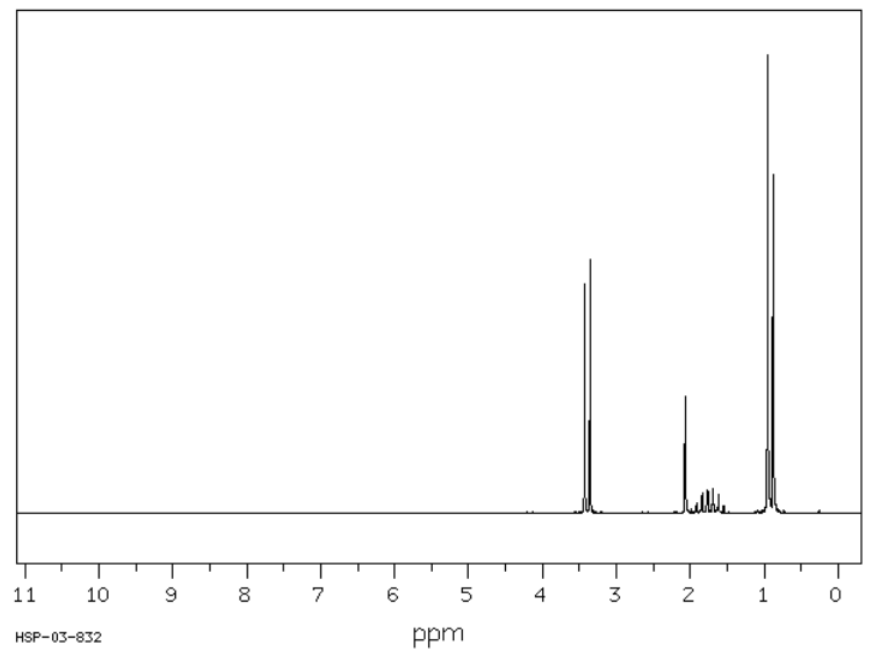


Exercise 3.5.4

The spectrum of isobutanol is shown below. Assign each peak to a different proton in the structure.



isobutanol or 2-methyl-1-propanol



Source: Modified from SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

Answer

3.4 ppm, doublet: CH-C**H**$_2$-O

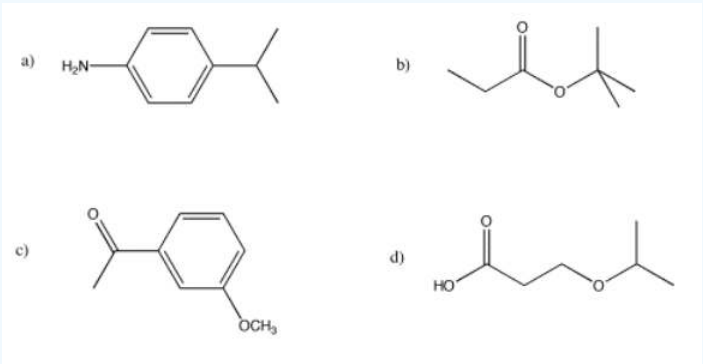
2.1 ppm, singlet: O**H**

1.7 ppm, nonet: $(CH_3)_2C\mathbf{H}CH_2$

0.9 ppm, doublet: $CH(C\mathbf{H}_3)_2$

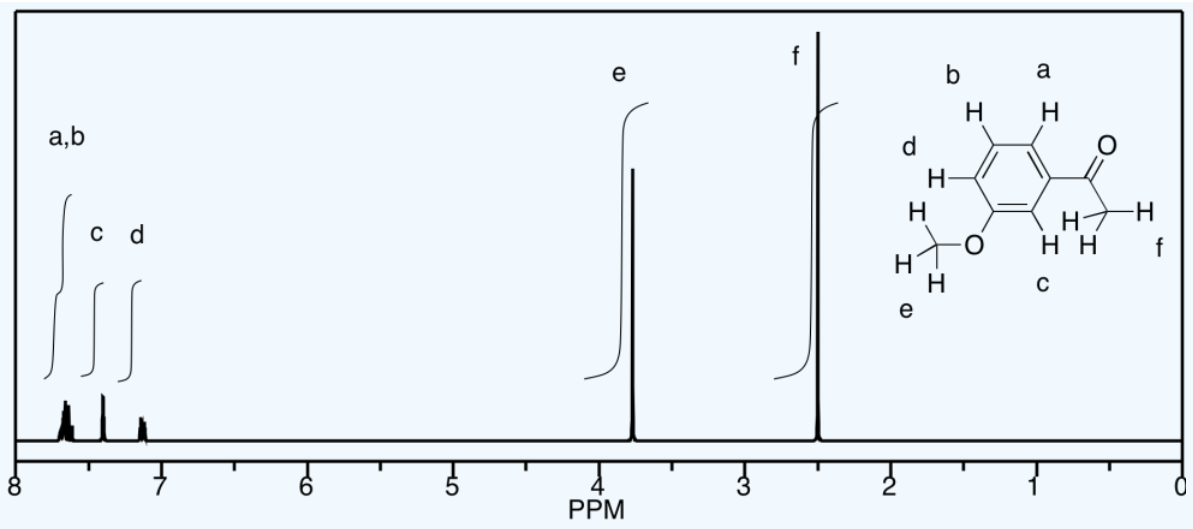
? Exercise 3.5.5

Sketch predicted ^{1}H NMR spectra, complete with coupling and integration, for the following structures:

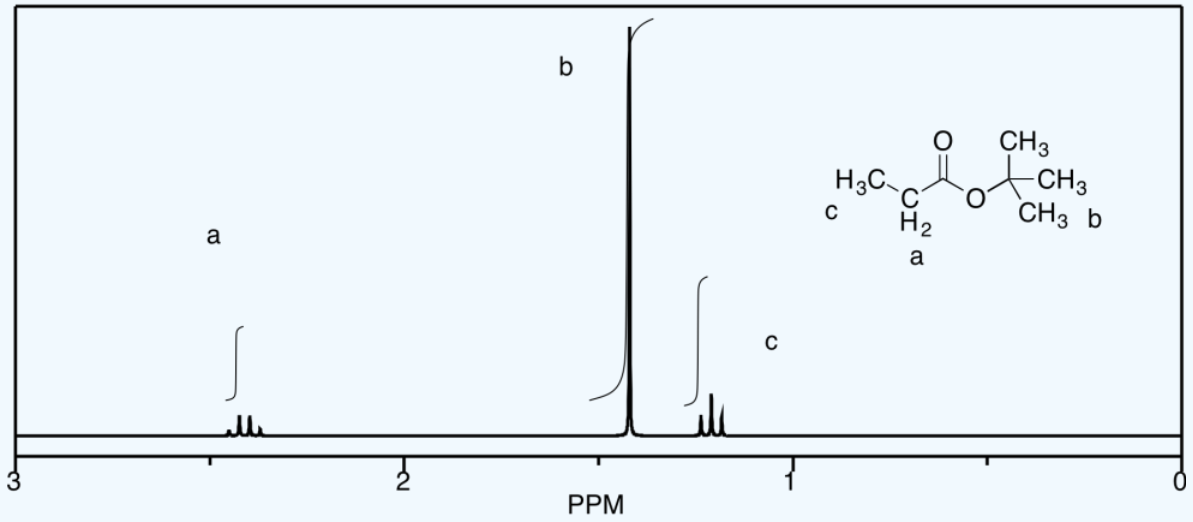


Answer

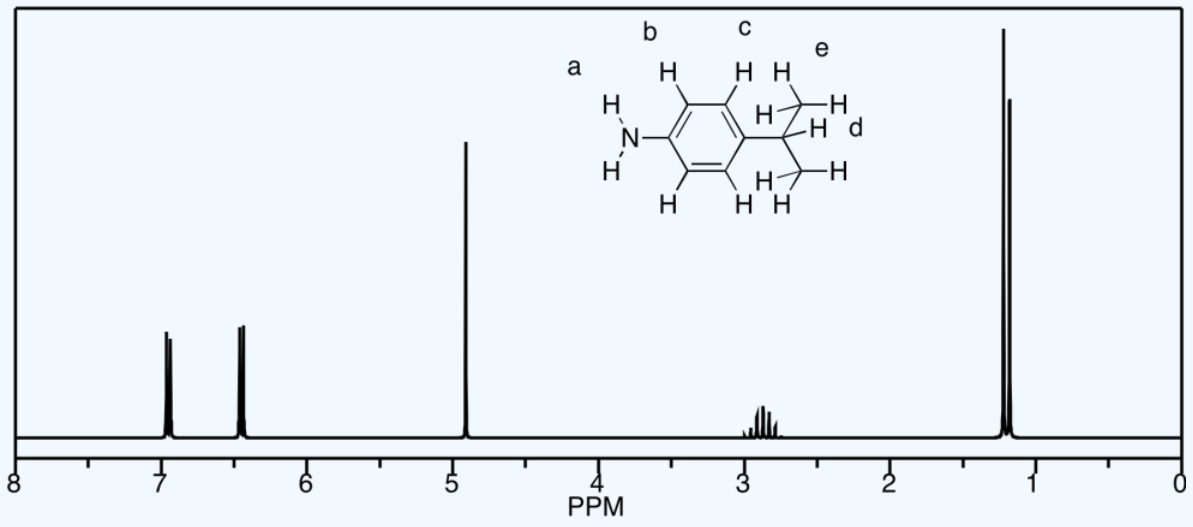
a) This is a simulated spectrum. The peaks at f, e, and c are singlets. The peak at d is a doublet. The peaks at a & b are unfortunately coincident, so their multiplicities are obscured, but they would be doublets & triplets, respectively.



b)

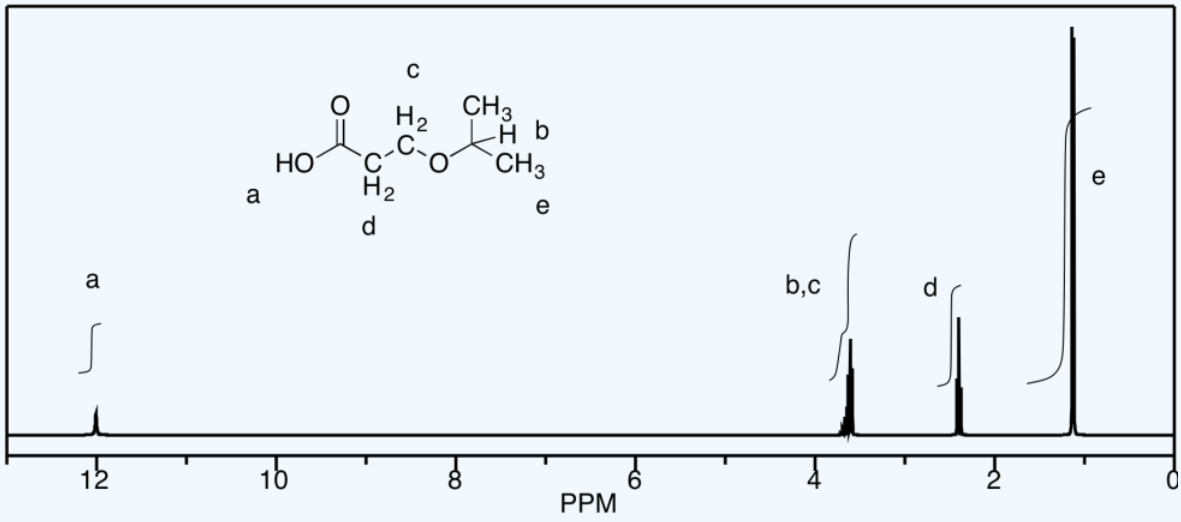


c)



https://chem.libretexts.org/@go/page/363279

d) The peaks at b and c unfortunately coincide, but they would be a septet and a triplet, respectively. Otherwise, a is a singlet, d is a triplet, and e is a doublet.

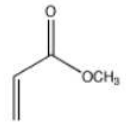


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3.6: More Complicated Coupling

The n + 1 rule (number of lines in a multiplet = number of neighbouring H + 1) will work for the majority of problems you may encounter. Occasionally, you may see more complicated coupling. The spectrum of methyl acrylate is a good example. There are a couple of points to note in this spectrum, beginning with the number of peaks.



methyl acrylate

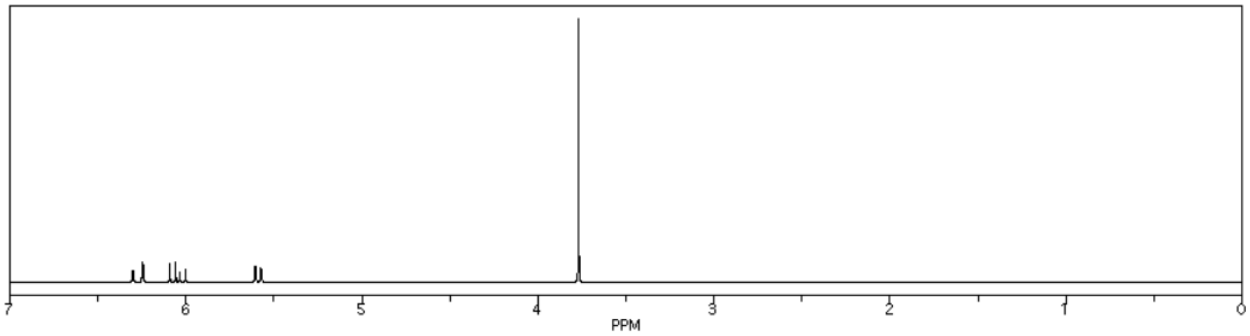


Figure **3.6.1**: ^{1}H NMR spectrum of methyl acrylate.

Source: Simulated spectrum.

- the vinyl portion of the spectrum (hydrogens adjacent to the C=C double bond) shows three peaks, not just two.
- although there are two protons on one vinyl carbon, each H is different because of cis/trans relationships: one H is cis to the carbonyl and the other is trans to it.
- these hydrogens are symmetry inequivalent.

In addition, there is a problem with coupling in the vinyl region.

- the proton adjacent to the carbonyl, at 6 ppm, has two neighbors and should give a triplet.
- instead, the peak from this proton shows four lines, not three.
- this peak is not a quartet; the middle two peaks are not three times as tall as the edge ones.
- the lines within this multiplet are symmetrically spaced, but not evenly; the middle space is smaller than the spaces on the edges.

This pattern is called a "doublet of doublets". The two symmetry-inequivalent neighbors on the other end of the double bond each act as if the other one isn't there. They couple to the proton next to the carbonyl independently, each one splitting the peak for this proton into a separate doublet.

There are a few cases in which this independent coupling will occur rather than the (n+1) type coupling we saw first. Generally, independent coupling occurs when protons are not freely rotating. That can happen if one of the protons is attached to a double-bonded carbon, because we can't rotate around a double bond. It may also happen with protons that are directly attached to the carbons of a ring.

To see why this happens, you need to know more about coupling.

- in coupling, magnetic information is shared between two protons. How fully this information is shared depends on the angle between the hydrogens as you look down the connecting C-C bond.
- for (n+1) coupling, the rotational angle about the C-C bond connecting the two protons (or 'dihedral angle' between the coupled hydrogens) must be unrestricted. The bond must be able to rotate freely.
- if the bond can rotate freely, any proton on the neighbouring carbon can assume any dihedral angle with the proton being observed. That means coupling information from one neighbouring proton is indistinguishable from another, and so all the

neighbouring protons affect the observed proton equally.

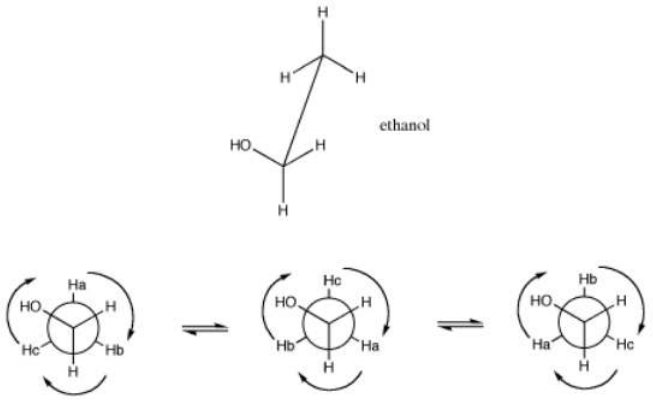
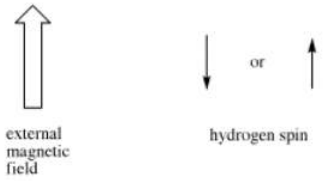
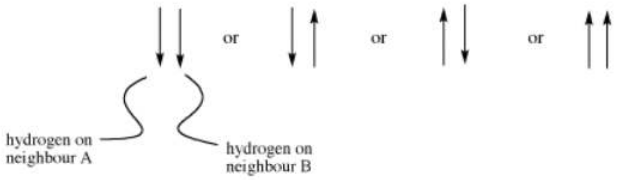


Figure **3.6.2**: A sawhorse projection (top) and Newman projection of ethanol (bottom), showing the angular relationship between hydrogens on neighbouring carbons. The angle between two groups on neighbouring carbons is called the dihedral angle. Because of free rotation about the C-C bond, all three hydrogens on the methyl have an equivalent spatial relationship to the hydrogens on the CH_2 group.

Sometimes coupling information is depicted as an arrow. This arrow stands for the coupling constant between two protons. The coupling constant is related to the spin of a hydrogen atom. The spin (related to magnetic moment) can be aligned with the external magnetic field (we will show it pointing up) or else against it; no other possibilities are allowed.



If there are two neighbouring hydrogens, both spins could be aligned with the external field, both could be aligned against it, or one could be aligned each way. That means there are three different magnetic combinations that will each have a different effect on the observed proton: increased magnetic field, decreased magnetic field, and no net effect (canceling out).



These three combinations result in the observed proton absorbing at three different frequencies, because the frequency it absorbs is sensitive to the magnetic field it experiences. Note that there are two ways to arrive at the middle possibility, with one neighbour spin up and the other spin down. Statistically this possibility is twice as likely as either both spins up or both spins down. It is thus twice as likely that the observed proton experiences that effect, and so the middle line in a triplet is twice as high as the other two lines.

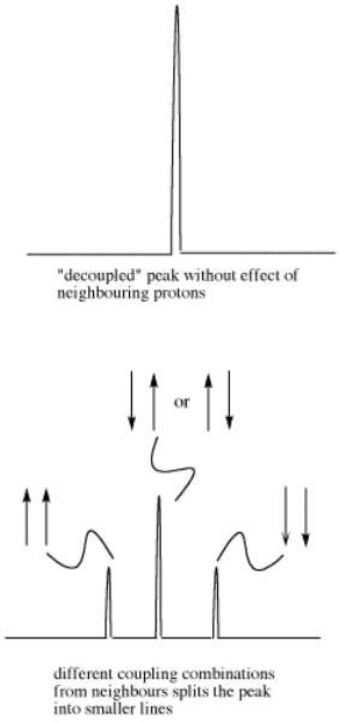
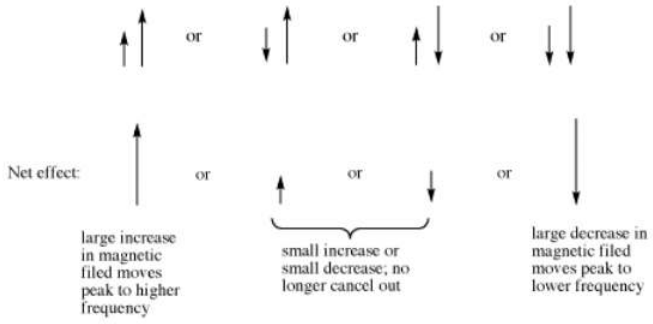


Figure **3.6.3**: Effects of neighbouring protons on an observed peak. This case assumes all the neighbouring protons have an equivalent effect (they have the same coupling constant with the observed proton).

However, the size of that arrow, the coupling constant, is only the same for two neighbouring hydrogens if they have the same spatial relationship with the observed hydrogen. That isn't always true.

- if the dihedral angle is limited, complex coupling occurs.
- complex coupling occurs because one neighbouring hydrogen can only adopt a limited range of dihedral angles. Another neighbouring proton can adopt a limited range of dihedral angles as well, but these two ranges do not overlap.

As a result, the two coupling constants are different. We can depict that situation using arrows of different lengths for the two neighbouring proton spins. Each spin can be either up or down, but now two opposing spins do not cancel out. The result is four spin combinations of equal probability, not just three.



The doublet of doublets is four lines of about equal heights. The distance between the two pairs of lines on each edge

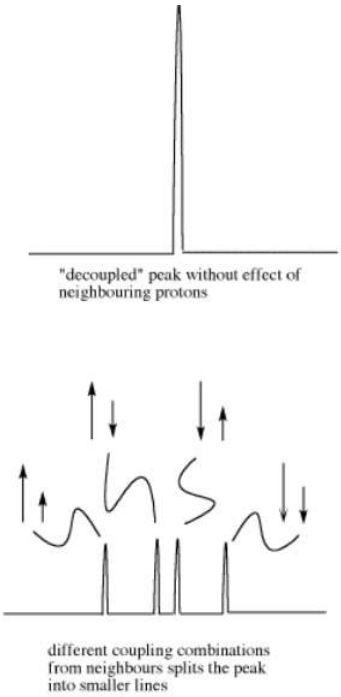


Figure **3.6.4**: Effects of neighbouring protons on an observed peak. This case assumes neighbouring protons have inequivalent effects (they have differing coupling constants with the observed proton).

The dihedral angle is limited in only a few specific cases:

- there is a double bond. Double bonds cannot rotate because that would require breaking the pi bond. In a pi bond, p orbitals on the two carbons must remain coplanar in order to overlap and form a bond.
- there is a ring. In a ring, there can't be complete rotation about a bond because the ring would twist into a pretzel.
- in some cases, there can be such large groups of atoms on either end of a bond that it is difficult to rotate the bond without having these groups crash into each other.

? Exercise 3.6.1

Sketch spectra for the following compounds.

a) allyl alcohol or 2-propene-1-ol, $HOCH_2CH=CH_2$

b) styrene or vinylbenzene, $C_6H_5CH=CH_2$

c) *trans*-1-chloropropene, $CH_3CH=CHCl$

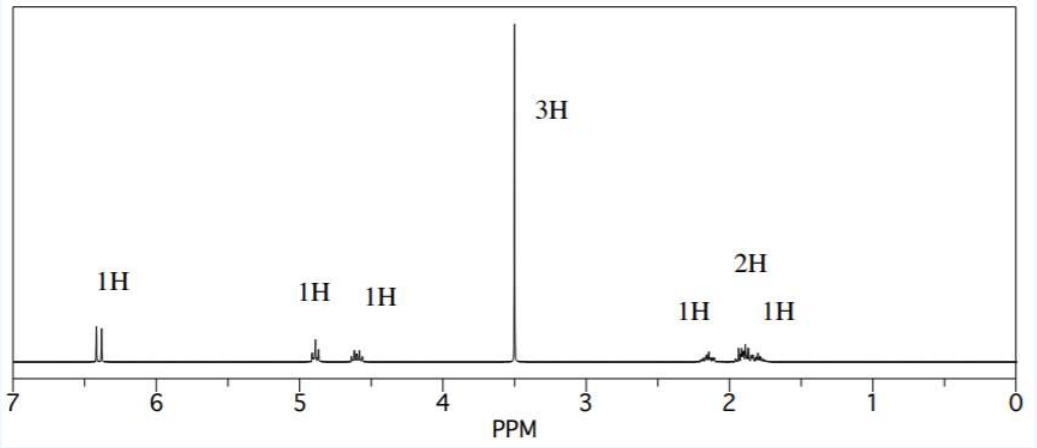
? Exercise 3.6.2

A compound was shown via high-resolution mass spectrometry to have the probable formula $C_6H_{10}O_2$.

a) What is the degree of unsaturation in this compoud?

b) IR spectroscopy gave the following data: 3105 (w), 2950 (m), 1517 (m), 1235 (s), 1056 (s), 715 (m) cm^{-1}. Provide a data table with possible assignments for these peaks.

c) ^1H NMR spectroscopy provided the following spectrum. Provide a data table with partial structures for each peak.



d) Suggest a likely structure for this compound

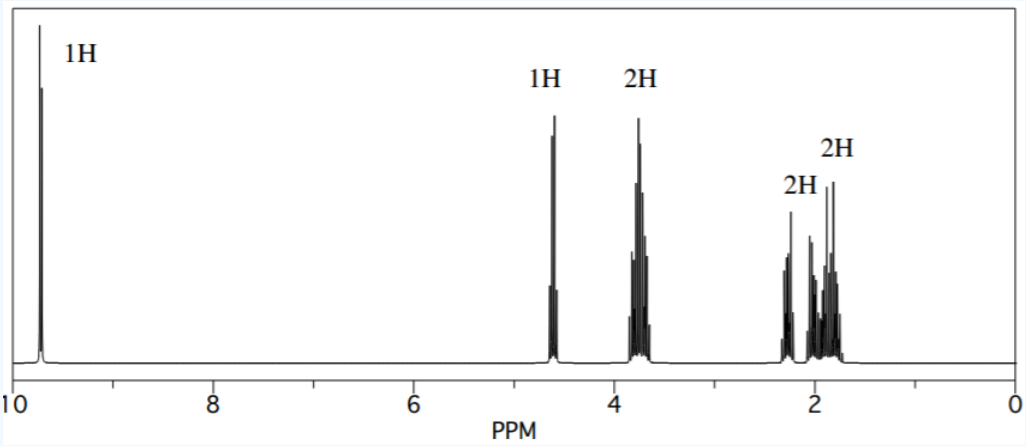
Exercise 3.6.3

A compound was shown via high-resolution mass spectrometry to have the probable formula $C_5H_8O_2$.

a. What is the degree of unsaturation in this compound?

b. IR spectroscopy gave the following data: 2950 (m), 2825 (m), 2716 (m), 1724 (s), 1505 (m), 1056 (w) cm^{-1}. Provide a data table with possible assignments for these peaks.

c. ^1H NMR spectroscopy provided the following spectrum. Provide a data table with partial structures for each peak.



d. Suggest a likely structure for this compound.

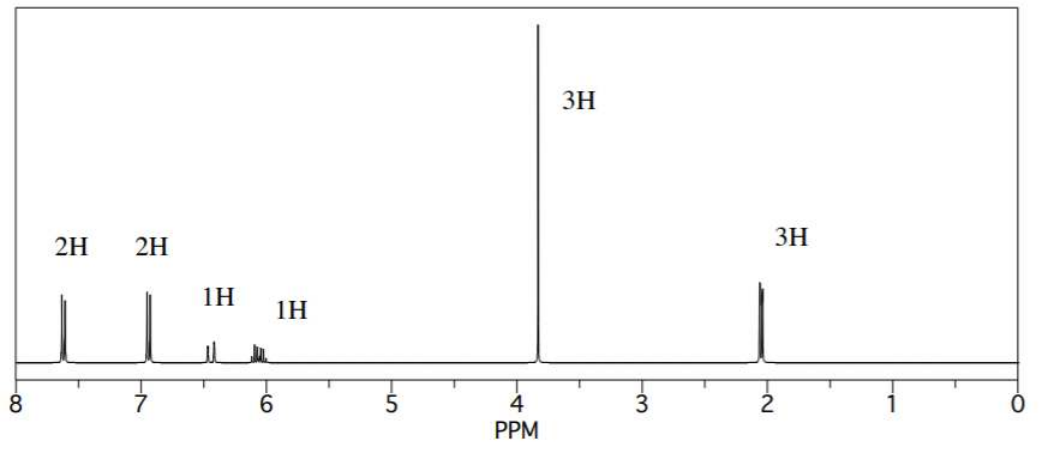
Exercise 3.6.4

A sample of a natural product was isolated from plant material and subjected to analysis.

a. IR spectroscopy gave the following data: 3097 (m), 2975 (m), 1600 (m), 1495 (m), 1235 (s), 1056 (s), 747 (m), 705 (m) cm^{-1}. Provide a data table with possible assignments for these peaks.

b. The compound was shown via high-resolution mass spectrometry to have the probable formula $C_{10}H_{12}O$. What is the degree of unsaturation in this compound?

c. ^{1}H NMR spectroscopy provided the following spectrum. Provide a data table with partial structures for each peak.



d. Suggest a likely structure for this compound.

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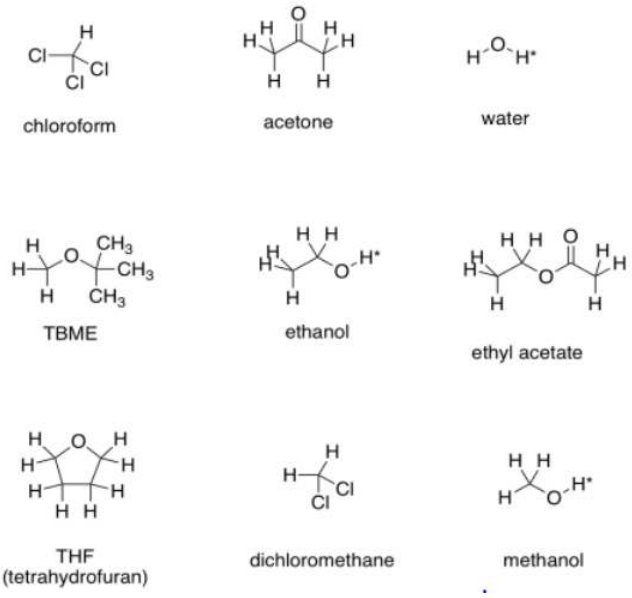
3.7: NMR in Lab- Solvent Impurities

One of the most complicated problems in lab is to deal with the analysis of a mixture. This situation is not uncommon when students run experiments in lab and analyse the data. For example, a student may have added a solvent as part of a purification procedure. Maybe the sample was recrystallized from methanol. Maybe the sample was purified by solvent extraction, and it still contains a little moisture from when it was exposed to the water. In these cases, the solvent will show up in the NMR spectrum.

- Sometimes solvents show up in the spectrum.
- In this case, you should probably make two completely separate sets of data tables for your analysis, one for each compound, or else one for the main compound and one for impurities.

As you go through a spectrum, you should think about any solvents the sample may have contacted. Look for evidence of those things in the spectrum, too.

Here are some examples of solvents that might be used in the lab. You can probably think of other ones, too.



The asterisks by the OH protons in these solvents indicate that these are "exchangeable positions". In protic solvents, or solvents capable of hydrogen bonding (any compound containing O-H or N-H bonds), the proton attached to the oxygen or nitrogen has some unusual behavior in the NMR spectrum. We do not usually observe multiplicity in peaks corresponding to these protons. Often the peaks are very broad, and sometimes they are missing altogether (especially if there is moisture in the sample).

? Exercise 3.7.1

See if you can predict what the NMR spetra of these solvents would look like.

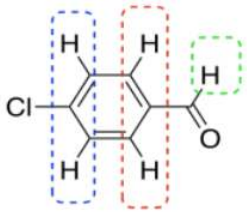
a) TBME b) acetone c) ethyl acetate d) THF e) dichloromethane f) chloroform

g) methanol h) ethanol i) water

Answer

a) TBME b) acetone c) THF d) methanol e) ethyl acetate

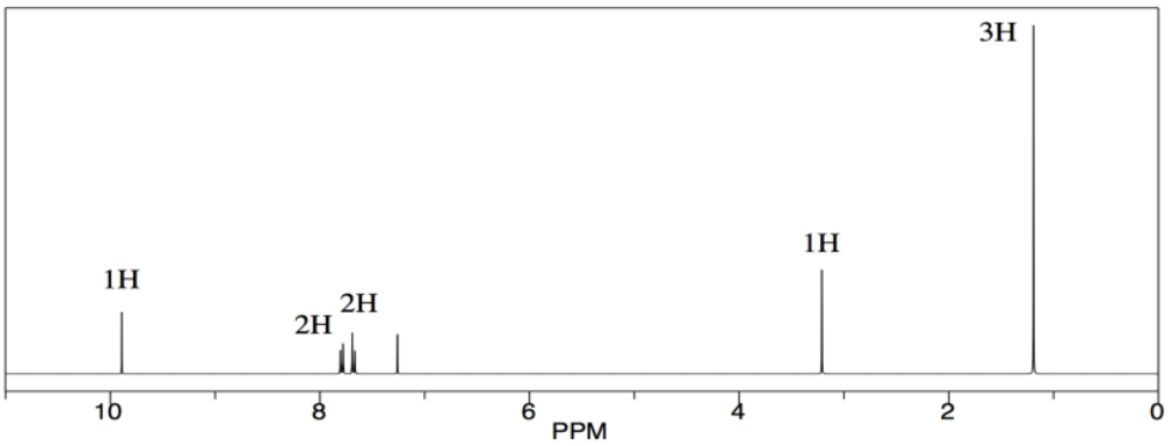
Let's look at an example. Maybe you worked with a sample of p-chlorobenzaldehyde in the lab.



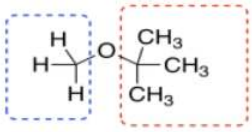
You think you know what that would look like in the NMR. All of the hydrogens are attached to sp^2 or trigonal planar carbons. They should all be somewhere in the left half of the spectrum, maybe between 5 and 10 ppm. Some of the hydrogens are symmetrically equivalent. There is a pair of hydrogens on the benzene ring that look the same as each other; they are closer to the chlorine. Another pair is closer to the carbonyl, the C=O unit. We expect to see two peaks in the NMR spectrum for these hydrogens, even though there are a total of four of them, because they are only in two groups. Because they are all on a benzene, we might even look closer to 7 ppm in the spectrum. Also, both sets of hydrogens have just one neighbour that is different from themselves. These hydrogens should both show up as doublets.

That's not all of the hydrogens in the molecule. There is also a hydrogen on the carbonyl. Because of the double bond to the electronegative oxygen, this position will be strongly deshielded. We should look for it closer to 10 ppm. It does not have any hydrogen neighbors, though. We expect to see a singlet.

The spectrum we see has all of those features. Note that this spectrum is integrated (the *area* of each peak has been measured), and it shows the peak at 10 ppm corresponds to 1H, whereas the ones closer to 7 ppm correspond to 2H each. That information corresponds to what we see in the structure.



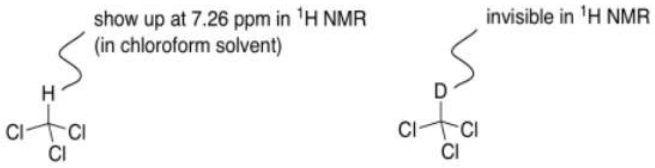
But we see other things, too. Maybe we know that the compound was once dissolved in TBME, $(CH_3)_3COCH_3$. All of the TBME probably evaporated, but you can never be too sure.



TBME has just two kinds of hydrogen, and they are both on tetrahedral or sp^3 carbons. They would probably show up in the right hand side of the spectrum, below 5 ppm. The ones on the carbon next to the other carbon would show up closer to 1 ppm. The ones on the carbon next to the oxygen would show up at 3 or 4 ppm. We do see those peaks in this spectrum.

Furthermore, there are only 3 hydrogens on the carbon next to the oxygen in TBME. There are 9 hydrogens on the methyl groups attached to the carbon. They are in a 1:3 ratio, so we should see that ratio reflected in the integration in the NMR.

There is one more peak in the spectrum, and it is an impurity of a sort, but it isn't part of the original sample. The singlet around 7 ppm is just chloroform, $CHCl_3$.



Now, the NMR solvent used here is actually deuterochloroform, $CDCl_3$. The heavy isotope of hydrogen, deuterium or ^2H, is used in this solvent. That's because we don't want the protons in the solvent to get in the way. ^2H shows up in a completely different area of the spectrum than ^1H, so it's invisible in a regular ^1H NMR spectrum. There is an awful lot of solvent in the NMR tube, and a tiny amount of the actual sample, and it has to be that way for the experiment to work. However, if we just used $CHCl_3$ as the solvent, we would see only one peak in the NMR spectrum: the $CHCl_3$ hydrogen. The sample we are interested in would show up, maybe, as tiny, tiny peaks. So instead we use $CDCl_3$, which is invisible in the hydrogen spectrum.

Well, deuterated solvents are very, very expensive, and the cost to make sure all of the hydrogen atoms in chloroform are replaced by deuteria would be prohibitive. So there is always a little bit of $CHCl_3$ still in the $CDCl_3$, and it shows up in the ^1H spectrum.

It's helpful to have a list of common solvent impurities on hand when you look at your spectrum. A few examples are provided in the following table, showing the data you would see from common solvents in an NMR spectrum taken *in chloroform*.

solvent	number of peaks	shift	multiplicity	integral ratio	assignment
water	1	1.56	br. s	-	O-**H**
acetone	1	2.17	s	-	(C=O)C**H**$_3$
chloroform	1	7.26	s	-	Cl_3C-**H**
t-butyl methyl ether	2	1.19	s	3	C(C**H**$_3$)$_3$
		3.22	s	1	O-C**H**$_3$
ethyl acetate	3	1.26	t	3	CH_2C**H**$_3$
		2.05	s	3	(C=O)C**H**$_3$
		4.12	q	2	OC**H**$_2$$CH_3$
tetrahydrofuran	2	1.85	m	1	CH_2-C**H**$_2$-CH_2
		3.76	m	1	CH_2-C**H**$_2$-O
methanol	2 (usually)	1.09	br s (may be absent)	1	O-**H**
		3.49	s	3	O-C**H**$_3$
ethanol	3 (usually)	1.25	t	1	CH_2C**H**$_3$
		1.32	br s (may be absent)	2	O-**H**
		3.72	q	3	OC**H**$_2$$CH_3$
dichloromethane	1	5.32	s	-	Cl_2C**H**$_2$
grease or alkanes	2	0.86	m	varies; smaller	CH_2C**H**$_3$
		1.26	m	varies; larger	CH_2C**H**$_2$$CH_2$ / CH_2C**H**$_2$$CH_3$

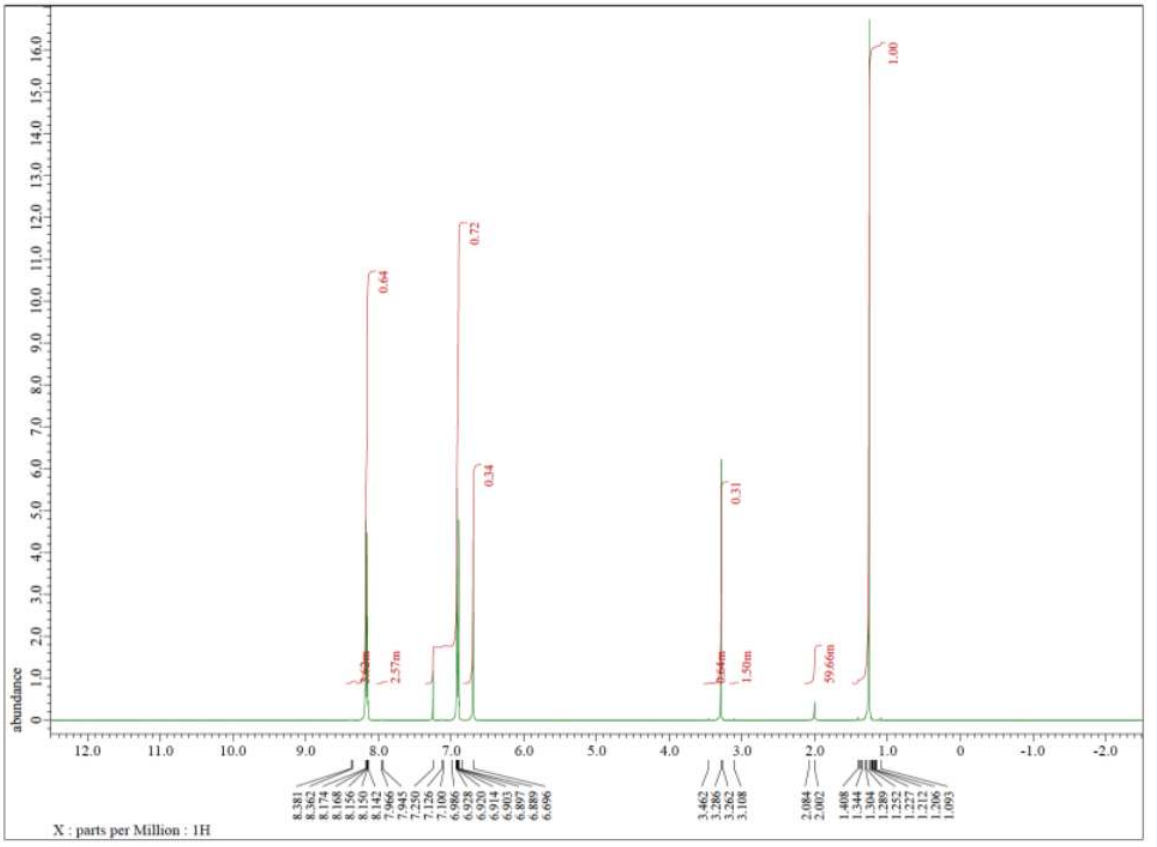
An excellent table, including shifts of a variety of impurities in different NMR solvents, can be found in the following article: Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem*. **1997**, *62*, 7512-7515.

Note that these compounds would show up at slightly different places if they were dissolved in something other than chloroform. Gottlieb's table lists where they would be seen in other common NMR solvents as well.

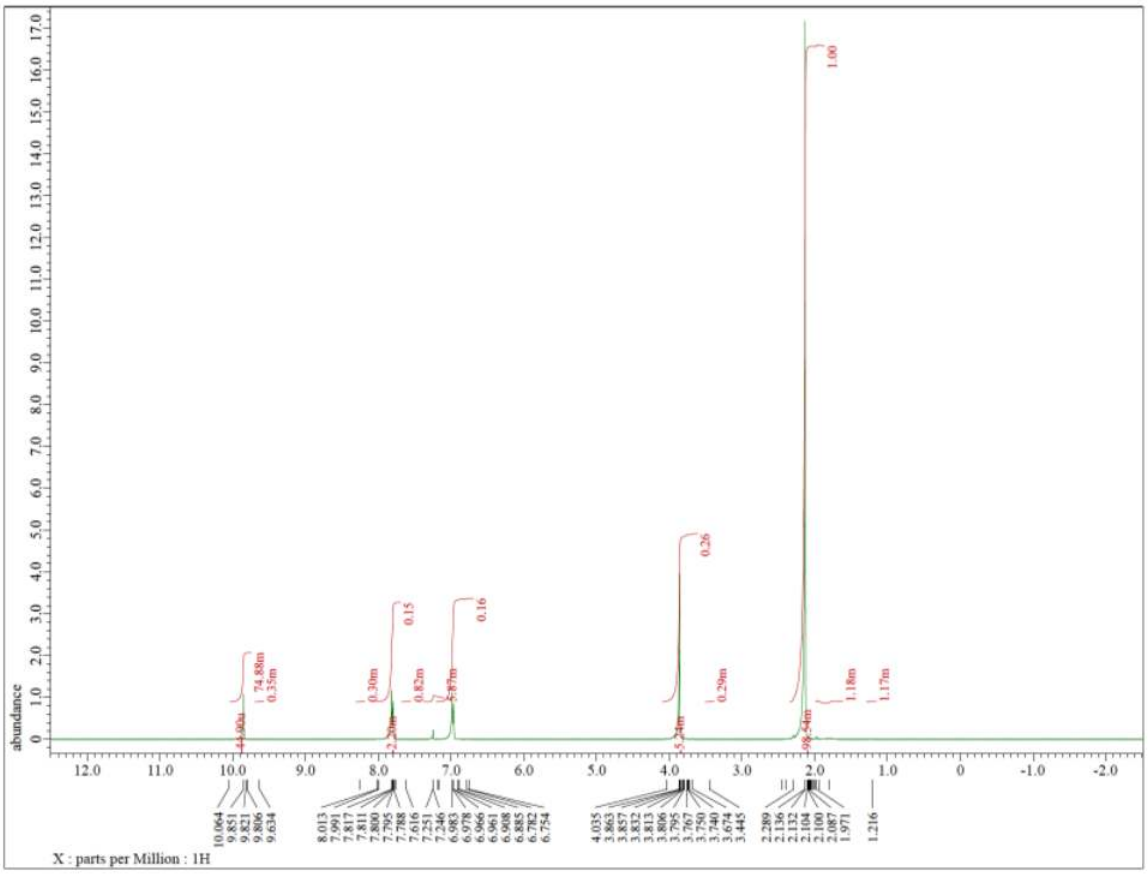
? Exercise 3.7.2

Each of the following spectra contains a solvent impurity: acetone, ethyl acetate, methanol, TBME, or THF. Match the spectrum to the impurity.

a)

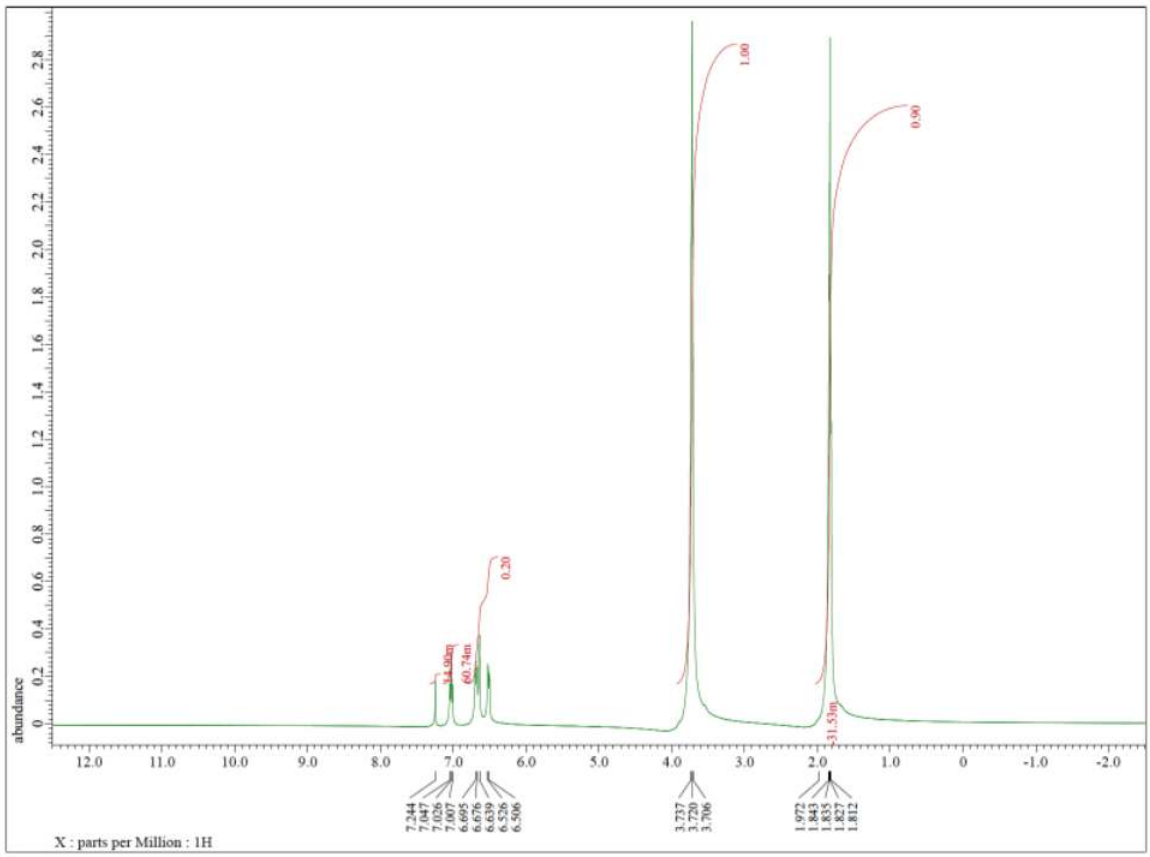


b)

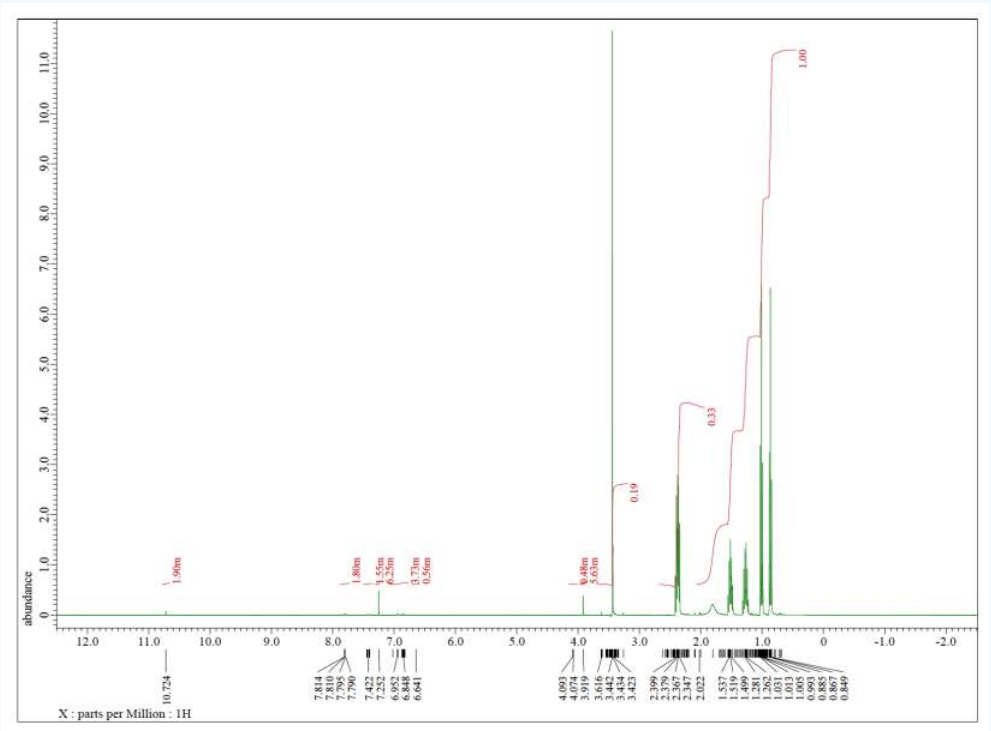


c)

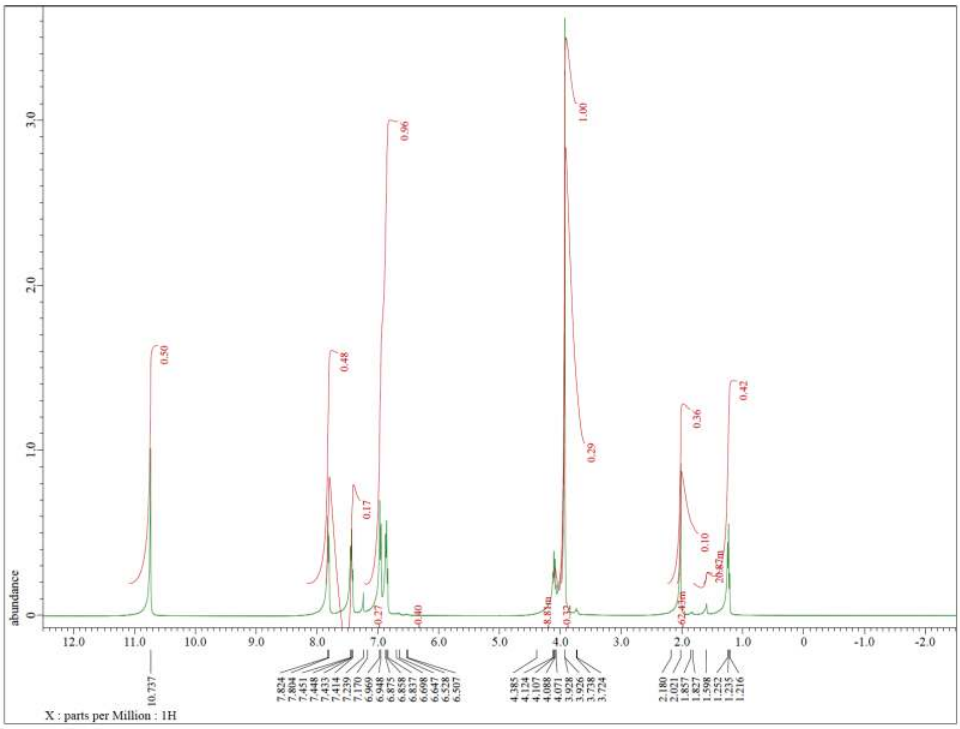
https://chem.libretexts.org/@go/page/363282


abundance
X : parts per Million : 1H
1.00
0.90
0.20
14.08m
60.74m
31.53m

d)


abundance
X : parts per Million : 1H
1.00
0.33
0.19
1.90m
1.80m
1.55m
6.28m
3.73m
0.56m
9.48m
5.63m
10.724

e)



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3.8: NMR in Lab- Monitoring Reaction Progress

If you are running a reaction, chances are you know what you started with. You may also have a pretty good idea of what you will be making. The big question is whether the reaction worked (or, maybe, nothing happened at all). If it worked, did you get the product you thought you would, or did you get something unexpected?

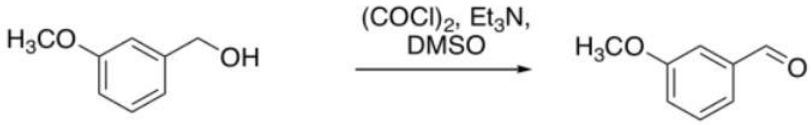
In these cases:

- You should draw attention to pieces of data that most strongly support your expected structure. This approach will demonstrate evaluative understanding of the data; that means you can look at data and decide what parts are more crucial than others.
- You should also draw attention to negative results: that is, peaks that might be there if this spectrum matched another, possible structure, but that are in fact missing.

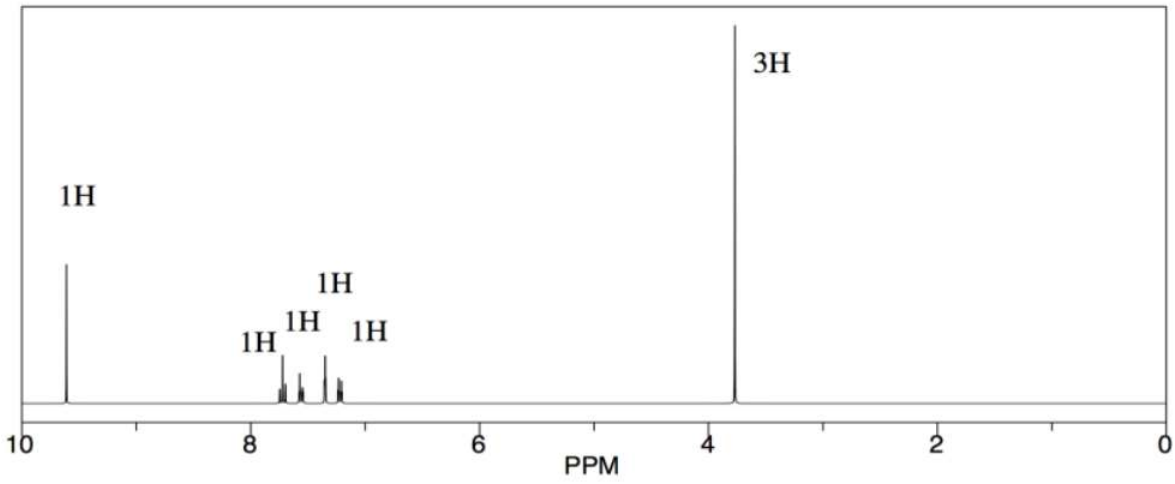
One of the most complicated problems to deal with is the analysis of a mixture. This situation is not uncommon when students run reactions in lab and analyse the data.

- Sometimes the spectra show a little starting material mixed in with the product.
- Sometimes spectra show only a little product and a lot of starting material.
- In these cases, you should probably make two completely separate sets of data tables for your analysis, one for each compound, or else one for the main compound and one for impurities.

Let's look at an example of a reaction. A student is running a type of reaction called an oxidation. She is starting with 3-methoxybenzyl alcohol and trying to convert it to 3-methoxybenzaldehyde. She follows the directions carefully, but how will she know whether she is successful?



She looks at the spectrum, and sees a group of aromatic hydrogens, and a large singlet near 4 ppm, which could be the hydrogens on the methoxy group. Those are reassuring, but they don't interest her that much, because they would appear in her spectrum whether the reaction had proceeded or not. Those peaks would all be pretty much the same in her starting material.



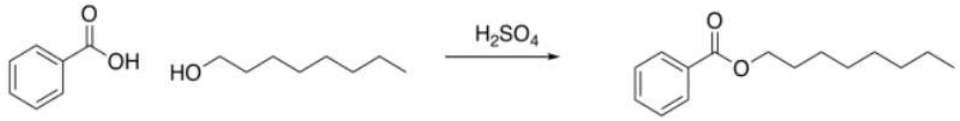
Instead, she notices the peak near 10 ppm. That's significant. Her product would have an aldehyde proton, and that would show up around 10 ppm. Maybe the reaction worked.

She also takes a look around 5 ppm. There is nothing there, and she thinks that's interesting, too. In her starting alcohol, she had protons on a carbon that was in between an arene and an oxygen, Ar-CH_2-OH. She knows that shift effects are additive in NMR: if

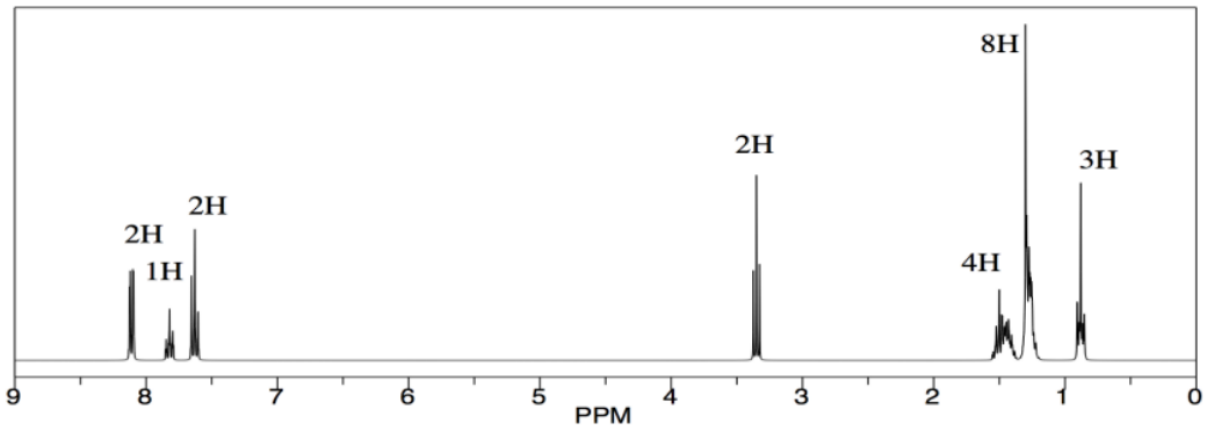
a CH_2 in general shows up around 1 ppm, but next to an oxygen it gets shifted to 4 ppm and next to an aromatic it gets shifted to 2 ppm, then if it is next to both it will shift to 5 ppm. There is nothing there. She no longer has an alcohol.

She makes an argument in her report that the reaction proceeded to form an aldehyde. She does not have the hubris to call the reaction "successful" or say it went "as expected". She just points out the presence of an aldehyde proton and the absence of the protons next to the alcohol. She gets an A on the report. Three years later, she is in medical school at Harvard.

Sometimes, things are more subtle. Let's look at another reaction. A student is performing an esterification reaction. He treats 1-octanol with benzoic acid and a drop of sulfuric acid. It's a Fischer esterification. He does not realize Fischer esterifications are equilibrium quagmires that never really make it one direction or another.



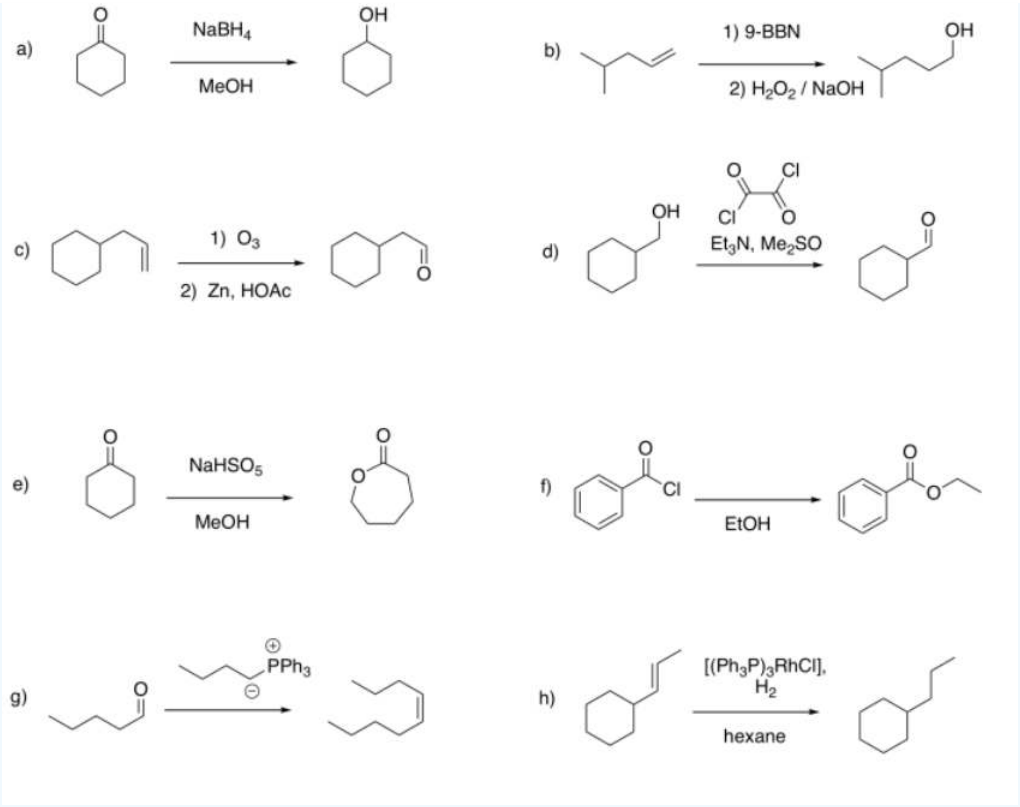
But when he sees the results, he suspects something is amiss. All the peaks are there -- the aromatics, the -CH_2-O, the long aliphatic chain -- but there is something about that methylene, that -CH_2-O, that bothers him. It shows up right around 3.5 ppm, exactly where it would in the starting alcohol. He thinks it should be just a little to the left in the ester, maybe around 4 ppm, because of the influence of the electron-withdrawing carbonyl. He thinks maybe the reaction did not proceed. It occurs to him to look for evidence of the OH protons, in both the alcohol and the benzoic acid, but he knows looking for that in the ^1H spectrum is usually a fool's errand, so he consults the IR evidence instead.

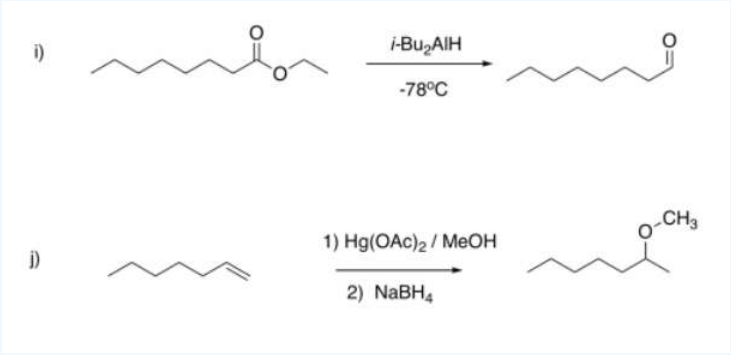


He makes an argument in the report that the reaction did not proceed, but yielded unreacted starting materials. He does not wring his hands about human error, but points out that esters can be both formed and cleaved in the presence of acid, and suggests an acid chloride route might be preferable. He still manages to get an A on the report.

? Exercise 3.8.1

Suggest diagnostic NMR peaks that could be used to determine whether each of the following reactions has proceeded.





Answer

a) appearance of CH-O near 3.5 ppm (multiplet, 1H)

b) appearance of CH_2-O near 3.5 ppm (triplet, 2H); disappearance of =CH near 5-6 ppm (mutiplets, total 3H)

c) appearance of HC=O near 10 ppm (triplet, 1H); disappearance of =CH near 5-6 ppm (mutiplets, total 3H)

d) appearance of HC=O near 10 ppm (triplet, 1H); disappearance of CH_2-O near 3.5 ppm (doublet, 2H)

e) appearance of CH_2-O near 3.5 ppm (triplet, 2H)

f) appearance of CH_2-O near 4 ppm (triplet, 2H)

g) appearance of =CH near 5-6 ppm (mutiplets, total 2H); disappearance of HC=O near 10 ppm (triplet, 1H);

h) disappearance of =CH near 5-6 ppm (mutiplets, total 2H); appearance of triplet:sextet:triplet pattern between 1-2 ppm

i) appearance of HC=O near 10 ppm (triplet, 1H); disappearance of CH_2-O near 3.5 ppm (doublet, 2H)

j) appearance of CH-O near 3 ppm (singlet, 3H) and 3.5 ppm (sextet, 1H); disappearance of =CH near 5-6 ppm (mutiplets, total 2H)

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3.9: NMR in Lab- Composition of Mixtures

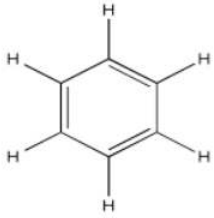
There will be cases in which you already know what the structure might be. In these cases:

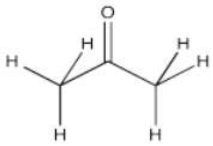
- You should draw attention to pieces of data that most strongly support your expected structure. This approach will demonstrate evaluative understanding of the data; that means you can look at data and decide what parts are more crucial than others.
- You should also draw attention to negative results: that is, peaks that might be there if this spectrum matched another, possible structure, but that are in fact missing.

One of the most complicated problems to deal with is the analysis of a mixture. This situation is not uncommon when students run reactions in lab and analyse the data.

- Sometimes the spectra show a little starting material mixed in with the product.
- Sometimes solvents show up in the spectrum.
- As you might expect, the minor component usually shows up as smaller peaks in the spectrum. If there are fewer molecules present, then there are usually fewer protons to absorb in the spectrum.
- In this case, you should probably make two completely separate sets of data tables for your analysis, one for each compound, or else one for the main compound and one for impurities.

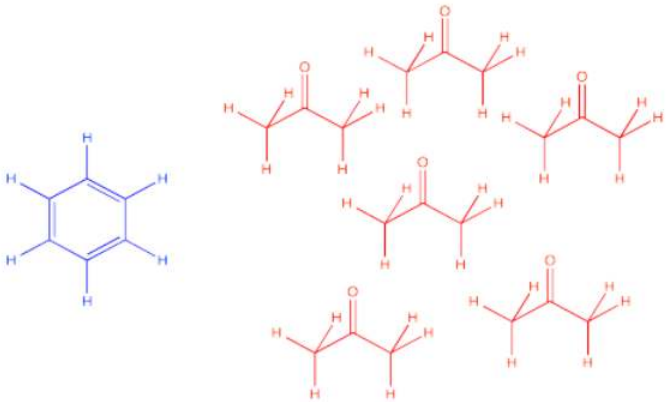
Remember that integration ratios are really only meaningful within a single compound. If your NMR sample contains some benzene (C_6H_6) and some acetone (CH_3COCH_3), and there is a peak at 7.15 that integrates to 1 proton and a peak at 2.10 ppm integrating to 6 protons, it might mean there are 6 protons in acetone and 1 in benzene, but you can tell that isn't true by looking at the structure.





There are six protons in the benzene, and they should all show up near 7 ppm. There are six protons in acetone, and they should all show up near 2 ppm. If there were 1 molecule of benzene for every molecule of acetone, then the integrations would be equal.

Assuming that small integral of 1H for the benzene is really supposed to be 6H, then the large integral of 6H for the acetone must also represent six times as many hydrogens, too. It would be 36 H. There are only six hydrogens in acetone, so it must represent six times as many acetone molecules as there are benzenes.



Integration ratio 1:6

In general, to calculate that ratio, we have to take the integral we see and correct for the number of hydrogens it is supposed to represent. If there are six hydrogens per molecule, and we divide the integral by six, then the result represents the relative amount

of that molecule in the sample.

For benzene: at 7.15 ppm, integral = 1H

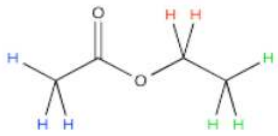
But 1H / 6H per molecule = 0.17 molecules

For acetone: at 2.10 ppm, integral = 6H

But 6H / 6H per molecule = 1 molecule

The ratio of acetone to benzene = 1 molecule acetone : 0.17 molecules benzene = 6 acetone : 1 benzene

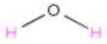
Sometimes a compound will have several peaks in an NMR spectrum because it has several unique hydrogens. For example, ethyl acetate has a few different peaks. What if you wanted to compare the amount of acetone to the amount of water?



peak near 2 ppm, integration 3H

peak near 4 ppm, integration 2H

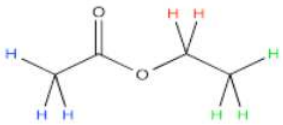
peak near 1 ppm, integration 3H



peak near 1.5 ppm, integration 2H

It might be tempting to just measure up all the integrals for the hydrogens in ethyl acetate and all the integrals for the hydrogens in water. Comparing those two numbers would tell you the ratio of ethyl acetate to water, right? Not exactly. Ethyl acetate has a lot more protons than water, so that isn't a fair comparison. Even in a 1:1 misture of water to ethyl acetate, the total integral for ethyl acetate should be much bigger than for water.

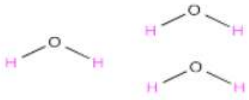
However, notice that peak near 4 ppm in ethyl acetate. It represents 2H, just like the peak for water. Comparing the integral for the peak at 4 to the integral for the peak at 1.5 would provide a pretty good ratio of ethyl acetate to water. The reason we choose the integral at 4 ppm is because it isn't close to any other peaks, so we are very confident that this integral represents only ethyl acetate and nothing else.



peak near 2 ppm, integration 3H

peak near 4 ppm, integration 2H

peak near 1 ppm, integration 3H



peak near 1.5 ppm, integration 6H

Because both peaks represent the same number of hydrogens, the integrals give a direct ratio of the number of molecules present. So, suppose the spectrum reports a raw integral of 27 for the peak at 1.5 ppm and 9 for the peak at 4 ppm. Remember, the integral is just reporting the relative area under the peak, rather than some absolute quantity, so the initial numbers we get might not sound like they correspond to a reasonable number of hydrogens. It's the ratio that matters, and the ratio of 27:9 is 3. If the integral at 1.5 ppm is three times bigger than the one at 4 ppm, there must be three times as many water molecules as ethyl acetate molecules.

For water: at 1.5 ppm, integral = 27H

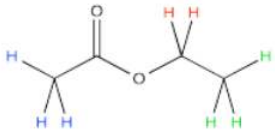
But 27H / 2H per molecule = 13.5 molecules

For ethyl acetate: at 4.2 ppm, integral = 9H

But 9H / 2H per molecule = 4.5 molecule

The ratio of water to ethyl acetate = 13.5 molecule water : 4.5 molecules ethyl acetate = 3 water : 1 ethyl acetate

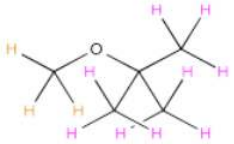
Sometimes there are several unique hydrogens in both compounds that you want to compare, so you will need to make a choice about which peaks to compare. For example, maybe you need to determine the ratio of ethyl acetate to TBME (^{tert}-butyl methyl ether, sometimes alternatively called MTBE) in a sample.



peak near 2 ppm, integration 3H

peak near 4 ppm, integration 2H

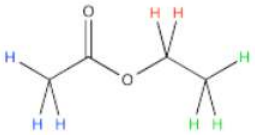
peak near 1 ppm, integration 3H



peak near 3 ppm, integration 3H

peak near 1 ppm, integration 9H

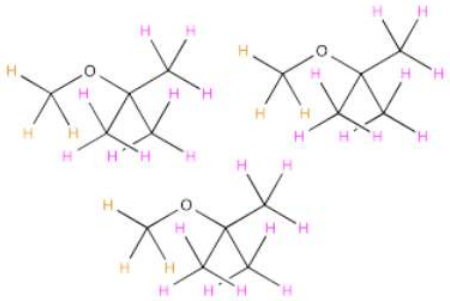
The easiest thing to do may be to compare the peak at 2 ppm in ethyl acetate with the peak at 3 ppm in TBME. They are both supposed to be 3H, so a comparison of those two integrals gives you a direct look at the ratio of molecules. For example, a 1:3 ratio between the peak at 2 ppm and the peak at 3 ppm would indicate a 1:3 ratio of molecules.



peak near 2 ppm, integration 3H

peak near 4 ppm, integration 2H

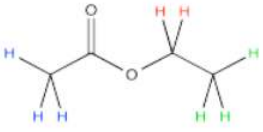
peak near 1 ppm, integration 3H



peak near 3 ppm, integration 9H

peak near 1 ppm, integration 27H

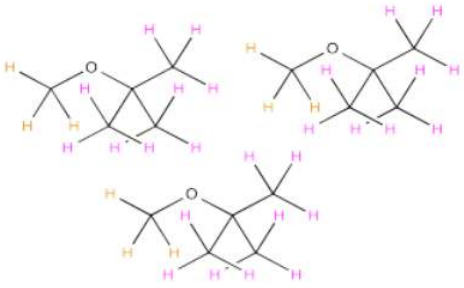
But what if, right before you made your NMR sample, you noticed a little schmutz on the NMR tube and decided to clean it with some acetone. As a result, you're pretty sure there is some acetone in your NMR sample. Unfortunately, that also shows up at 2 ppm, so you're not quite sure what part of the integral at 2 ppm is telling you about the acetone and what part is telling you about the ethyl acetate.



peak near 2 ppm, integration ???

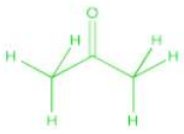
peak near 4 ppm, integration 2H

peak near 1 ppm, integration ???



peak near 3 ppm, integration 9H

peak near 1 ppm, integration ???



2 ppm, integration ???

Don't worry. You can still resort to comparing the peak at 4 ppm in ethyl acetate, which you can see very clearly, with the peak at 3 ppm in TBME, also in the clear. The only trouble is that you have to take into account that one peak represents 2H per molecule and the other peak represents 3H per molecule. You need to adjust for that by, for example, multiplying the integral at 3 ppm by 2/3. You're cutting it down so you can compare it to a peak that would only represent 2H rather than 3H. You are putting it on an equal footing with the peak from the ethyl acetate, so that you can compare the number of molecules present, not just the number of H in each molecule.

Suppose this students measures those two raw integrals at 4 ppm and 3 ppm, and gets values of 127H and 38H.

For ethyl acetate: at 4.2 ppm, integral = 127H

But 127H / 2H per molecule = 63.5 molecules

For TBME: at 3.10 ppm, integral = 38H

But 38H / 3H per molecule = 12.67 molecule

The ratio of ethyl acetate to TBME = 63.5 molecule ethyl acetate : 12.67 molecules TBME = 5 ethyl acetate : 1 TBME

Sometimes, you may be asked to express the make-up of the sample in terms of **percent composition** rather than as a ratio. Converting ratios to percentages involves dividing one part of the ratio by the sum of both parts.

% ethyl acetate = $\frac{5}{5+1} \times 100\% = 83.3\%$ ethyl acetate

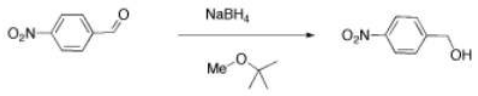
% TBME = $\frac{1}{5+1} \times 100\% = 16.7\%$ TBME

or %TBME = $100 - 83.3\% = 16.7\%$

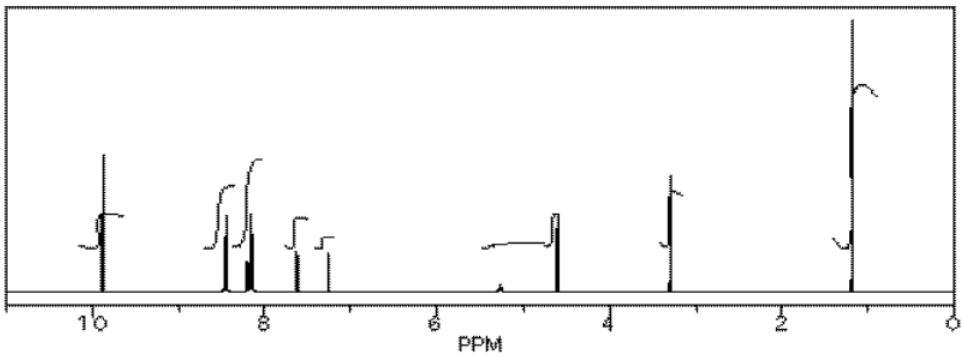
If you have decided that you can identify two sets of peaks in the 1H spectrum, analysing them in different tables makes it easy to keep the integration analysis completely separate too ; 1 H in one table will not be the same size integral as 1 H in the other table unless the concentrations of the two compounds in the sample are the same.

However, comparing the ratio of two integrals for two different compounds can give you the ratio of the two compounds in solution, just as we could determine the ratio of benzene to acetone in the mixture described above.

We will look at two examples of sample mixtures that could arise in lab. Results like these are pretty common events in the labIn the first example, a student tried to carry out the following reaction, a borohydride reduction of an aldehyde. The borohydride should give a hydride anion to the C=O carbon; washing with water should then supply a proton to the oxygen, giving an alcohol.

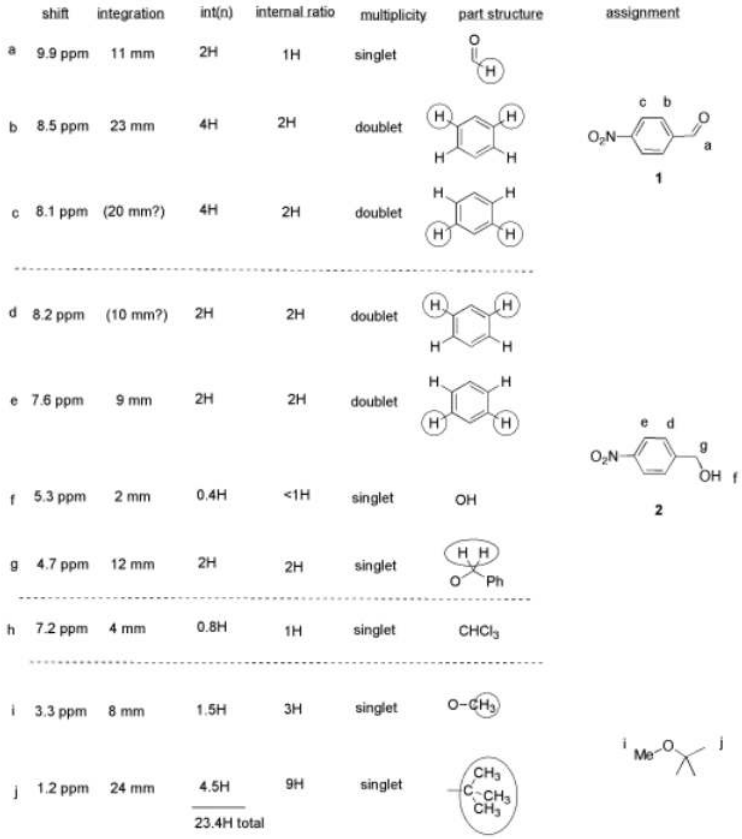


Her reaction produced the following spectrum.



(simulated data)

From this data, she produced the table below.



Notice how she calculated that ratio. She found a peak in molecule 1, the aldehyde, that she was pretty sure corresponded to the aldehydic hydrogen, the H attached to the C=O; in other words, the CH=O. She found another peak from molecule 2, the alcohol, that she was pretty sure represented the two hydrogens on the carbon attached to oxygen, the CH_2-O.

The integrals for those two peaks are equal. They are both 2H in her table. However, she notes that within each molecule, the first integral really represents 1H and the second represents 2H. That means there must be twice as many of molecule 1 as there are molecule 2. That way, there would be 2 x CH=O, and its integral would be the same as the 1 x CH_2-O in the other molecule.

One way to approach this kind of problem is to:

- choose one peak from each of the two compounds you want to compare.
- decide how many hydrogens each peak is supposed to represent in a molecule. Is it supposed to be a CH2, a CH, a CH3?
- divide the integral value for that peak by that number of hydrogens it is supposed to represent in a molecule.
- compare the two answers (integral A / ideal # H) vs (integral B / ideal # H).
- the ratio of those two answers is the ratio of the two molecules in the sample.

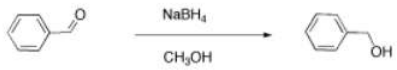
So there is twice as much aldehyde as alcohol in the mixture. In terms of these two compounds alone, she has 33% alcohol and 66% aldehyde. That's $\frac{1}{1+2} \times \%$ for the alcohol, and $\frac{2}{1+2} \times 100\%$(2/(1+2))for the aldehyde. That calculation just represents the amount of individual component divided by the total of the components she wants to compare.

There are a number of things to take note of here.

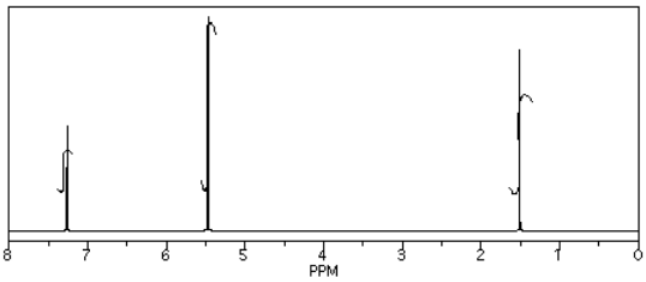
- Her reaction really didn't work very well. She still has majority starting material, not product.
- She will get a good grade on this lab. Although the experiment didn't work well, she has good data, and she has analyzed it very clearly.

- She has separated her data table into different sections for different compounds. Sometimes that makes it easier to analyze things.
- She has noted the actual integral data (she may have measured the integral with a ruler) and also converted it into a more convenient ratio, based on the integral for a peak that she felt certain about.
- She went one step further, and indicated the internal integration ratio within each individual compound.
- She calculated the % completion of the reaction using the integral data for the reactant and product, and she made clear what part of the data she used for that calculation. A similar procedure could be done if a student were just trying to separate two components in a mixture rather than carry out a reaction.
- She also calculated the overall purity of the mixture, including a solvent impurity that she failed to remove.
- However, $CHCl_3$ is not included in her analysis of purity. $CHCl_3$ really isn't part of her sample; it was just present in the NMR solvent, so it does not represent anything in the material she ended up with at the end of lab.

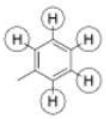
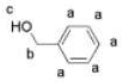
Another student carried out a similar reaction, shown below. He also finished the reaction by washing with water, but because methanol is soluble in water, he had to extract his product out of the water. He chose to use dichloromethane for that purpose.



He obtained the following data.



From this data, he constructed the following table.

	shift	integration	int(n)	multiplicity	partial structure	assignment
a	7.3 ppm	16 mm	5H	singlet		
b	5.4 ppm	64 mm	2H	singlet		
c	1.6 ppm	37 mm	1H	singlet	OH	

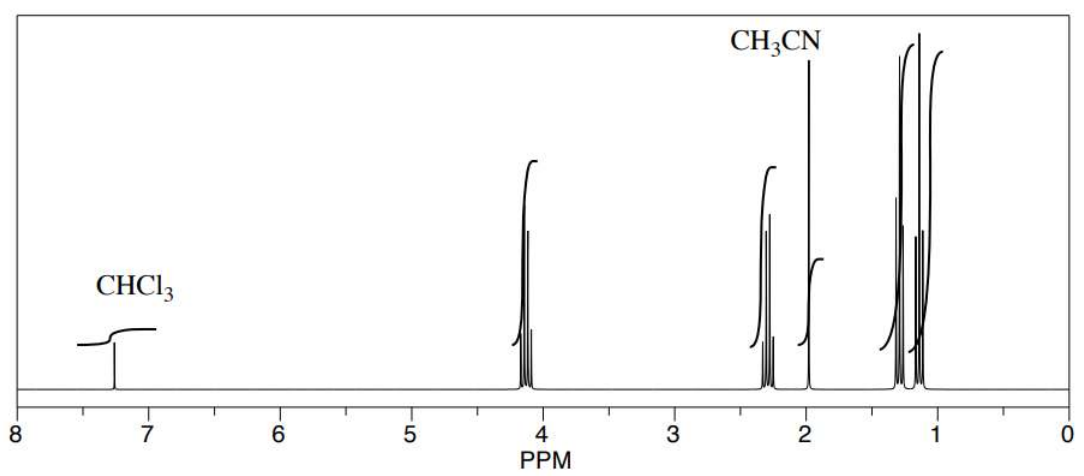
There are some things to learn about this table, too.

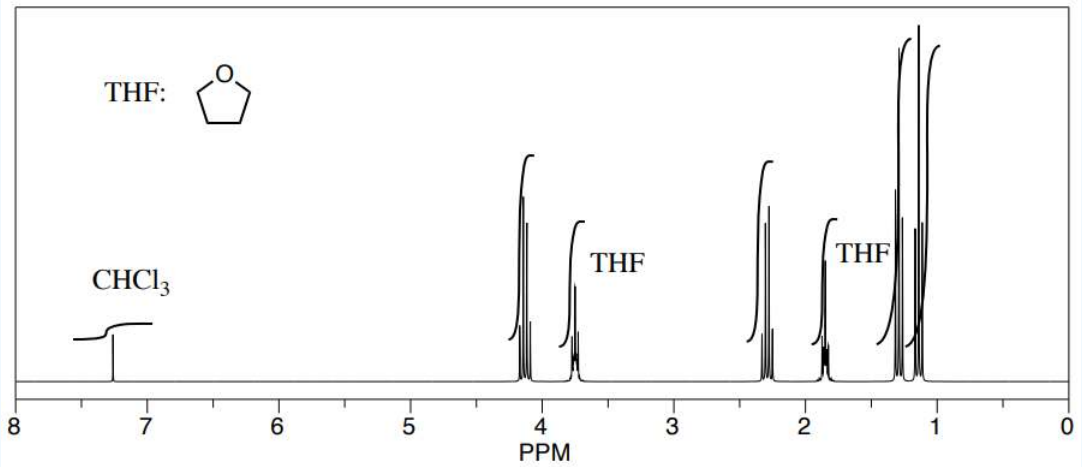
- Does the integration ratio really match the integral data? Or is this just wishful thinking?
- This table might reflect what he wants to see in the data. But what else could be in the data?
- $CHCl_3$ is often seen in NMR spectra if $CDCl_3$ is used for the NMR sample. It's there, at 7.2 ppm.
- "Leftover" or residual solvent is very common in real lab data. There it is, CH_2Cl_2 from the extraction, at 5.4 ppm.
- What about water? Sometimes people don't dry their solutions properly before evaporating the solvent. There is probably water around 1.5 to 1.6 ppm here.

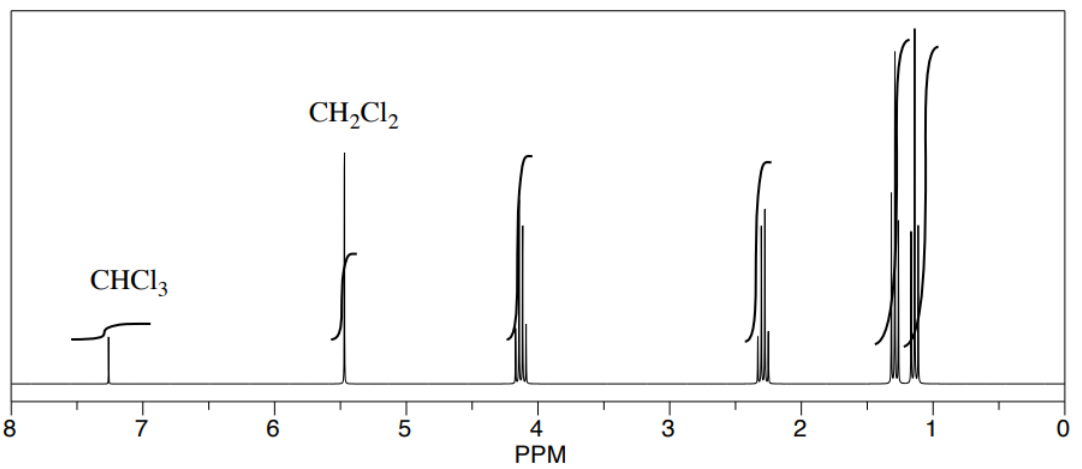
This student might not get a very good grade; the sample does not even show up in the spectrum, so he lost it somewhere. But his analysis is also poor, so he will really get a terrible grade.

Exercise 3.9.1

Three students performed a synthesis of a fragrant ester, ethyl propanoate, $CH_3CH_2CO_2CH_2CH_3$. During their reactions, they each used a different solvent. The students were able to see peaks in the NMR spectrum for ethyl propanoate, as well as peaks for chloroform ($CHCl_3$, in the $CDCl_3$ they used to make their NMR samples).







They were also able to determine that they had some leftover solvent in their samples by consulting a useful table of solvent impurities in NMR (which they found in Goldberg et. al., *Organometallics* **2010**, *29*, 2176-2179).

a. What is the ratio of leftover solvent to ethyl propanoate in each sample?
b. What is the percent of each sample that is leftover solvent?

Answer

a) student 1: Let's use the H_2C-O peak of ethyl propanoate at 4 ppm and the acetonitrile methyl at 2 ppm. The ratio appears to be 2:1, but they represent 2 protons and 3 protons, respectively. That means the ratio of molecules is 2/2:1/3 = 3:1 ethyl propanoate : acetonitrile.

student 2: We'll use the H_2C-O peak of ethyl propanoate at 4 ppm and the H_2C-O peak of THF at 3.5 ppm. The ratio appears to be 3:2, but they represent 2 protons and 4 protons, respectively. That means the ratio of molecules is 3/2:2/4 = 12:4 = 3:1 ethyl propanoate : THF.

student 3: Look at the H_2CCl_2 peak of dichloromethane at 5 ppm and the H_2C-O peak of THF at 4 ppm. The ratio appears to be 1:2, and they both represent 2 protons, so the ratio of molecules is 1:2 dichloromethane : ethyl propanoate.

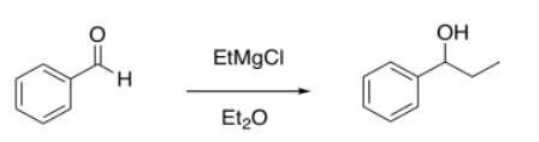
b) student 1: The sample is $[\frac{1}{1+3}] \times 100\% = 25$ acetonitrile.

student 2: The sample is $[\frac{1}{1+3}] \times 100\% = 25$ THF.

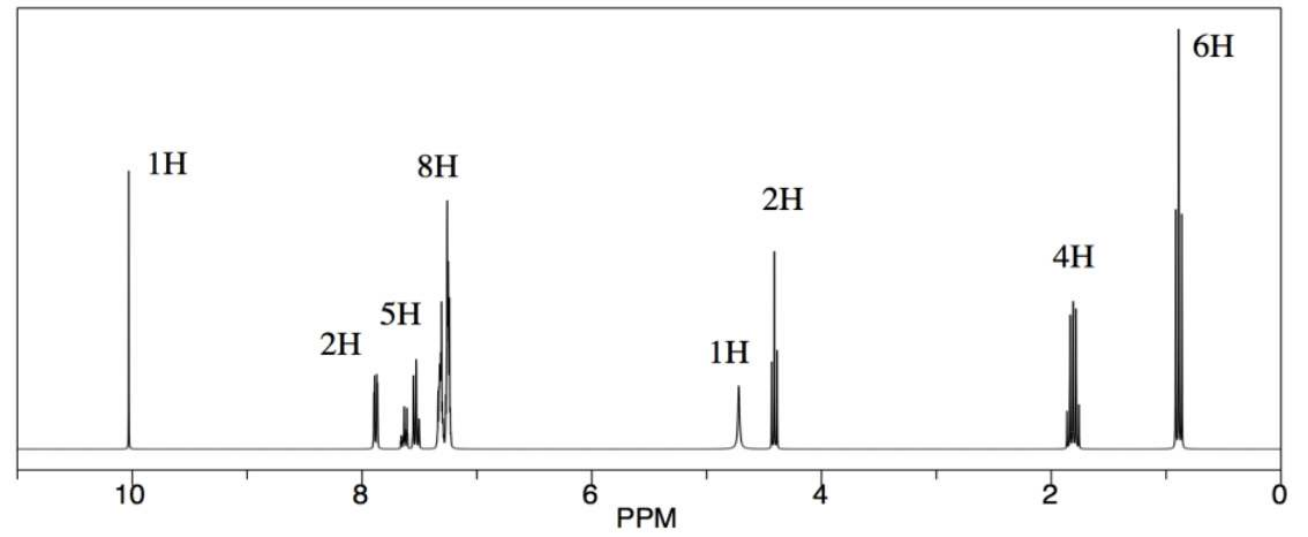
student 3: The sample is$[\frac{1}{1+2}] \times 100\% = 33$ acetonitrile.

Exercise 3.9.2

A student attempted to add a Grignard reagent to benzaldehyde.



She obtained the following data (well, this is a simulated spectrum). What was the composition of her product?



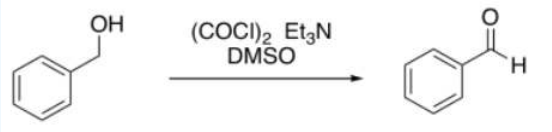
Answer

The obvious NMR handles are the H-C=O aldehyde proton at 10 ppm for benzaldehyde and the alcohol-adjacent H-C-O proton at 4.5 ppm for 1-phenylpropanol.

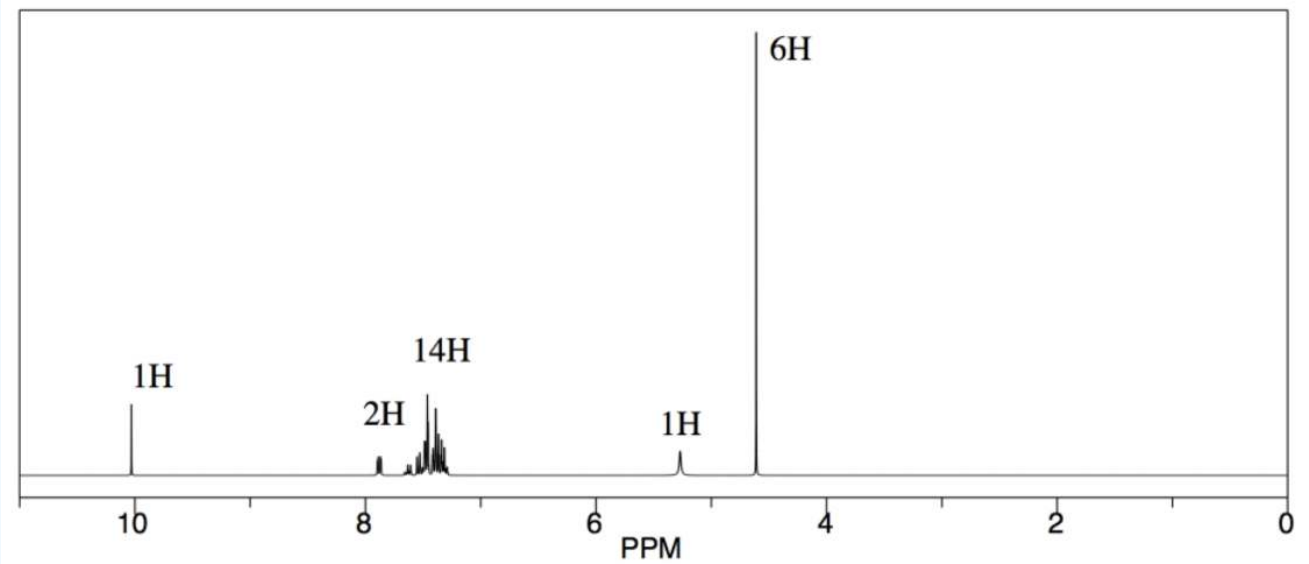
Each of those peaks represents one proton, so the integral ratio of 1:2 suggests a ratio of bezaldehyde to 1-phenylpropanol of of 1:2. That translates into 33% benzaldehyde, 67% 1-phenylpropanol.

Exercise 3.9.3

A student attempted to run a Swern oxidation on benzyl alcohol.



She obtained the following data (simulated spectrum). What was the composition of her product?



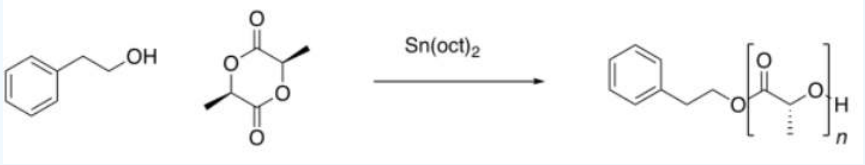
Answer

The NMR handles here are the H-C=O aldehyde proton at 10 ppm for benzaldehyde and the alcohol-adjacent H_2C-O protons near 5 ppm for benzyl alcohol.

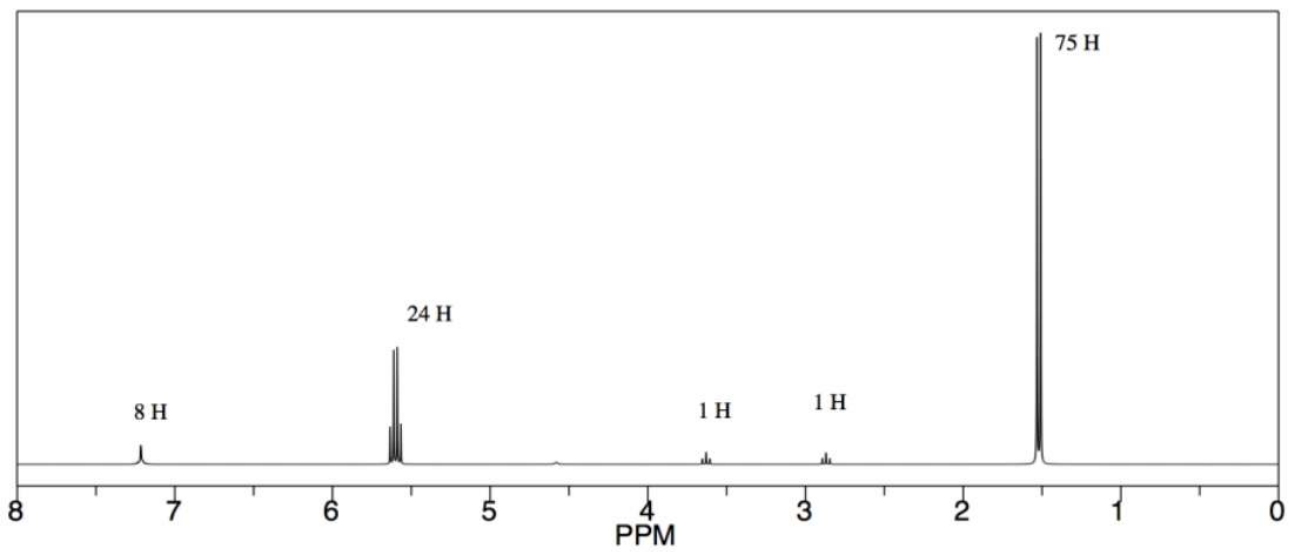
In this case, we need to correct for the differing numbers of protons represented by each peak: 1H for the aldehyde peak but 2H for the alcohol one. The integral ratio of 1:6 therefore suggests a ratio of bezaldehyde to 1-phenylpropanol of of 1:3. That translates into 25% benzaldehyde, 75% 1-phenylpropanol.

Exercise 3.9.4

A student attempted to carry out a ring-opening trans-esterification polymerization.



She obtained the following data (simulated spectrum). She knows that the alcohol should act as the initial nucleophile and should be found at the end of the polymer chain. What is the degree of polymerization (i.e. the number of repeating units in the chain)?



Answer

We could use the peak corresponding to the O-CH-C=O proton above 5 ppm for the repeat unit and the peak for the CH_2-O proton in the initiator/end group near 3.5 ppm. The integral ratio is 24:1, but they represent different numbers of hydrogens, so the repeat unit to end group ratio is really 24/1:1/2, or 48:1. The degree of polymerization is 48.

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3.10: 13C-NMR Spectroscopy

The ^{12}C isotope of carbon - which accounts for up about 99% of the carbons in organic molecules - does not have a nuclear magnetic moment, and thus is NMR-inactive. Fortunately for organic chemists, however, the ^{13}C isotope, which accounts for most of the remaining 1% of carbon atoms in nature, has a magnetic dipole moment just like protons. Most of what we have learned about ^{1}H-NMR spectroscopy also applies to ^{13}C-NMR, although there are several important differences.

The magnetic moment of a ^{13}C nucleus is much weaker than that of a proton, meaning that NMR signals from ^{13}C nuclei are inherently much weaker than proton signals. This, combined with the low natural abundance of ^{13}C, means that it is much more difficult to observe carbon signals: more sample is required, and often the data from hundreds of scans must be averaged in order to bring the signal-to-noise ratio down to acceptable levels. Unlike ^{1}H-NMR signals, the area under a ^{13}C-NMR signal cannot easily be used to determine the number of carbons to which it corresponds. The signals for some types of carbons are inherently weaker than for other types – peaks corresponding to carbonyl carbons, for example, are much smaller than those for methyl or methylene (CH_2) peaks. For this reason, peak integration is generally not useful in ^{13}C-NMR spectroscopy.

The resonance frequencies of ^{13}C nuclei are lower than those of protons in the same applied field - in an instrument with a 7.05 Tesla magnet, protons resonate at about 300 MHz, while carbons resonate at about 75 MHz. This is fortunate, as it allows us to look at ^{13}C signals using a completely separate 'window' of radio frequencies. Just like in ^{1}H-NMR, the standard used in ^{13}C-NMR experiments to define the 0 ppm point is tetramethylsilane (TMS),

although of course in ^{13}C-NMR it is the signal from the four equivalent *carbons* in TMS that serves as the standard. Chemical shifts for ^{13}C nuclei in organic molecules are spread out over a much wider range than for protons – up to 200 ppm for ^{13}C compared to 10-12 ppm for protons (see Table 3 for a list of typical ^{13}C-NMR chemical shifts).

The chemical shift of a ^{13}C nucleus is influenced by essentially the same factors that influence a proton's chemical shift: bonds to electronegative atoms and diamagnetic anisotropy effects tend to shift signals downfield (higher resonance frequency). In addition, sp^2 hybridization results in a large downfield shift. The ^{13}C-NMR signals for carbonyl carbons are generally the furthest downfield (170-220 ppm), due to both sp^2 hybridization and to the double bond to oxygen.

Exercise 5.15

How many sets of non-equivalent carbons are there in each of the molecules shown in exercise 5.2?

Exercise 5.16

How many sets of non-equivalent carbons are there in:

a) methylbenzene

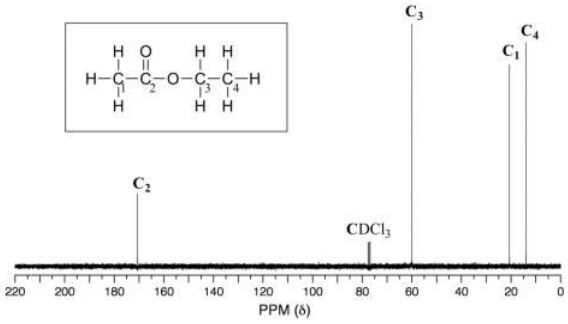
b) 2-pentanone

c) 1,4-dimethylbenzene

d) triclosan

(all structures are shown earlier in this chapter)

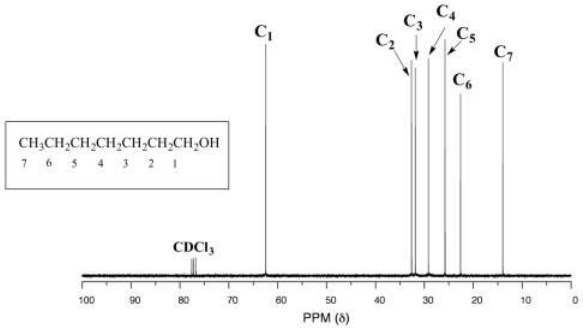
Because of the low natural abundance of ^{13}C nuclei, it is very unlikely to find two ^{13}C atoms near each other in the same molecule, and thus *we do not see spin-spin coupling between neighboring carbons in a ^{13}C-NMR spectrum*. ^{13}C nuclei are coupled to nearby protons, however, which results in complicated spectra. For clarity, chemists generally use a technique called **broadband decoupling**, which essentially 'turns off' C-H coupling, resulting in a spectrum in which all carbon signals are singlets. Below is the proton-decoupled ^{13}C-NMR sectrum of ethyl acetate, showing the expected four signals, one for each of the carbons. We can also see a signal for the carbon atom in the deuterated chloroform ($CDCl_3$) solvent (although a detailed discussion is beyond our scope here, it is interesting to note that this signal is split into a triplet by deuterium, which is NMR active and has *three* possible spin states rather than two). We can ignore the solvent signal when interpreting ^{13}C-NMR spectra.



While broadband decoupling results in a much simpler spectrum, useful information about the presence of neighboring protons is lost. However, another NMR technique called DEPT (Distortionless Enhancement by Polarization Transfer) allows us to determine how many hydrogens are bound to each carbon. This information is usually provided in problems in which you are asked to interpret the ^{13}C-NMR spectrum of an unknown compound. (Details of how the DEPT technique works is beyond the scope of this book, but will be covered if you take a more advanced course in spectroscopy.)

One of the greatest advantages of ^{13}C-NMR compared to ^{1}H-NMR is the breadth of the spectrum - recall that carbons resonate from 0-220 ppm relative to the TMS standard, as opposed to only 0-12 ppm for protons. Because of this, ^{13}C signals rarely overlap, and

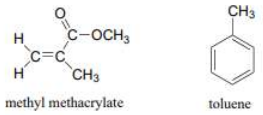
we can almost always distinguish separate peaks for each carbon, even in a relatively large compound containing carbons in very similar environments. In the proton spectrum of 1-heptanol we saw earlier only the broad singlet of the alcohol proton (H_a) and the triplet for (H_b) are easily analyzed. The other proton signals overlap, making analysis difficult. In the ^{13}C spectrum of the same molecule, however, we can easily distinguish each carbon signal, and we know from this data that our sample has seven nonequivalent carbons. (Notice also that, as we would expect, the chemical shifts of the carbons get progressively lower as they get farther away from the deshielding oxygen.)



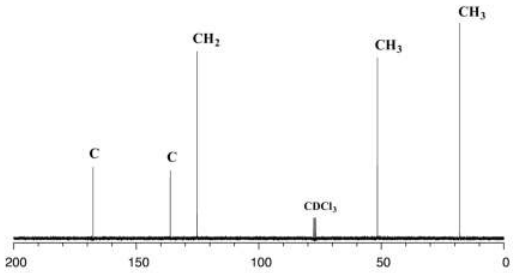
This property of ^{13}C-NMR makes it very helpful in the elucidation of larger, more complex structures.

Exercise 5.17

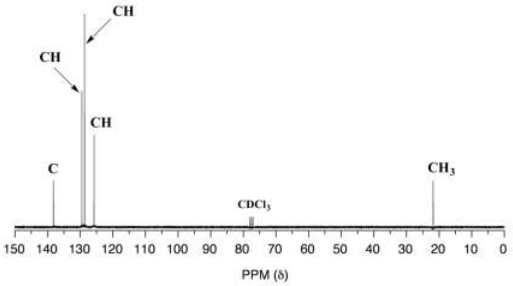
Below are ^{13}C-NMR spectra for methylbenzene (common name toluene) and methyl methacrylate. Match the spectra to the correct structure, and make peak assignments.



Spectrum A:



Spetrum B:



Exercise 5.18

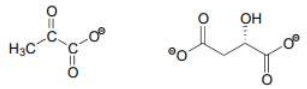
^{13}C-NMR data for some common biomolecules are shown below (data is from the Aldrich Library of ^{1}H and ^{13}C NMR). Match the NMR data to the correct structure, and make complete peak assignments.

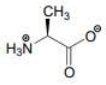
spectrum a: 168.10 ppm (C), 159.91 ppm (C), 144.05 ppm (CH), 95.79 ppm (CH)

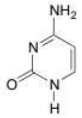
spectrum b: 207.85 ppm (C), 172.69 ppm (C), 29.29 ppm (CH_3)

spectrum c: 178.54 ppm (C), 53.25 ppm (CH), 18.95 ppm (CH_3)

spectrum d: 183.81 ppm (C), 182. 63 ppm (C), 73.06 ppm (CH), 45.35 ppm (CH_2)





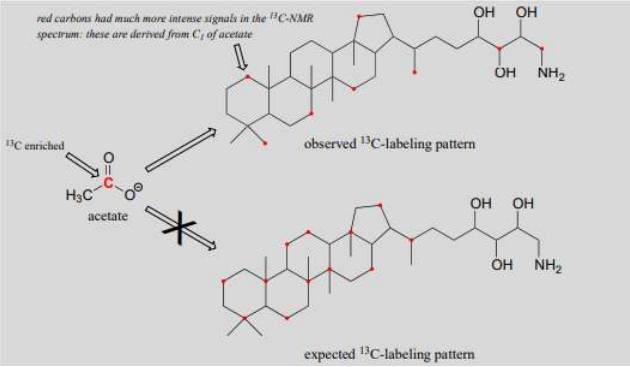


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^{13}C-NMR in Isotopic Labeling Studies

Although only about 1 out of 100 carbon atoms in a naturally occurring organic molecule is a 13C isotope, chemists are often able to synthesize molecules that are artificially enriched in 13C at specific carbon positions. This can be very useful in biochemical studies, because it allows us to 'label' one or more carbons in a small precursor molecule and then trace the presence of the 13C label through a biosynthetic pathway all the way to the final product, providing insight into how the biosynthesis occurs. For example, scientists were able to grow bacteria in a medium in which the only source of carbon was acetate enriched in 13C at the C1 (carbonyl) position. When they isolated an isoprenoid compound called amino-bacterio-hopanetriol synthesized by the bacteria and looked at its 13C-NMR spectrum, they observed that the 13C label from acetate had been incorporated at eight specific

positions. They knew this because the 13C-NMR signals for these carbons were much stronger compared to the same signals in a control (unlabeled) compound.



This result was very surprising - the scientists had expected a completely different pattern of 13C incorporation based on what they believed to be the isoprenoid biosynthesis pathway involved. This unexpected result led eventually to the discovery that bacteria synthesize isoprenoid compounds by a completely different pathway then yeasts, plants, and animals. The newly discovered bacterial metabolic pathway is currently a key target for the development of new antibiotic and antimalaria drugs. (Eur. J. Biochem. 1988, 175, 405).

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3.11: Symmetry in Spectroscopy

Butane shows two different peaks in the ^{13}C NMR spectrum, below. Note that:

- the chemical shifts of these peaks are not very different from methane. The carbons in butane are in a similar environment to the one in methane.
- there are two distinct carbons in butane: the methyl, or CH_3, carbon, and the methylene, or CH_2, carbon.
- the methyl carbon absorbs slightly upfield, or at lower shift, around 10 ppm.
- the methylene carbon absorbs at slightly downfield, or at higher shift, around 20 ppm.
- other factors being equal, methylene carbons show up at slightly higher shift than methyl carbons.

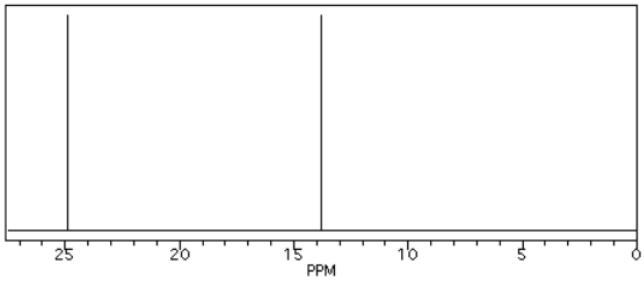


Figure **3.11.1**: Simulated ^{13}C NMR spectrum of butane (showing only the upfield portion of the spectrum).

In the ^{13}C NMR spectrum of pentane (below), you can see three different peaks, even though pentane just contains methyl carbons and methylene carbons like butane. As far as the NMR spectrometer is concerned, pentane contains three different kinds of carbon, in three different environments. That result comes from symmetry.

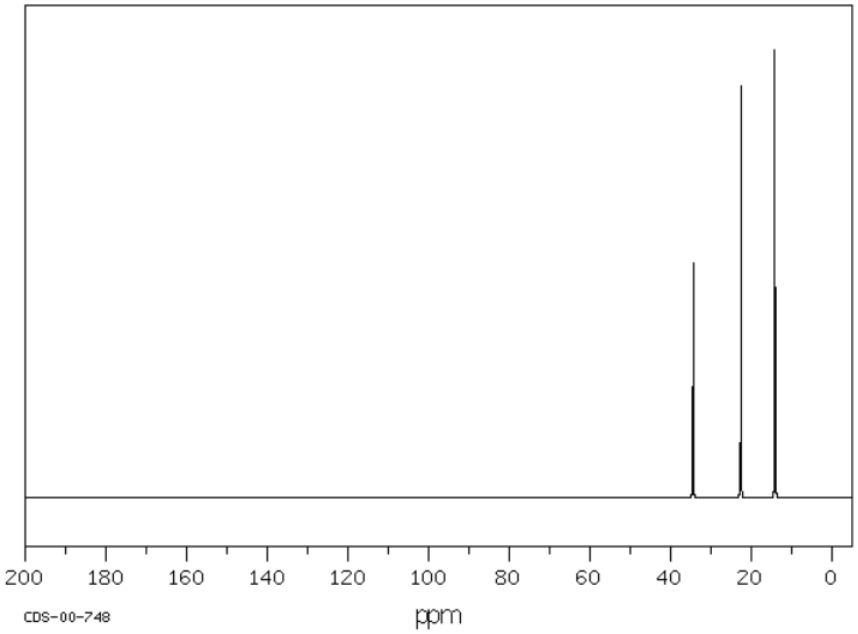


Figure **3.11.2**: Simulated ^{13}C NMR spectrum of butane (showing only the upfield portion of the spectrum).

In the ^{13}C NMR spectrum of pentane (below), you can see three different peaks, even though pentane just contains methyl carbons and methylene carbons like butane. As far as the NMR spectrometer is concerned, pentane contains three different kinds of carbon, in three different environments. That result comes from symmetry.

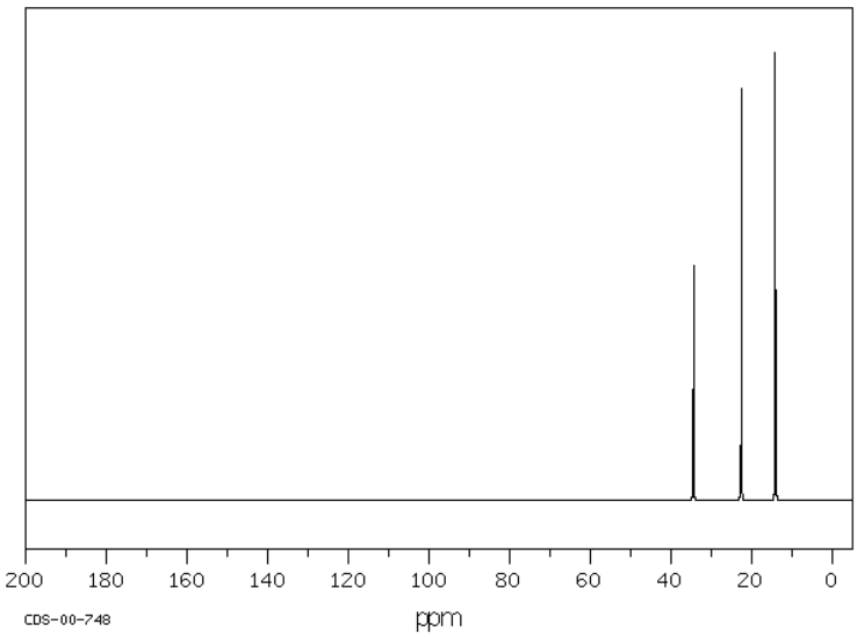


Figure **3.11.3**: ^{13}C NMR spectrum of pentane. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

Symmetry is an important factor in spectroscopy. Nature says:

- atoms that are symmetry-inequivalent can absorb at different shifts.
- atoms that are symmetry-equivalent must absorb at the same shift.

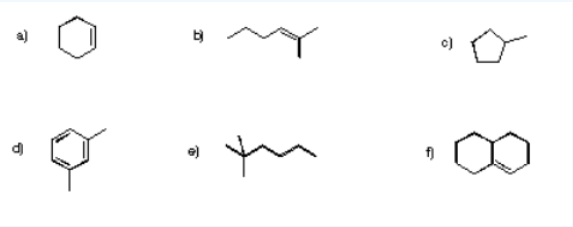
To learn about symmetry, take a model of pentane and do the following:

- make sure the model is twisted into the most symmetric shape possible: a nice "W".
- choose one of the methyl carbons to focus on.
- rotate the model 180 degrees so that you are looking at the same "W" but from the other side.
- note that the methyl you were focusing on has simply switched places with the other methyl group. These two carbons are symmetry-equivalent via two-fold rotation.

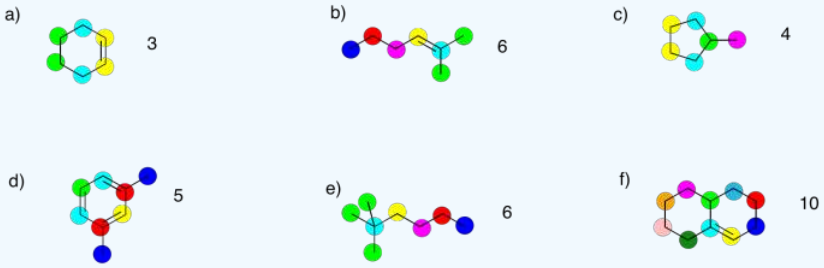
By the same process, you can see that the second and fourth carbons along the chain are also symmetry-equivalent. However, the middle carbon is not; it never switches places with the other carbons if you rotate the model. There are three different sets of inequivalent carbons; these three groups are not the same as each other according to symmetry.

? Exercise 3.11.1

Determine how many inequivalent carbons there are in each of the following compounds. How many peaks do you expect in each ^{13}C NMR spectrum?



Answer



Exercise 3.11.2

Based on an IR spectrum, you have determined that your sample is a saturated hydrocarbon; it contains only C-C and C-H bonds. Assuming a straight chain structure with no branches, what could be the structure in the following cases:

a. 3 peaks in the ^{13}C spectrum
b. 4 peaks in the ^{13}C spectrum
c. 5 peaks in the ^{13}C spectrum

Answer

Based on an IR spectrum, you have determined that your sample is a saturated hydrocarbon; it contains only C-C and C-H bonds. Assuming a straight chain structure with no branches, what could be the structure in the following cases:

3 peaks in the ^{13}C spectrum 4 peaks in the ^{13}C spectrum 5 peaks in the ^{13}C spectrum

Practically speaking, there is only so much room in the spectrum from one end to the other. At some point, peaks can get so crowded together that you can't distinguish one from another. You might expect to see ten different peaks in eicosane, a twenty-carbon alkane chain, but when you look at the spectrum you can only see seven different peaks. That may be frustrating, because the experiment does not seem to agree with your expectation. However, you will be using a number of methods together to minimize the problem of misleading data.

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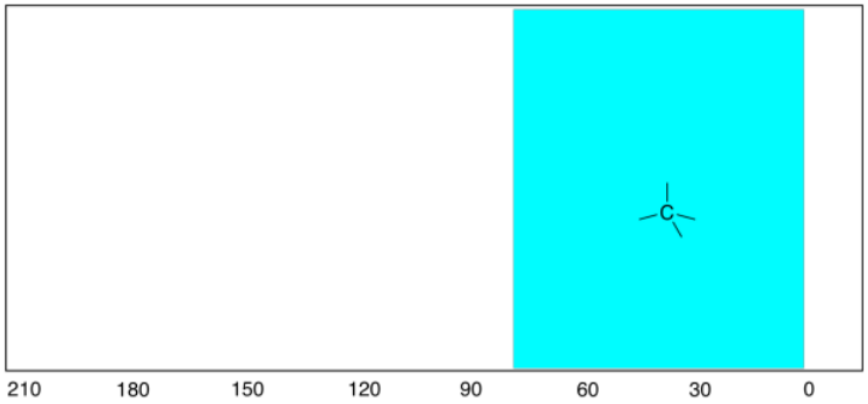
3.12: Factors in Chemical Shift- Carbon Geometry

As in IR spectroscopy, the frequency at which different carbons absorb in the NMR spectrum is pretty predictable. There are two main factors that control the shift. These two factors are :

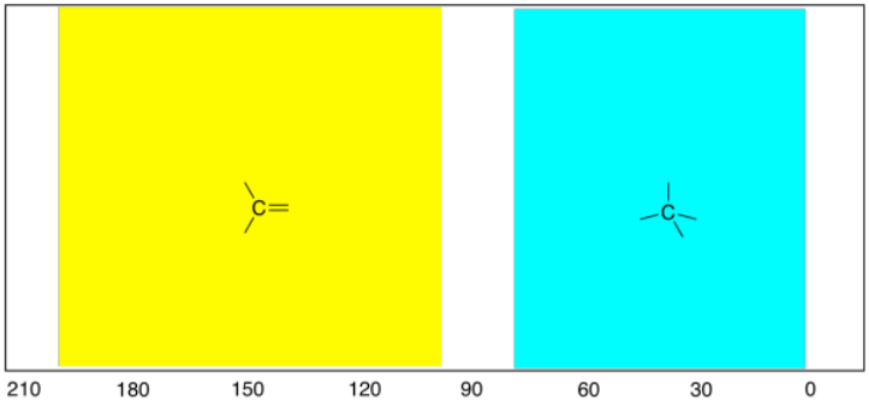
- the geometry around the carbon atom.
- the electronegativity of the other atoms attached to the carbon.

First we'll look at the influence of geometry.

In all of the hydrocarbon spectra seen above, the only peaks observed are at the right-hand end of the spectrum. The ^{13}C spectrum ranges from about 0 ppm to about 200 ppm, and all of the peaks we observed were well below 100 ppm. One of the things that those compounds had in common (cyclohexane, butane, pentane) was that they contain only tetrahedral (or sp^3) carbons. And, in fact, that kind of carbon atom generally shows up below 100 ppm (typically below 80 ppm) in the ^{13}C spectrum.



That's an important trend to know, because tetrahedral carbons are quite common in nature. Another shape of carbon atom, trigonal planar, is also pretty common. In contrast to the tetrahedral carbons, these carbons show up in the left-hand half of the spectrum, between 100 and 200 ppm.



As a *general* rule:

- sp^2 or trigonal planar carbons absorb in the left half of the spectrum (100 - 200 ppm).
- sp^3 or tetrahedral carbons absorb in the right half of the spectrum (0 - 100 ppm).

In the ^{13}C NMR spectrum of another hydrocarbon, 1-hexene, most of the peaks show up at the right-hand end, but two others show up farther to the left. A comparison of the structures will tell you that these two peaks are from the double-bonded carbons.

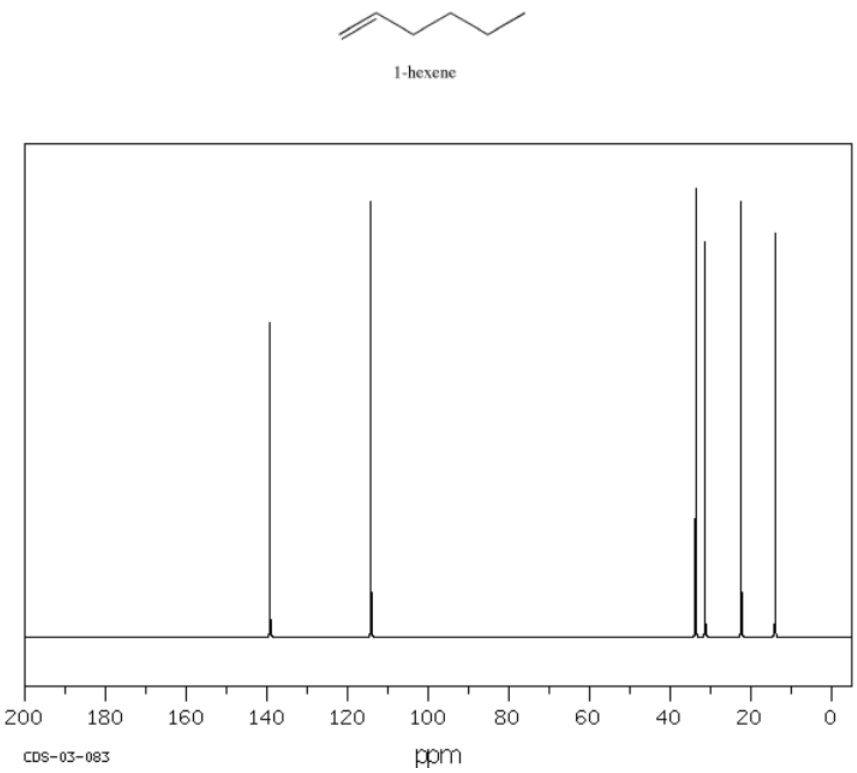
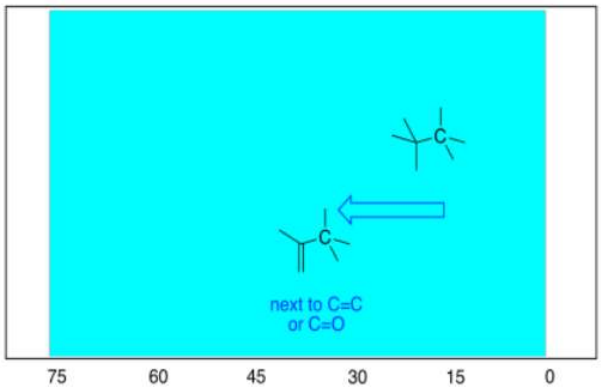


Figure 3.12.1: ^{13}C NMR spectrum of 1-hexene. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

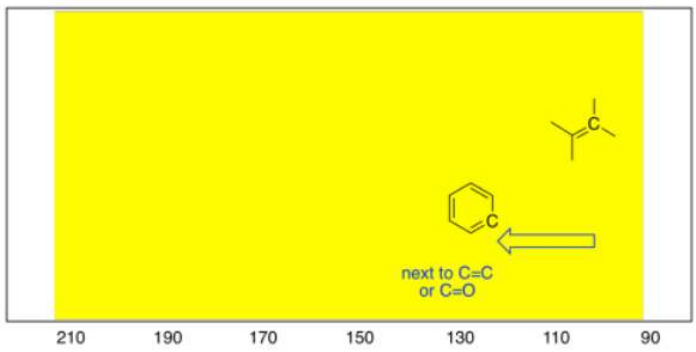
The alkene, 1-hexene, shows four peaks below 20 ppm and two near 100 ppm. The two carbons that absorb near 100 ppm are the two trigonal carbons that form the alkene functional group; the others are tetrahedral carbons.

Remember, a general rule means that there will be exceptions. You might see sp^2 carbons at 210 ppm or 95 ppm, for example. You are not likely to see them at 30 ppm, however.

There are some more subtle factors that influence the shift of a carbon atom in the spectrum, having to do with what the neighbouring groups are in the compound. For example, a tetrahedral carbon shifts a little bit downfield if it is next to a trigonal planar carbon. The reason has to do with the way the magnetic field that is used in this experiment recruits the electrons of double bonds, essentially magnetizing them, as well.

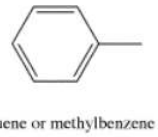


The same thing happens if trigonal planar carbons are near other trigonal planar carbons. Just as in the tetrahedral case, these sp^2 carbons can be pulled to the left under the influence of neighbouring double bonds. As a result, carbons in benzene rings show up slightly to the left of carbons in alkenes.



- sp^2 carbons in alkenes show up near the upfield end of the sp^2 half of the spectrum (usually around 100-120 ppm).
- sp^2 carbons in aromatic systems like benzene absorb a little farther downfield than alkenes (around 120-160 ppm).

Another compound that contains both sp^2 and sp^3 carbons is toluene or methylbenzene. Its ^{13}C NMR spectrum shows one peak near 30 ppm and four between 120 and 130 ppm.



toluene or methylbenzene

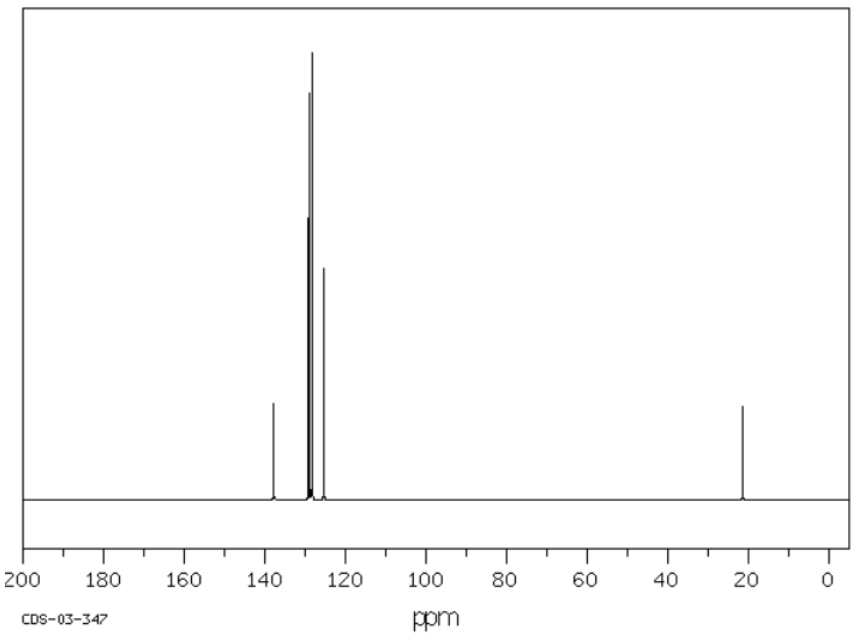
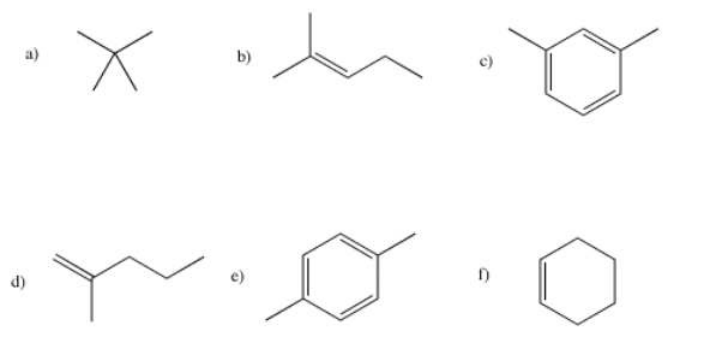


Figure **3.12.2**: ^{13}C NMR spectrum of toluene. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

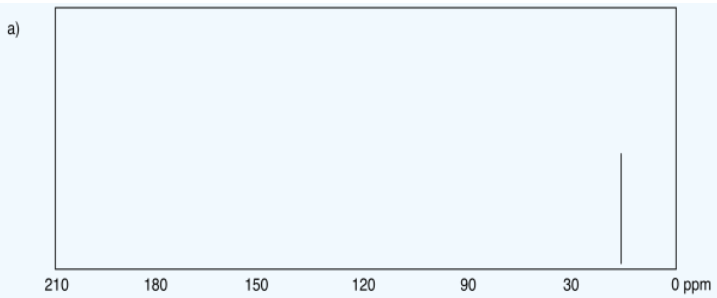
? Exercise 3.12.1

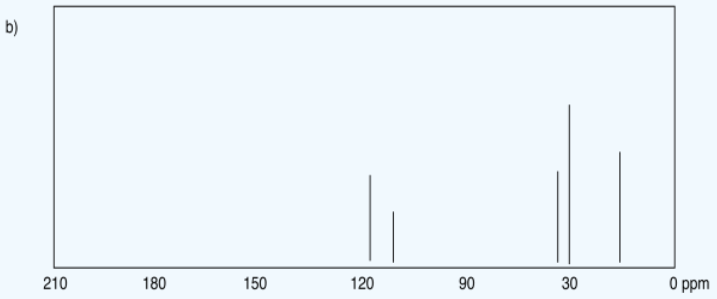
Draw an approximate ^{13}C NMR spectrum for each of the following compounds. You will need to take into account symmetry and carbon geometry.

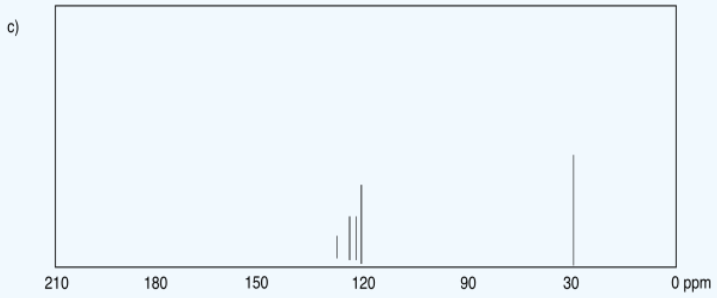


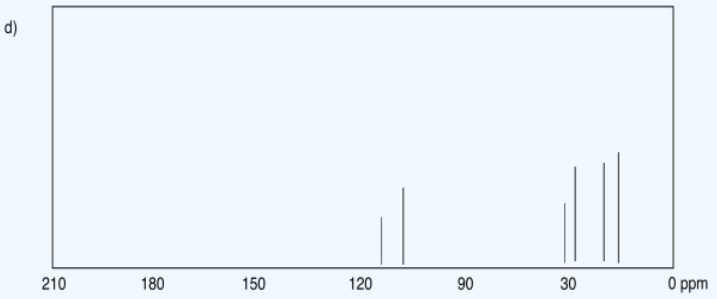
Answer

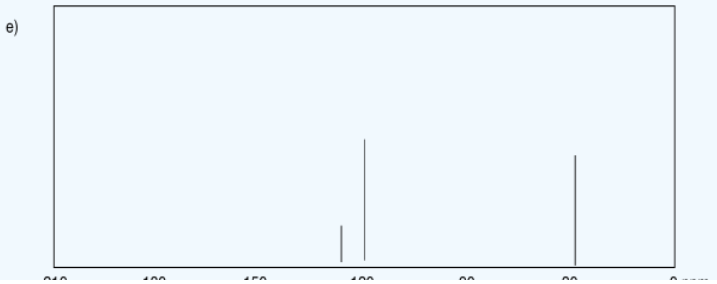
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? Exercise 3.12.2

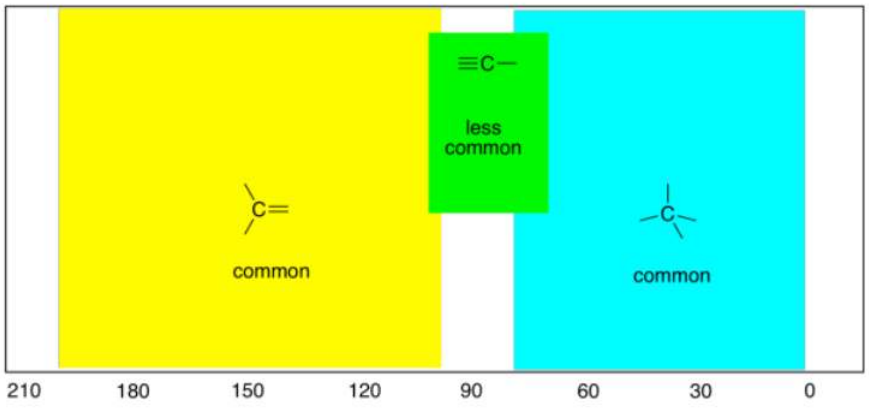
Determine whether the following peaks represent sp^2 (trigonal planar) or sp^3 (tetrahedral) carbon atoms.

a) 27 ppm b) 198 ppm c) 112 ppm d) 15 ppm e) 79 ppm f) 164 ppm

Answer

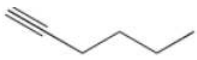
a) sp^3 b) sp^2 c) sp^2 d) sp^3 e) sp^3 f) sp^2

In addition, there are also linear carbons in organic chemistry, although they are much less common as tetrahedral and trigonal carbons. Linear or sp carbons absorb at about 60 to 100 ppm, sort of in the middle of the spectrum. Mostly they are seen around 60-80 ppm, so they overlap considerably with sp^3 carbons.



- sp or linear carbons absorb around 60-100 ppm.
- clearly, some sp^3 carbons absorb at frequencies similar to sp carbons. Be careful.

One example of a compound containing sp carbons is 1-hexyne. Its spectrum is shown below.



1-hexyne

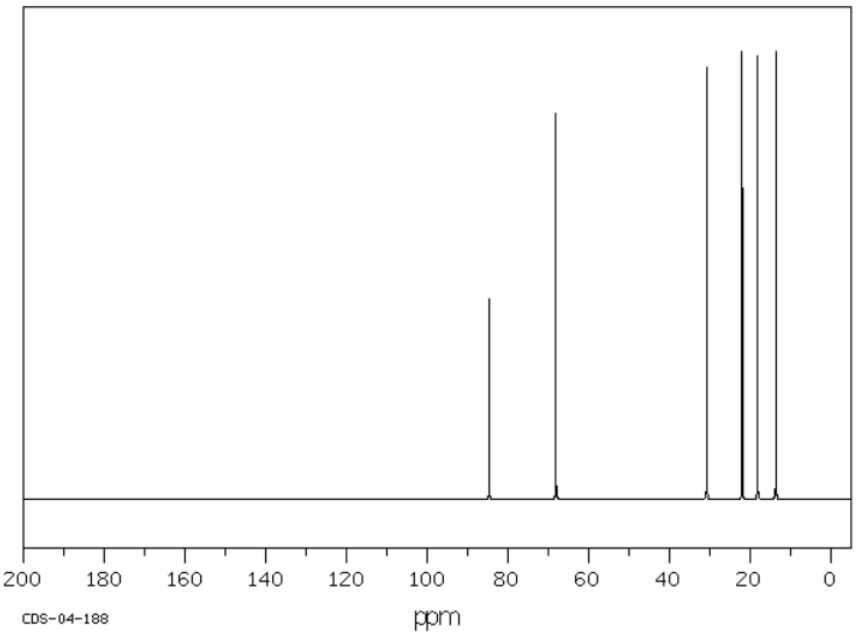


Figure **3.12.3**: ^{13}C NMR spectrum of 1-hexyne. Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

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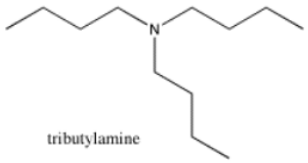
- **4.4: Factors in Chemical Shift- Carbon Geometry** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

3.13: Factors in Chemical Shift- Electronegativity

Electronegativity is a second factor that influences NMR spectra. The frequency of radio waves absorbed by an atom depends on the magnetic field experienced at the nucleus. The magnetic field experienced at the nucleus depends on the amount of electron density around the atom. Consequently:

- the more electron density present, the further upfield the shift in the spectrum.
- the less electron density present around the atom, the further downfield the shift.

Tributylamine has an NMR spectrum with four peaks, one for each inequivalent carbon in the structure. These peaks are spread out just a little bit more than in a hydrocarbon; there are more peaks showing up further downfield. The carbon next to the nitrogen is the one that shows up furthest downfield.



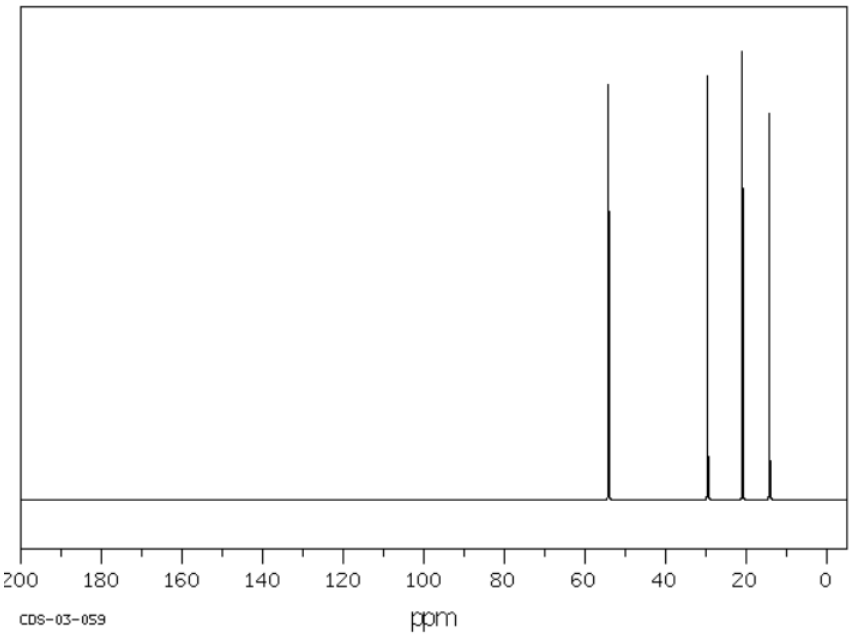
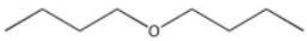


Figure **3.13.1**: ^{13}C NMR spectrum of tributylamine.

Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

- usually, a tetrahedral carbon shows up in the upfield half of the spectrum.
- the region from about 0 to 100 ppm can be thought of as the sp^3 window.
- an electronegative atom moves a peak further downfield within the sp^3 window.

Dibutyl ether has peaks that show up even further downfield. As in tributylamine, the carbon next to the heteroatom, in this case an oxygen, shows up the furthest downfield. The other carbons in the chain also show up a little farther downfield than they would in butane, but the further from the oxygen they are, the less effect the oxygen has on them. This is a typical inductive effect. In an inductive effect, atoms have an effect on each other through sigma bonds, but the further apart the atoms are the smaller the effect.



dibutyl ether or butyl ether

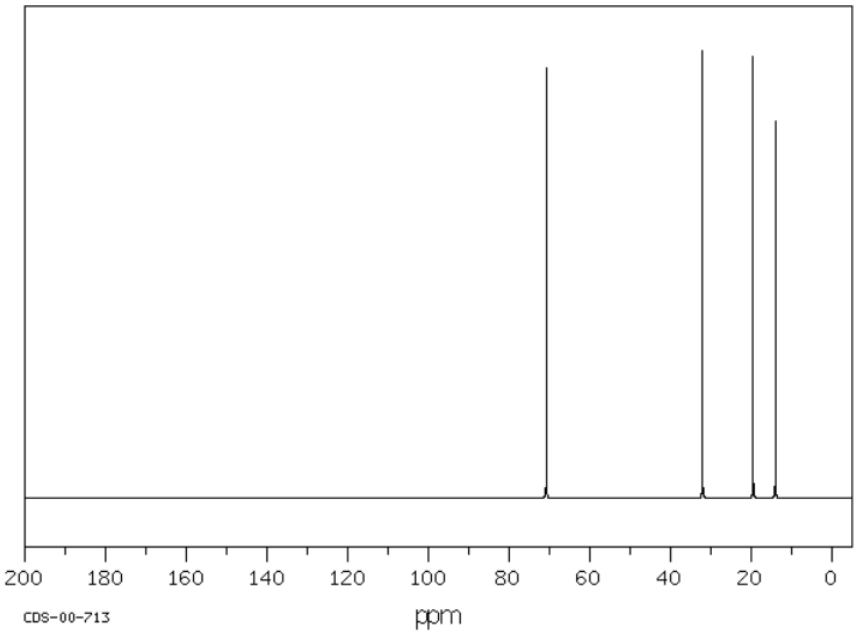
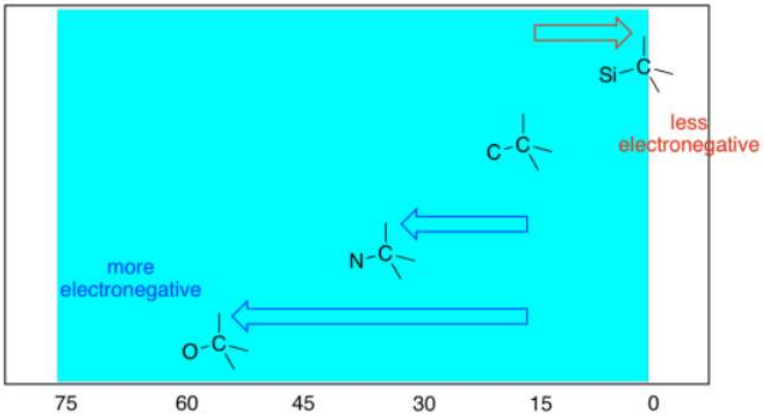


Figure **3.13.2**: ^{13}C NMR spectrum of butyl ether.

Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

Notice that the absorbance of a carbon next to an oxygen atom was shifted even more to the left than a carbon next to a nitrogen atom. The more electronegative the neighbour, the greater the effect. You would probably expect a less electronegative neighbour than carbon will result in a shift to the right, and generally that's the case.



In summary:

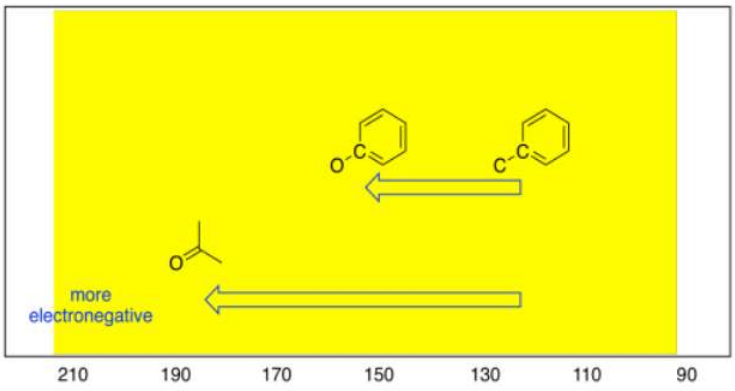
- electronegative elements draw attached carbons downfield.
- the more electronegative the element, the farther downfield the attached carbon.
- electronegative elements also have an effect on atoms further down the chain, drawing them downfield.
- the farther the atom is from the electronegative atom, the smaller the effect.
- the effect of electronegative atoms on their neighbors is called an inductive effect.

Methane (CH_4) absorbs at about 5 ppm in the ^{13}C NMR spectrum. Chloromethane absorbs at about 30 ppm. Since chlorine is about as electronegative as nitrogen, the effect of a chlorine or a nitrogen on an attached carbon are similar.

Dichloromethane or methylene chloride (CH_2Cl_2) shows up at about 55 ppm, and trichloromethane or chloroform ($CHCl_3$) at about 80 ppm. The more bonds there are to an electronegative element, the further downfield the carbon absorbs. In the case of a chlorinated carbon, each additional chlorine moves the peak about 25 ppm further downfield.

- the effect of electronegativity is additive.
- the more electronegative elements attached to a carbon, the farther downfield it absorbs.

These trends are also seen among sp^2 carbons. An oxygen atom attached to an sp^2 carbon results in a downfield shift, to about 160 ppm. On the other hand, if a trigonal planar carbon is double bonded to an oxygen atom, the shift can be much farther; it actually ranges from 160 to 210 ppm, depending on what else is attached to the carbon, and is most commonly seen around 180 ppm.

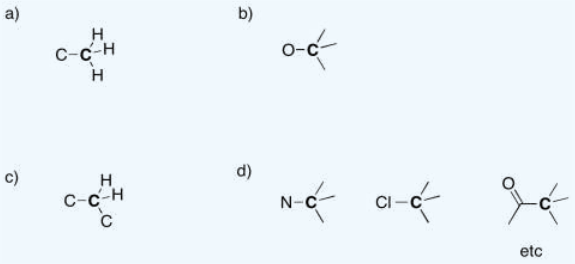


Exercise 3.13.1

Suggest an assignment for the following ^{13}C NMR peaks:

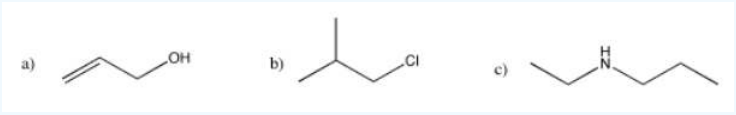
a) 12 ppm b) 58 ppm c) 22 ppm d) 41 ppm

Answer

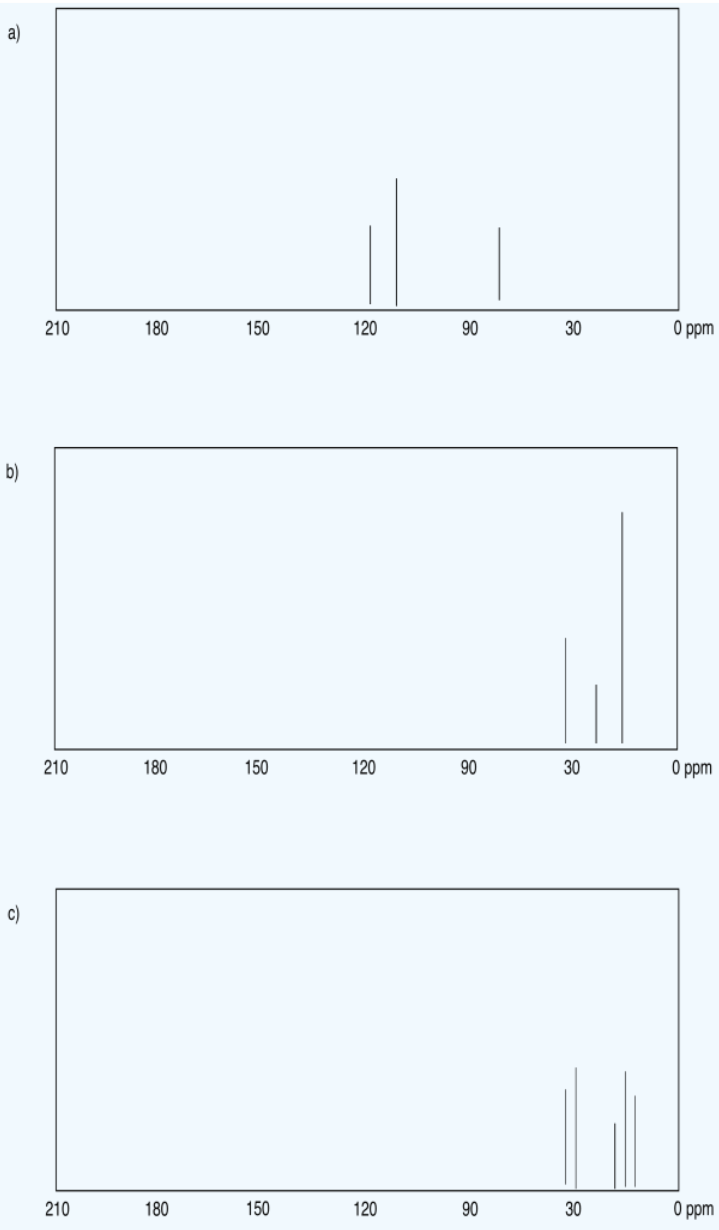


Exercise 3.13.2

Draw the predicted ^{13}C NMR spectra for the following compounds.



Answer

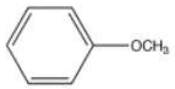


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3.14: More on Electronic Effects

Methoxybenzene or anisole has six carbons, but only four peaks in the spectrum because of symmetry. These peaks are all above 100 ppm, but some peaks are as far downfield as 160 ppm.



methoxybenzene

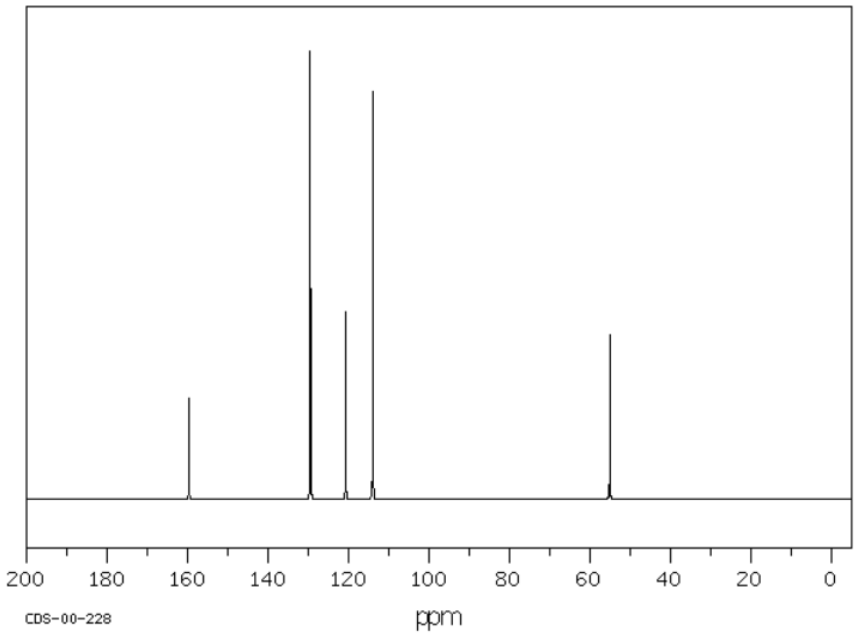
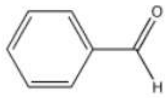


Figure **3.14.1**: ^{13}C NMR spectrum of methoxybenzene (anisole).

Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

- usually, a trigonal planar carbon shows up in the downfield half of the spectrum.
- the region from about 100 to 200 ppm can be thought of as the sp^2 window.
- an electronegative atom moves a peak further downfield within the sp^2 window.

Benzaldehyde has peaks between 130 and 140 ppm, as well as one near 190 ppm. Just as in the sp^3 region of the spectrum, when a carbon is attached to an electronegative element, it moves further downfield, and since the carbonyl (or C=O) carbon in the aldehyde has two bonds to oxygen, it shows up considerably downfield. The carbonyl carbon in some ketones can show up as far as 210 ppm.



benzaldehyde

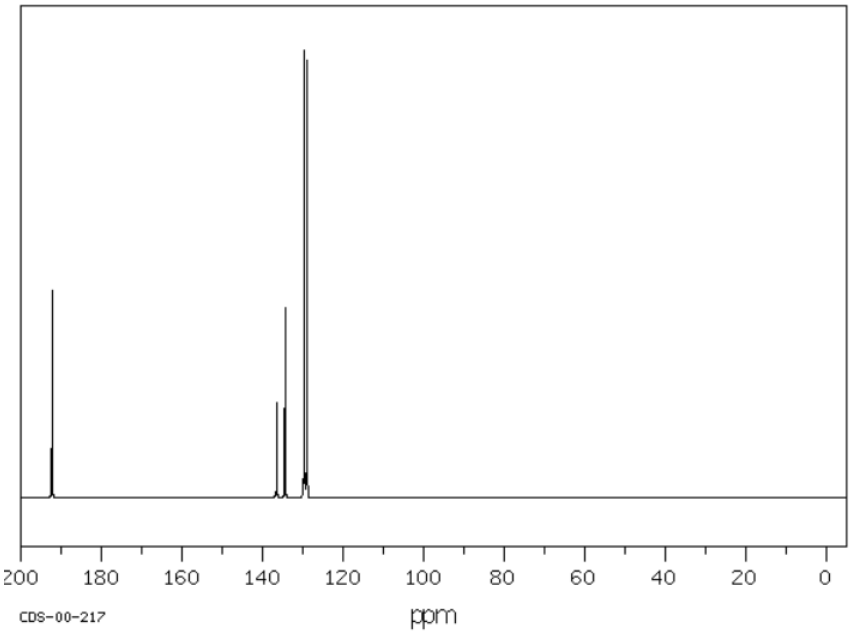


Figure **3.14.2**: ^{13}C NMR spectrum of benzaldehyde.

Source: SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 15 August 2008)

- Carbonyl carbons may show up even further downfield than 200 ppm.
- Carbonyl carbons have a great deal of positive charge and low electron density.

? Exercise 3.14.1

Suggests possible assignments for the following chemical shifts in a ^{13}C NMR spectrum.

a) 127 ppm b) 11 ppm c) 196 ppm d) 65 ppm e) 111 ppm

f) 154 ppm g) 210 ppm h) 28 ppm i) 170 ppm j) 42 ppm

Answer

a) 127 ppm



b) 11 ppm



c) 196 ppm



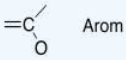
d) 65 ppm



e) 111 ppm



f) 154 ppm



g) 210 ppm



h) 28 ppm



i) 170 ppm



j) 42 ppm

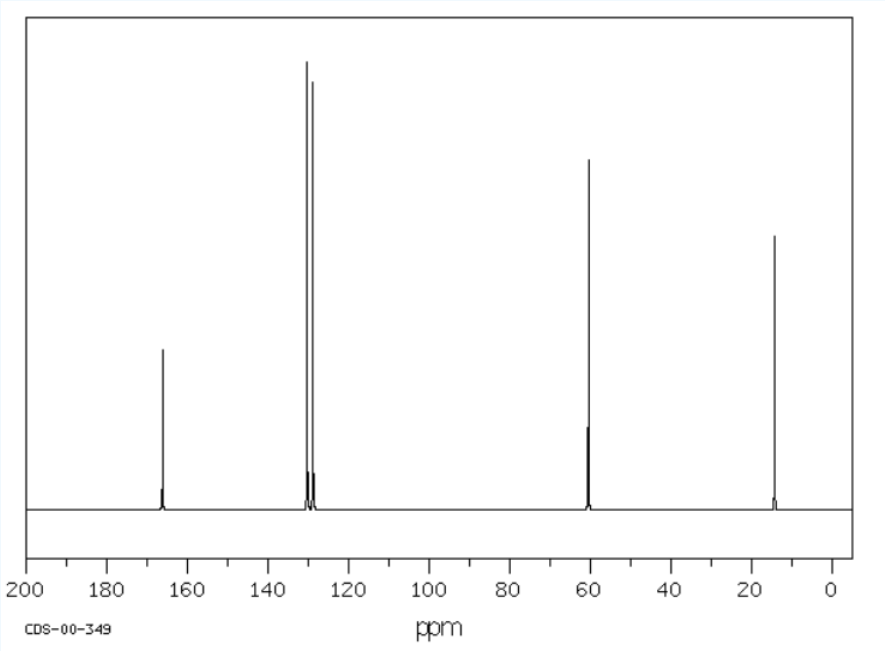


? Exercise 3.14.2

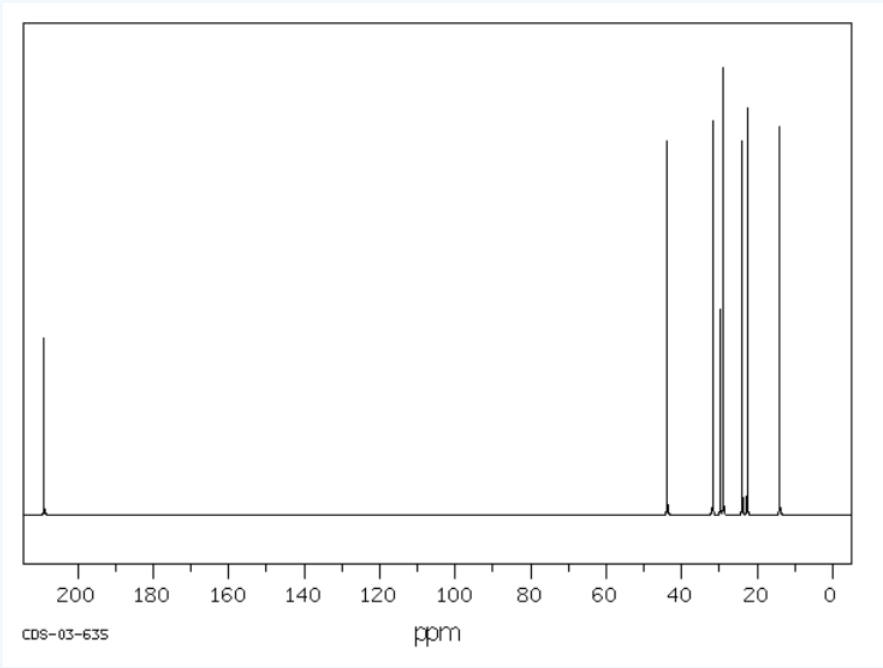
Suggest possible structures for the following spectra.

Source: SDBSWeb : riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology of Japan, 19 August 2008)

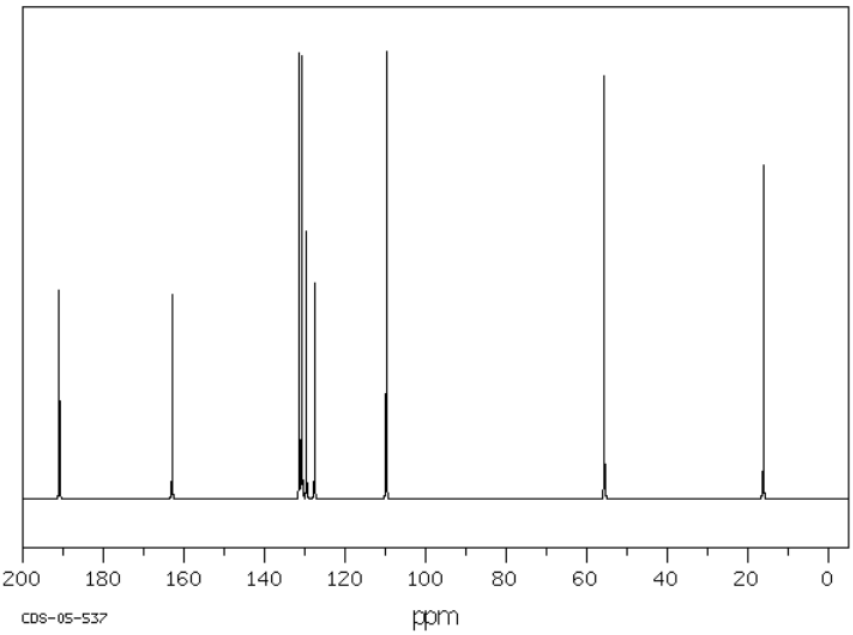
a)


200
180
160
140
120
100
80
60
40
20
0
CDS-00-349
ppm

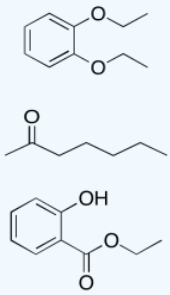
b)


200
180
160
140
120
100
80
60
40
20
0
CDS-03-635
ppm

c)



Answer



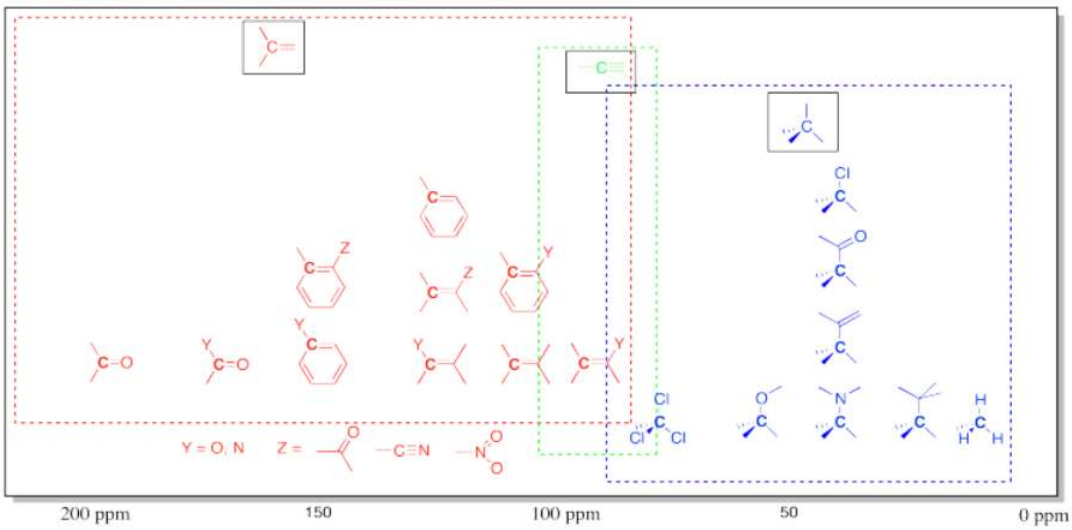
There are subtle effects of electronegativity in saturated hydrocarbons like hexane. Carbons in different positions in those compounds show up at different shifts. In general, a methyl group (CH_3) will show up farther upfield than a methylene group (CH_2), which will in turn show up further upfield from a methyne group (CH). This trend is related to the difference in electronegativity between a carbon and a hydrogen. Carbon is slightly more electronegative than a hydrogen. As a result, a carbon atom that is bonded to a number of hydrogen atoms has a very slight negative charge. That means it absorbs further upfield. A carbon that is bonded to a number of carbons is more neutral, is not quite so shielded, and shows up a little more downfield.

Unless there are bigger electronegative effects due to heteroatoms such as oxygen,

- methyl (CH_3) groups show up furthest upfield.
- methylene (CH_2) groups show up next furthest upfield.
- methyne (CH) groups show up furthest downfield.

We can use NMR spectroscopy as a diagnostic tool to determine the structure of a compound. ^{13}C NMR spectroscopy is useful in highlighting whether there are any double bonds in a molecule, whether there are any heteroatoms such as oxygen, and how many different kinds of carbons there are. That last point isn't the same as the number of carbons, but is related to the symmetry of the molecule.

Table 3.14.1: Approximate chemical shifts in ^{13}C NMR spectroscopy.



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3.15: Constructing Partial Structures in NMR Spectroscopy and Combined Structure Determination

When you look at an IR spectrum, you immediately see little chunks of the structure, because you see individual bonds. You know at a glance that the compound contains a C=O bond or an O-H bond. That can be very reassuring, because you can quickly imagine what you are dealing with.

NMR spectra often take more work. You may have to put pencil to paper to come up with a structure. The work pays off, because you can get a much more detailed picture of the structure.

Let's start with a ^{13}C NMR spectrum. Suppose you had peaks in the spectrum at 200, 35 and 15 ppm. We might assign these three peaks as follows:

shift (ppm)	**partial structure**
200	sp^2 **C**=O
35	sp^3 **C**-C=O
30	sp^3 **C**-C=O
15	sp^3 **C**-C

We are saying that the first carbon is in the sp^2 or trigonal planar region, and that it is so far downfield because of a double bond to oxygen. The other two carbons are in the sp^3 or tetrahedral region. One of them isn't very far downfield; it is probably just attached to another sp^3 carbon. The other two, at 35 and 30 ppm, are both a little further downfield. That's around the right place for a tetrahedral carbon attached to a trigonal planar carbon; that is, these carbons are each attached to either a double bond or a carbonyl.

In the partial structure, we always **bold** or <u>underline</u> the carbon that corresponds to the peak we are discussing. If you don't do that, it isn't clear whether the peak at 30 comes from a carbon next to the carbonyl (C=O), or the carbon in the carbonyl itself. Also, on the peak at 15, we want to make clear that we are talking about a single carbon atom; leaving the partial structure as C-C somehow implies that this spectroscopy observes bonds, but it does not. IR spectroscopy observes bonds. ^{13}C NMR spectroscopy observes carbon atoms.

Now, suppose we look at the ^{1}H NMR spectrum for the same compound. Maybe we see three peaks this time. There is a quartet integrating for 2H at 2.3 ppm, a singlet integrating for 3H at 2.1 ppm, and a triplet integrating for 3H at 1.1 ppm. We enter those characteristics in a table. This time, there are three features to explain for each peak.

shift	**integ.**	**multipl.**	**partial structure**
2.3	2H	quartet	CH_3-C**H**$_2$-C=O
2.1	3H	singlet	C**H**$_3$-C=O
1.1	3H	triplet	C**H**$_3$-CH2

First of all, we need to explain the shift. All of these peaks are in the upfield end of the spectrum (below 5 ppm), so they are likely from hydrogens on sp^3 or tetrahedral carbons. The first two are slightly downfield, just past 2 ppm. That suggests that the sp3 carbons they are attached to may in turn be attached to sp^2 carbons: either double bonds or carbonyls. We already know there is a carbonyl from the ^{13}C spectrum, so let's assume that's what is causing the shift near 2 ppm. The third peak, at 1.1 ppm, is in the normal range; this hydrogen is on a tetrahedral carbon, likely attached to other tetrahedral carbons.

To demonstrate what the integration is telling us, we just show the correct number of hydrogens. There are two hydrogens responsible for the peak at 2.3 ppm. Three others are responsible for the peak at 2.1 ppm, and another three give rise to the peak at 1.1 ppm.

Finally, we need to explain the muliplicity. The peak at 2.3 ppm is a quartet, so by the "n+1" rule it must be next to a CH_3 group. The peak at 1.1 ppm is a triplet, so it must be next to a CH_2 group. (It does not take long to figure out that these two peaks represent hydrogens that are next to each other.) Finally, the peak at 2.1 ppm is a singlet. It has no hydrogen neighbors at all.

Notice we do not need to know what the structure is in order to fill in these partial structures. We are just writing down what the data is telling us. From there, it isn't very far to determine the overall structure.

? Exercise 3.15.1

Fill in partial structures for the following peaks.

a) 10.1 ppm, 1H, triplet b) 3.4 ppm, 1H, septet c) 7.3 ppm, 2H, triplet

d) 5.4 ppm, 1H, quartet e) 1.4 ppm, 2H, sextet f) 8.0 ppm, 1H, singlet

g) 2.1 ppm, 3H, singlet h) 6.8 ppm, 2H, doublet i) 0.9 ppm, 6H, doublet

Answer

Aromatic (benzene etc) peaks are labeled "Ar" to distinguish from alkene peaks that show up further upfield (lower shift). Also, some peaks may be in two symmetric positions and are labeled with "x2".

a) 10.1 ppm, 1H, triplet, CH_2-C**H**=O b) 3.4 ppm, 1H, septet, O-C**H**$(CH_3)_2$

c) 7.3 ppm, 2H, triplet, CH=C**H**-CH x 2 (Ar) d) 5.4 ppm, 1H, quartet, CH_3-C**H**=C

e) 1.4 ppm, 2H, sextet, CH_3-C**H**$_2$-CH_2 f) 8.0 ppm, 1H, singlet, C=C**H**-C (Ar)

g) 2.1 ppm, 3H, singlet, C**H**$_3$-C=C or C**H**$_3$-C=O or C**H**$_3$-N; need context to choose

h) 6.8 ppm, 2H, doublet, CH=C**H**-C x 2 (Ar) i) 0.9 ppm, 6H, doublet, CH-C**H**$_3$ x 2

? Exercise 3.15.2

Identify the errors in the following partial structures:

a) 3.6 ppm, 2H, triplet, C**H**$_2$-CH_2 b) 2.1 ppm, 2H, singlet, C**H**$_3$-C=C

c) 7.4 ppm, 2H, doublet, CH=C**H**$_2$-C d) 1.8 ppm, 2H, quintet, C**H**$_2$-CH_4

e) 7.8 ppm, 1H, triplet, -C**H**=CH_2 f) 1.7 ppm, 1H, nonet, NH_2-C**H**$(CH_3)_2$

Answer

Identify the errors in the following partial structures:

a) 3.6 ppm, 2H, triplet, C**H**$_2$-CH_2 the first carbon must be attached to O to have a shift at 3.6 ppm

b) 2.1 ppm, 2H, singlet, C**H**$_3$-C=C the integral says only 2H, not 3H

c) 7.4 ppm, 2H, doublet, CH=C**H**$_2$-C the shift implies aromatic, so there can only be one H per carbon; must be symmetry

d) 1.8 ppm, 2H, quintet, C**H**$_2$-CH_4 there can't be four hydrogens on one carbon; must be some hydrogens on each side

e) 7.8 ppm, 1H, triplet, -C**H**=CH_2 the shift implies aromatic, so there can only be one H per carbon; must be one one each side

f) 1.7 ppm, 1H, nonet, NH_2-C**H**$(CH_3)_2$ an attached nitrogen would shift this hydrogen past 2 ppm; also, coupling is rarely seen across O or N, so the two neighbouring H on the left are probably on a carbon.

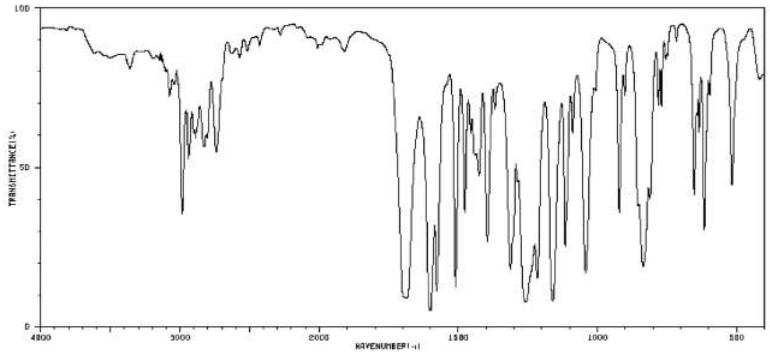
There are a many ways we can use NMR spectroscopy to analyse compounds. One common application is in determination of an unknown structure. Given the MS, IR, ^{13}C and ^{1}H NMR spectra, what might be the structure of an unknown sample?

It is often easiest to start with the IR spectrum.

- identify at least three peaks in the IR spectrum. Which peaks seem to tell you the most information about this compound?
- don't think with your head; think with your hands. Write down ideas on the spectrum.
- if you are working on a formal proof of structure, on a class test or a lab report, you may be required to enter your data in a table correlating wavenumber with peak assignment:

cm^{-1}	asst

For example, a student might obtain the following IR spectrum.



From that information, she constructs the following table. She might even write this table, by hand, directly on her spectrum. She makes useful notes on the edges, and might even include some guesses, which she later crosses out, but does not erase. She is assisted in this task by consulting an IR table, that suggests what some of these peaks might mean.

frequency (cm^{-1})	description	assignment
3400	weak, broad	OH (water?)
2990	medium, sharp	sp3 C-H
2800 & 2700	medium, sharp	aldehyde C-H
1700	strong	C=O
1250	strong	C-O
1150	strong	(C-O ??)
825	strong	C=C-H bending

Remember:

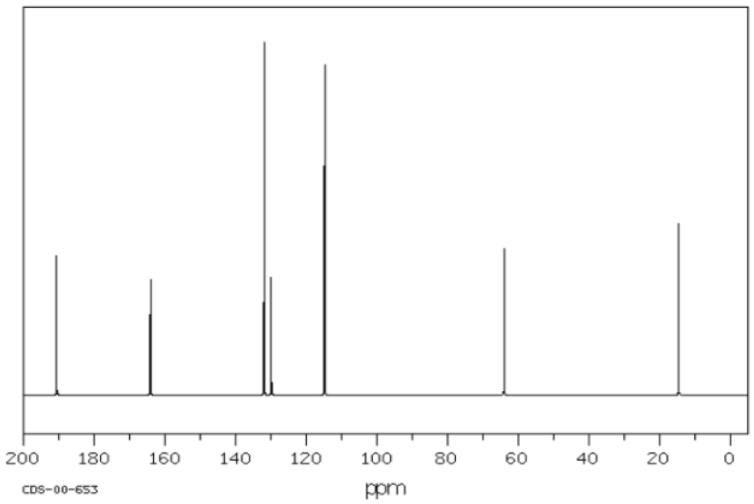
- make special note of what atoms are present in the compound: C, H, N, O...
- also note your initial ideas about specific functional groups that may be present.
- if you are unsure of an assignment, put a question mark beside it to signal this uncertainty.
- some data may need to be discarded later if it is not consistent with other data.

Look at the ^{13}C spectrum.

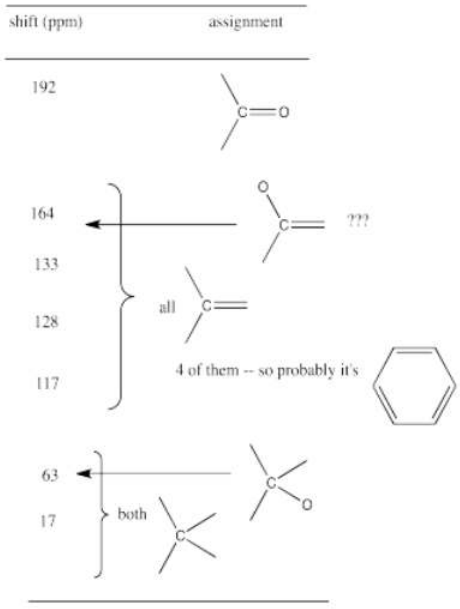
- How many different carbons are there, based on the number of peaks in the spectrum? This is the first step in estimating the molecular formula.
- Do you have reason to believe there is symmetry in the structure? In the entire compound or just part of it? Adjust the number of carbons you think you are dealing with.
- As in IR spectroscopy, begin assigning peaks, either on the spectrum or, if required, in a table:

ppm	asst

For example, a student might obtain the following ^{13}C NMR spectrum:



From that information, she puts together the following table:



Remember:

- you will be able to assign all peaks in the NMR spectrum, not just a few like in IR.

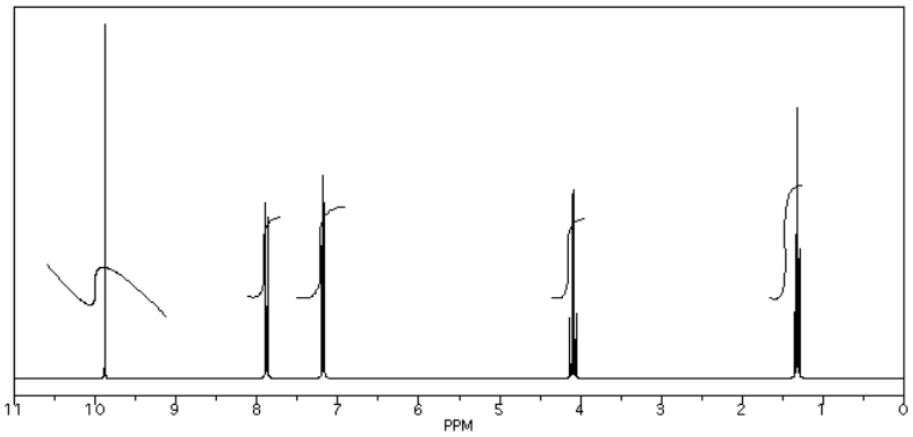
As in ^{13}C NMR, you should be able to assign all peaks in the ^{1}H NMR spectrum. You may be able to do so by making notes on the spectrum. If you think you know the structure, you may be able to draw it and note which peak belongs with which proton.

A formal proof of structure might require a table of assignments.

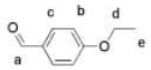
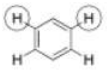
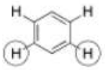
ppm	int	mult	partial structure	assignment

- This table demonstrates your ability to read the spectrum. Can you decide what ratio of protons is suggested by the integral line? Can you decide whether a peak is a quartet?
- The partial structure column should explain the shift, integration and multiplicity for the peak in that row. It should not show any other information from elsewhere in the structure. This restriction forces you to demonstrate a thorough understanding of the data in a way that "getting the right answer" does not.
- The partial structure column is best filled in with drawings, not words. The drawing is a partial structure.
- Because the partial structure will show the protons absorbing at the shift in that row as well the neighbouring protons, you need to distinguish between them in your picture. Most people circle or underline or make **bold** the protons that show up at the shift given in that row.
- When finished with the partial structure column, you should be able to link the partial structures together to make an entire structure in the assignment column.

An example of a spectrum and its accompanying data table is given below. Here is the spectrum:



Here is a data table:

	shift	integration	int(n)	multiplicity	partial structure	assignment
a	9.7 ppm	11 mm	1H	singlet		
b	7.5 ppm	23 mm	2H	doublet		
c	8.1 ppm	21 mm	2H	doublet		
d	3.8 ppm	24 mm	2H	quartet		
e	1.2 ppm	35 mm	3H	triplet		

Things to note:

- This student has used two integration columns instead of just one.
- The first column shows the integral measured from the spectrum. She probably used a ruler.
- The second column, which she called int(n), contains a convenient ratio taken from the raw data. This ratio is easier to use in her assignments.
- Also note that the peak at 9.7 ppm does not have a very good integral. There is either a "phasing" or a "level & tilt" problem here that can be corrected using the NMR software, but this is sometimes difficult to do. If she had taken an automatic printout of this integral measurement, she would have gotten a strange number; in this case, it would be about -5, because the end of the integral line is lower than the start. It clearly isn't a negative number of hydrogens, though. She has instead measured the vertical rise in the integral and recorded that; it isn't perfect, but is a fair estimate in this case.

There are a couple of additional tools that can help to confirm the structure at this point. Alternatively, if the structure is still elusive, these tools might help to produce some ideas.

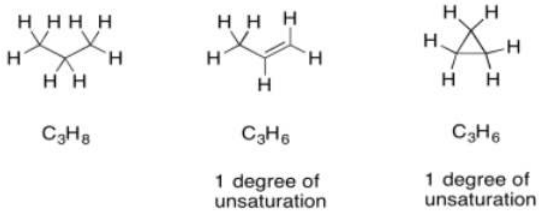
The first tool is the formula. Once we have NMR tables, we can begin guessing at the numbers of carbons and hydrogens in the structure. With the addition of an IR table, we can begin guessing at the presence of other atoms, such as oxygen or maybe nitrogen.

For example, in the ^{13}C NMR table above, there were seven peaks. That means there are probably at least seven carbons. We can start off the molecular formula as C_7. However, there may be additional carbons if there is some symmetry. There may also be a few carbons that do not show up very well in the spectrum. If you have ever obtained a real ^{13}C NMR spectrum, you will know that carbonyl peaks can be hard to find, especially if there are no hydrogens attached to the carbonyl. In the table above, it looked like there was a benzene, so maybe there werereally six carbons in the aromatic region, and not just four carbons. That would mean the formula, so far, is C_9.

In the ^{1}H NMR table, the integrals added up to a total of 10H. So, maybe the formula is C_9H_{10}.

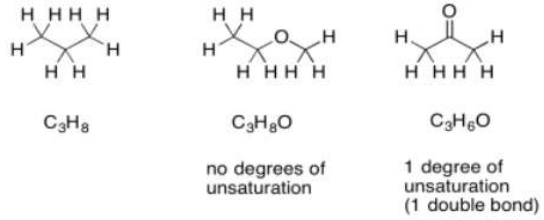
Furthermore, the IR table suggested the possible presence of two different oxygen atoms. The formula may actually be $C_9H_{10}O_2$.

Once we have a formula, we actually get a great deal of information automatically. One of the most important pieces is "units of unsaturation" or "degrees of unsaturation" (DU). The DU is the result of a formal comparison of the C/H ratio in the compound to that in a normal alkane. In a normal alkane, the formula is always C_nH_{2n+2}. If you picture a long hydrocarbon chain, there will be two hydrogens on each carbon along the chain, plus one more hydrogen at either end of the chain. However, an alkene contains one pi bond, and at the site of that pi bond there are two hydrogen atoms missing from that alkane formula. A simple alkene always has the formula C_nH_{2n}. That missing pair of hydrogens in the formula is called a degree of unsaturation.

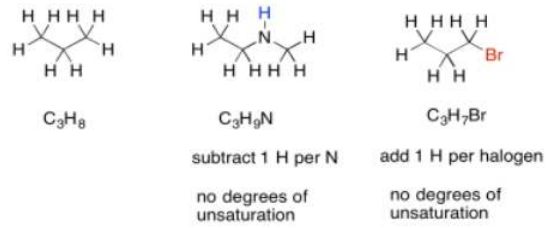


The same thing also happens to the formula if there is a ring present. One DU can correspond to the presence of a double bond or a ring. If DU=2, there may be two double bonds, two rings, or one of each.

If there are oxygen atoms present in the formula, we can just ignore them and pay attention to the hydrocarbon part. Conceptually, because oxygen forms two bonds, we can think of it as squeezing in between any two atoms in a hydrocarbon structure to form a new compound. The ratio of carbon to hydrogen is unchanged. If there is a degree of unsturation in a formula containing oxygen, it simply suggests the presence of a ring or a double bond, just like in a hydrocarbon.



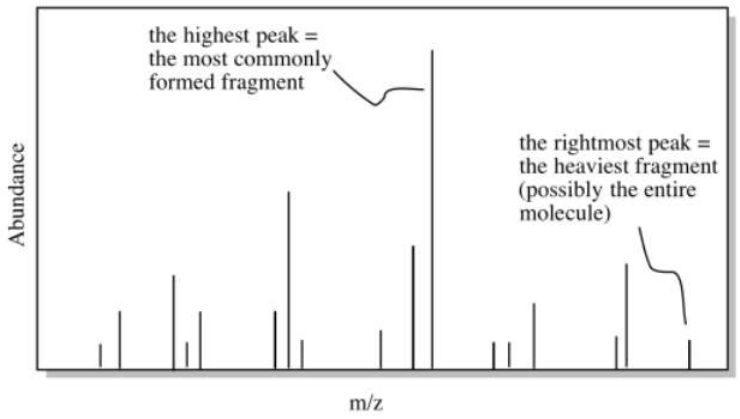
Sometimes, if there are other atoms present, we need to adjust the formula to take them into account. For example, any time a halogen is found in the structure, it conceptually replaces a hydrogen atom. In order for a halogen to be found in the structure, there would have to be one fewer hydrogen atoms in order to open up a spot for the halogen. To adjust for the presence of a halogen, we need to add one hydrogen into the formula, then compare it to the standard alkane formula.



Nitrogen, on the other hand, has three bonds. Unlike oxygen, if we squeeze it in between two other atoms, it still needs one extra bond. It always brings an extra hydrogen into the formula. To adjust for the presence of nitrogen, we need to subtract one H from the formula, then compare it to the standard alkane formula.

In the formula we just calculated, we have $C_9H_{10}O_2$. We can ignore the oxygens and look at the C9H10. If this were a saturated hydrocarbon with nine carbons, its formula would be C_9H_{20} (since 2 x 9 + 2 = 20). We are missing five pairs of hydrogens, so DU = 5. That is a lot. However, if we have one benzene in the structure, that would account for three double bonds and one ring all at once. That four degrees of unsaturation. An additional carbonyl would bring the number up to the required five. If we had not yet arrived at the idea of a benzene ring, this comparison might make us think of it. Alternatively, if we knew about the benzene but hadn't yet spotted the carbonyl, we might be on the lookout for it now.

Once we have a possible formula, another useful tool is mass spectrometry (MS). Even if you don't know much about mass spectrometry, the basic idea is simple. A mass spectrometer takes a molecules and bashes it into little pieces, then measures the molecular weights of each of those fragments. If you are lucky when you run the experiment, some of the molecules are left intact, and you get the molecular weight of the entire molecule, too.

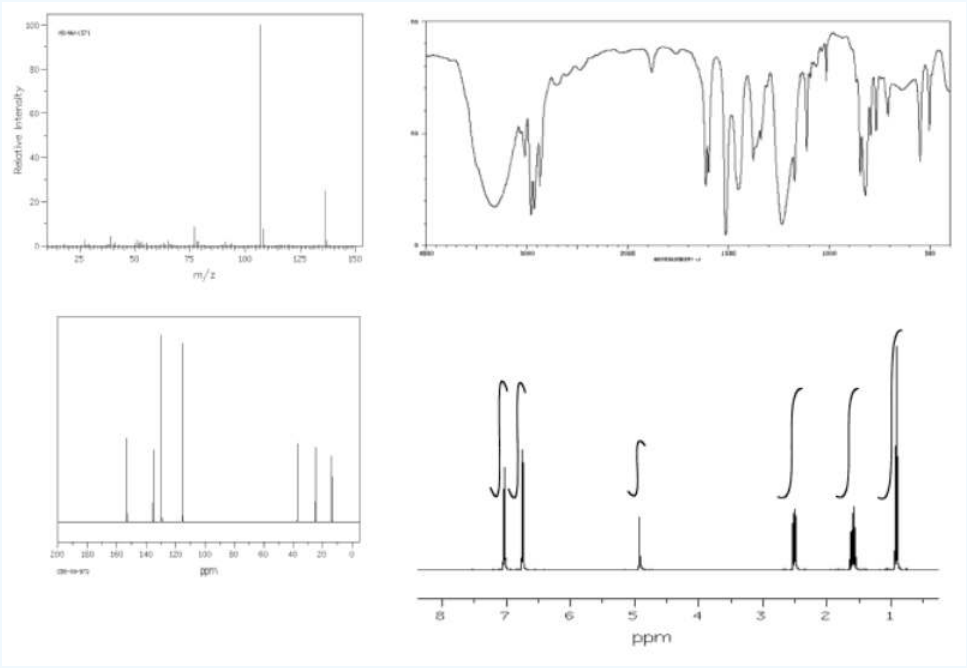


If we calculate the molecular weight based on the formula and compare it to the possible molecular weight from the mass spectrum, we might get confirmation that we are on the right track. Alternatively, maybe our calculated molecular weight will come up short. If we are off by 16, maybe we have missed an oxygen atom somewhere. If we are off by 14, maybe we have missed a carbon and a pair of hydrogens. This information might help us to correct some mistakes.

In the above example, the formula leads to a molecular weight of 150 g/mol. If the mass spectrum did not match, we would want to check our work to see if we overlooked something.

? Exercise 3.15.3

Using the approach outlined above, build a case for the structure of the compound represented by the data below.



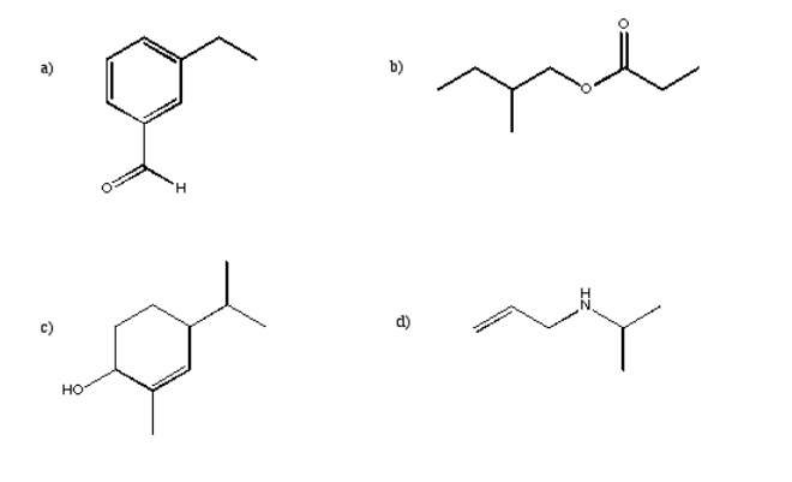
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3.16: More Practice

Exercise 3.16.1

For each of the following structures, indicate how many peaks would be found in the ^{13}C spectrum.



Exercise 3.16.2

Sketch the expected ^{13}C spectrum for each of the structures in the previous question.

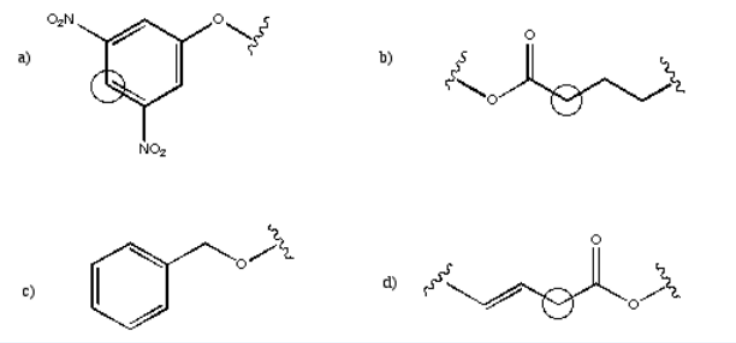
Exercise 3.16.3

Suggest possible assignments for peaks found at the following positions in the ^{13}C NMR spectrum.

a) 63 ppm b) 114 ppm c) 205 ppm d) 35 ppm e) 165 ppm f) 175 pp

Exercise 3.16.4

Suggest the approximate chemical shift for the circled carbons in the following partial structures.



Exercise 3.16.5

Explain why, in the following cases, chemical shift is slightly different from the normal range described.

a) chlorofom ($CHCl_3$): H on sp^3 carbon; normally 0-5 but here at 7.27 ppm.

b) vinyl ether ($C\mathbf{H}_2$=CHOCH=C$\mathbf{H}_2$): H on sp^2 carbon normally 5-7 but here at 4.5 ppm.

c) nitrobenzene ($C_6H_5NO_2$): H on sp^2, aromatic carbon normally 7-8 but here 8.5 ppm

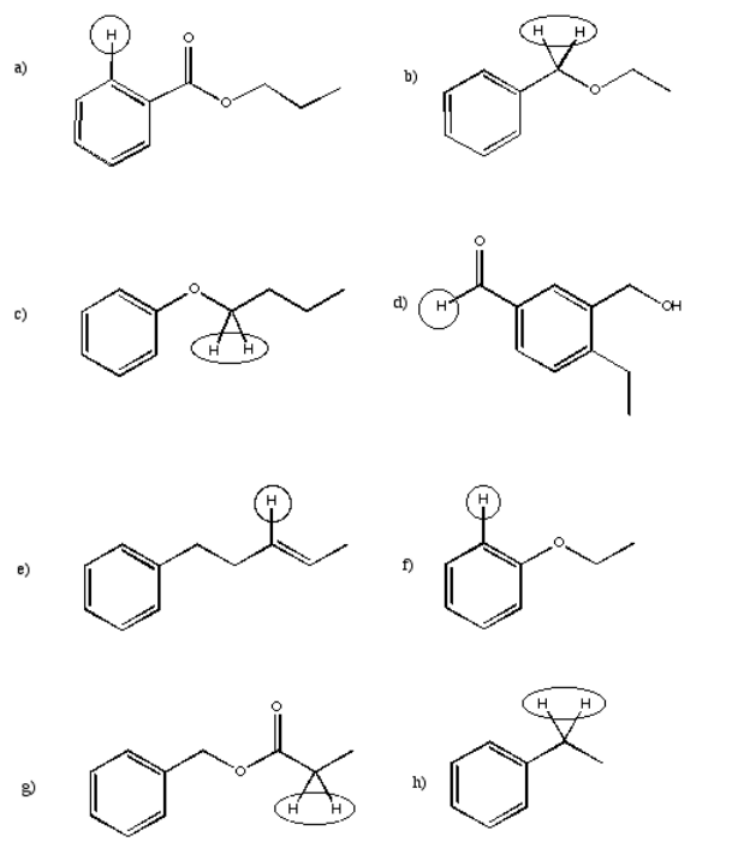
Exercise 3.16.6

Suggest possible assignments for peaks found at the following positions in the ^1H NMR spectrum.

a) 7.4 ppm b) 12.1 ppm c) 3.6 ppm d) 10.1 ppm e) 8.2 ppm f) 2.1 ppm g) 5.8 ppm

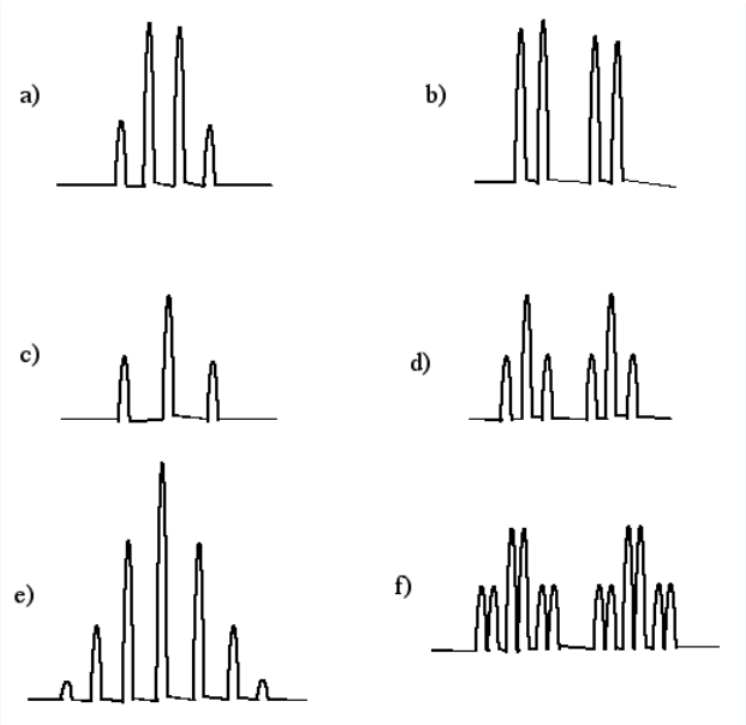
Exercise 3.16.7

Suggest the approximate chemical shift for the circled protons in the following partial structures.



Exercise 3.16.8

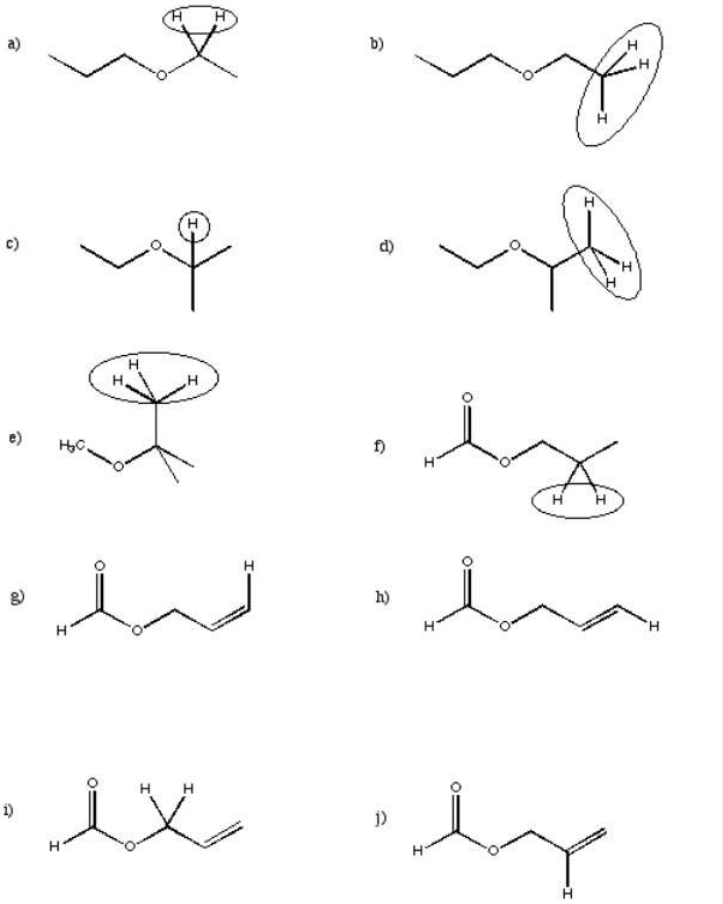
Suggest the arrangement of neighbouring hydrogens for the following peaks in the ^1H NMR spectrum and draw a partial structure.



Exercise 3.16.9

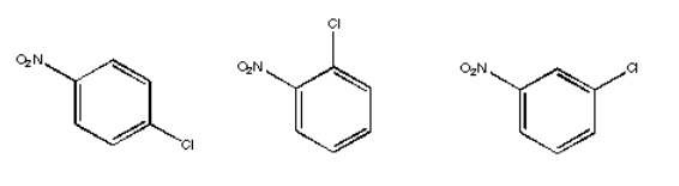
Sketch peak shapes for the circled protons in the following partial structures.

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Exercise 3.16.10

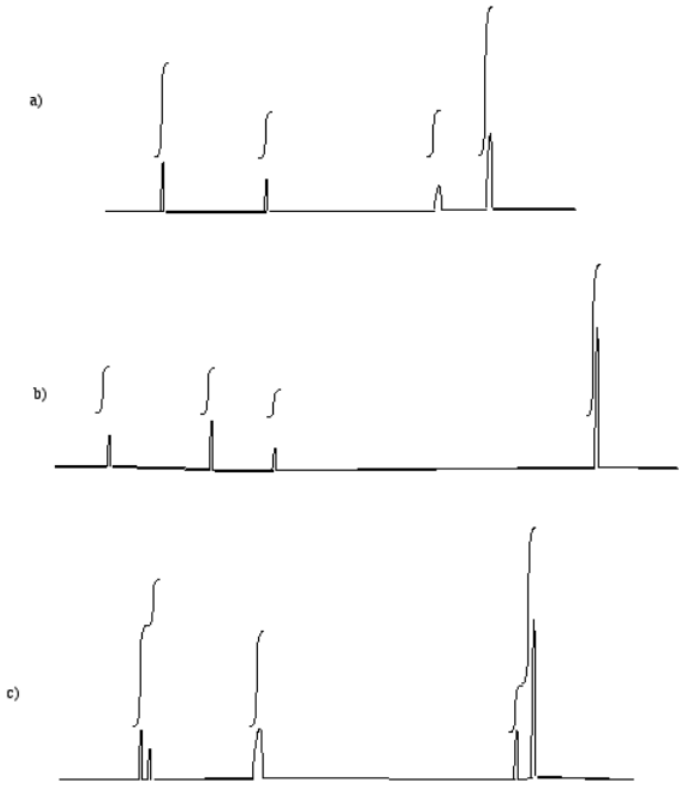
Describe the different coupling patterns in the aromatic region of the ^{1}H NMR spectra of the following isomers.



Exercise 3.16.11

Assign the relative number of protons at each position based on the integral lines shown.

https://chem.libretexts.org/@go/page/363285



Exercise 3.16.12

Suggest partial structures for the following data, given in string form.

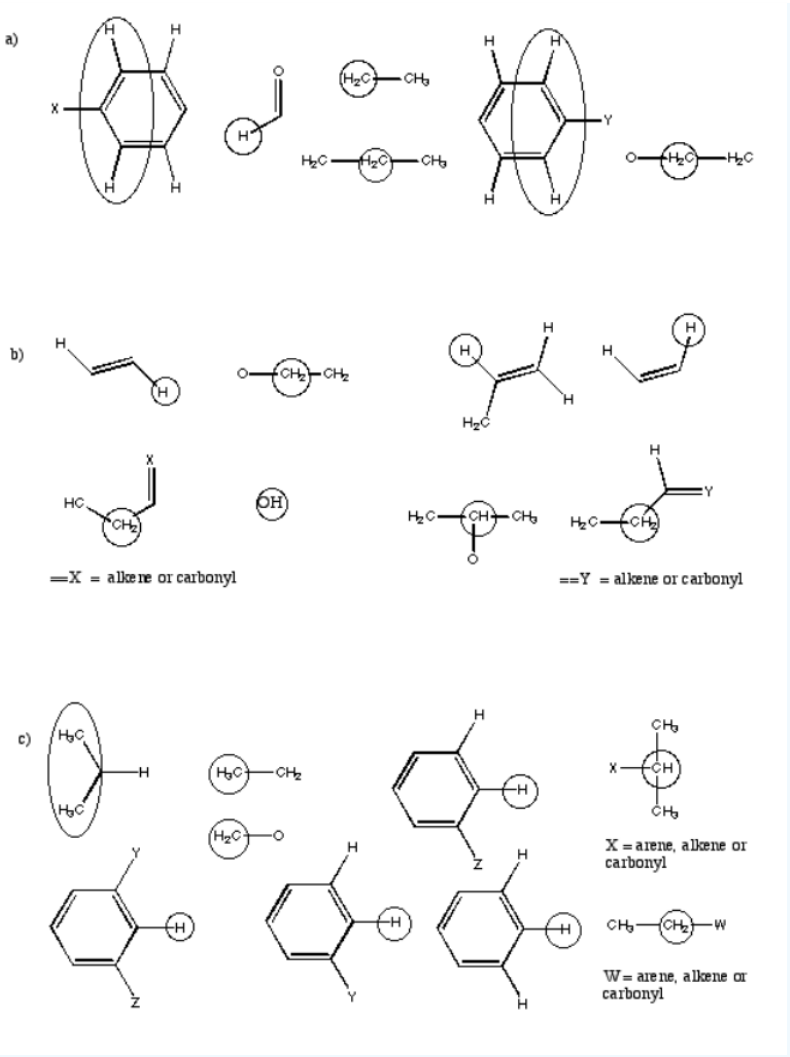
a) 8.05 ppm (doublet, 2H) b) 3.25 ppm (septet, 1H) c) 2.65 ppm (nonet, 1H)

d) 6.55 ppm (broad singlet, 1H) e) 0.94 ppm (triplet, 3H) f) 2.33 ppm (broad singlet, 2H)

g) 8.65 ppm (singlet, 1H) h) 2.05 ppm (quartet, 2H) i) 6.21 ppm (doublet of doublets, 1H)

Exercise 3.16.13

Suggest complete structures from the following sets of partial structures.

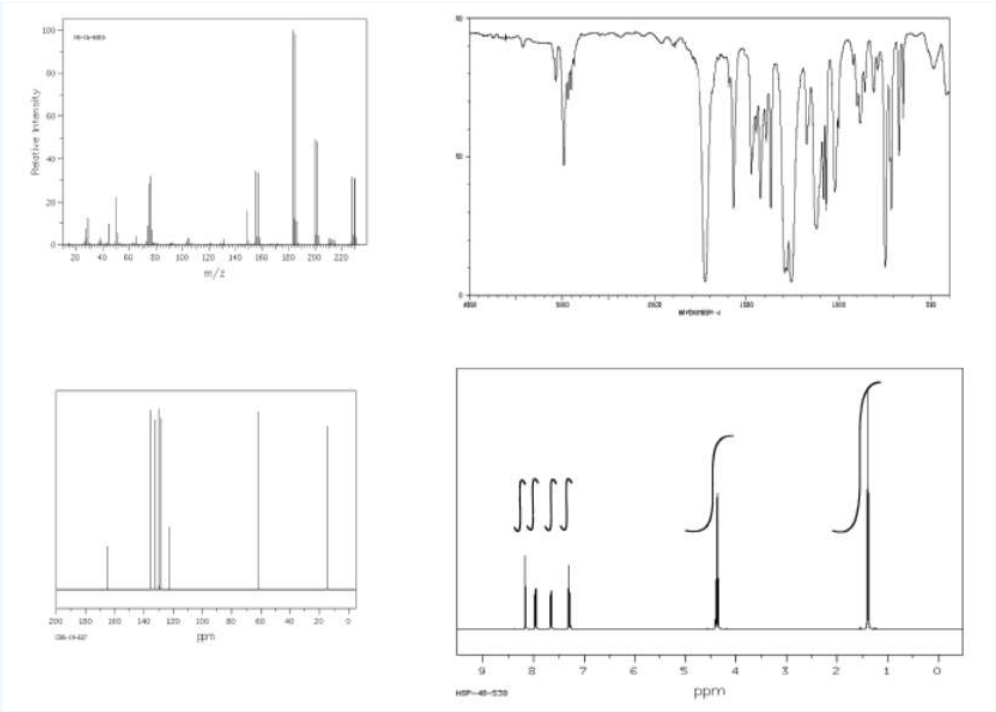


Exercise 3.16.14

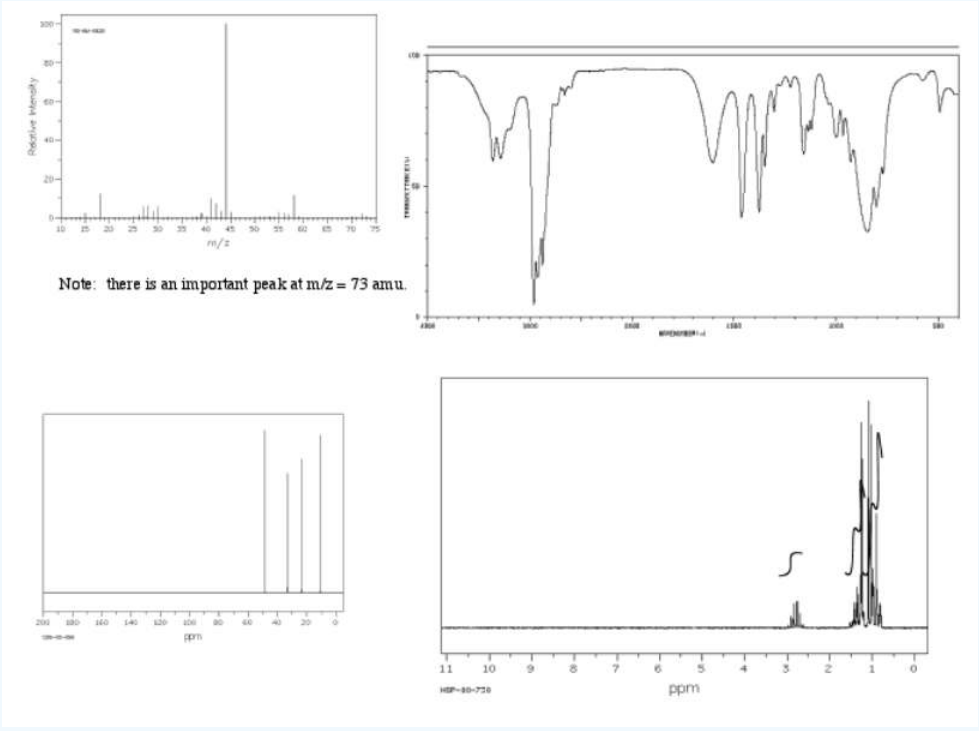
Show complete analysis of the following spectral data and propose a structure in each case.

a)

https://chem.libretexts.org/@go/page/363285

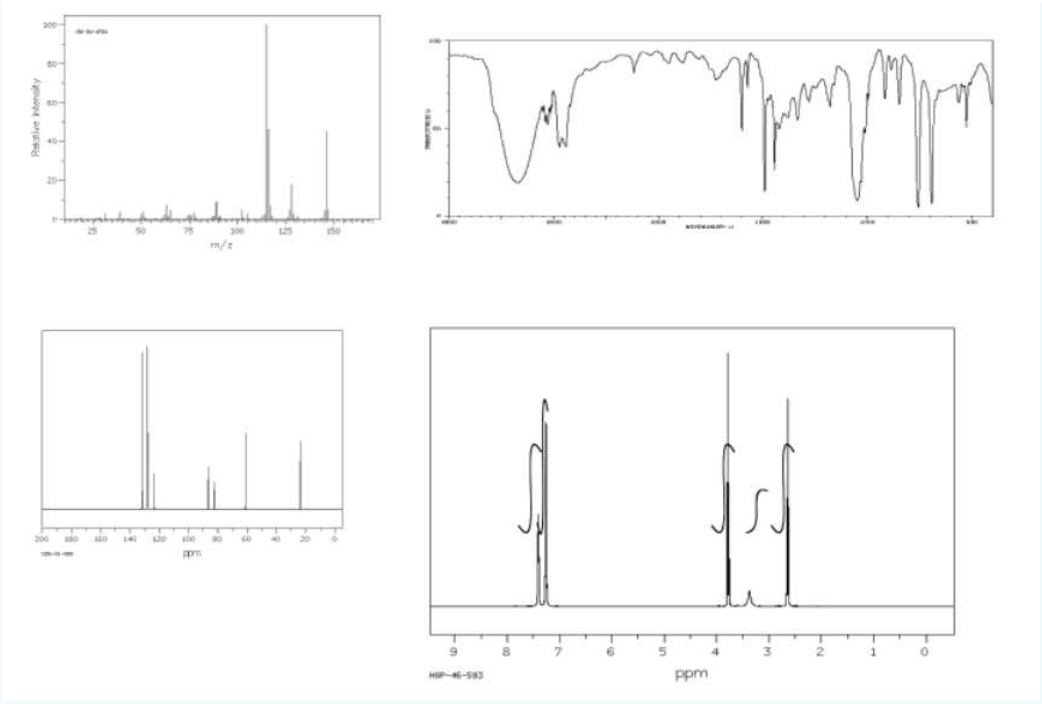


b)

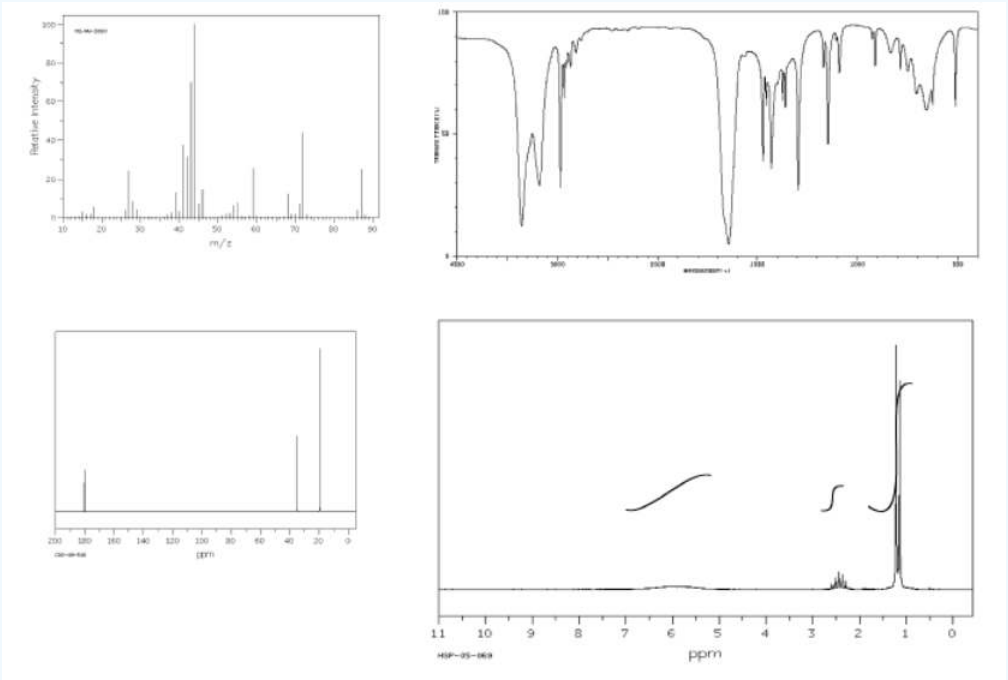


c)

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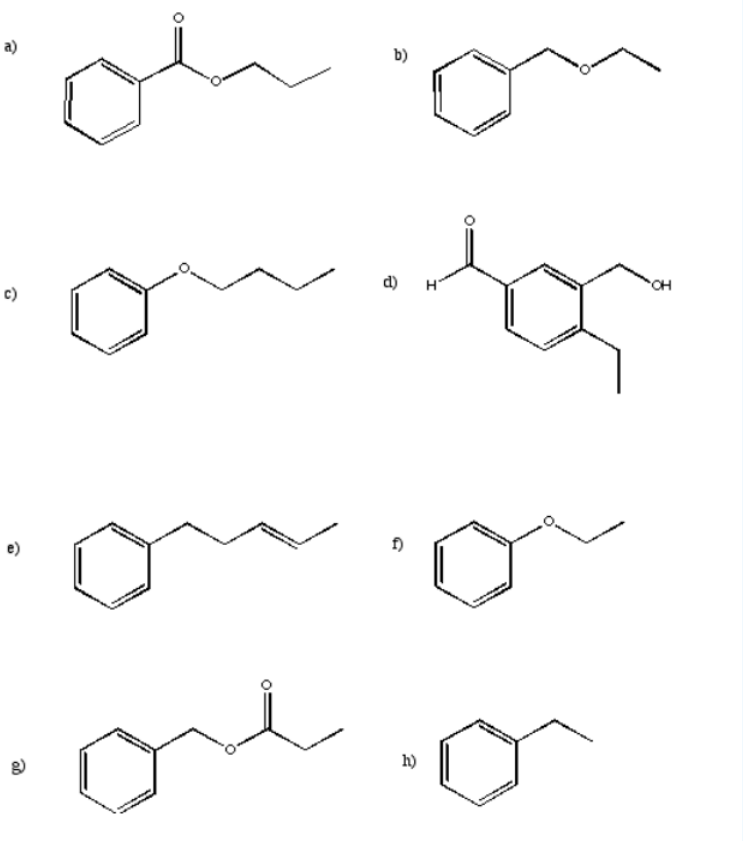
d)



Exercise 3.16.15

Sketch the expected ^{1}H spectrum for each of the following structures.

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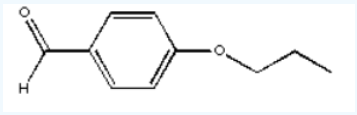


? Exercise 3.16.16

Draw what the NMR spectrum of ethylbenzene, $CH_3CH_2C_6H_5$, would look like if it was contaminated with an equal amount of tert-butyl methyl ether, $(CH_3)_3COCH$

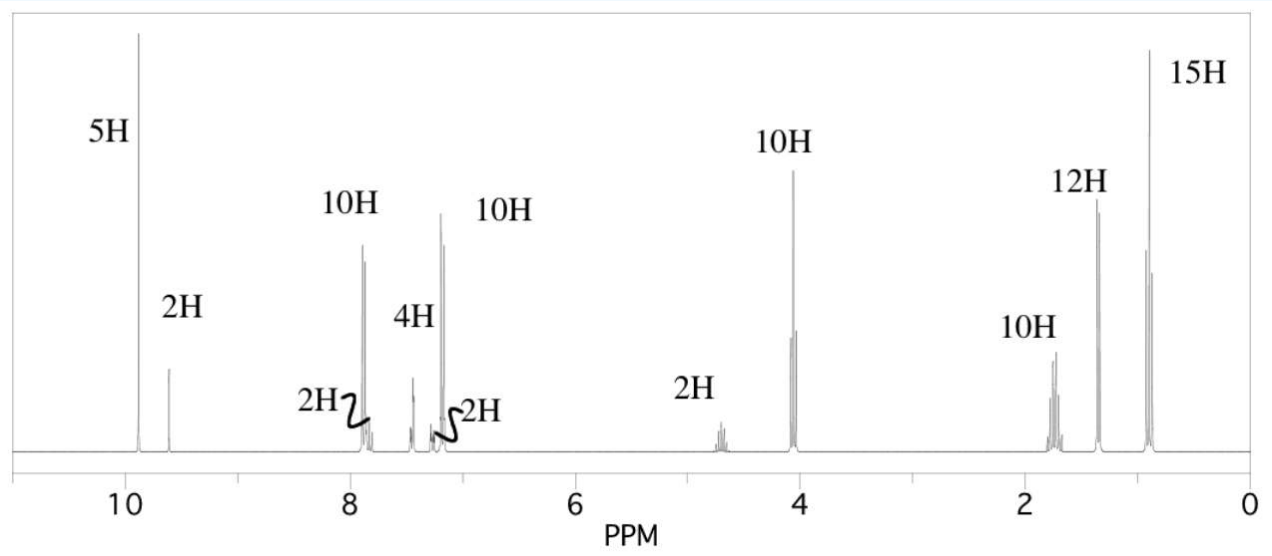
? Exercise 3.16.17

The following NMR spectrum, of the aldehyde shown, is contaminated with another isomer.



a. Identify the peaks corresponding to each isomer.
b. Identify which peaks correspond to which proton in each isomer.

c. Identify the ratio of isomers in the sample.



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SECTION OVERVIEW

3.17: 2D NMR

3.17.1: COSY Spectra

3.17.2: TOCSY Spectra

3.17.3: HMBC and HMQC Spectra

3.17.4: NOESY Spectra

3.17.5: More Practice with 2D

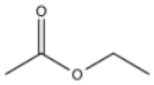
3.17.6: 2D NMR Solutions

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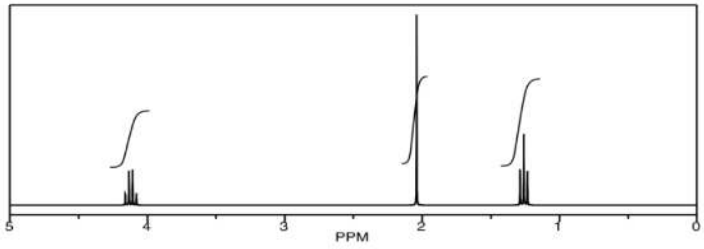
3.17.1: COSY Spectra

In 2D NMR, correlation peaks are used to help establish the structure.

Let's start with a simple compound, ethyl acetate.

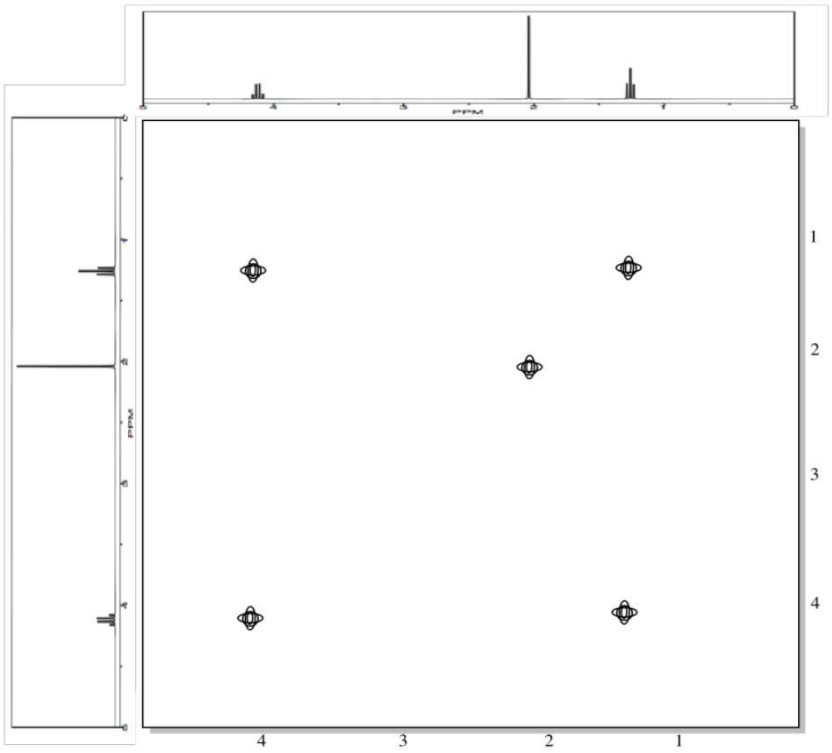


The ^{1}H NMR spectrum is not very complicated.



In **homonuclear correlation spectroscopy (COSY)**, we can look for hydrogens that are coupled to each other. In ethyl acetate, it's pretty clear where they are. There is a quartet and a triplet; the hydrogens corresponding to those two peaks are probably beside each other in the structure.

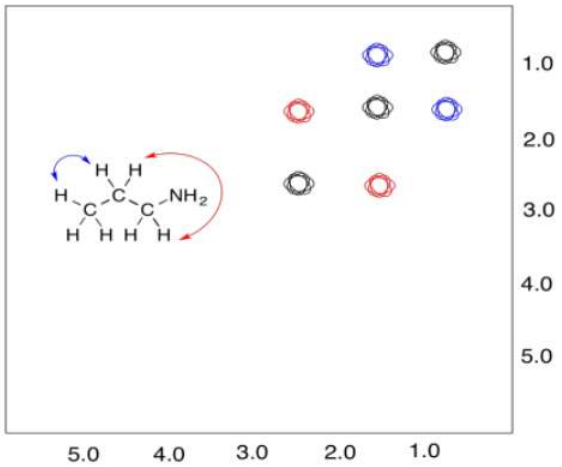
The COSY spectrum simply takes that ^{1}H spectrum and spreads it out into two dimensions. Instead of being displayed as a row of peaks, the peaks are spread out into an array. In the following simulated COSY spectrum, the peaks are displayed along one axis. The same peaks are also displayed along the other axis. In the middle of the plot, the peaks are shown plotted against each other -- that is, there is a peak at 1.25 ppm on the y axis and along the x axis, so there is a data point on the plot at (1.25, 1.25). Other such peaks appear along the diagonal stretching from the upper right to the lower left through the middle of the plot. There are three peaks appearing along that diagonal line; these three peaks basically show us what we already saw in the regular ^{1}H NMR spectrum.



The interesting peaks are the ones that do not appear along the diagonal. Those peaks indicate which hydrogens are coupled to which other hydrogens. The hydrogens at 1.25 ppm are coupled to the ones at 4.2 ppm, and that gives a "cross-peak" at (1.25, 4.20). There is also a cross-peak at (4.20, 1.25), because that relationship goes both ways.

What does it mean to be coupled? It means that magnetic information is transmitted between the atoms. How can we tell? Essentially, we can send a pulse of electromagnetic radiation into one set of hydrogens and look for a response somewhere else. Of course, if we send a pulse of radio waves at a frequency that will be absorbed by a particular hydrogen, we will see a response in that hydrogen itself. That's why we see the peaks on the diagonal. However, we also see responses from other hydrogens that are magnetically linked to the original one.

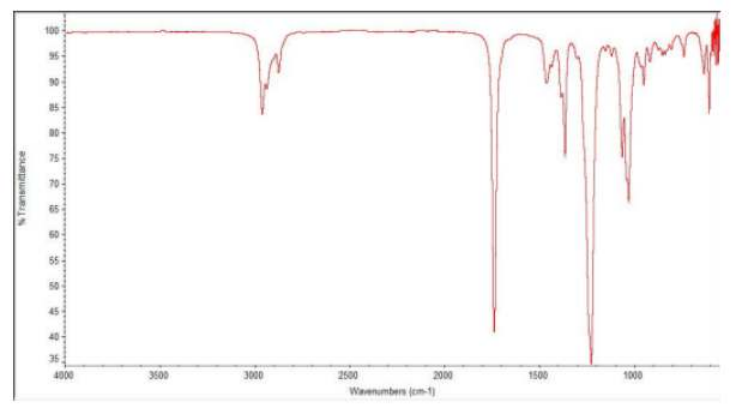
A second example is shown below. This time, the compound is propanamine. In propanamine, there would again be a diagonal set of peaks, shown in black, corresponding to the peaks in the regular proton spectrum. In addition, two different sets of protons are coupled. The methyl group is coupled to the methylene in the middle of the molecule; that cross-peak is shown in blue. The methylene in the middle is also coupled to the methylene next to the nitrogen; that cross-peak is shown in red.

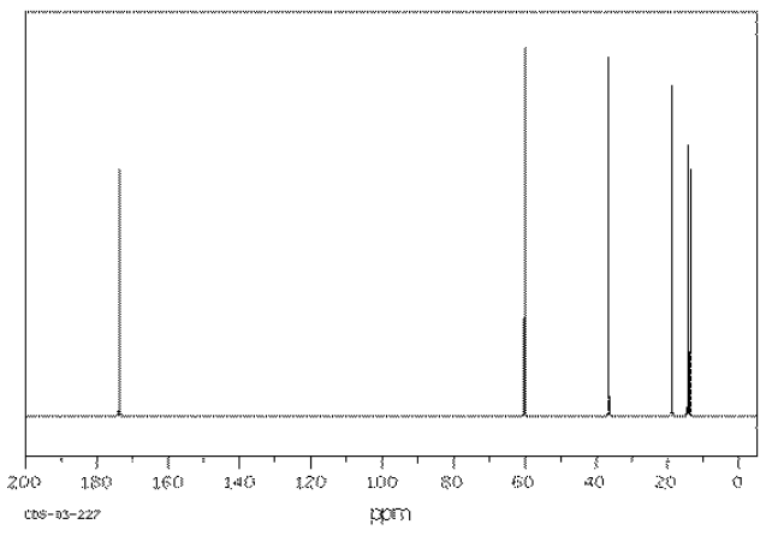


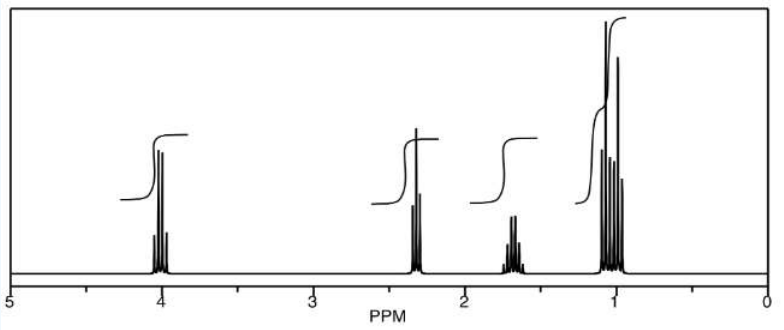
	^{13}C	^{1}H	COSY
a	10	0.9	1.5
b	28	1.5	0.9, 2.6
c	43	2.6	1.5

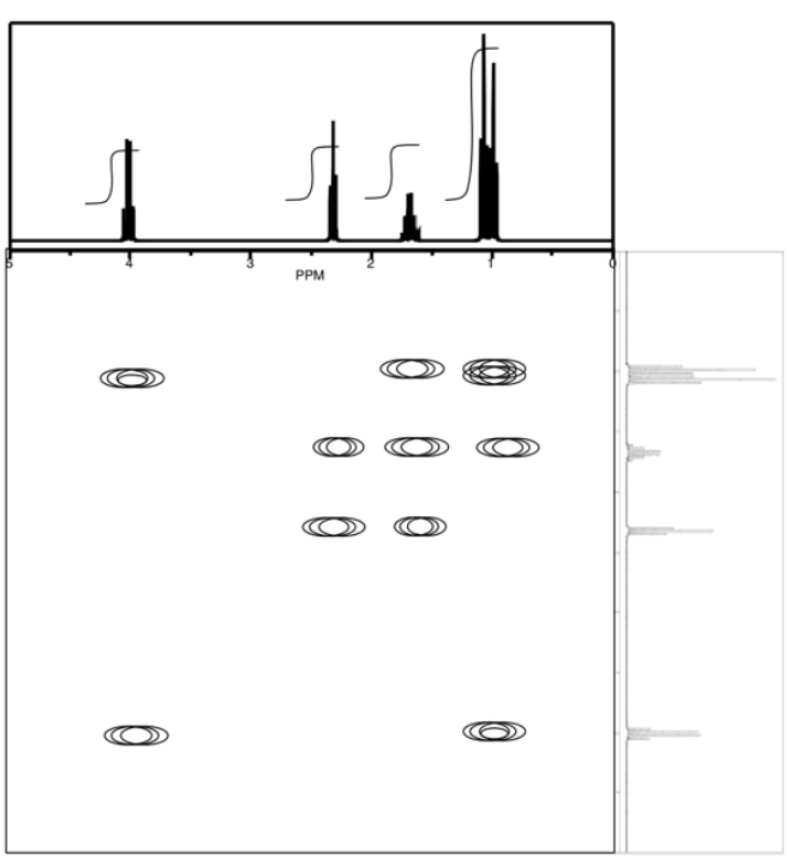
Exercise 3.17.1.1

Provide analyses of the following spectra and propose a structure for the compound.







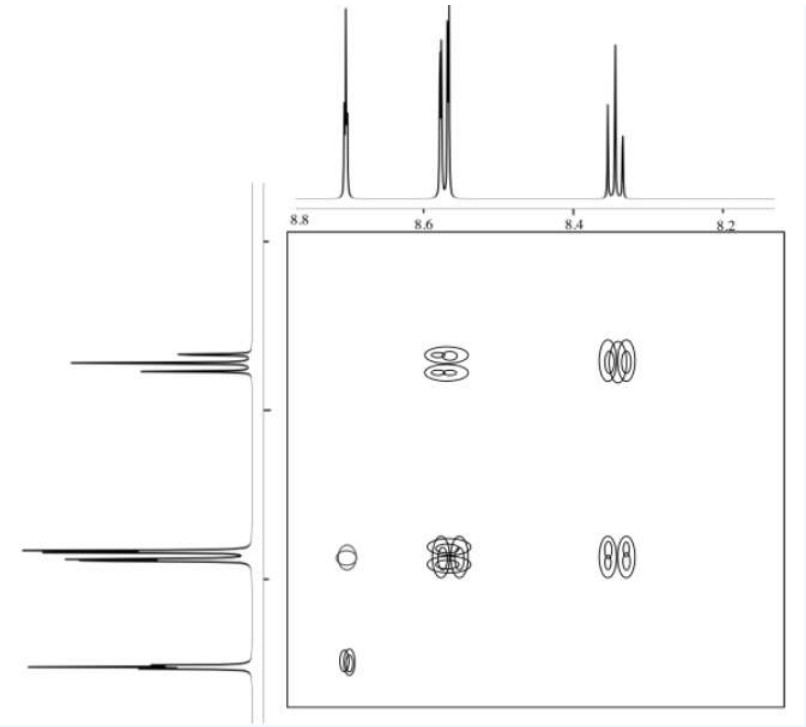


Answer

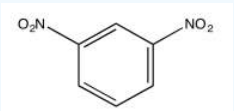
ethyl butanoate

Exercise 3.17.1.2

The following COSY spectrum is for an isomer of dinitrobenzene. Which isomer is it?

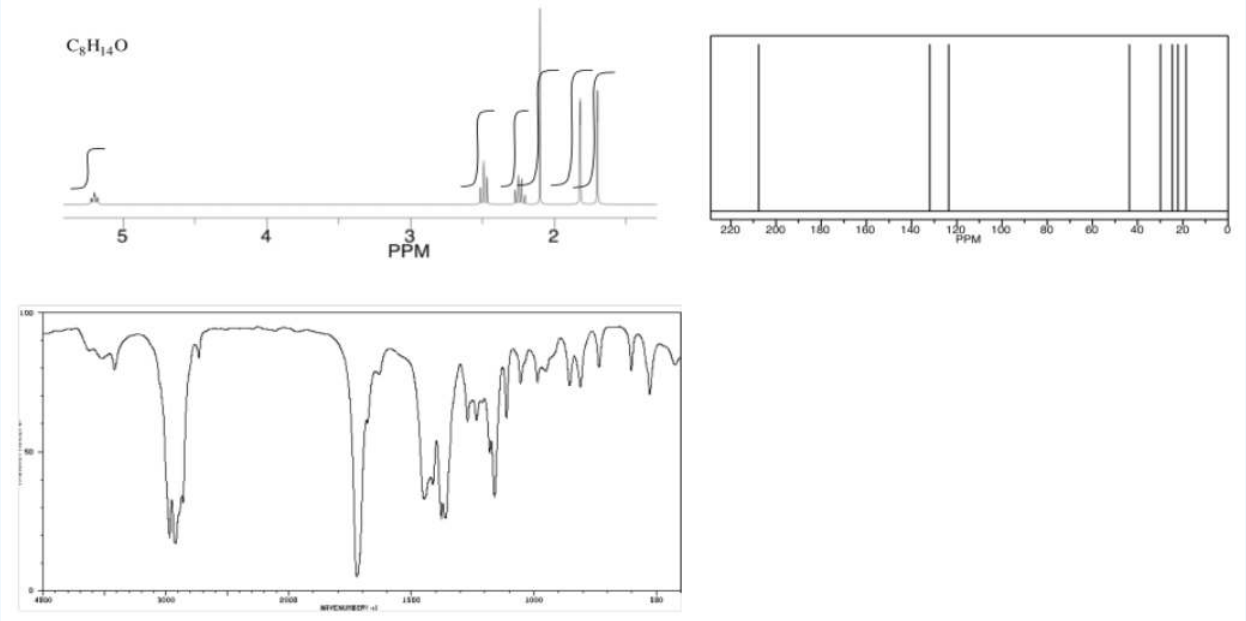


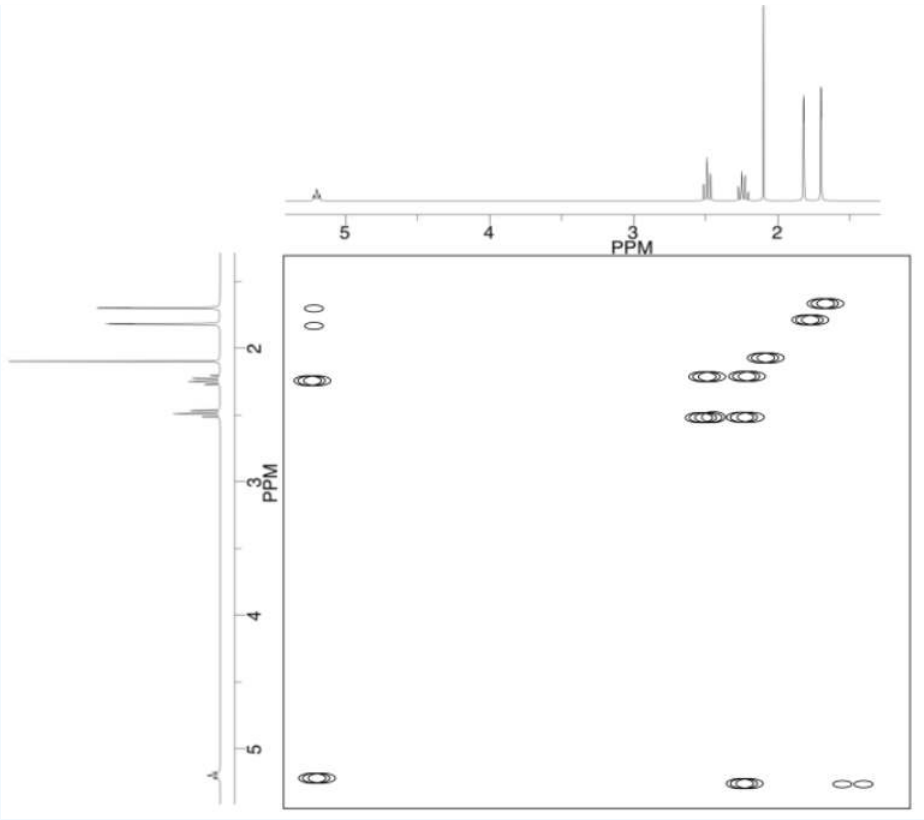
Answer



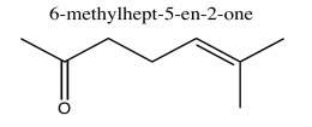
Exercise 3.17.1.3

Analyse the data in the following spectra and propose a structure for the compound.





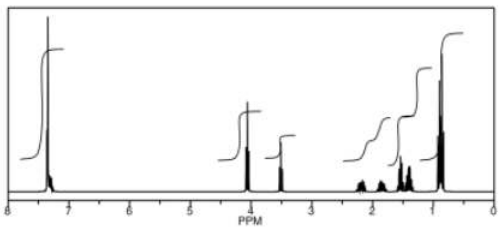
Answer

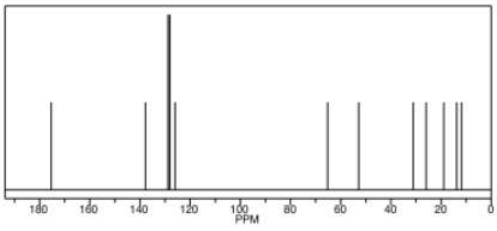


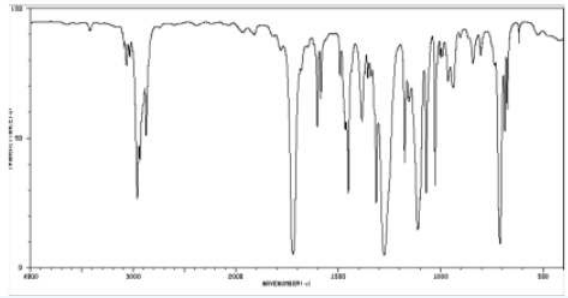
Exercise 3.17.1.4

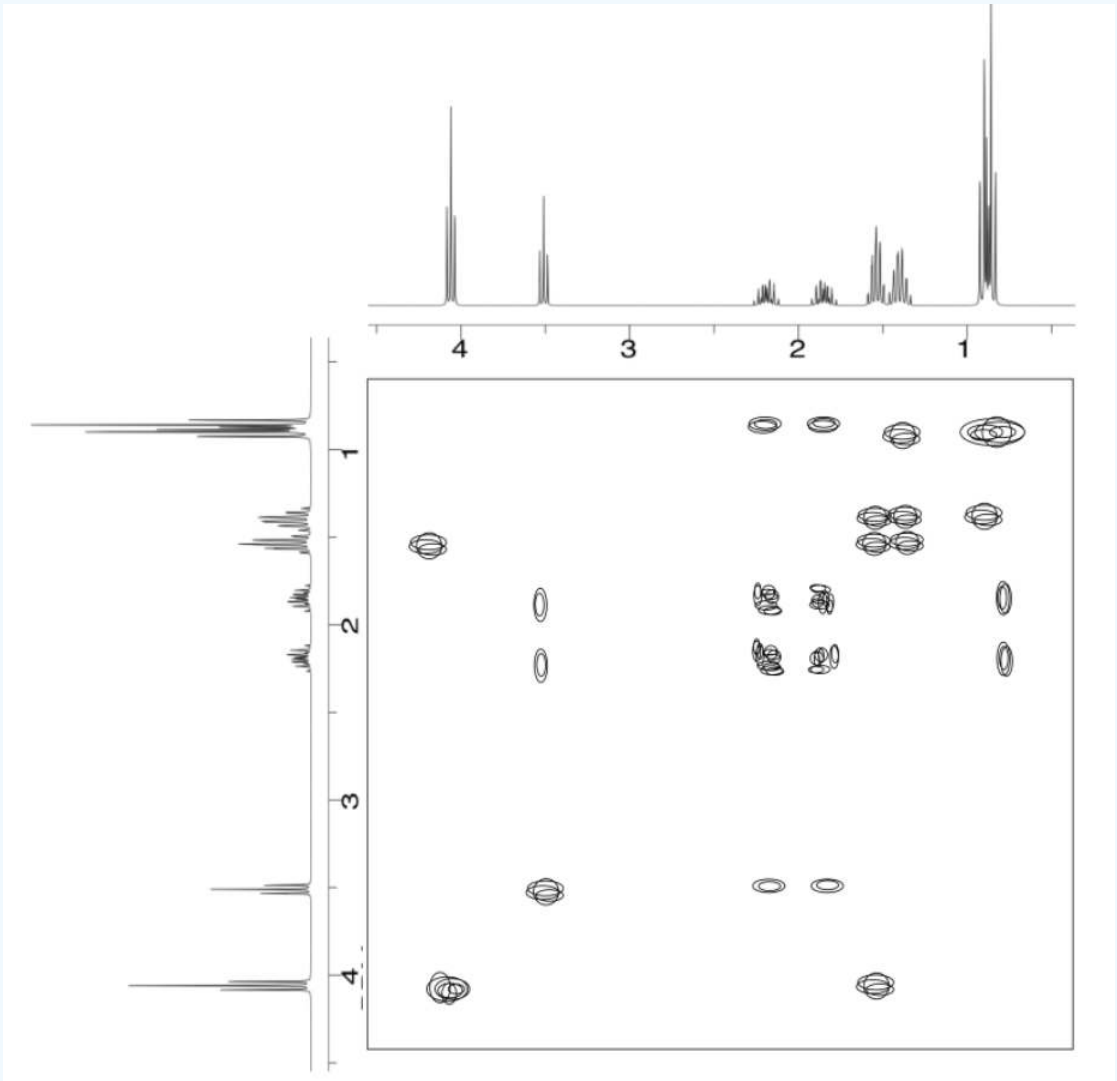
Analyse the data in the following spectra and propose a structure for the compound.

$C_{14}H_{20}O_2$

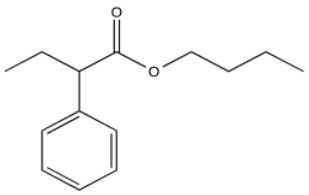








Answer

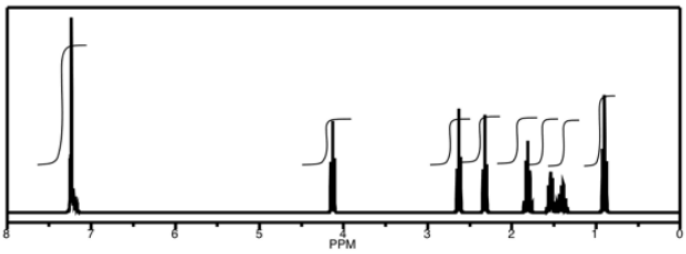


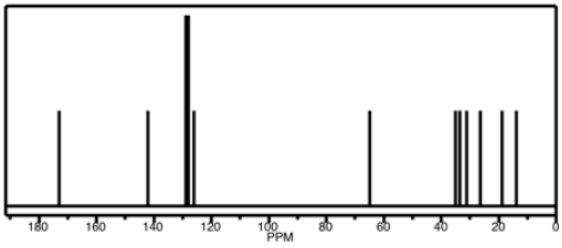
butyl 2-phenylbutanoate

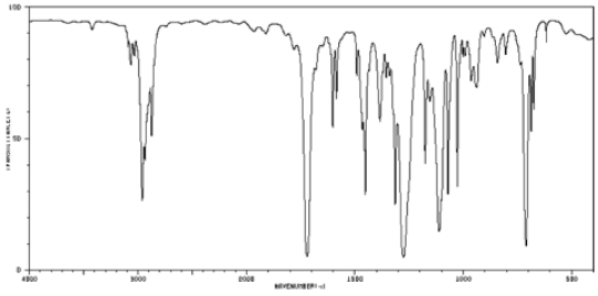
Exercise 3.17.1.5

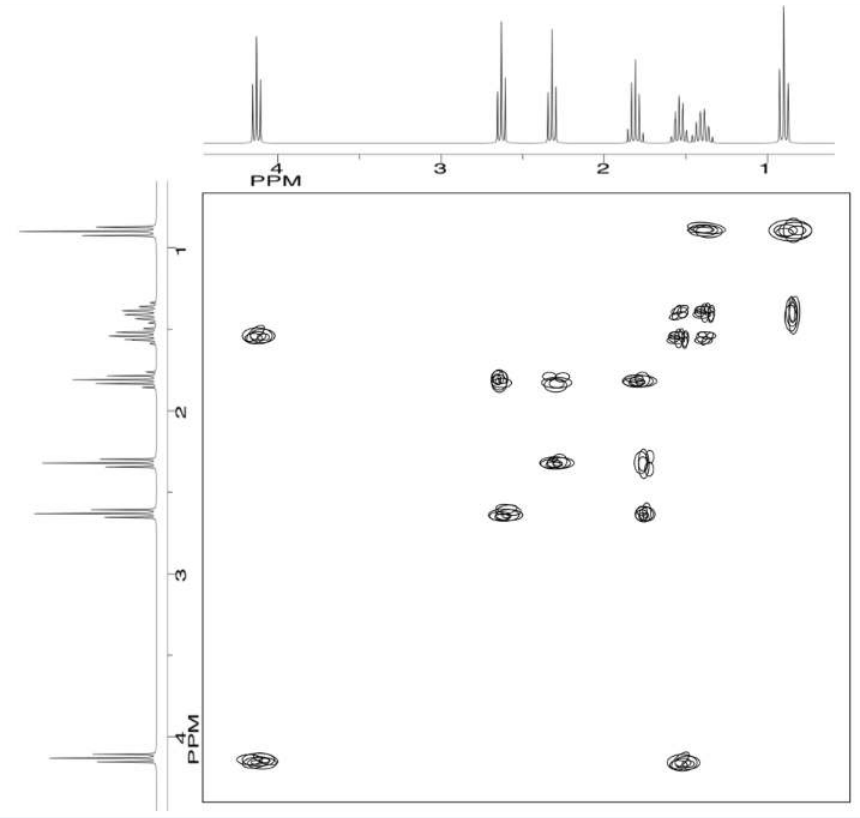
Analyse the data in the following spectra and propose a structure for the compound.

$C_{14}H_{20}O_2$

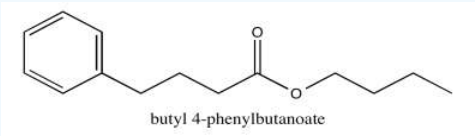








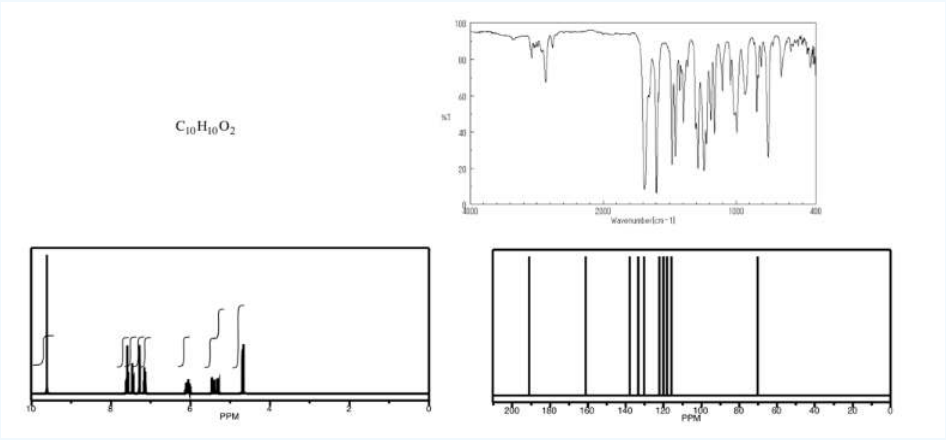
Answer



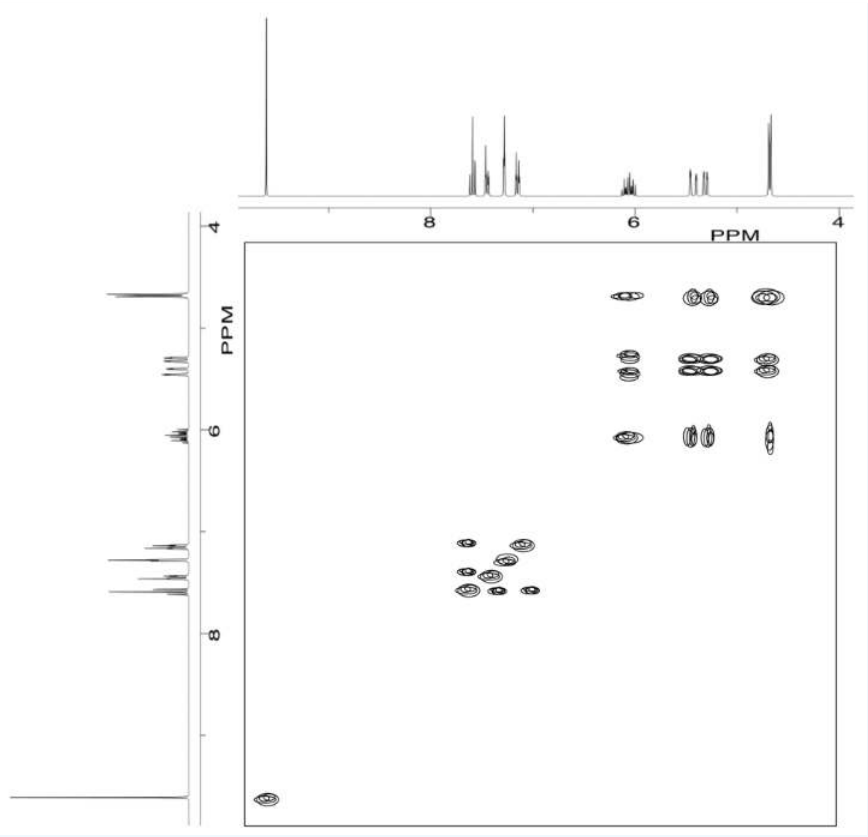
butyl 4-phenylbutanoate

Exercise 3.17.1.6

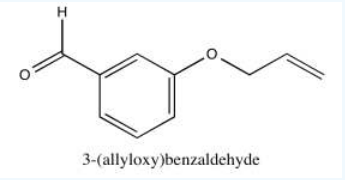
Analyse the data in the following spectra and propose a structure for the compound.



https://chem.libretexts.org/@go/page/363288



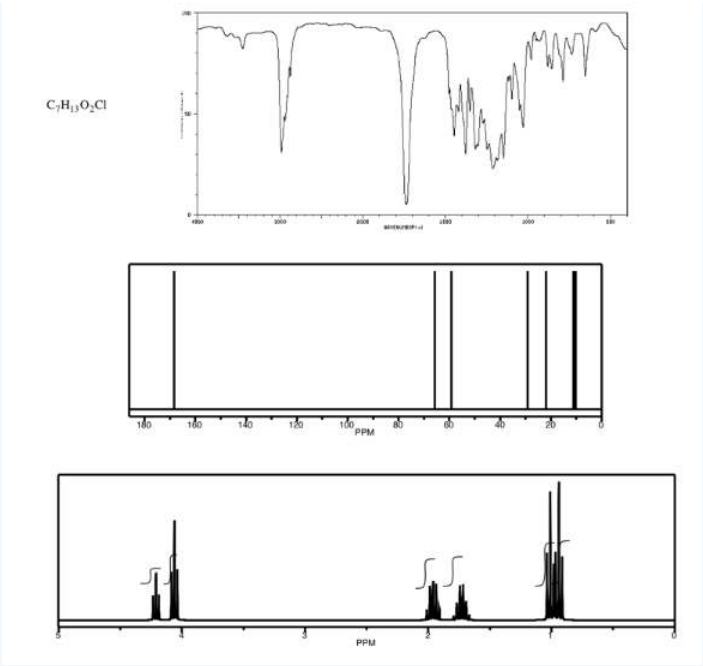
Answer

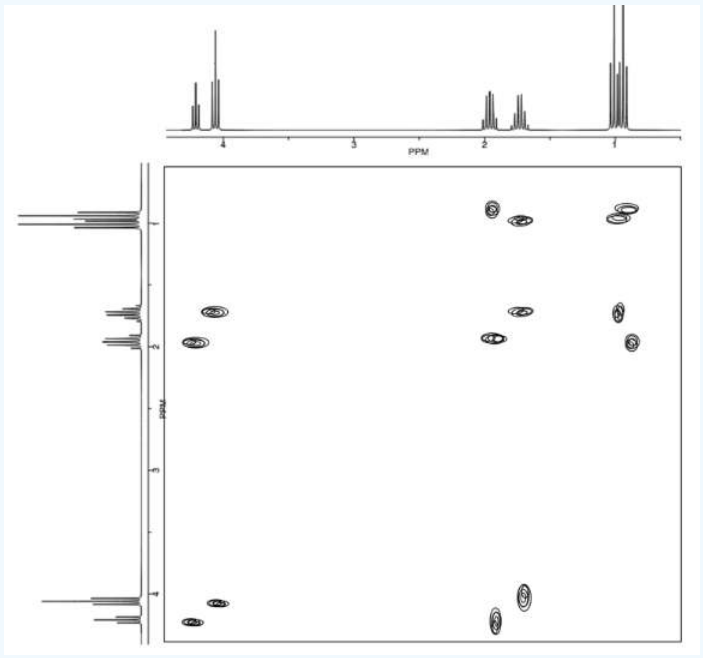


3-(allyloxy)benzaldehyde

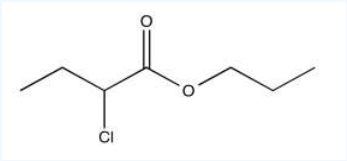
Exercise 3.17.1.7

Analyse the data in the following spectra and propose a structure for the compound.



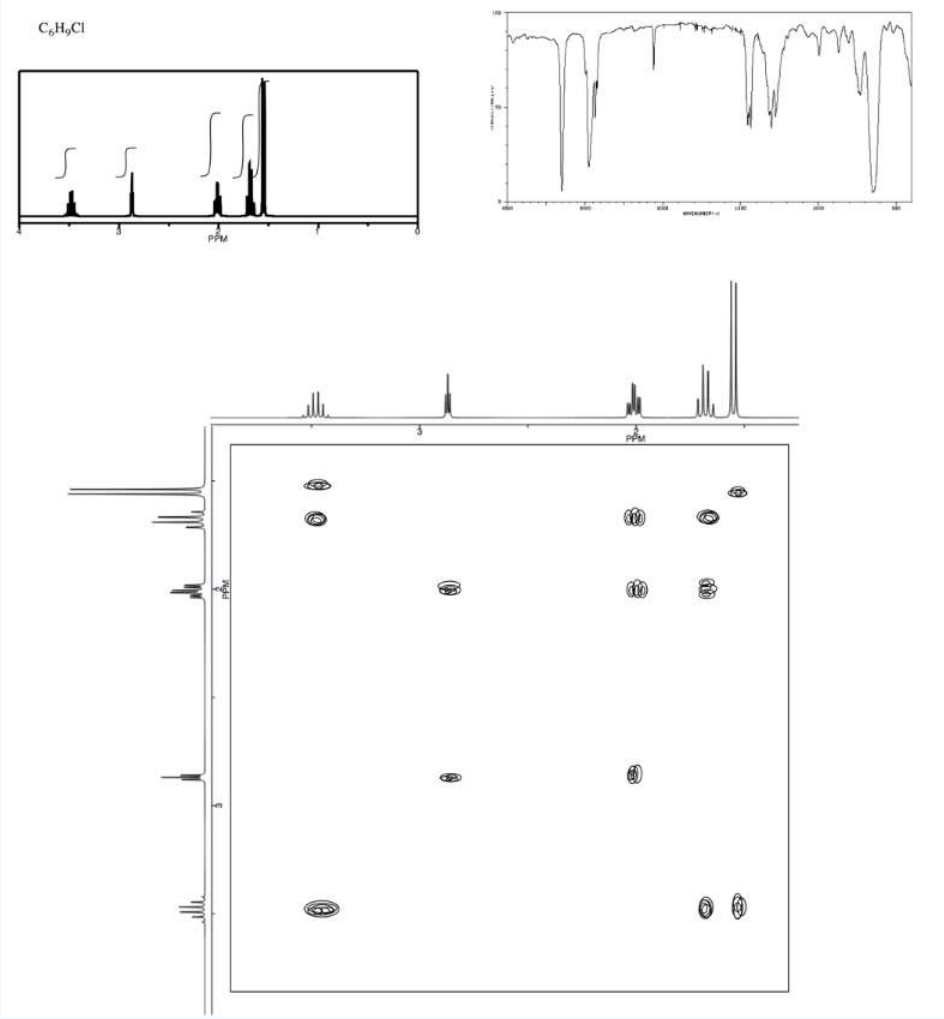


Answer

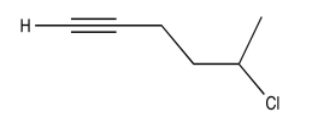


Exercise 3.17.1.8

Analyse the data in the following spectra and propose a structure for the compound.

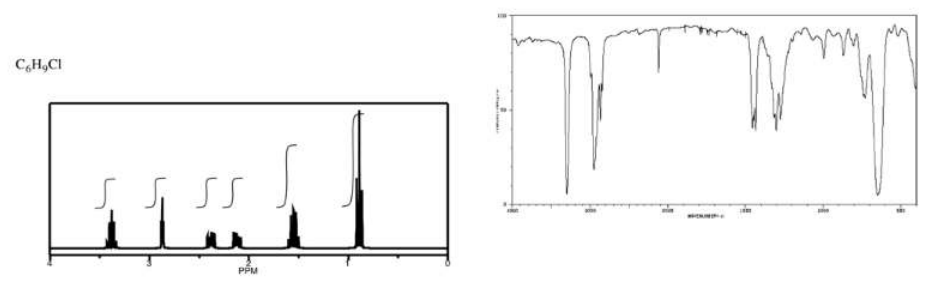


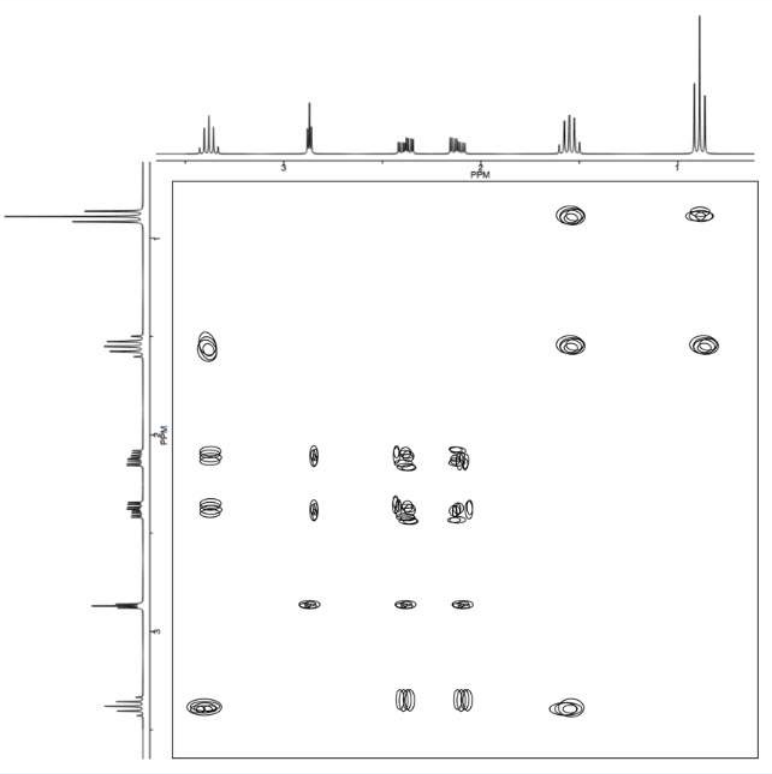
Answer



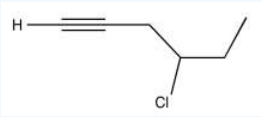
Exercise 3.17.1.9

Analyse the data in the following spectra and propose a structure for the compound.



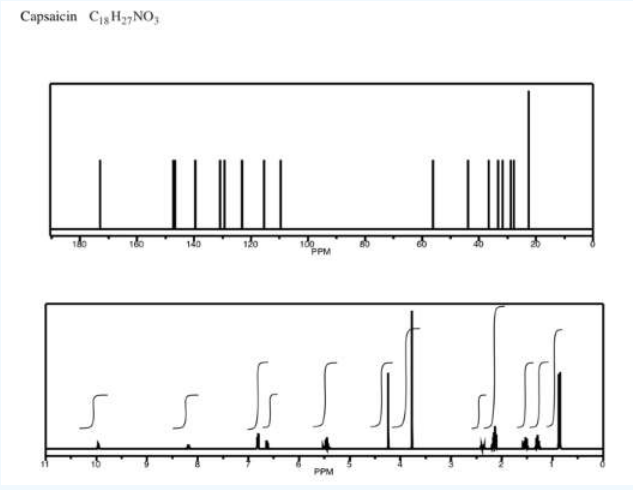


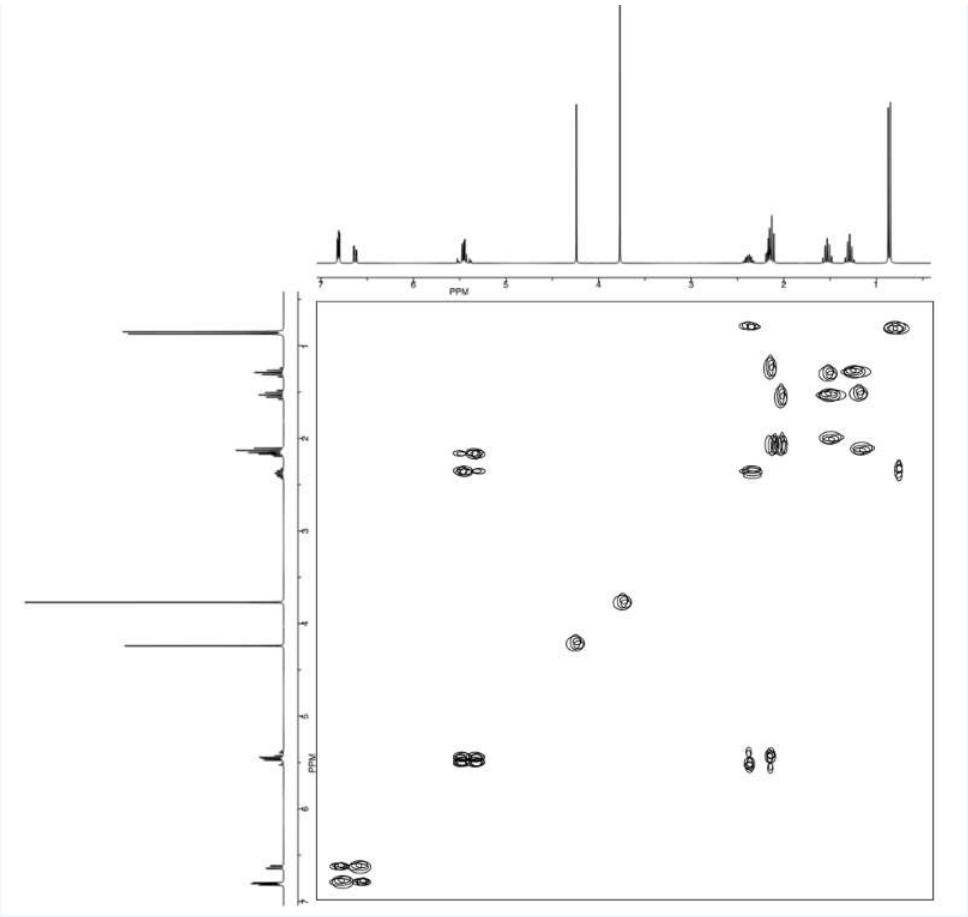
Answer



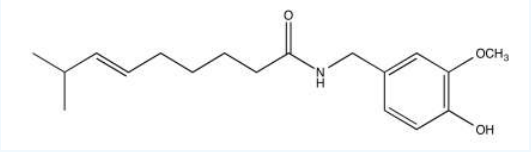
Exercise 3.17.1.10

Analyse the data in the following spectra and propose a structure for the compound.



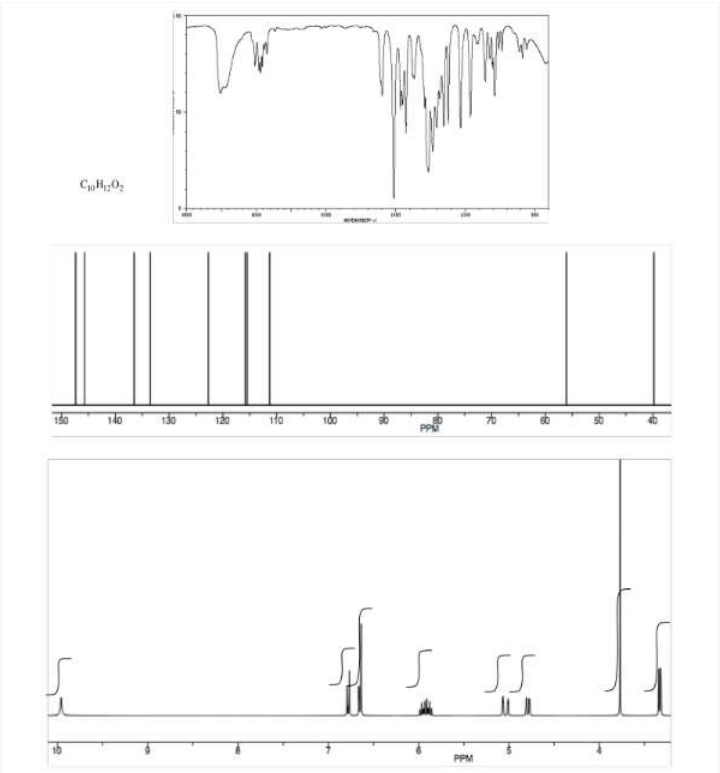


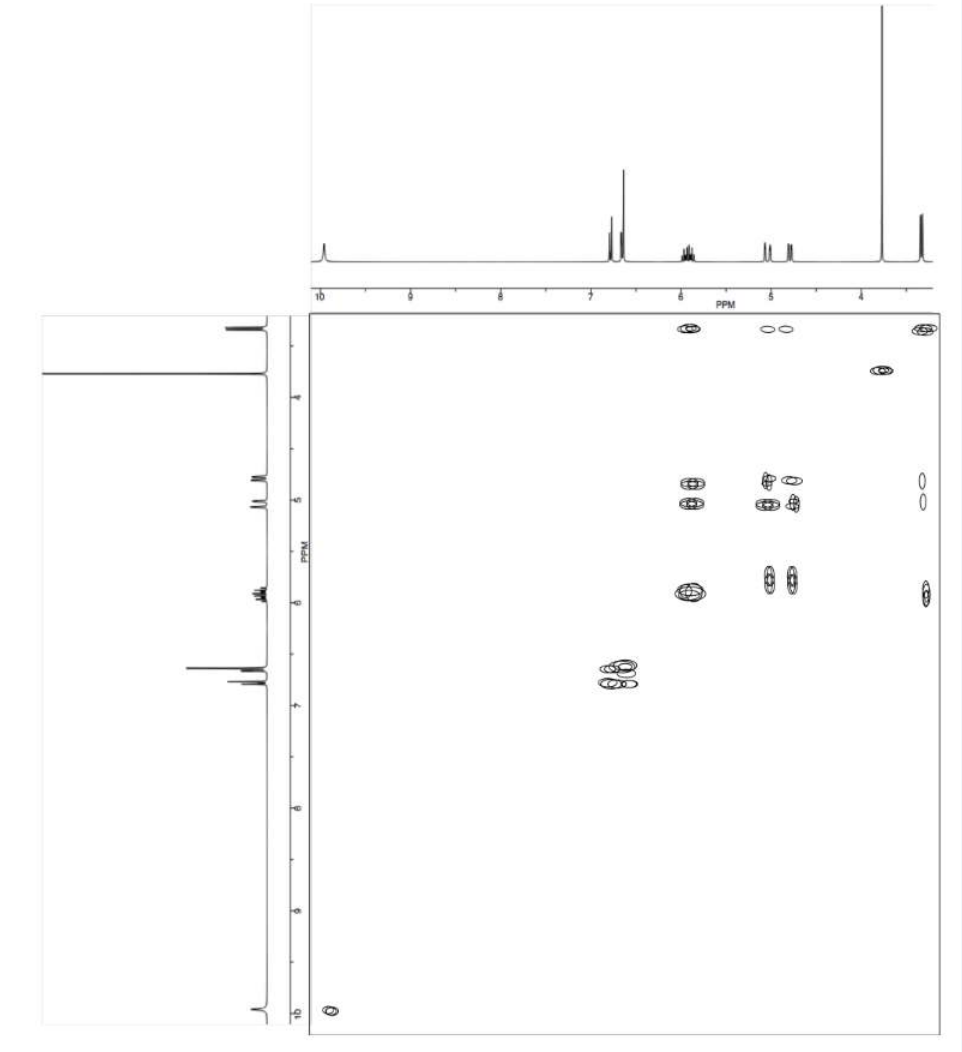
Answer



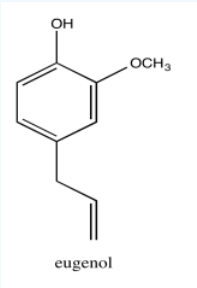
Exercise 3.17.1.11

Analyse the data in the following spectra and propose a structure for the compound.


$C_{10}H_{12}O_2$
150
140
130
120
110
100
90
80
70
60
50
40
PPM
10
9
8
7
6
5
4
PPM



Answer

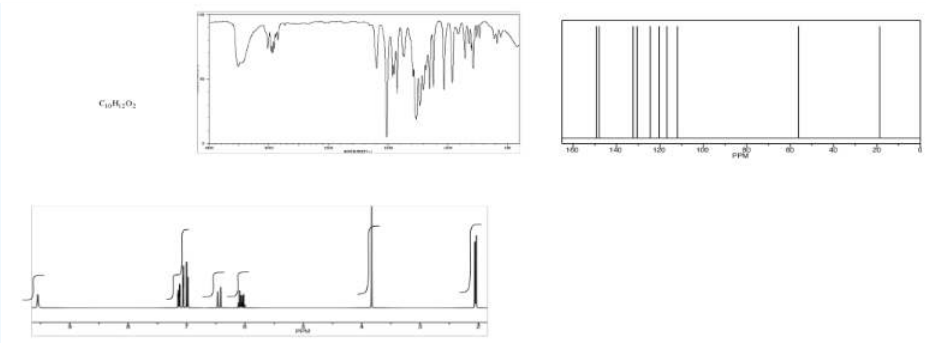


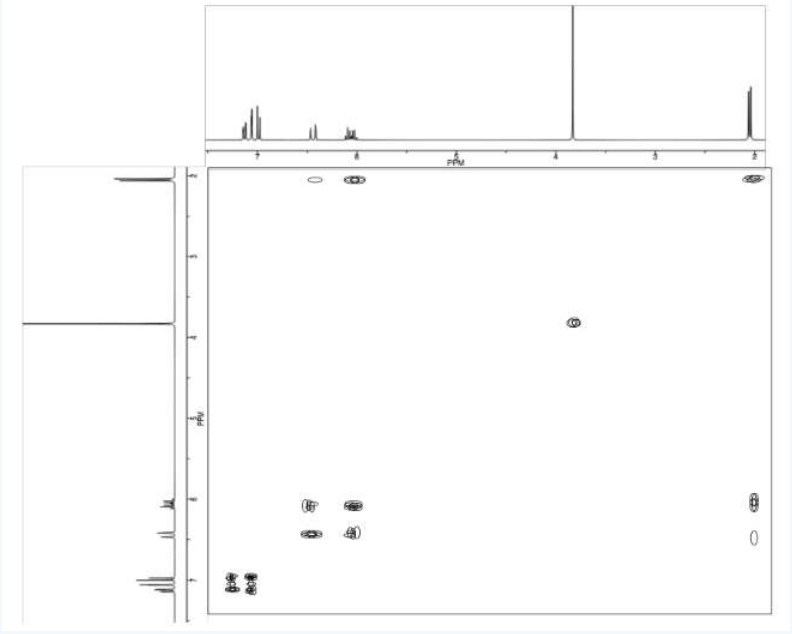
eugenol

Exercise 3.17.1.12

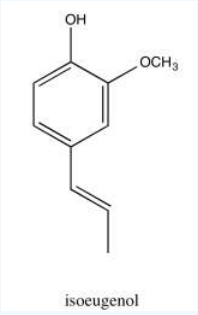
Analyse the data in the following spectra and propose a structure for the compound.

https://chem.libretexts.org/@go/page/363288





Answer



isoeugenol

* Sources:

Selected IR and ^{13}C NMR spectra from SDBS (National Institute of Advanced Industrial Science and Technology, Japan, Spectral Database for Organic Compounds, http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi, accessed December, 2015).

^{1}H NMR and COSY spectra simulated.

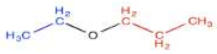
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- **5.1: COSY Spectra** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

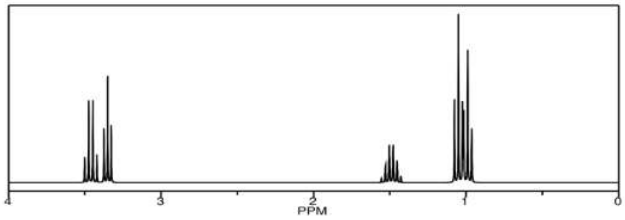
3.17.2: TOCSY Spectra

Total Correlation Spectroscopy, or **TOCSY**, is almost exactly the same as regular COSY. However, instead of just showing that two protons are coupled, it shows an entire spin system together. That means it shows this proton is connected to that proton, but that proton is connected to this other one, which is connected to that one over there. A TOCSY spectrum displays an entire chain of protons, each of which is coupled to the next.

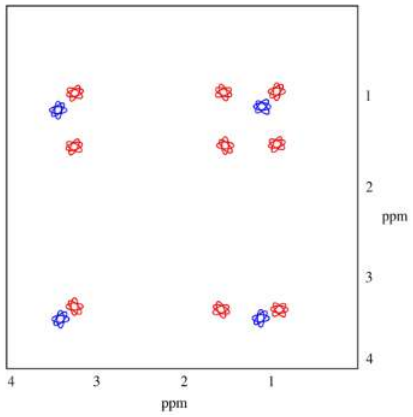
As an example, we'll look at ethoxypropane. It has a two-carbon chain and a three-carbon chain, but the two chains are separated from each other by an oxygen atom.



The ^{1}H NMR spectrum is shown below. It isn't all that complicated. However, if we wanted to know exactly which peak belonged to which hydrogen, we may have some trouble. In particular, how could we conclusively tell those two triplets apart near 1 ppm? An educated guess would put the methyl of the ethyl chain downfield, farther to the left. Can we confirm that suspicion?



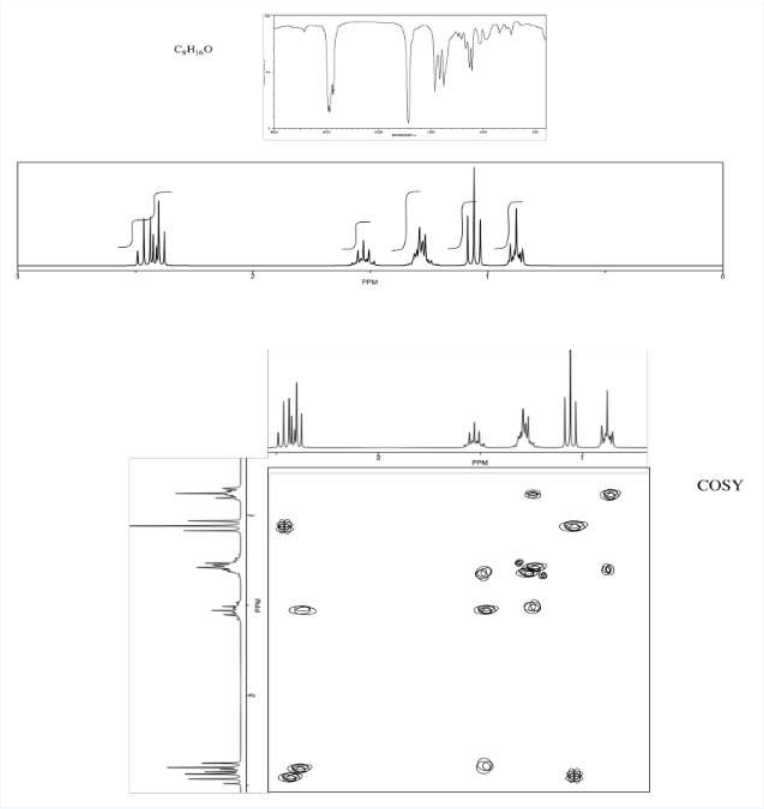
The TOCSY spectrum shows what we need to see in order to be sure. These spectra don't really show up color-coded, but red and blue have been added to make things more clear. The blue part is exactly what we would see in a COSY spectrum. The hydrogen at 1.1 is coupled to the one at 3.4. The red part is slightly different from the COSY; not only does it show the coupling between the hydrogen at 1.0 and the one at 1..5, but it also includes the hydrogen at 3.3, because that one is also coupled to the one at 1.5. The entire chain of coupled hydrogens is linked together.

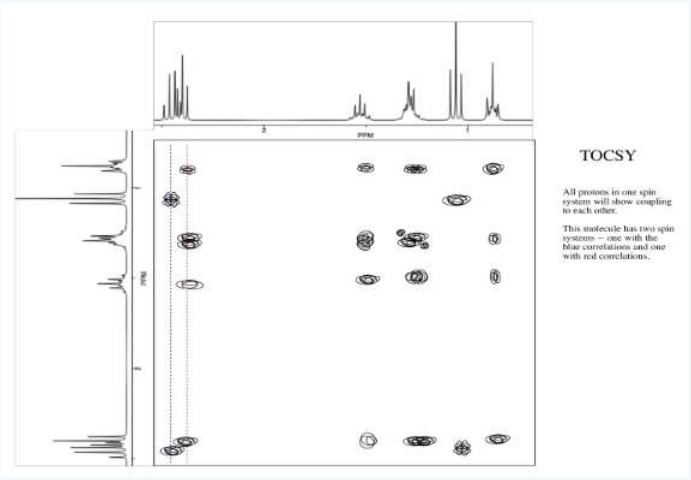


At a glance, the TOCSY spectrum tells us we have a two-carbon chain because we see two peaks in a row (or, really, a two by two array). It also tells us we have a chain of three peaks because we can see three peaks in a row (or a three by three array).

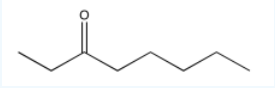
Exercise 3.17.2.1

Identify the compound.



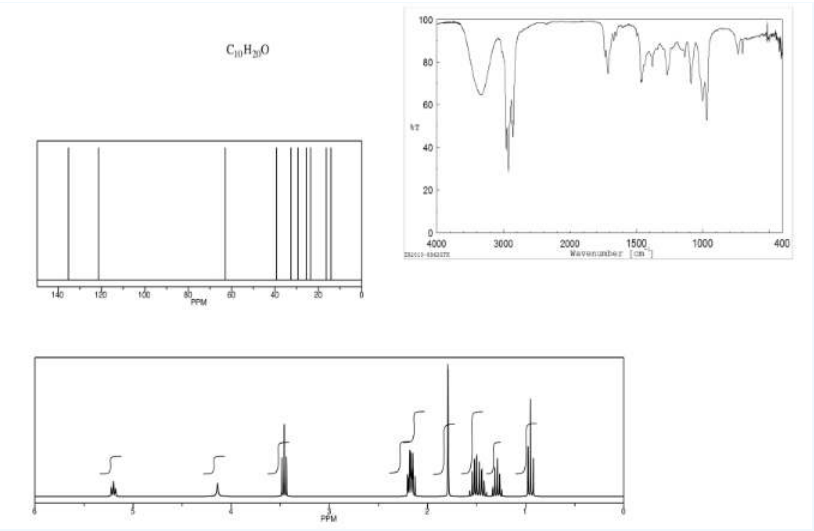


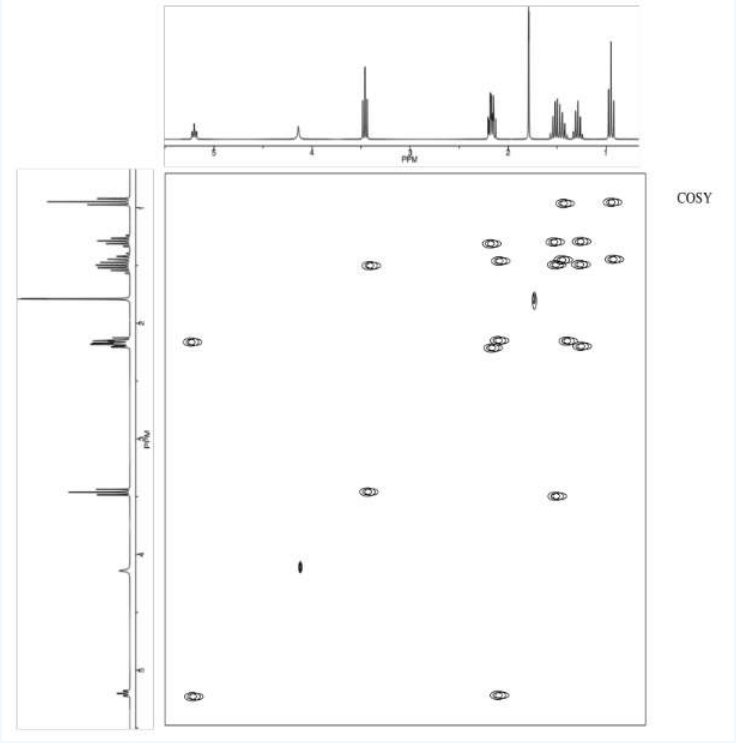
Answer



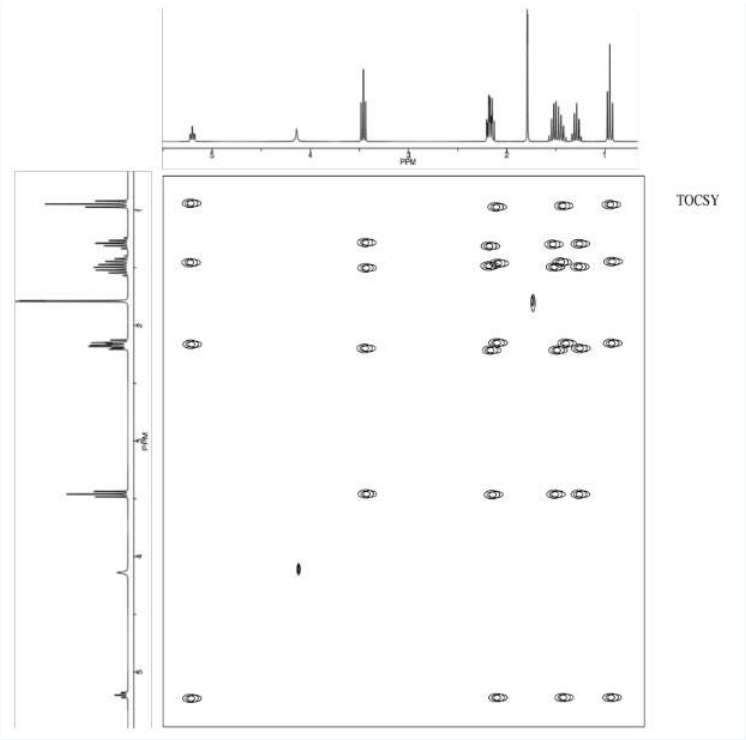
Exercise 3.17.2.2

Identify the compound.

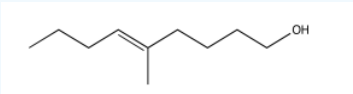




https://chem.libretexts.org/@go/page/363289

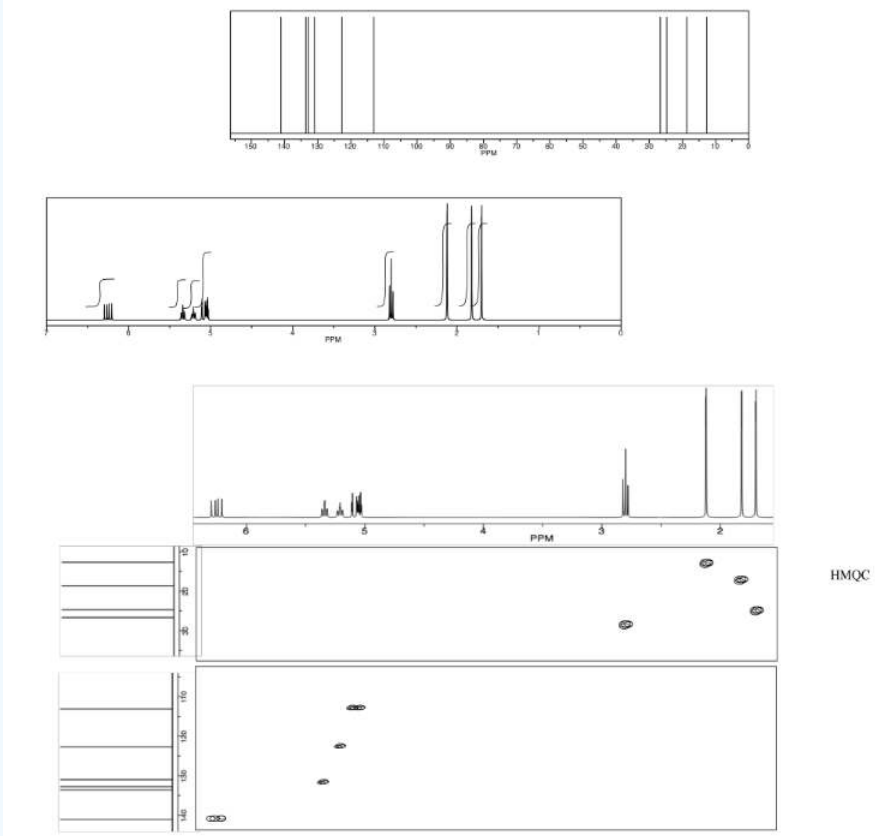


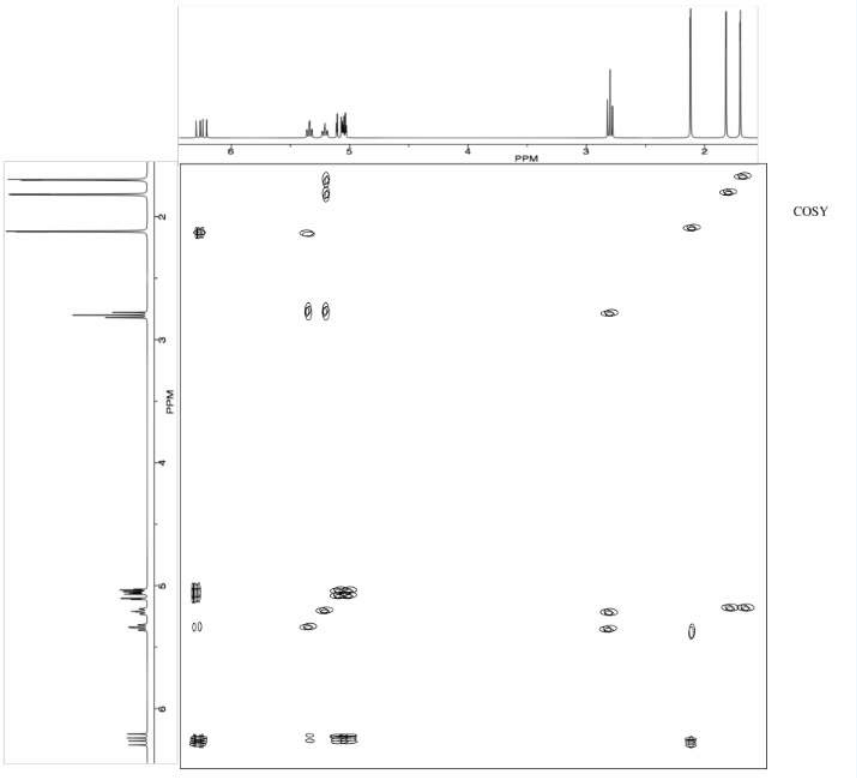
Answer

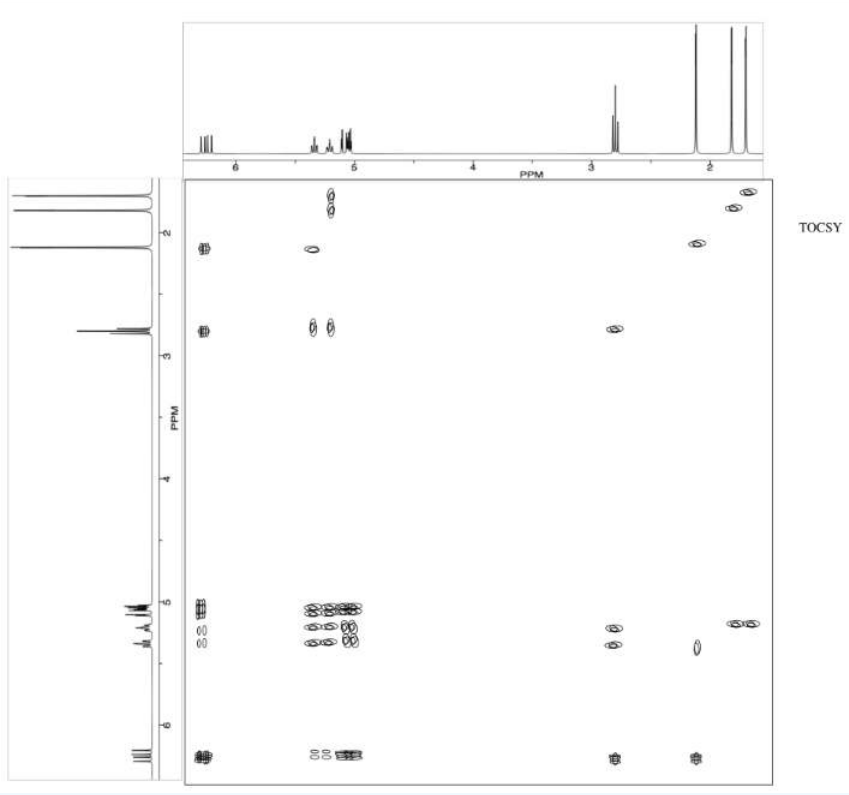


Exercise 3.17.2.3

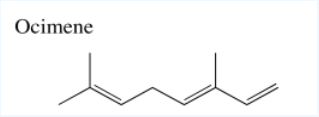
Identify this compound


PPM
PPM
PPM
HMQC


PPM
PPM
COSY



Answer



*Sources:

Selected IR spectra from SDBS (National Institute of Advanced Industrial Science and Technology, Japan, Spectral Database for Organic Compounds, http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi, accessed December, 2015).

^{1}H NMR, ^{13}C NMR, TOCSY and COSY spectra simulated.

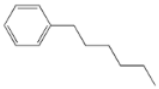
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- **5.2: TOCSY Spectra** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

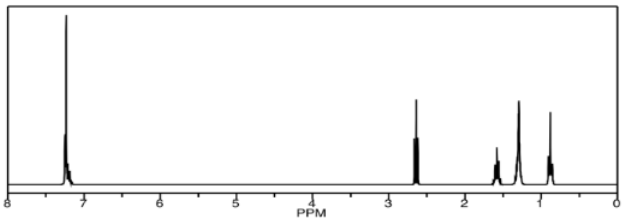
3.17.3: HMBC and HMQC Spectra

Just as COSY spectra show which protons are coupled to each other, HMBC (and the related HMQC) give information about the relative relationships between protons and carbons in a structure. In an HMQC spectrum, a ^{13}C spectrum is displayed on one axis and a ^{1}H spectrum is displayed on the other axis. Cross-peaks show which proton is attached to which carbon. COSY spectra show 3-bond coupling (from H-C-C-H), whereas HMQC shows a 1-bond coupling (just C-H).

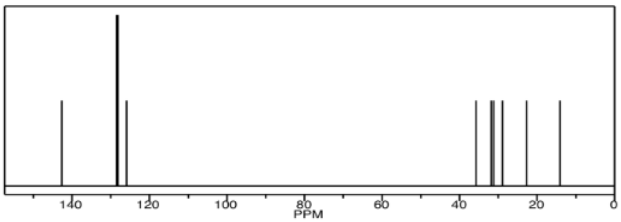
Take a look at n-hexylbenzene. There are lots of similar positions in this structure, so it may be hard to tell peaks apart in either the proton or carbon NMR spectrum.



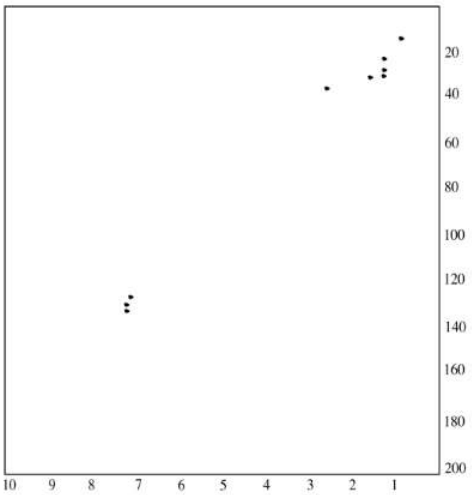
Indeed, the ^{1}H spectrum has some unique peaks but also a couple of large multiplets.



Similarly, there are a couple of carbons that show up at the same place in the ^{13}C NMR spectrum.



An HMQC experiment will help spread things out into two dimensions. Looking along the x axis, we can see that several peaks were clustered together near 7 ppm and near 1.3 ppm. Even looking along the y axis, we can see a couple of carbon peaks have separated out from each other around 33 ppm.

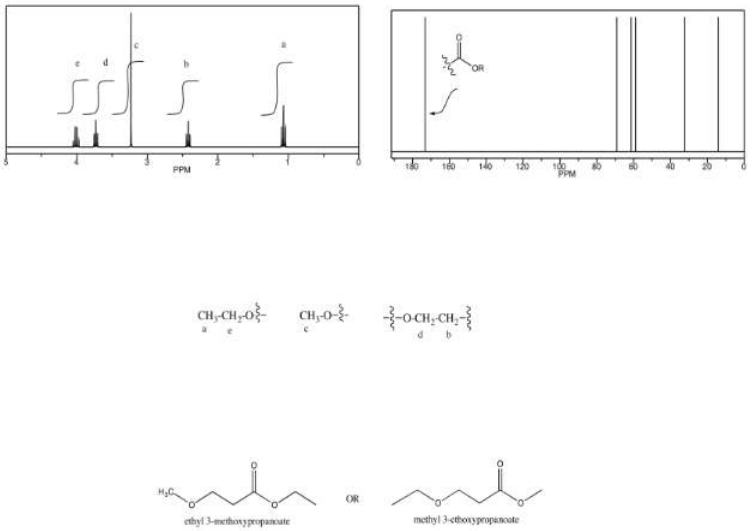


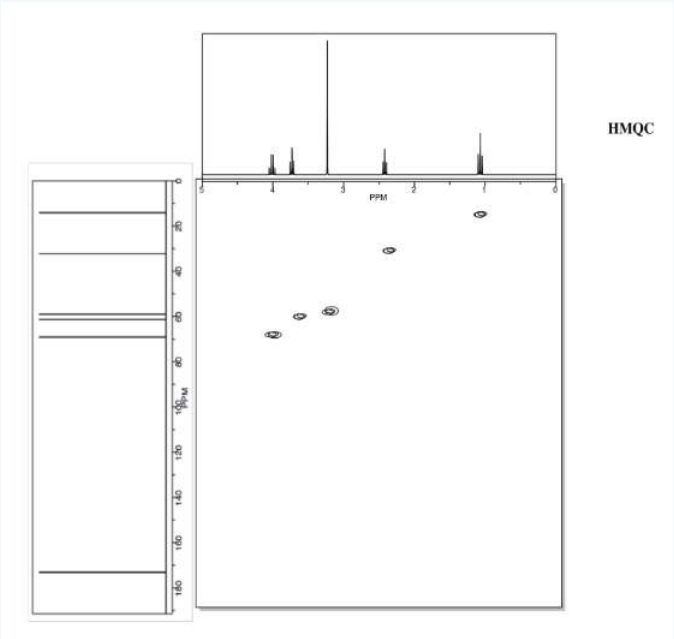
An HMBC spectrum looks very similar to an HMQC spectrum, except that it shows 2-bond, 3-bond or sometimes even 4-bond coupling (not H-C, but H-C-C or H-C-C-C or even H-C-C-C-C). Instead of seeing which carbon is directly attached to a hydrogen,

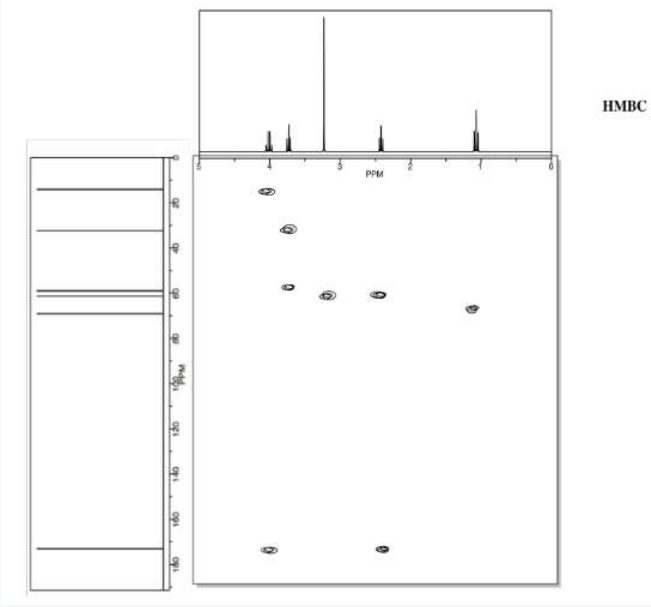
we see which carbon is next to that one, so that we begin to see how the molecule connects.

Exercise 3.17.3.1

Analyse the data to determine which of the two isomers (below) we are dealing with.

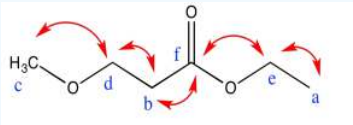






HMBC

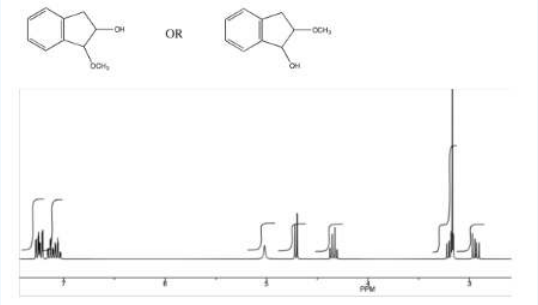
Answer



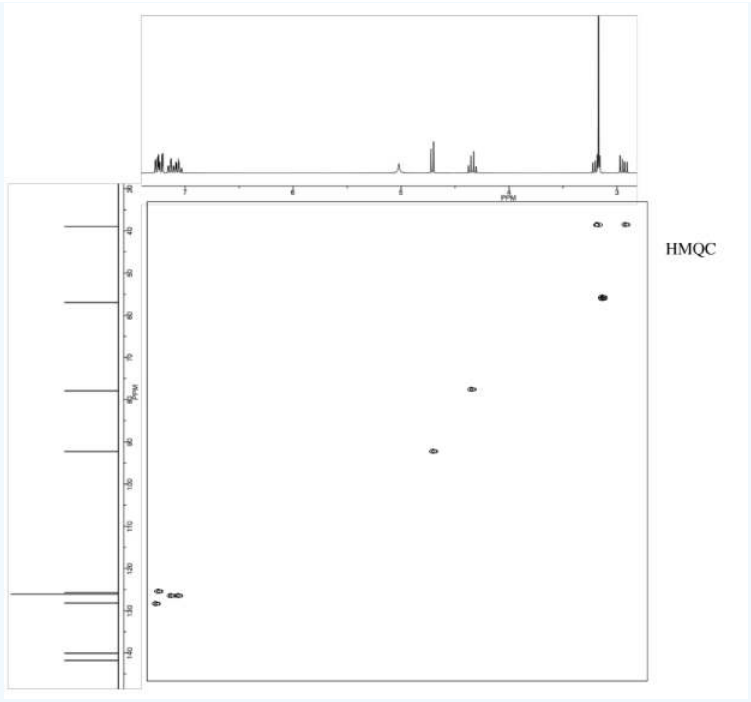
	^{1}H	^{13}C	HMBC
a	1.1	15	e
b	2.4	32	d, f
c	3.2	58	d
d	3.7	63	b, c
e	4.0	69	a, f
f	-	172	b, e

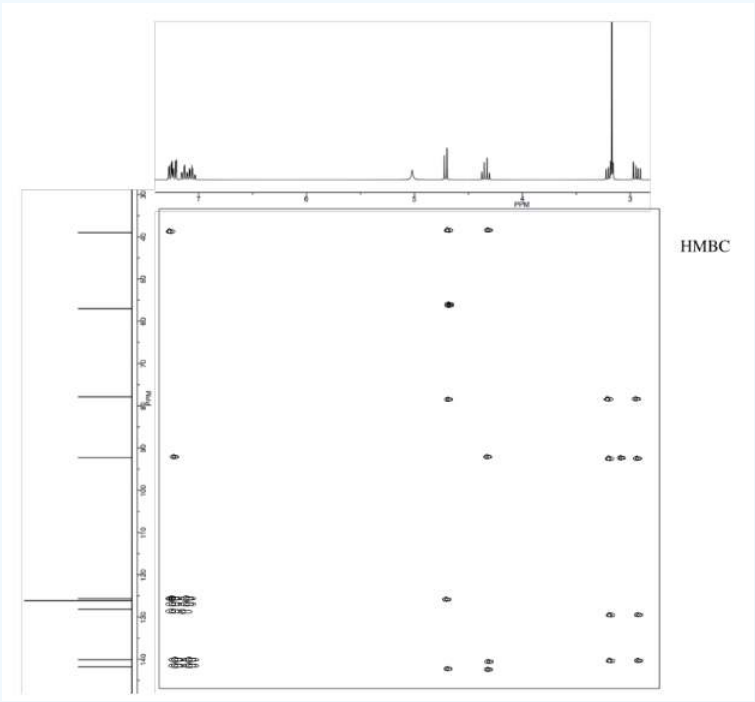
Exercise 3.17.3.2

Analyze the data to determine which of the two isomers (below) we are dealing with.

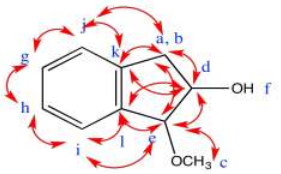


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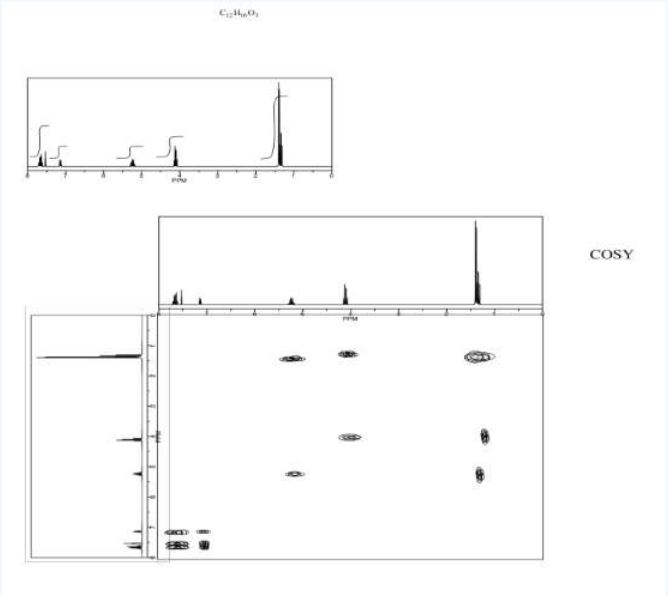
Answer



	^{1}H	^{13}C	HMBC
a	2.8	38	d, e, j, k
b	3.2		
c	3.2	57	e
d	4.4	78	a/b, e, k, l
e	4.7	92	a/b, c, d, i, l
f	5.0	-	-
g	7.1	127	h, i, j, k, l
h	7.2	127	g, i, j, k, l
i	7.3	126	e, g, h, j, k, l
j	7.4	129	a/b, g, h, i, k, l
k	-	140	a/b, d, g, h, i, j, l
l	-	142	d, e, g, h, i, j, k

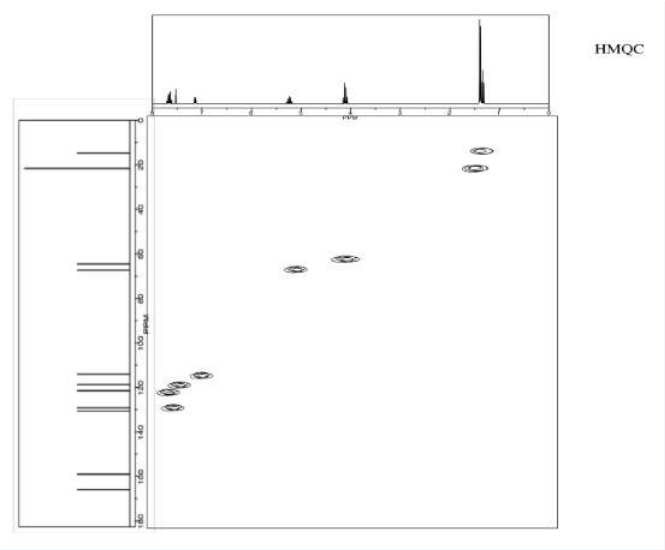
Exercise 3.17.3.3

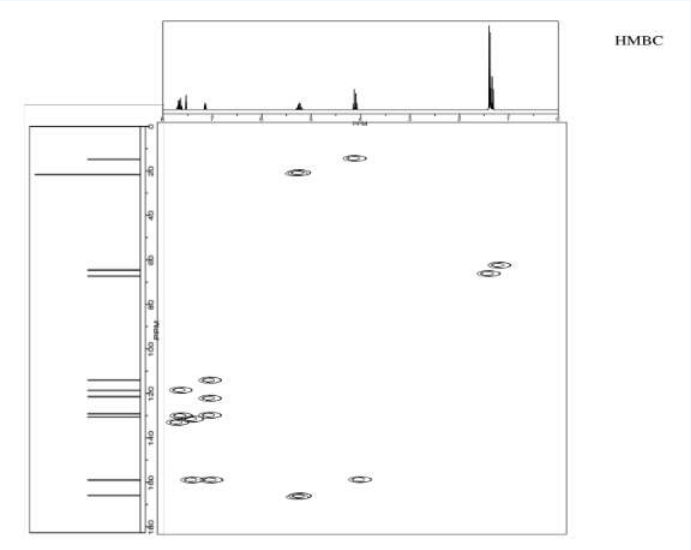
Analyse the data to determine the structure of the compound.



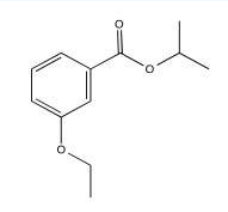
COSY

https://chem.libretexts.org/@go/page/363290

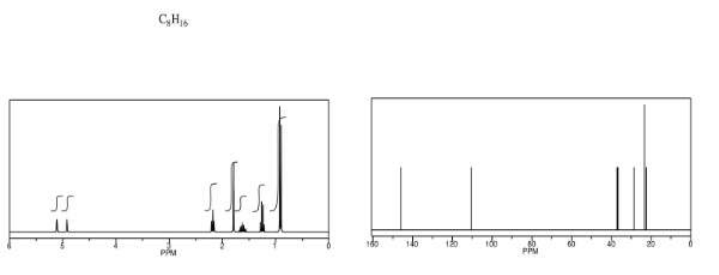


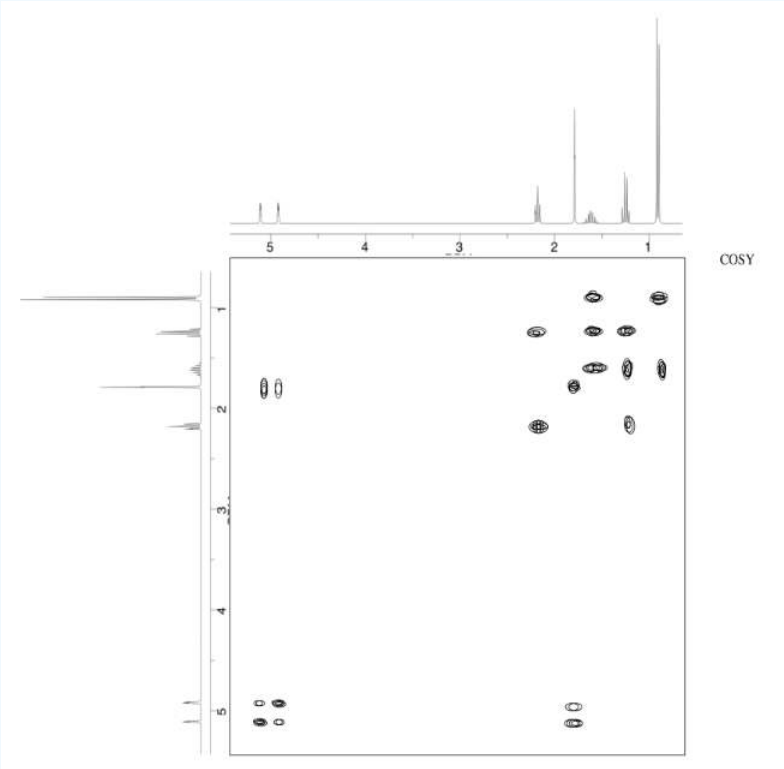


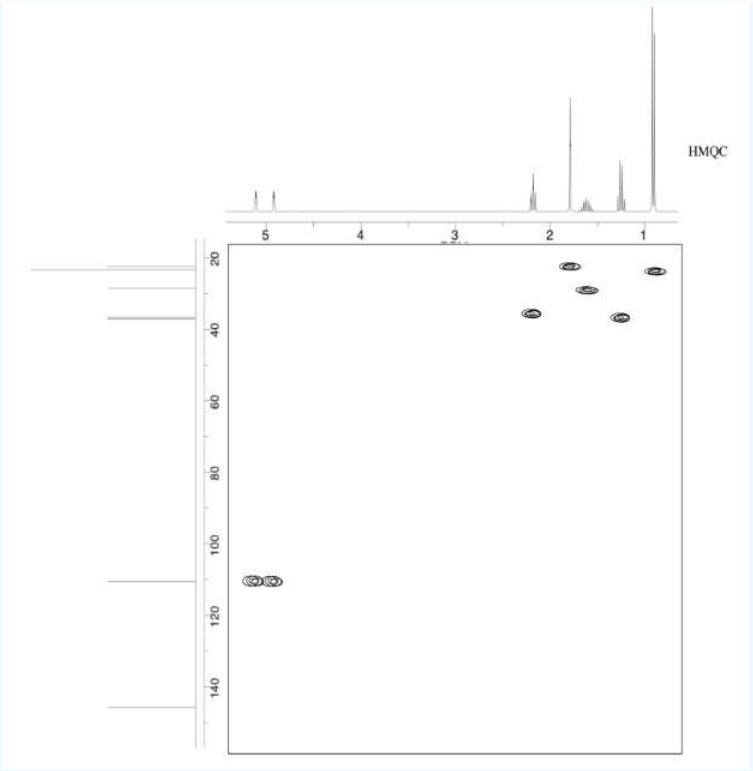
Answer

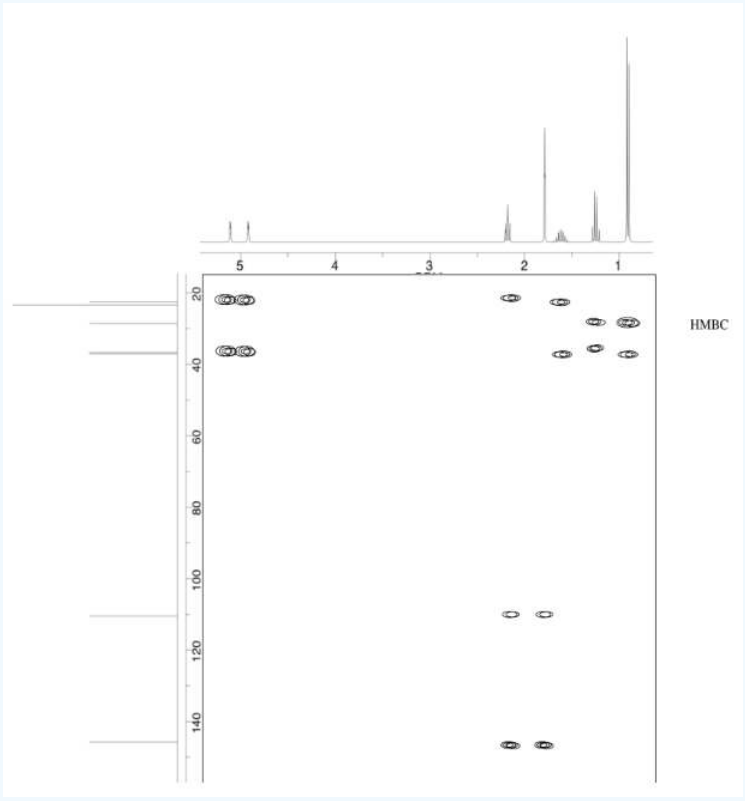


Exercise 3.17.3.4


C_8H_{16}
PPM
PPM

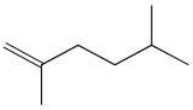

5
4
3
2
1
COSY





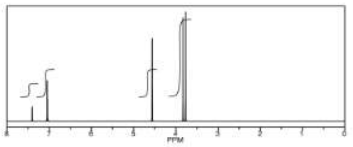
Answer

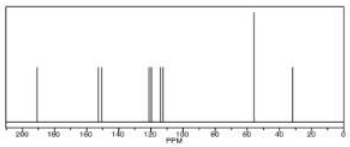
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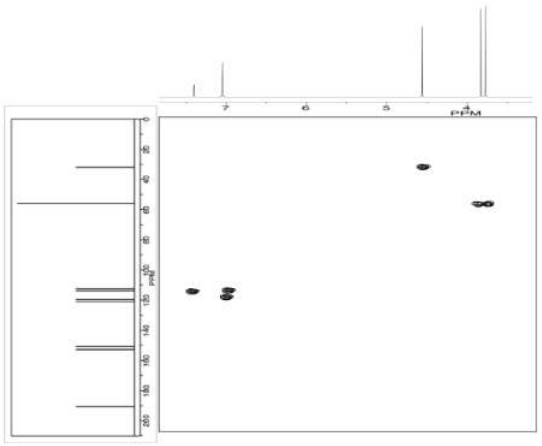


2,5-dimethylhex-1-ene

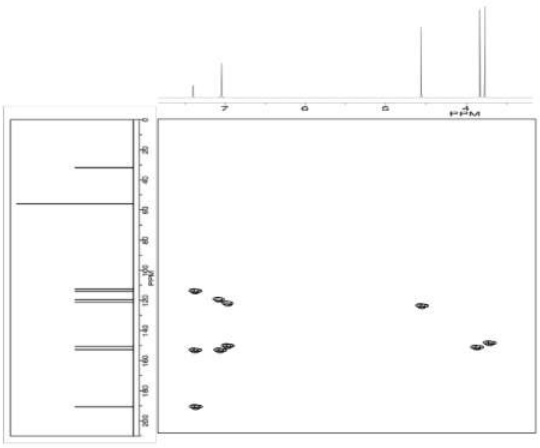
Exercise 3.17.3.5





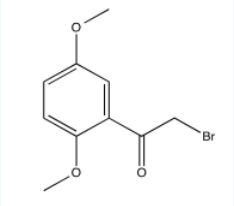


HMQC

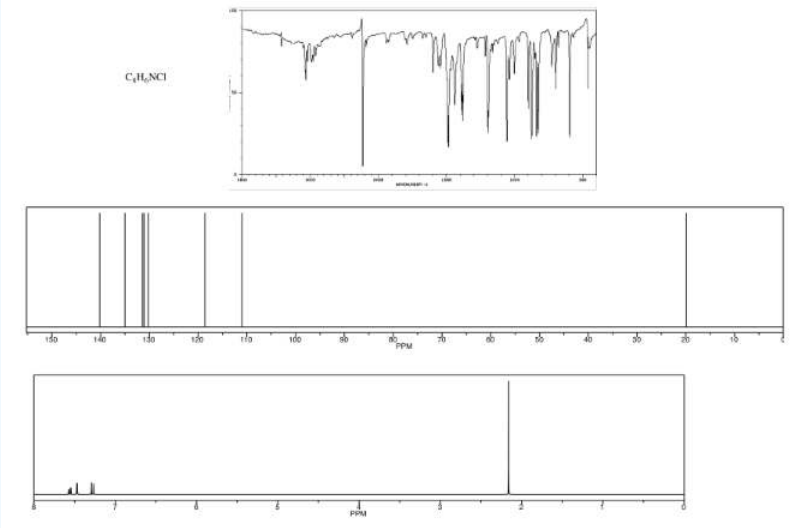


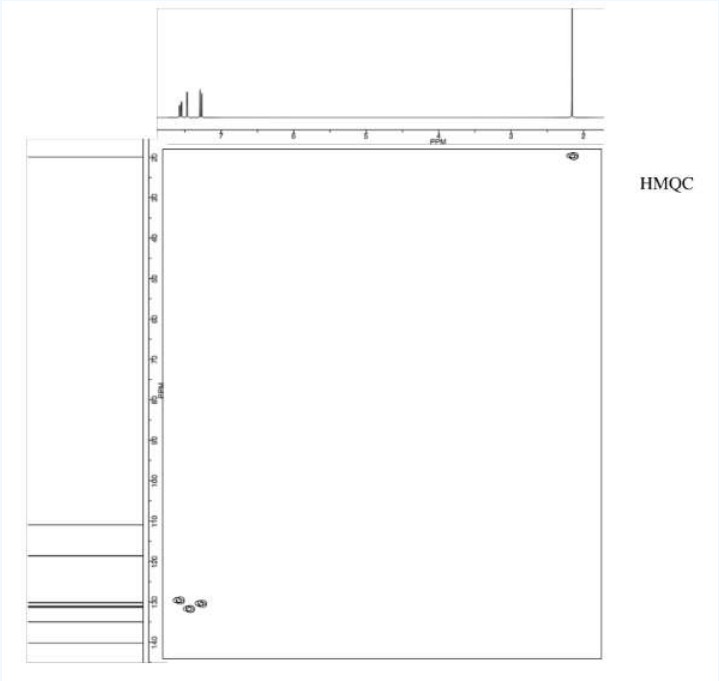
HMBC

Answer

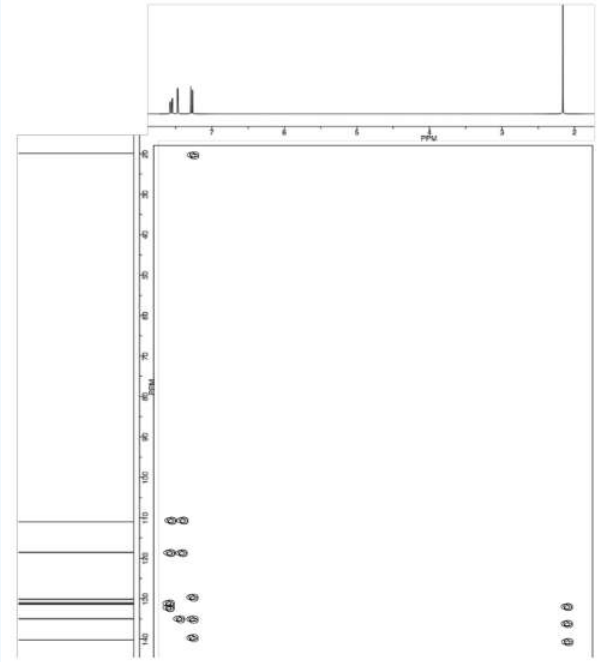


Exercise 3.17.3.6



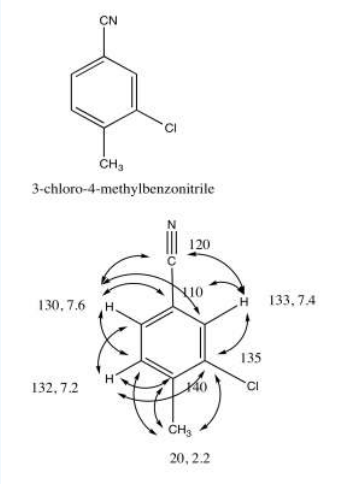


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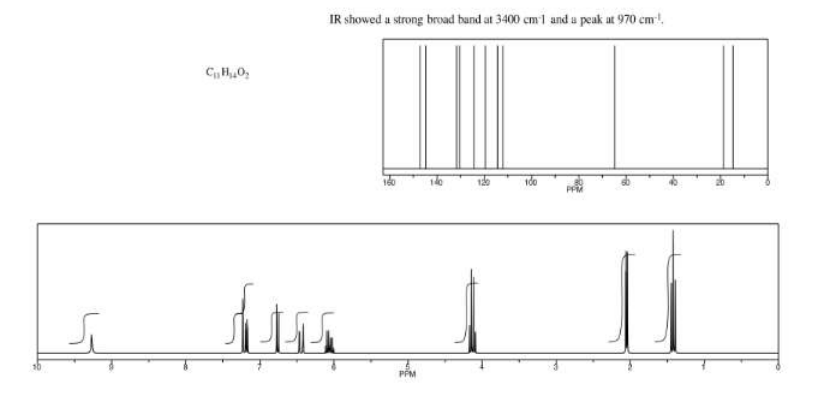


HMBC

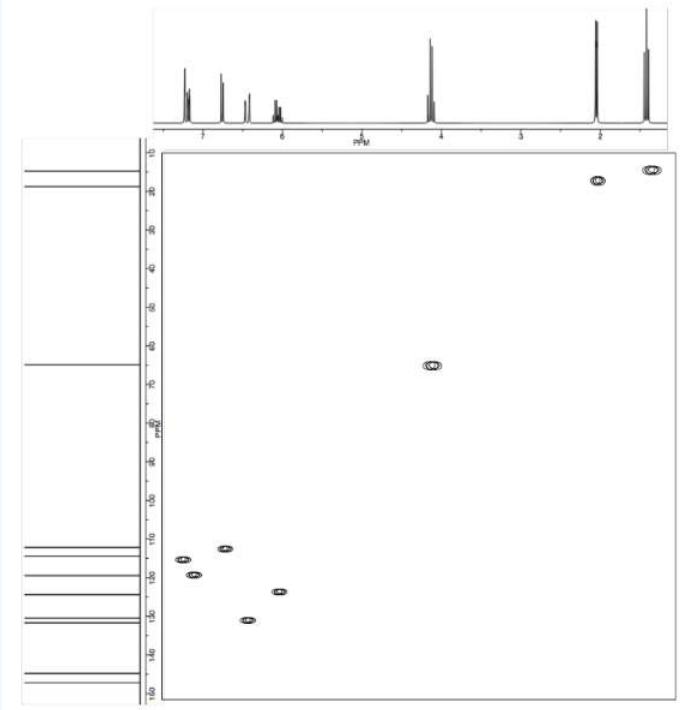
Answer



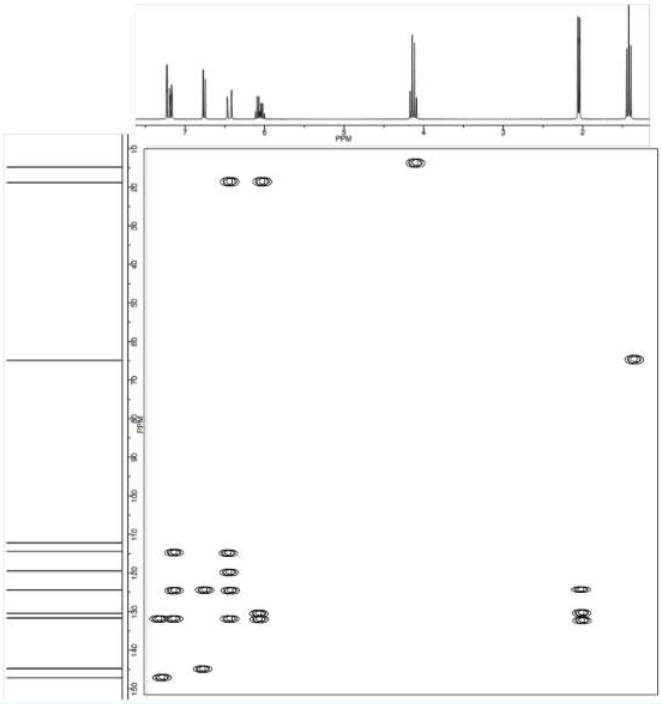
Exercise 3.17.3.7



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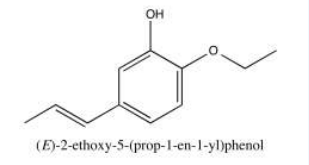


HMQC



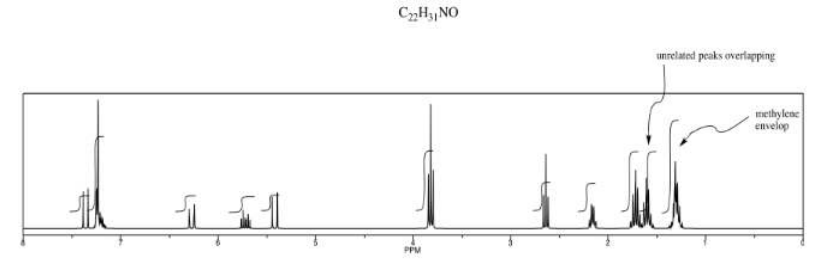
HMBC

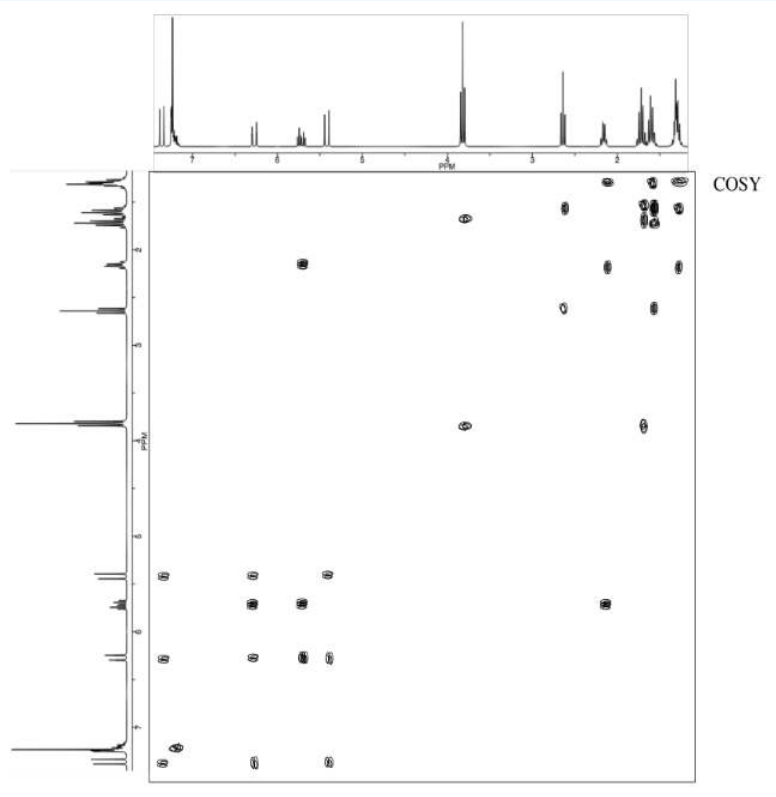
Answer

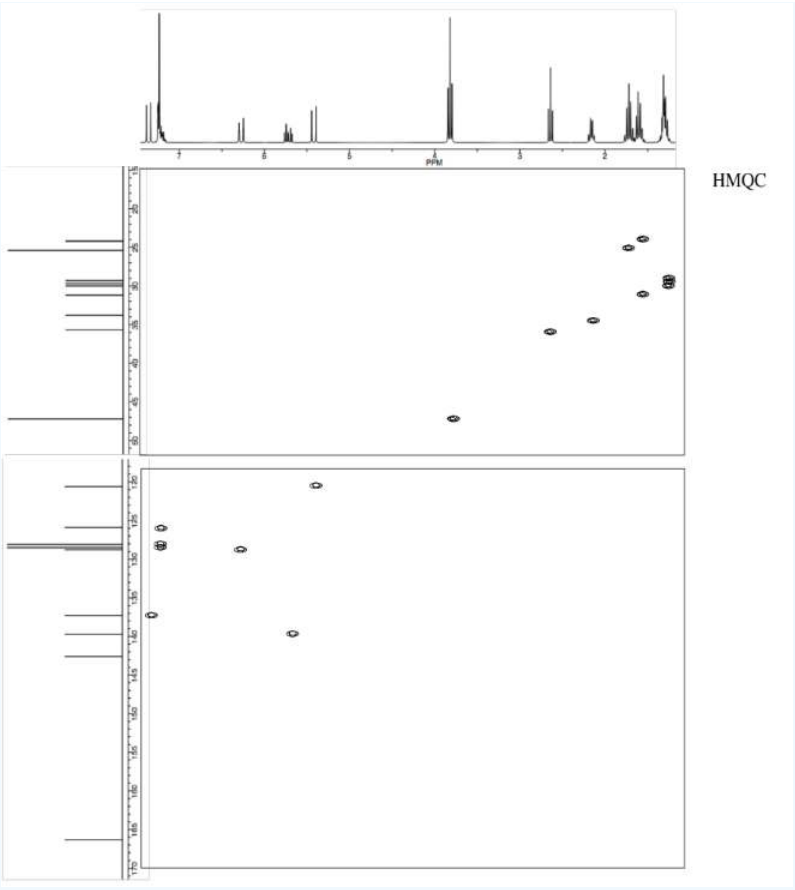


(*E*)-2-ethoxy-5-(prop-1-en-1-yl)phenol

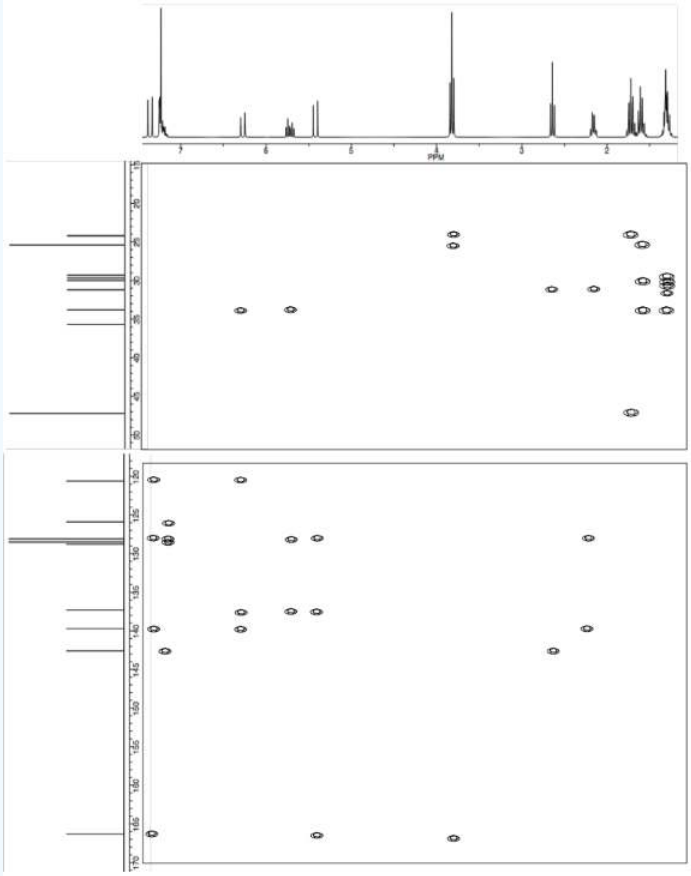
Exercise 3.17.3.8



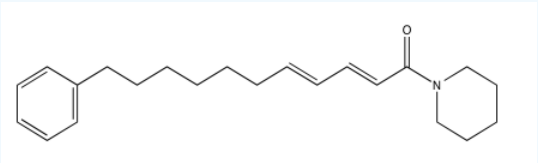




https://chem.libretexts.org/@go/page/363290



Answer



*Sources:

Selected IR spectra from SDBS (National Institute of Advanced Industrial Science and Technology, Japan, Spectral Database for Organic Compounds, http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi, accessed December, 2015).

^{1}H NMR, ^{13}C NMR, HMBC and HMQC spectra simulated.

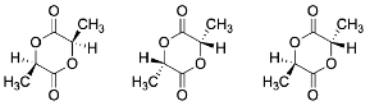
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3.17.4: NOESY Spectra

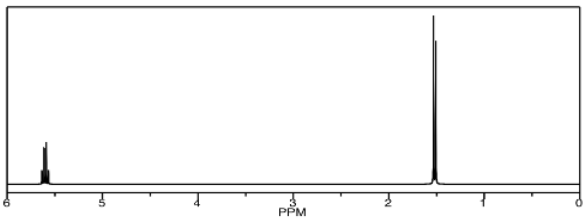
Nuclear Overhauser Effect Spectroscopy, or **NOESY**, shows through-space interactions within the molecule, rather than the through-bond interactions seen in the other methods. This method is especially useful for determining stereochemical relationships in a molecule. In two stereoisomers, the atoms are all connected in exactly the same order, through exactly the same bonds. A COSY or an HMBC spectrum wouldn't be able to distinguish between these isomers.

However, in a relatively rigid conformer, one hydrogen in one stereoisomer may be locked on the same side of the molecule as another group. If information could be transmitted from that group to that proton, we would know that they were near each other in space, and we would know which stereoisomer we have. For example, there are three different stereoisomers of lactide. Lactide is a product of the fermentation of corn and soybeans; it can be polymerized to make a sort of brittle plastic, PLA. PLA is used for food packaging because it can be composted in industrial and municipal waste management sites.

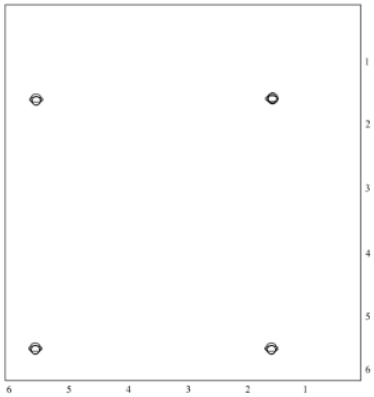


How would we know which isomer we were dealing with? Telling L-LA and D-LA apart may be difficult. They are enantiomers of each other and so they have the same physical properties. However, provided someone else has already figured out which is which, we could use optical rotation and compare the value we measure to the reported one.

On the other hand, we could easily tell the meso-LA from either the D-LA or the L-LA, because it would be the diastereomer of either of them. It would have different physical properties, including different NMR spectra. We could carefully compare the spectrum below to reported spectra for meso-LA and L-LA (or D-LA) to see which isomer we have.



On the other hand, we could just take a NOESY spectrum. In meso-LA, the methyl on one end of the molecule is on the same face of the ring as the hydrogen on the other end. We may be able to see that through-space relationship. We wouldn't see it in L-LA or D-LA, though.

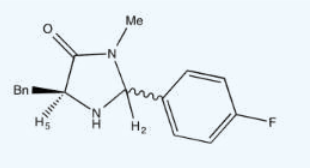


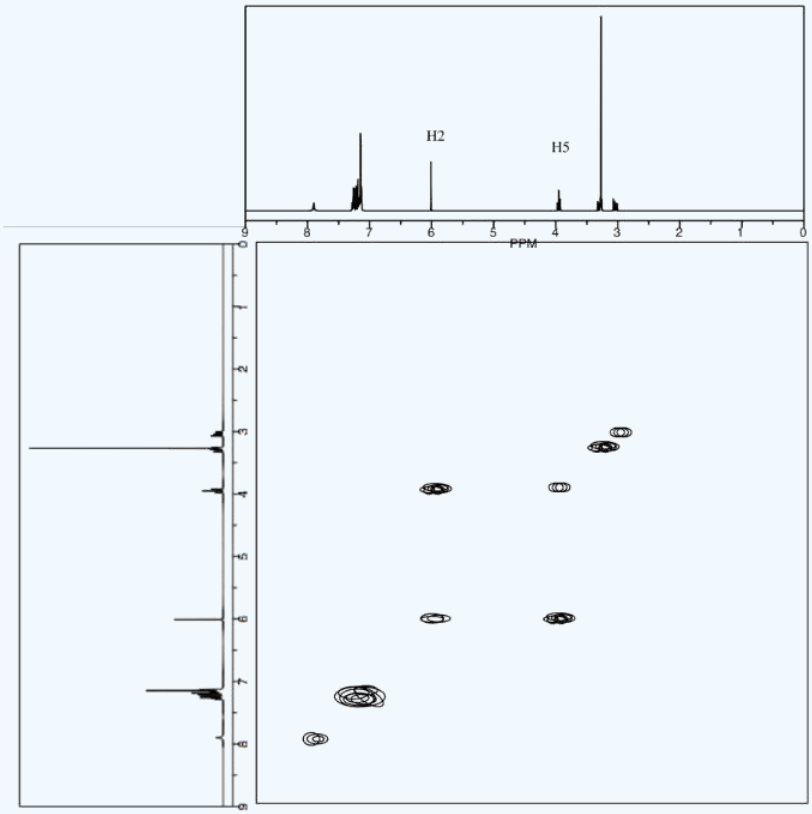
Just like in a COSY spectrum, all of the peaks that show up along the diagonal of a NOESY spectrum are simple the ones we would see in a regular ^{1}H spectrum. The peaks that show up off the diagonal tell us about through-space relationships. In this case, the relationship between the methyl hydrogen and the alpha hydrogen suggest we have a sample of meso-LA.

ROESY is a similar method that works better in some cases.

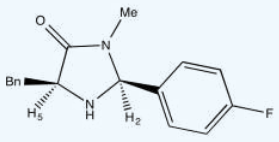
Exercise 3.17.4.1

Draw the relative stereochemistry of this compound based on the NOESY spectrum.



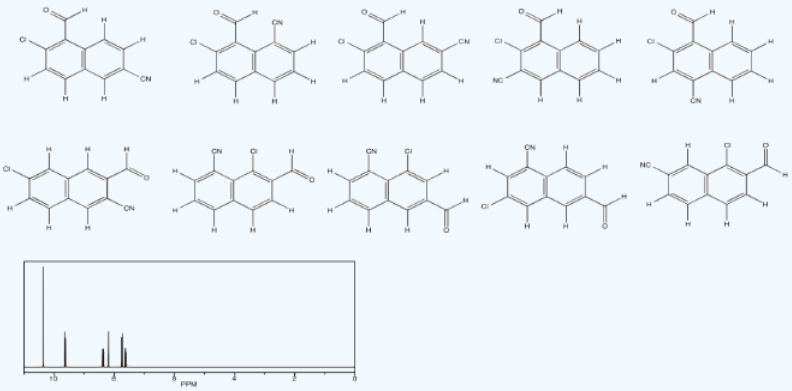


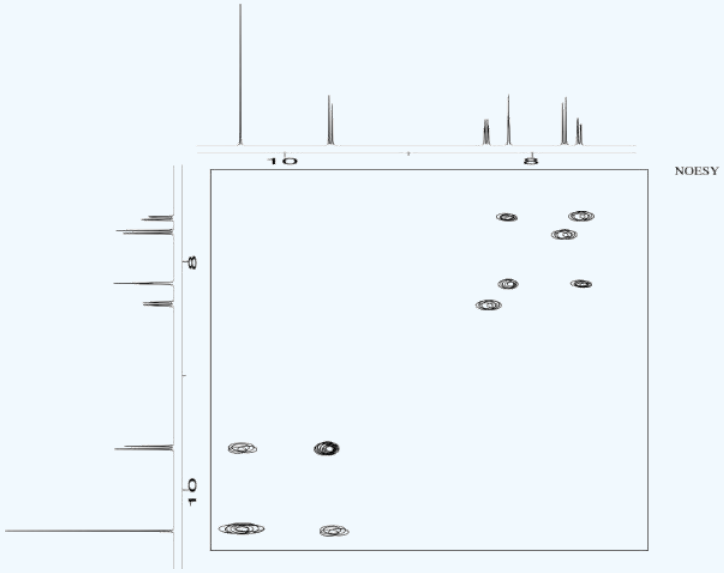
Answer



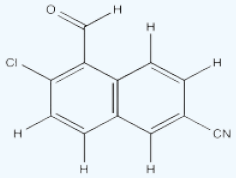
Exercise 3.17.4.2

Use NOESY to determine which isomer below is present.



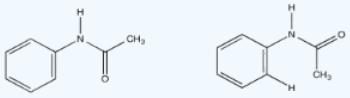


Answer

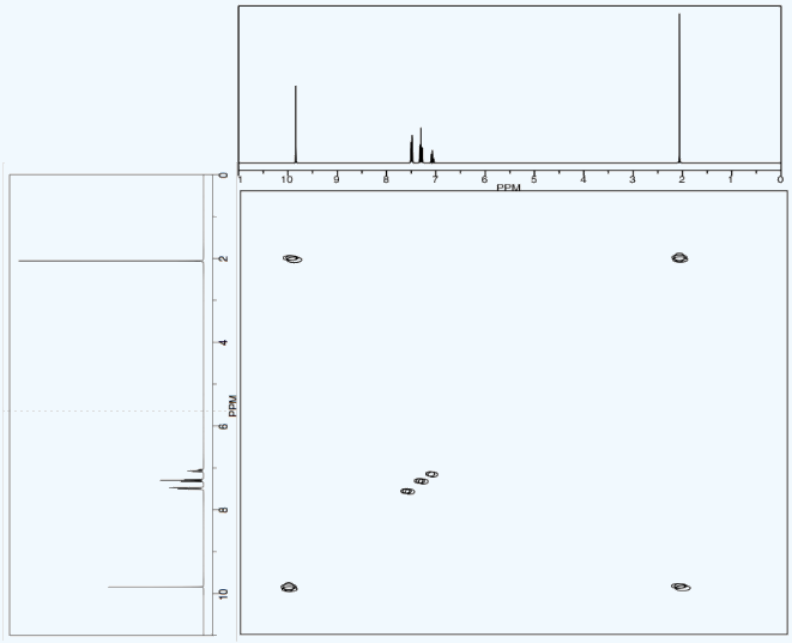


Exercise 3.17.4.3

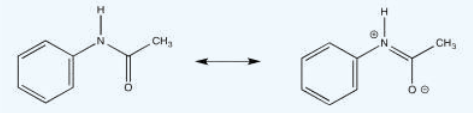
Acetanilide has two different conformers. They do not easily interconvert.



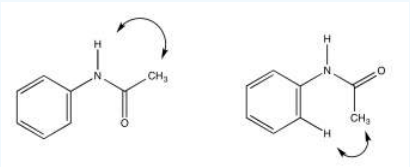
a. Explain (using pictures) why there isn't free rotation around the amide bond.
b. Use double headed arrows to predict nOe correlations.
c. Use the NOESY spectrum to determine which conformer is observed at room temperature.



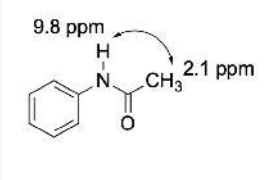
Answer a



Answer b

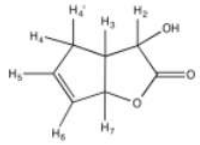


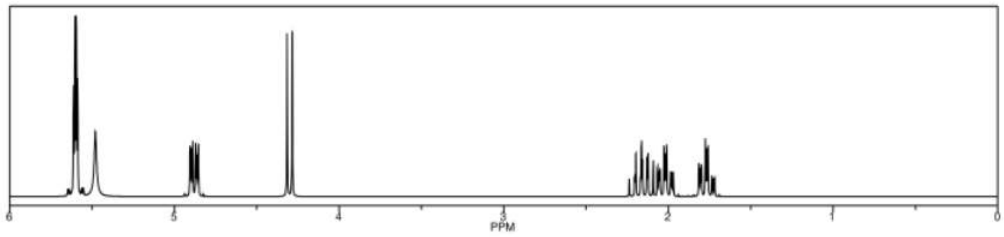
Answer c



Exercise 3.17.4.4

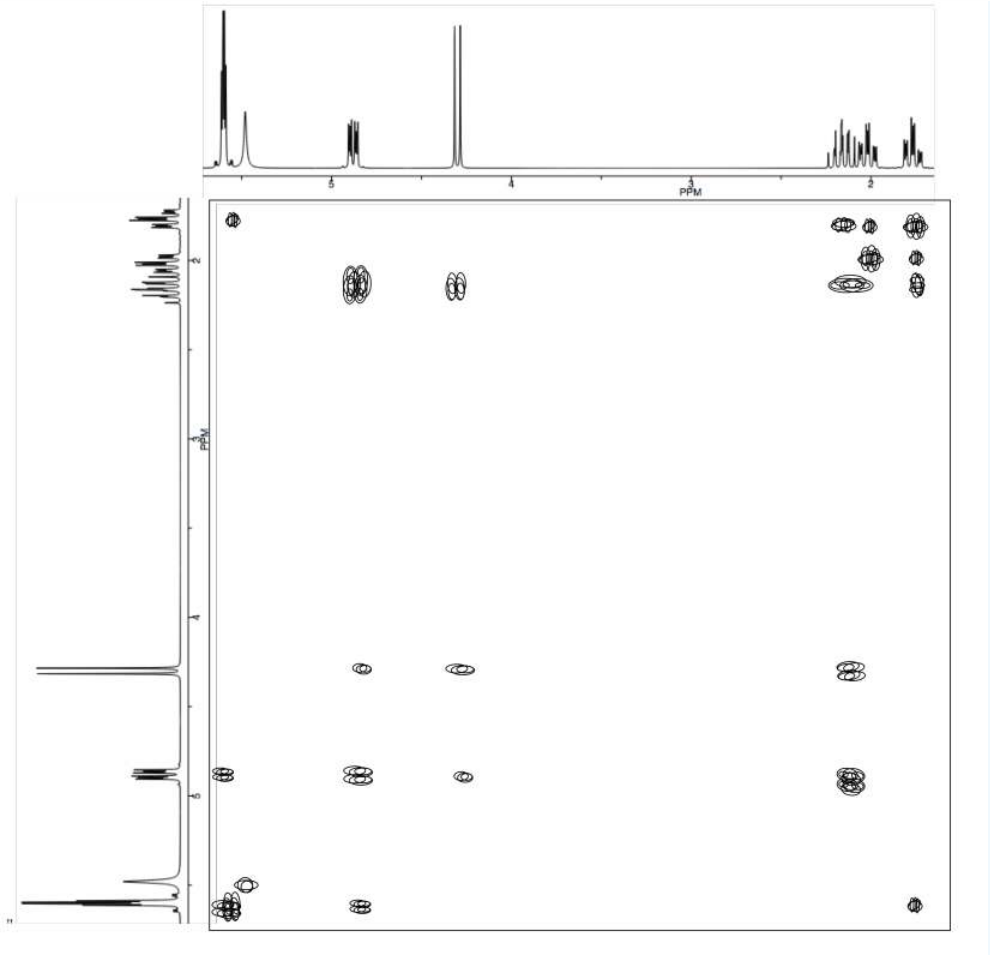
a) Complete the table of ^{1}H assignments for the following compound:



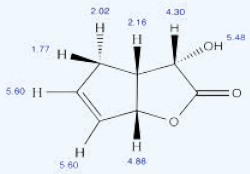


Proton	δ ppm
OH	5.48
H2	
H3	
H4	
H4'	2.02
H5	
H6	
H7	

b) Use the NOESY to assign the relative configuration.

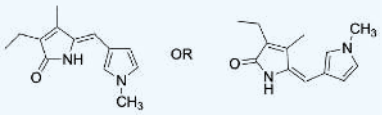


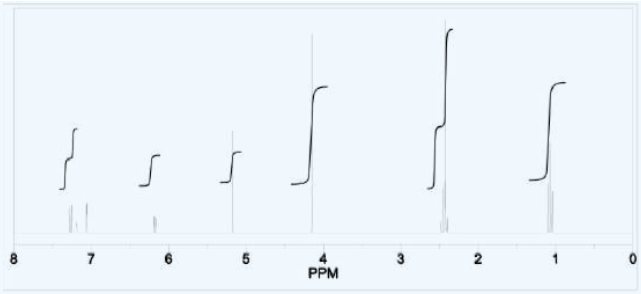
Answer b

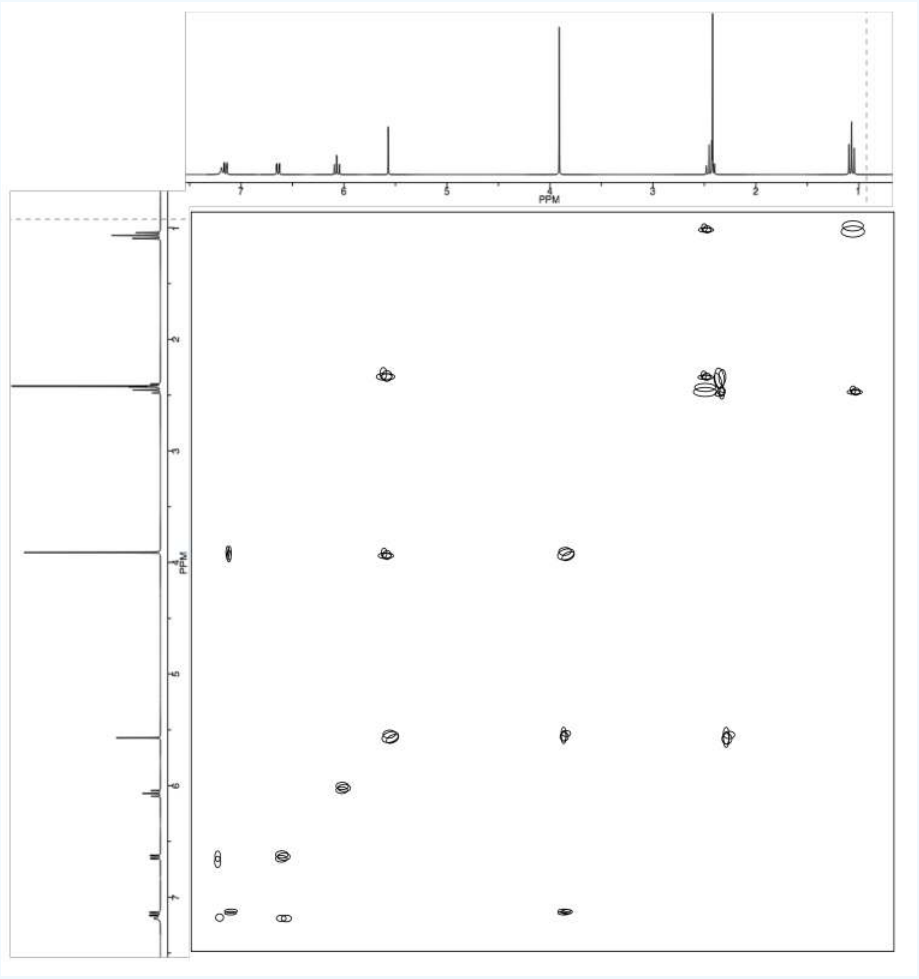


Exercise 3.17.4.5

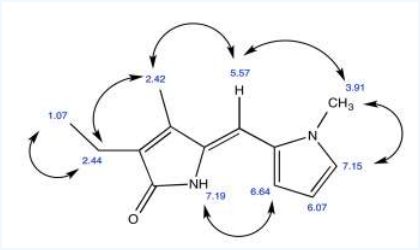
Draw the relative stereochemistry of this compound based on the NOESY spectrum.




8
7
6
5
4
PPM
3
2
1
0


PPM
PPM

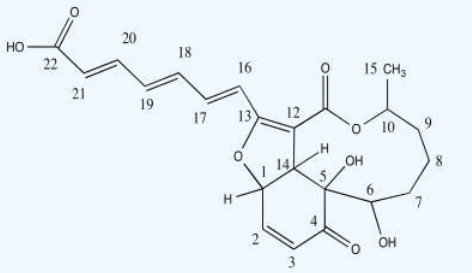
Answer


5.57
2.42
3.91
H
CH3
1.07
N
2.44
7.15
NH
7.19
6.64
6.07
O

Exercise 3.17.4.6

Dictyosphaeric Acid A is an antimicrobial compound isolated from an undescribed *Penicillium sp.* in an alga *Dictyosphaeria versluyii* collected in Fiji (Bugni, Janso, Williamson, Feng, Bernan, Greenstein, Carter, Maiese and Ireland, *J. Nat. Prod*. **2004**, *67*, 1396-1399).

a. Circle all the chiral centers.



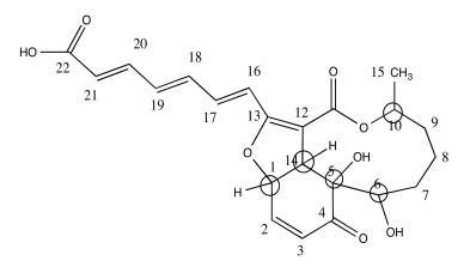
The researchers used nOe (ROESY) to determine stereochemical relationships.

H	ROESY
1	2, 14
2	1, 3
3	2
4	
5	
6	8b, 9b
7a	7b
7b	7a, 14
8a	
8b	6
9a	10, 15
9b	6, 10, 15
10	9a, 9b, 15
11	
12	
13	
14	1, 7b
15	9a, 9b, 10

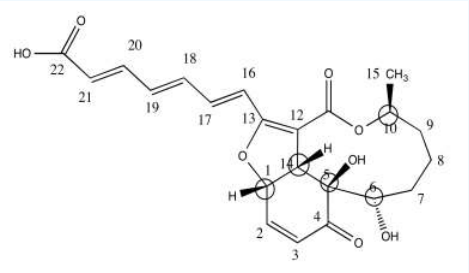
b. Use the data to put the substituents on this structure with wedges/dashes

c. Include key nOe correlations with the curved arrows.

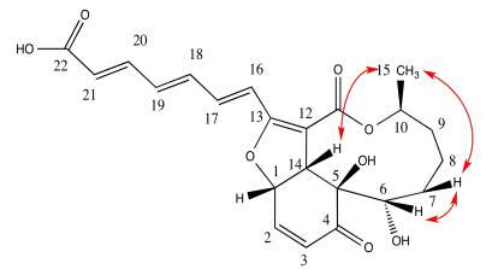
Answer a



.**Answer b**

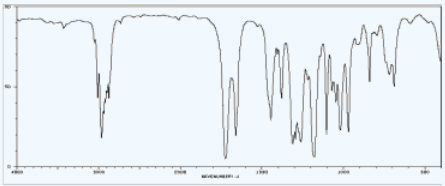


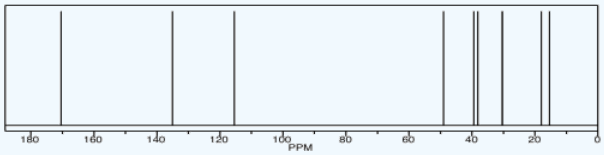
Answer c

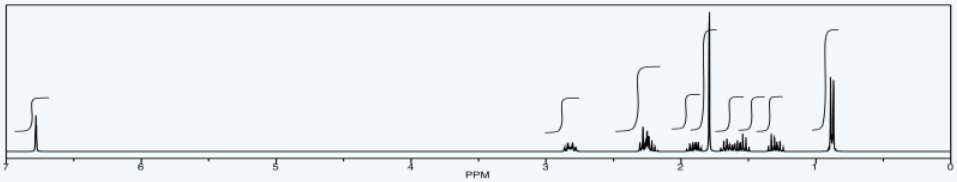


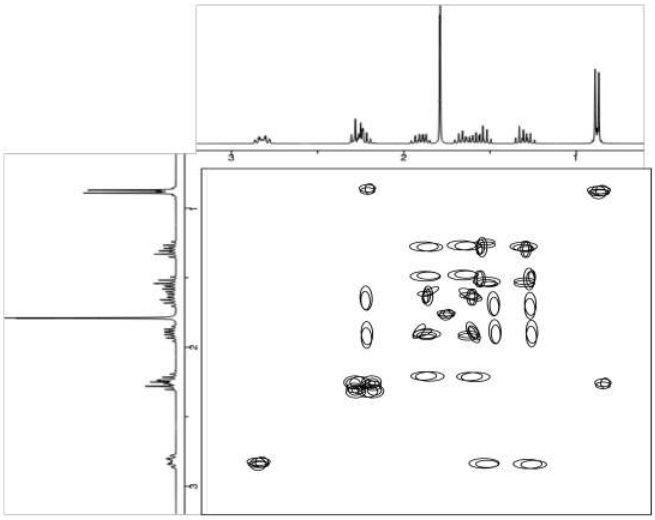
Exercise 3.17.4.7

analyze the following data and propose a structure for the compound, formula $C_{10}H_{14}O_2$.

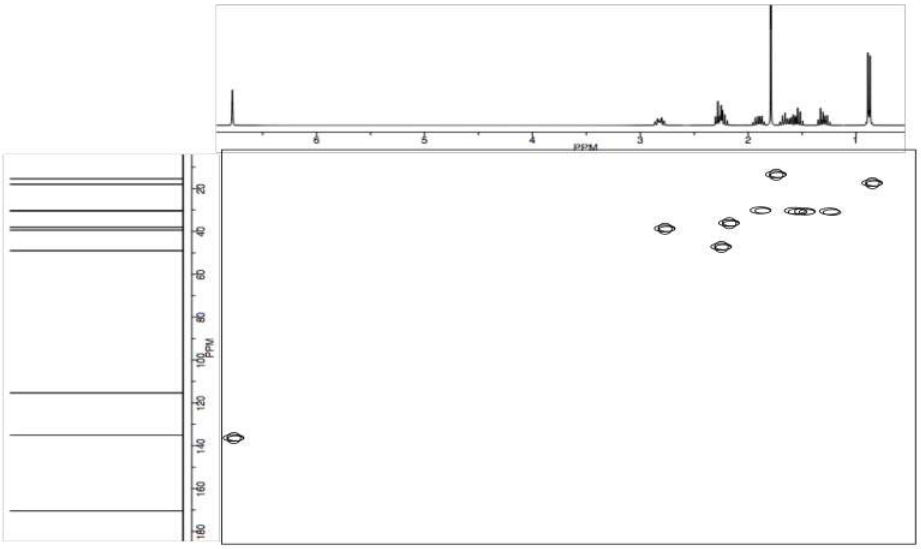






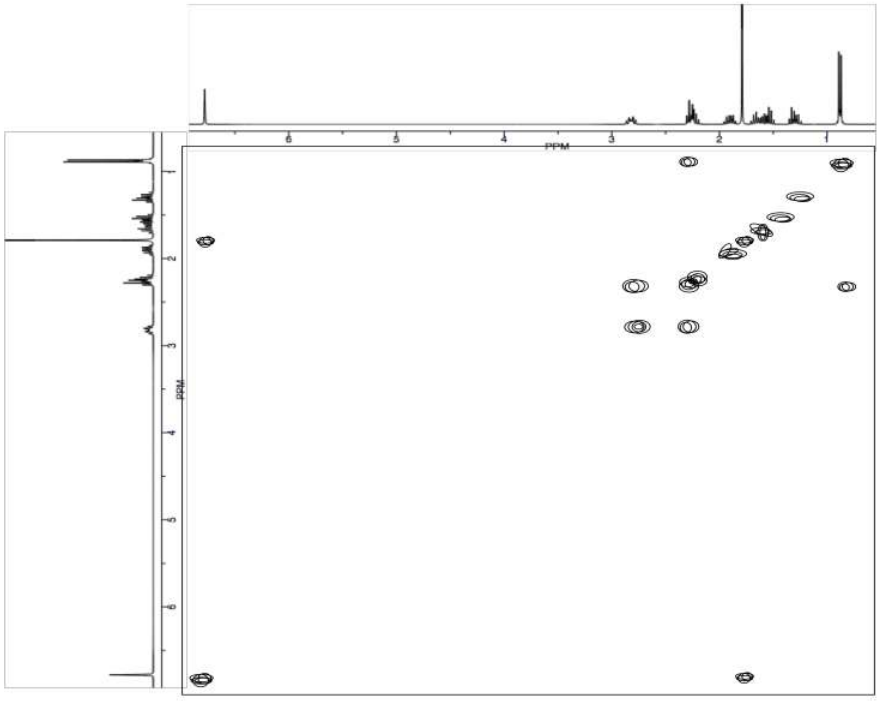


COSY



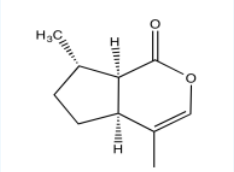
HMQC

https://chem.libretexts.org/@go/page/363291



NOESY

Answer



Catnip (nepetalactone)

Sources

Selected IR spectra from SDBS (National Institute of Advanced Industrial Science and Technology, Japan, Spectral Database for Organic Compounds, http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi, accessed December, 2015).

^{1}H NMR, ^{13}C NMR and NOESY spectra simulated.

This page titled 3.17.4: NOESY Spectra is shared under a CC BY-NC license and was authored, remixed, and/or curated by Chris Schaller.

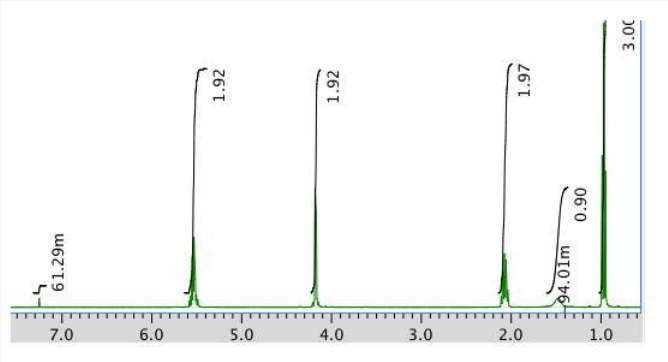
- **5.4: NOESY Spectra** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

3.17.5: More Practice with 2D

The following problems involve real samples. Note that you may need to check for peaks due to solvent. Helpful tables may be found here.

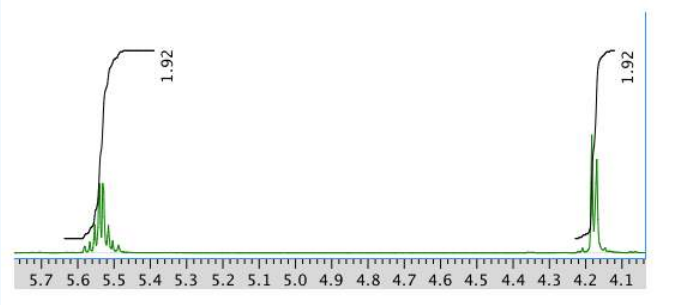
Exercise 3.17.5.1

The following problems involve real samples. Note that you may need to check for peaks due to solvent. Helpful tables may be found here.

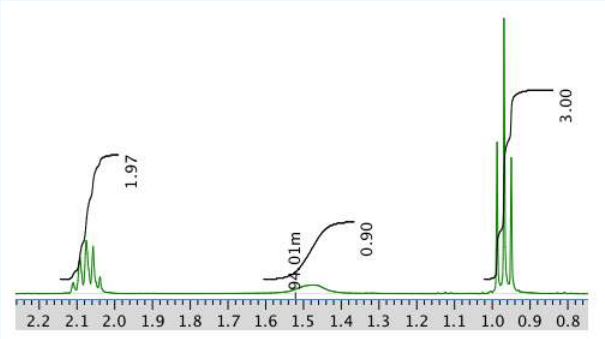


Note that the m beside one of the integral values stands for milli (one thousandth). 61.29m = 0.06129 units.

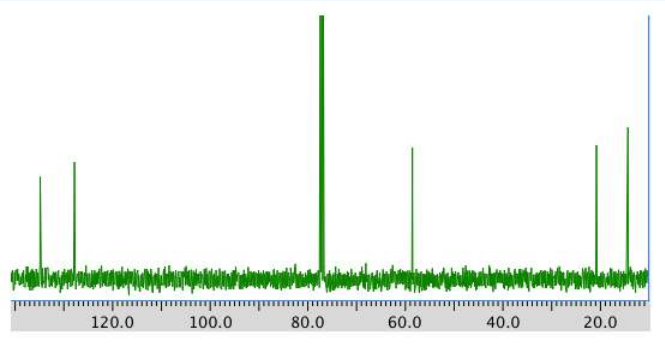
An expansion of the ^{1}H NMR spectrum:



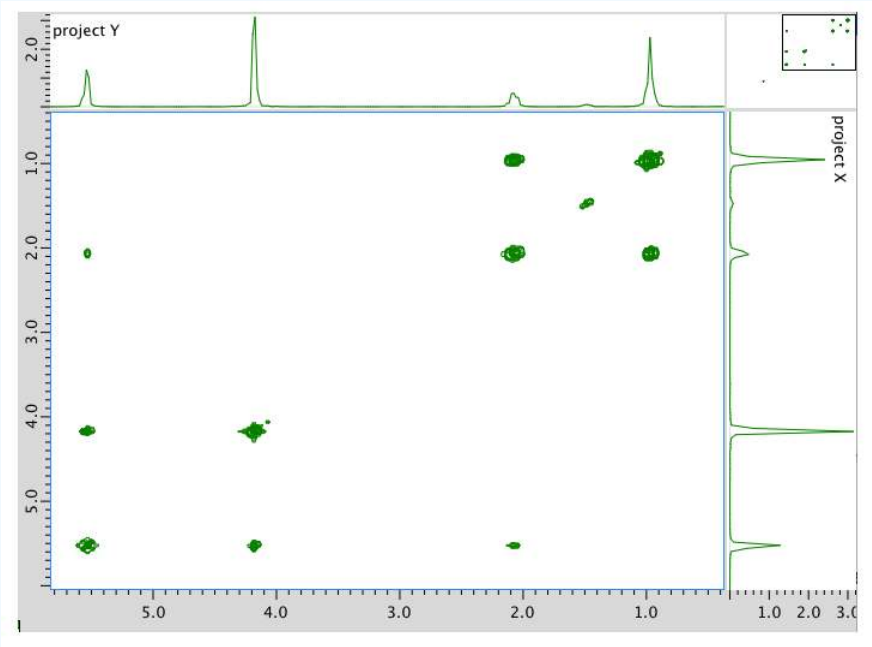
Another expansion:



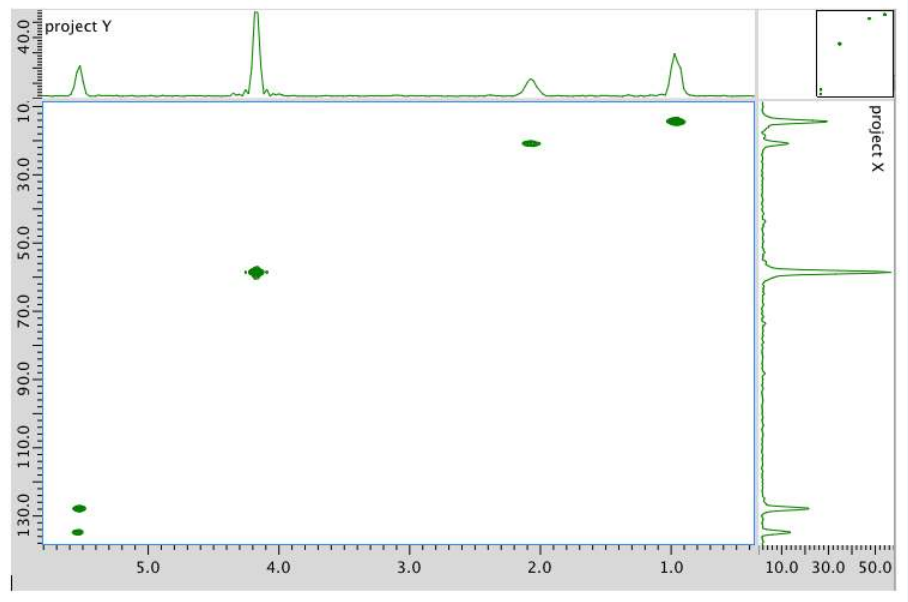
A ^{13}C NMR spectrum:



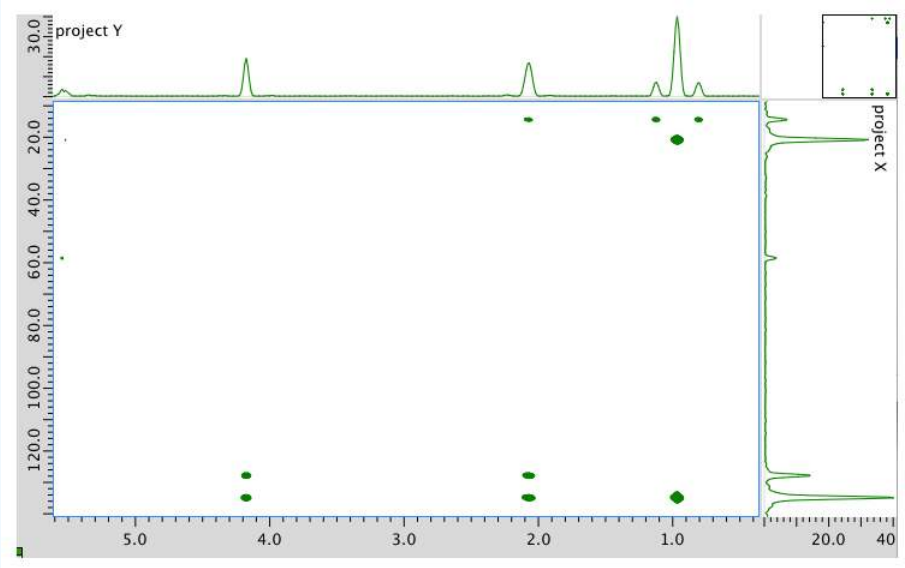
COSY spectrum:



HMQC spectrum:



HMBC spectrum:



Answer

^{1}H NMR

Chemical shift (ppm)	Integration	Multiplicity	Partial Structure
5.54	2H	multiplet	C**H**=C (x 2)
4.17	2H	doublet	O-C**H**$_2$-CH
2.08	2H	quintet	CH-C**H**$_2$-CH$_3$
1.47	1H	boad singlet	OH
0.95	3H	triplet	CH$_2$-C**H**$_3$

* total # H: 10

^{13}C NMR

Chemical shift (ppm)	Type of carbon
134	sp^2
128	sp^2
58	sp^3-O
21	sp^3
14	sp^3

*total # C: 5

COSY

Assignment	^{1}H	COSY
A	0.95	2.08
B	2.08	0.95, 5.54
C	4.17	5.54
D	5.54	2.08
E	5.54	4.17

*HMQC indicates two hydrogens at 5.54 are in two different environments

HMQC

Assignment	^{13}C	^{1}H
A	14	0.95
B	21	2.08
C	58	4.17
D	128	5.54
E	134	5.54

Formula:

$C_5H_{10}O$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $\mathbf{5\times 12) + (10\times 1) + (1\times 16) = 86}$

Compare C_5H_{10} ratio to C_5H_{12} in hydrocarbon

Degrees of unsaturation = \(\frac{(2 \times 5) + 2 - 10}{2} = 1 unit (1 double bond)

The data tables should be consitent with this structure:

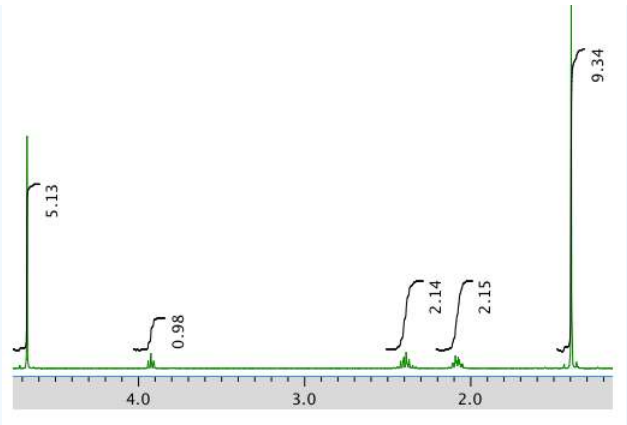
pent-2-en-1-ol (could be *cis* or *trans* based on this analysis)

Exercise 3.17.5.2

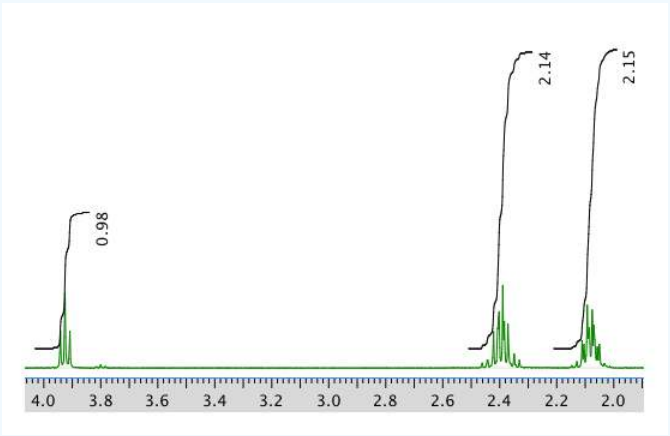
Present an analysis of the following data and propose a structure.

MW: 202 amu

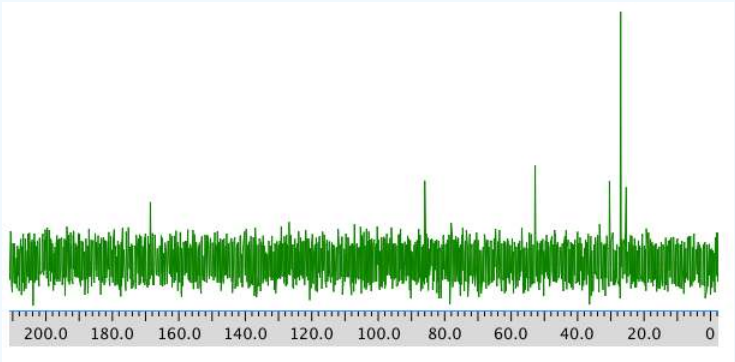
The full ^{1}H NMR spectrum in D_2O:



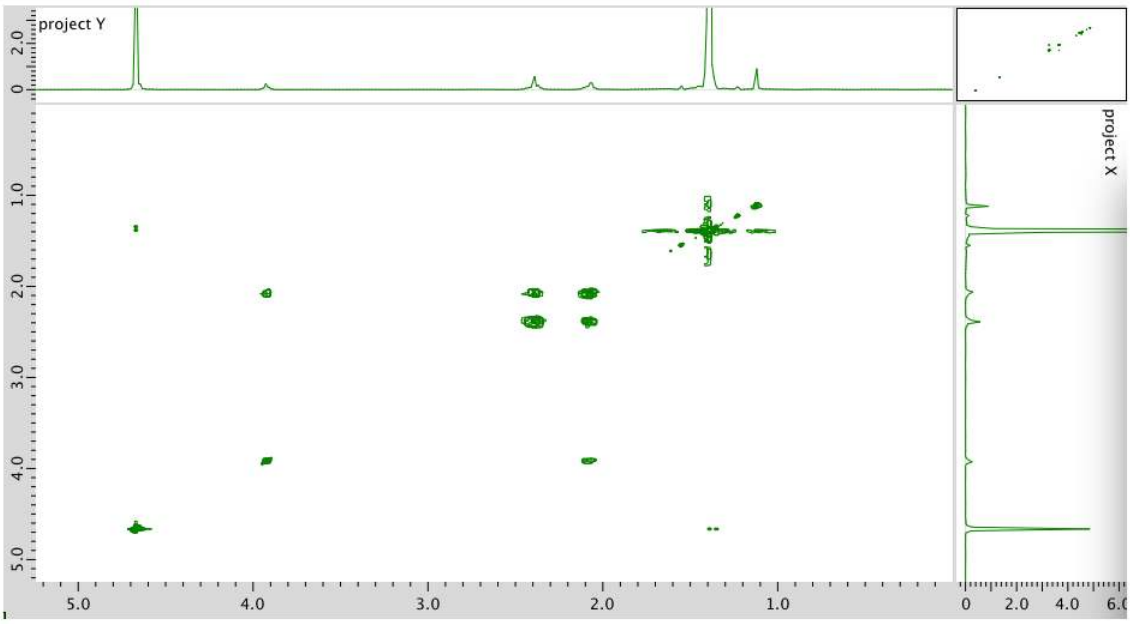
An expansion:



^{13}C NMR:



COSY:



Answer

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial structure
4.7	5H	singlet	solvent
3.93	1H	triplet	CH_2-C**H**-N
2.40	2H	multiplet	CH_2-C**H**$_2$?
2.09	2H	multiplet	C**H**$_2$-CH_2?
1.4	9H	singlet	C(C**H**$_3$)$_3$

*Total number of H: 19 H

^{13}C NMR:

Chemical shift (ppm)	Type of carbon
170	sp^2 (C=O)
80	sp^3 (C-O)
52	sp^3 (C-N)
32	sp^3
28	sp^3
26	sp^3

*Total number of C: 6 apparent, but two more suggested by symmetry (3 methyl groups in ^{1}H NMR) for 8 C; a third extra suggested by MW fit for 9 C

COSY:

Assignment	^{1}H	COSY
Solvent	4.7	--
B	3.93	2.40
D	2.40	2.09
C	2.09	2.40, 2.09
A	1.4	--

Formula:

$C_9H_{18}O_3N_2$ (extra O indicated from shift in ^{13}C, ^{1}H NMR; second O suggested by C=O in ^{13}C NMR; additional CO needed to fit MW)

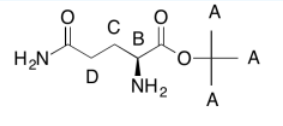
FW = $(9\times 12)+(18\times 1)+(3\times 16)+(2\times 14)=202$

FW = ((9 \times 12) + (18 \times 1) + (3 \times 16) + (2 \times 14) = 202\)

Compare C_9H_{18} to C_9H_{22} for the corresponding hydrocarbon corrected for two nitrogens (therefore two extra hydrogens)

Degrees of unsaturation = $\frac{(2\times 9)+2+2-10}{2}=2$ units (2 double bonds)

The data tables should be consistent with this structure:

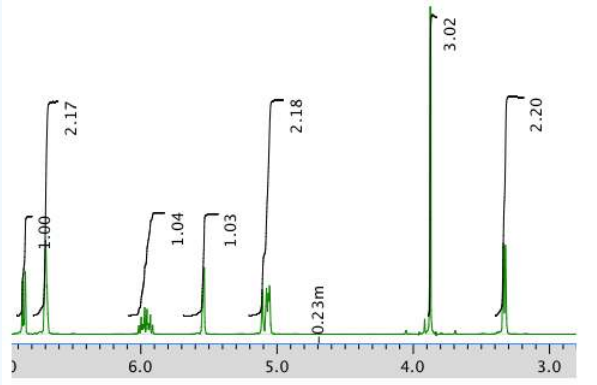


Exercise 3.17.5.3

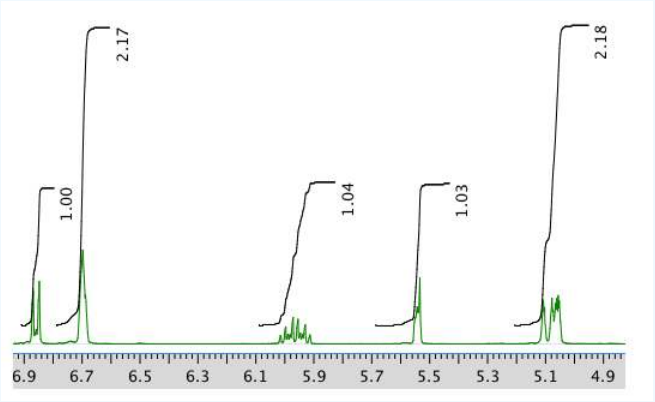
Present an analysis of the following data and propose a structure.

MW: 164 amu

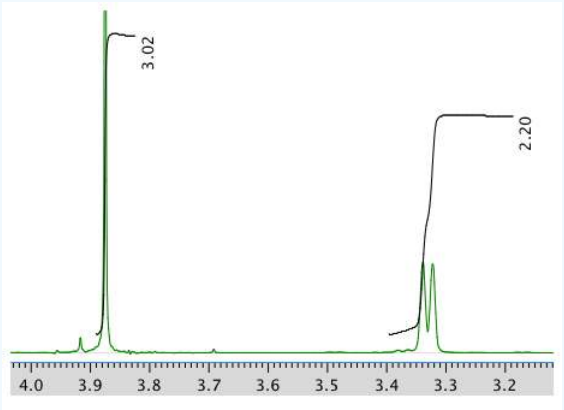
The full ^{1}H NMR spectrum in $CDCl_3$:



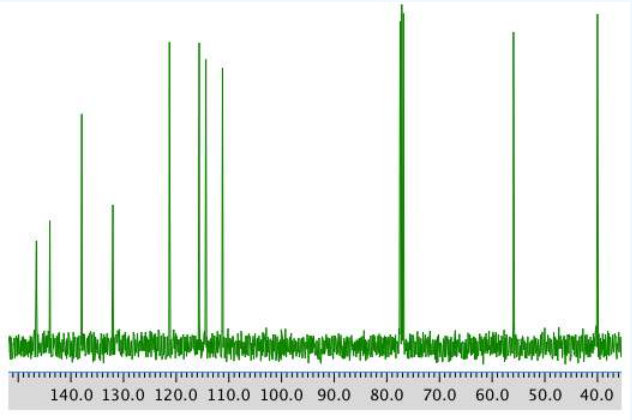
An expansion of the ^{1}H NMR spectrum:



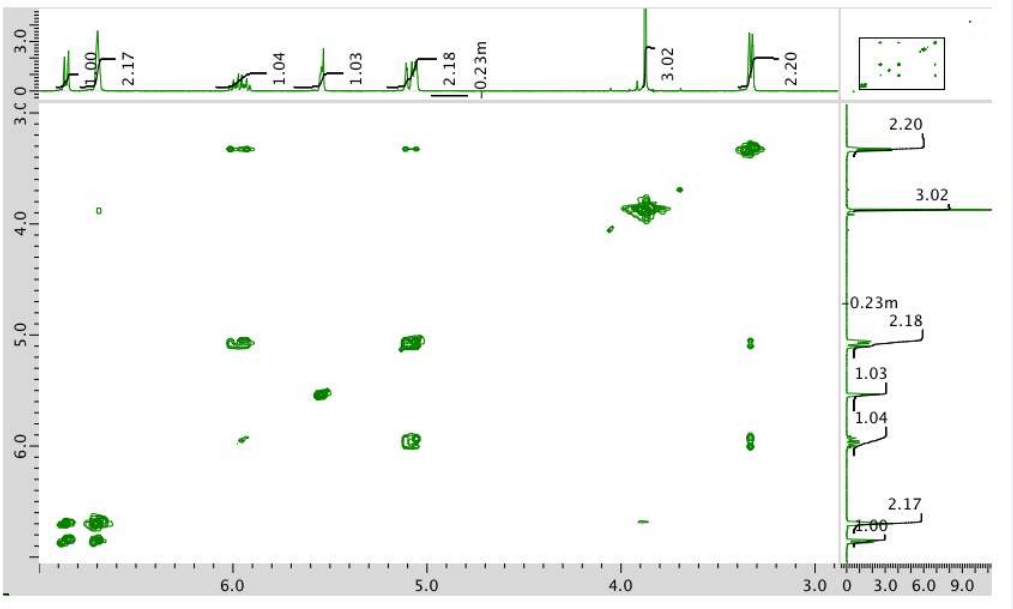
Another expansion:



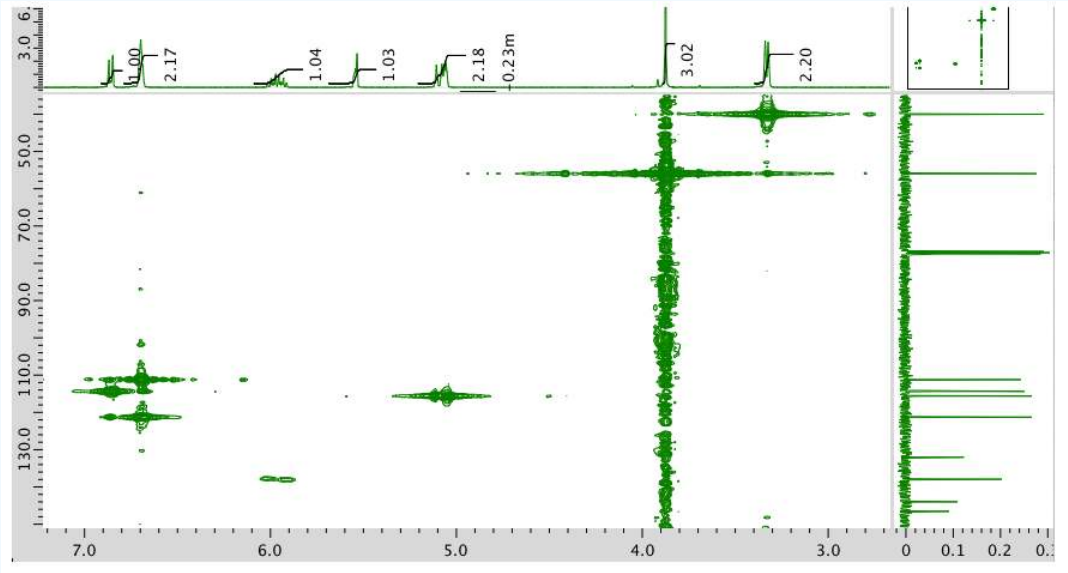
^{13}C NMR spectrum:



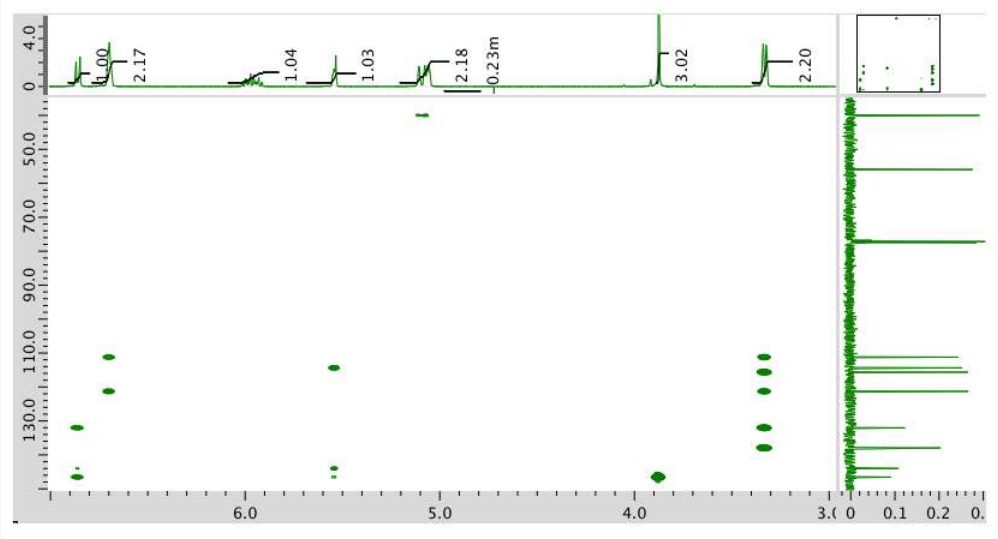
COSY spectrum:


1.00
2.17
1.04
1.03
2.18
0.23m
3.02
2.20
3.0
4.0
5.0
6.0
2.20
3.02
0.23m
2.18
1.03
1.04
2.17
1.00
6.0
5.0
4.0
3.0
0
3.0
6.0
9.0

HMQC:

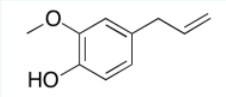

1.00
2.17
1.04
1.03
2.18
0.23m
3.02
2.20
50.0
70.0
90.0
110.0
130.0
7.0
6.0
5.0
4.0
3.0
0
0.1
0.2

HMBC:



Answer

The data should be consistent with this structure:

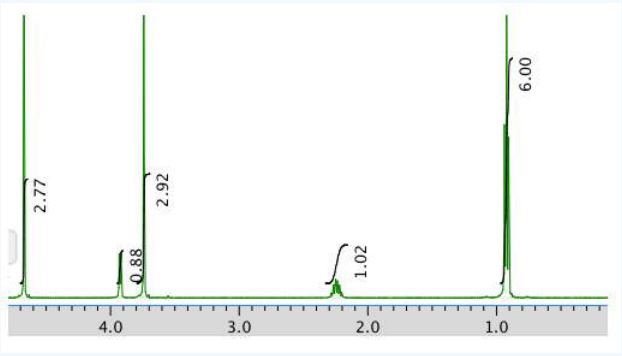


Exercise 3.17.5.4

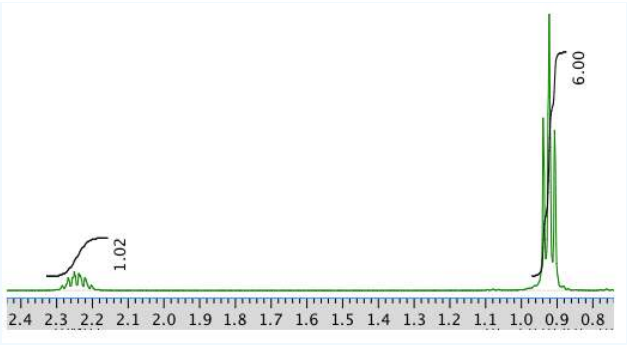
Present an analysis of the following data and propose a structure.

MW: 131 amu

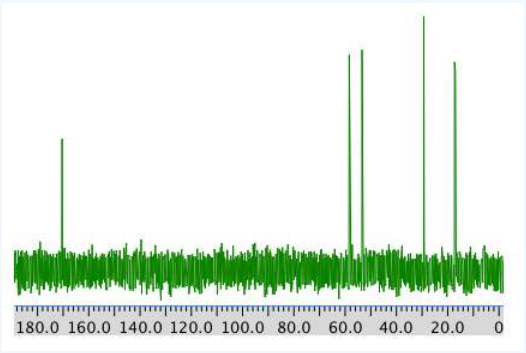
The full ^{1}H NMR spectrum in D_2O:



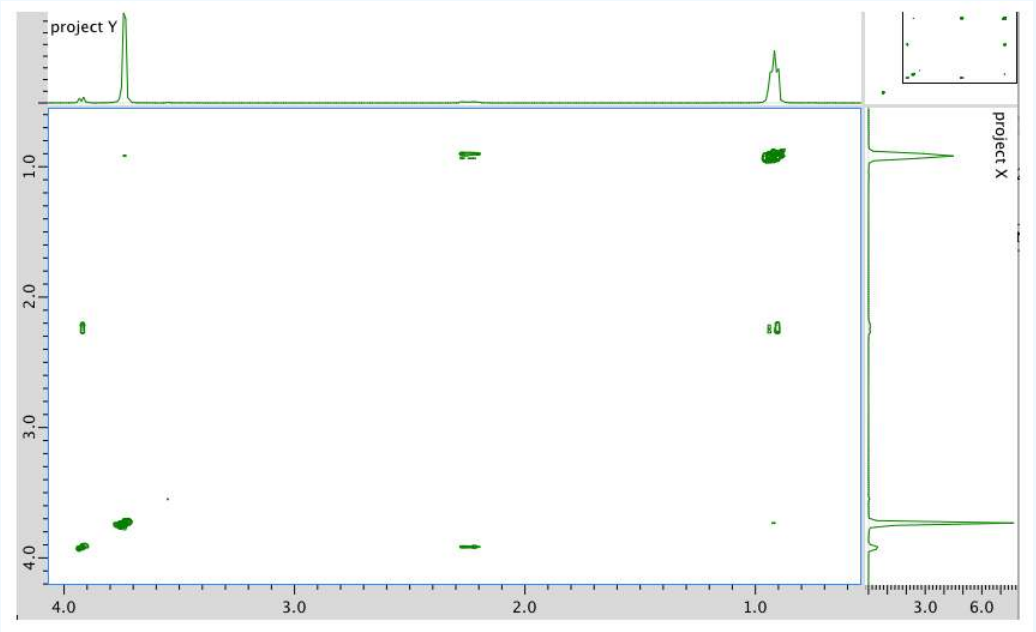
An expansion:



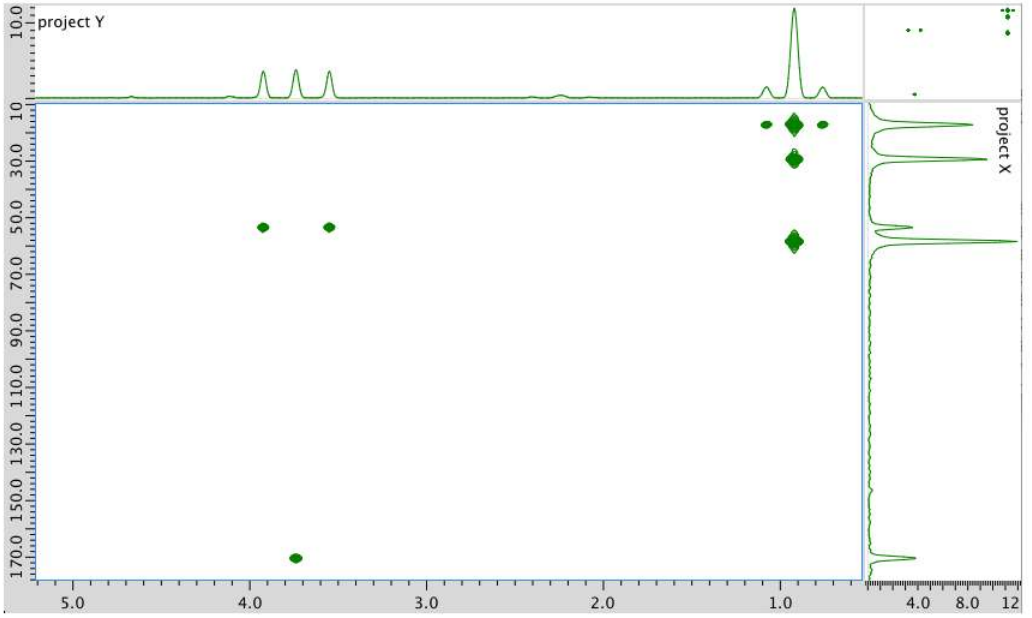
13C NMR:



COSY:



HMBC:



Answer

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial Structure
4.71	--	singlet	solvent
4.17	1H	doublet?	CO-C**H**-N
3.75	3H	singlet	O-C$\mathbf{H}_3$
2.25	1H	multiplet	CH-C**H**-$(CH_3)_2$
0.92	6H	triplet?	2 x C$\mathbf{H}_3$

^{13}C NMR:

Chemical shift (ppm)	Type of carbon
170	sp^2 C=O
60	sp^3 C-N
52	sp^3 C-O
30	sp^3 C
19	sp^3 C

COSY:

Assignment	^{1}H	COSY
A	4.17	2.25
B	3.75	--
C	2.25	4.17
D	0.92	2.25

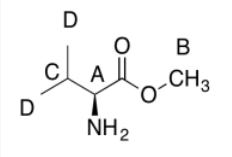
Formula:

$C_6H_{13}O_2N$ (1 O indicated from shift in ^{13}C, ^1H NMR)

FW = $(6\times 120+(13\times 1)+(2\times 16)+(1\times 14)=131$

Degrees of unsaturation = $\frac{(2\times 6)+2+1-13}{2}=1$ unit (1 double bond)

The data should be consistent with this structure:

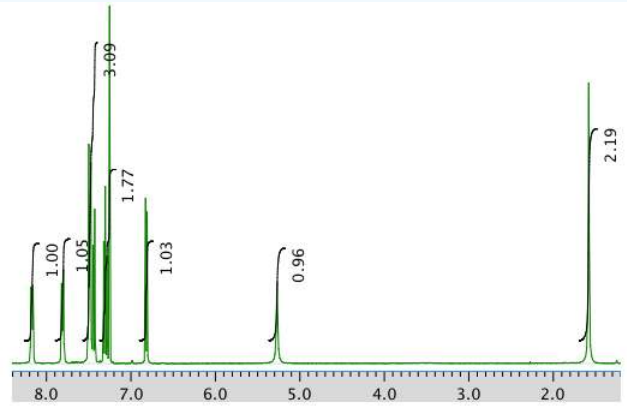


Exercise 3.17.5.5

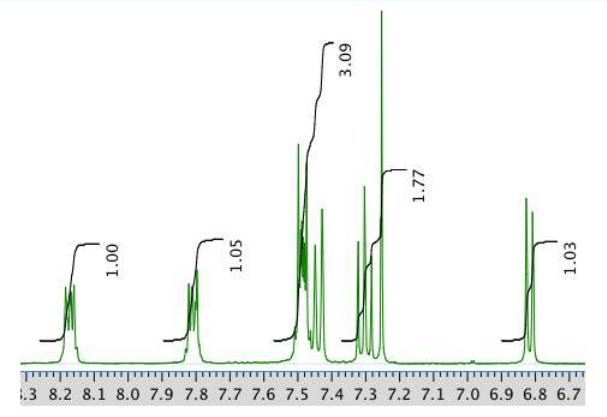
Present an analysis of the following data and propose a structure.

MW: 144 amu

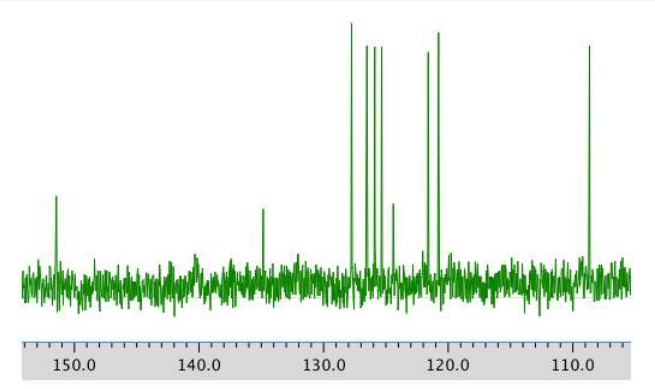
The ^{1}H NMR spectrum in $CDCl_3$:



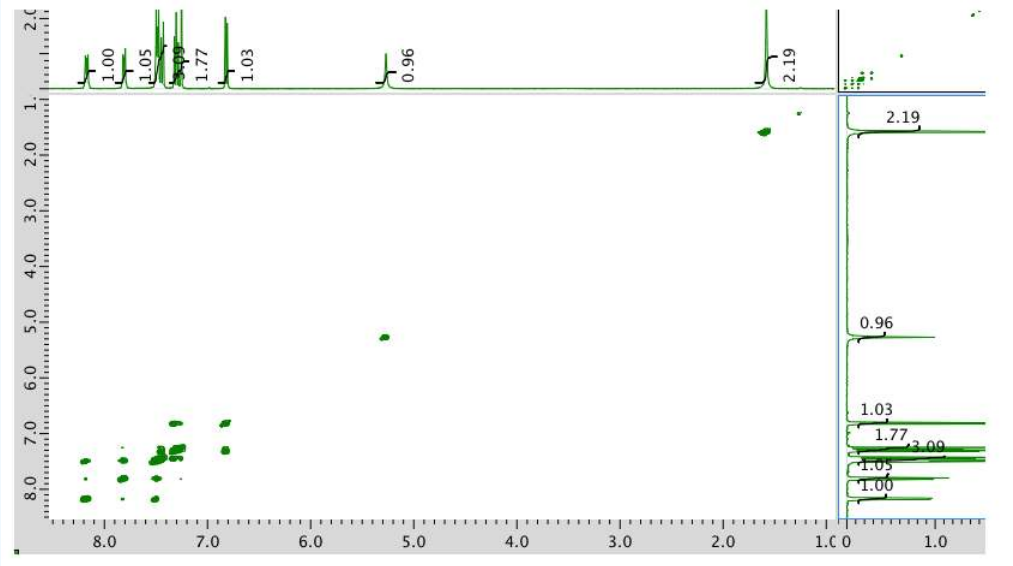
An expansion of the ^{1}H NMR spectrum:



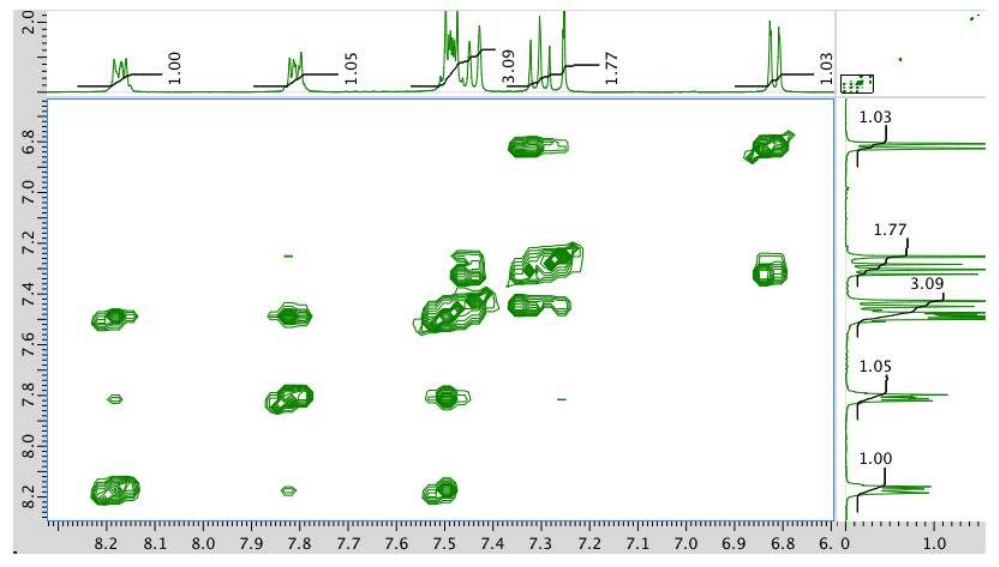
^{13}C NMR spectrum:



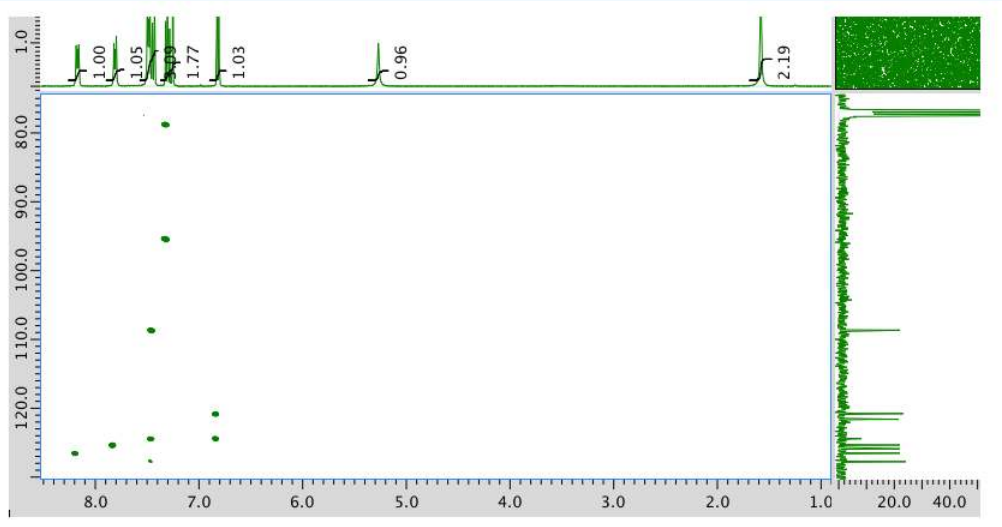
COSY:



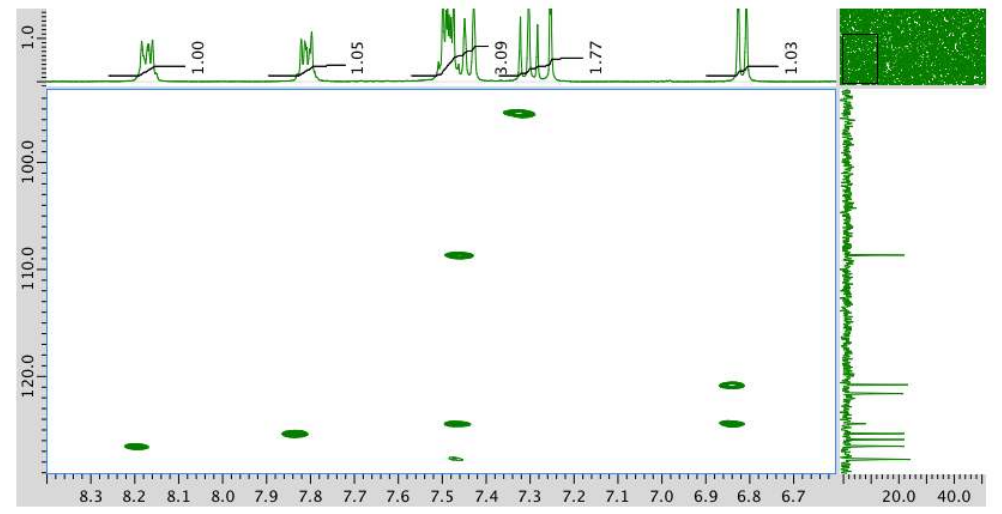
An expansion of the COSY spectrum:



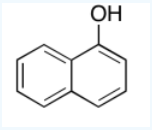
HMBC:



An expansion of the HMBC spectrum:



Answer

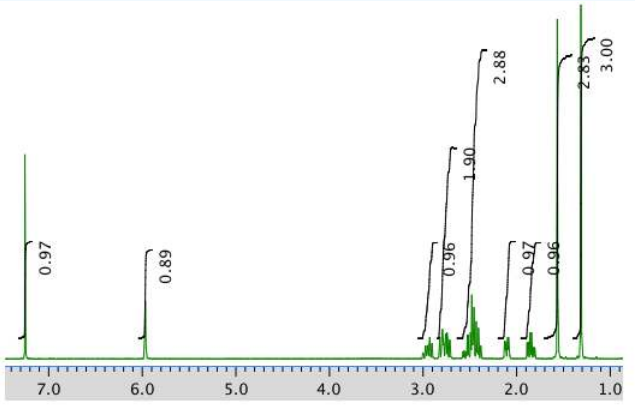


Exercise 3.17.5.6

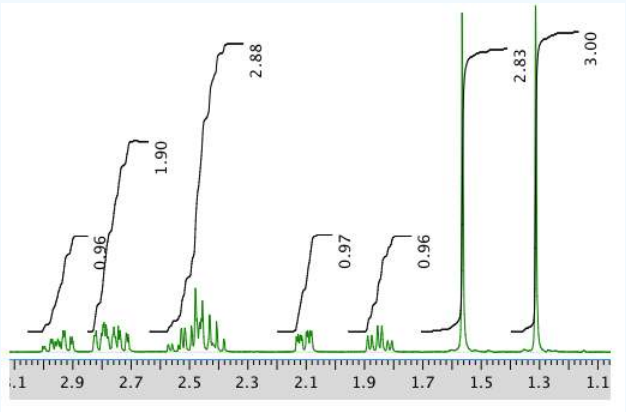
Present an analysis of the following data and propose a structure.

MW: 164 amu

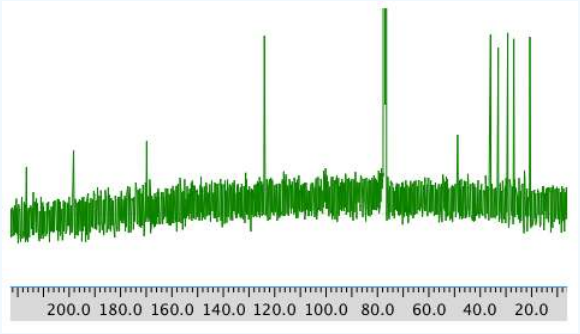
The full ^{1}H NMR spectrum in $CDCl_3$:



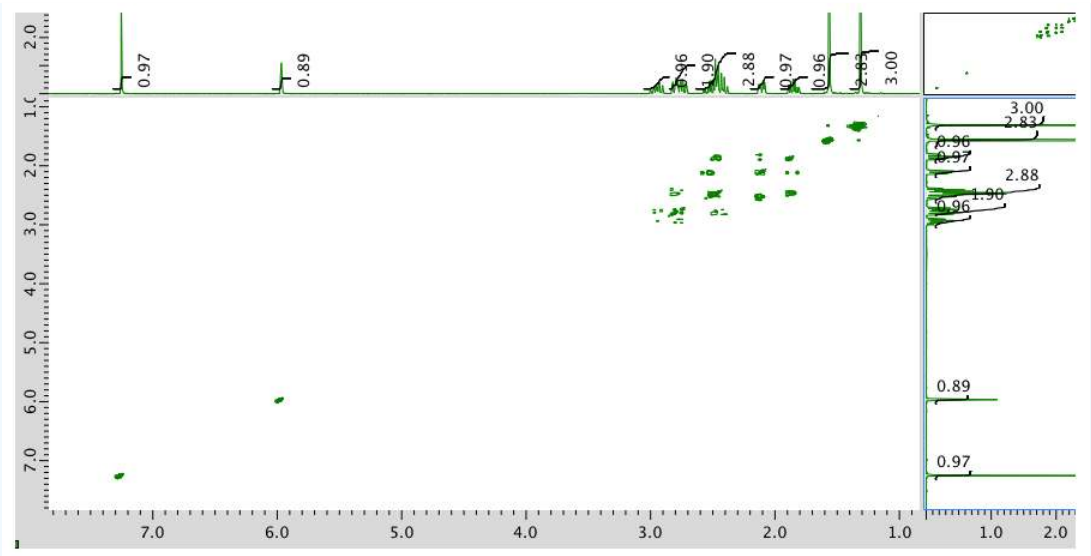
AN expansion:



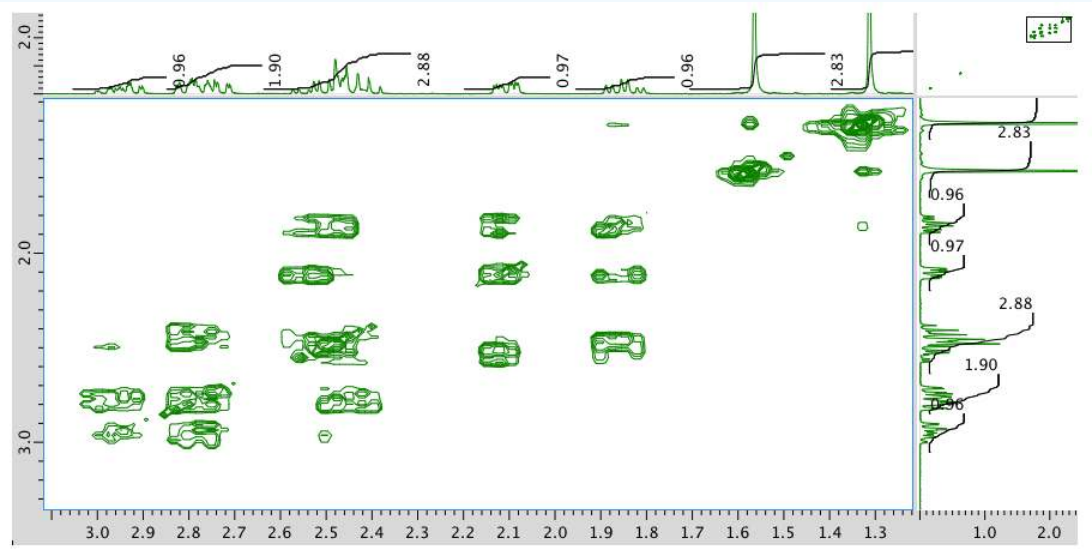
13C NMR:



COSY:

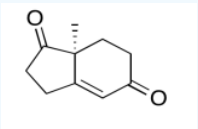


Expansion of COSY spectrum:



Answer

The data should be consistent with this structure:

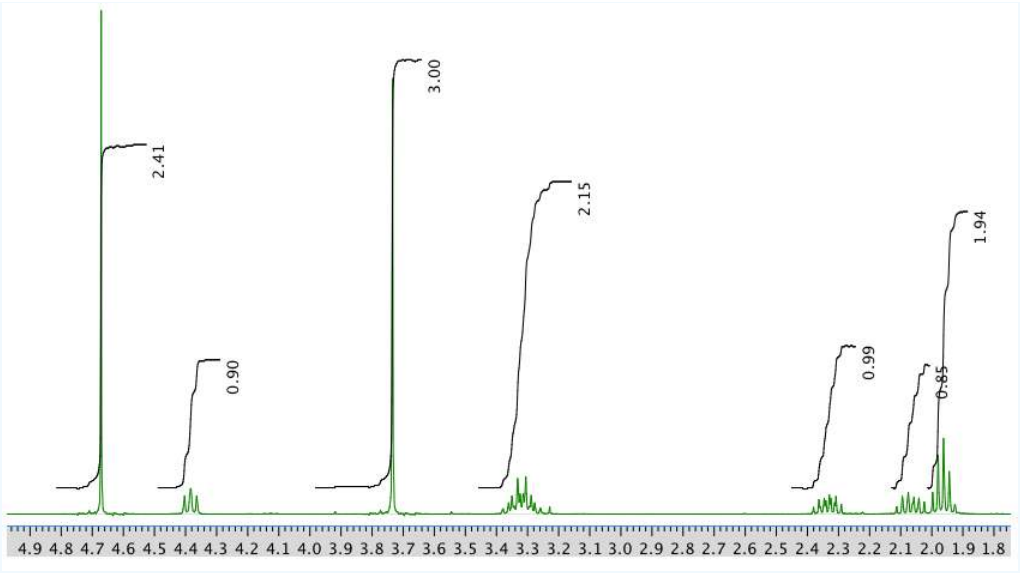


Exercise 3.17.5.7

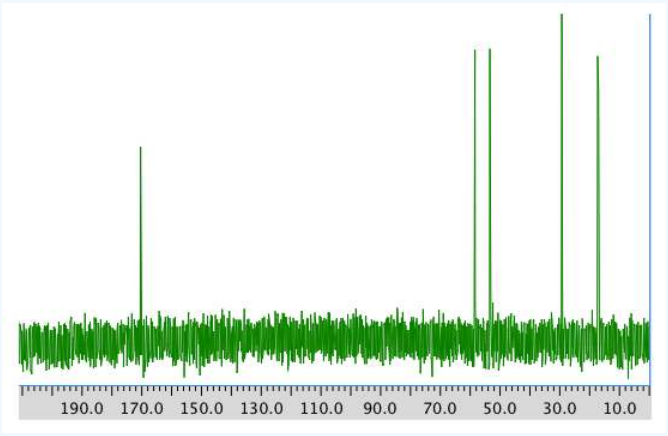
Present an analysis of the following data and propose a structure.

MW: 129 amu

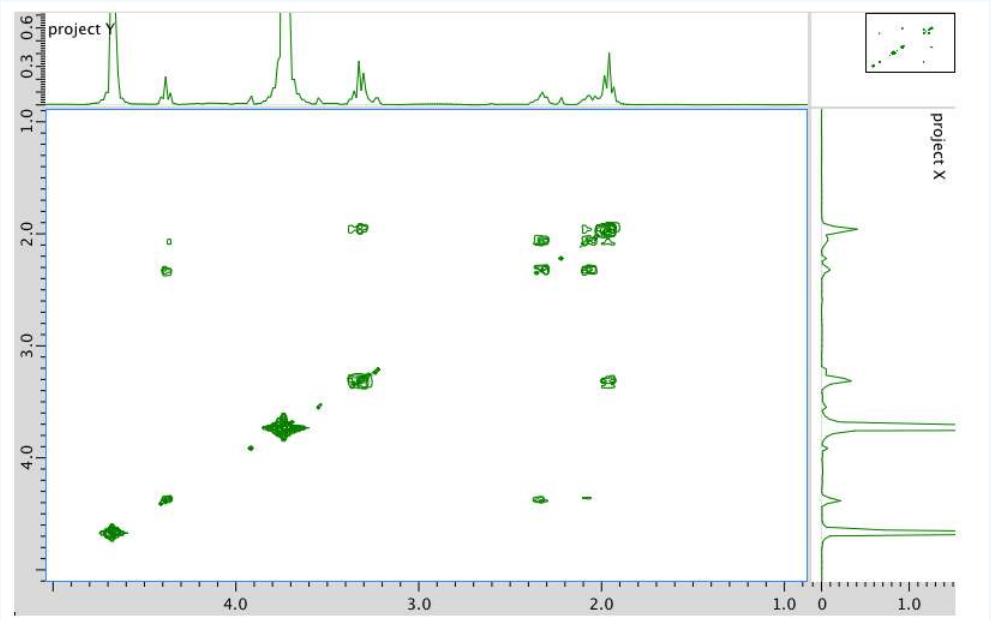
The full ^{1}H NMR spectrum in D_2O:



^{13}C NMR spectrum:

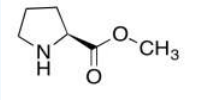


COSY spectrum:



Answer

The data should be consistent with this structure:

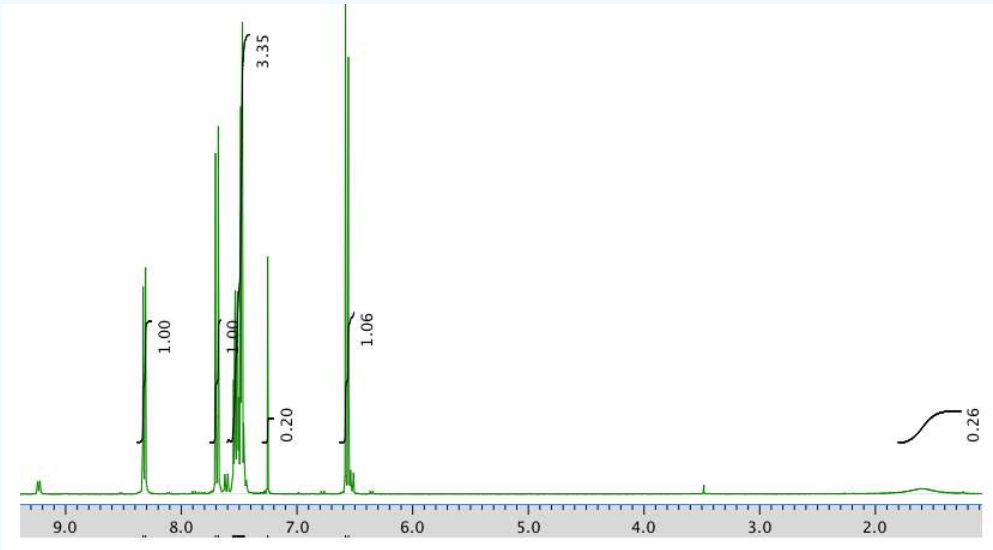


Exercise 3.17.5.8

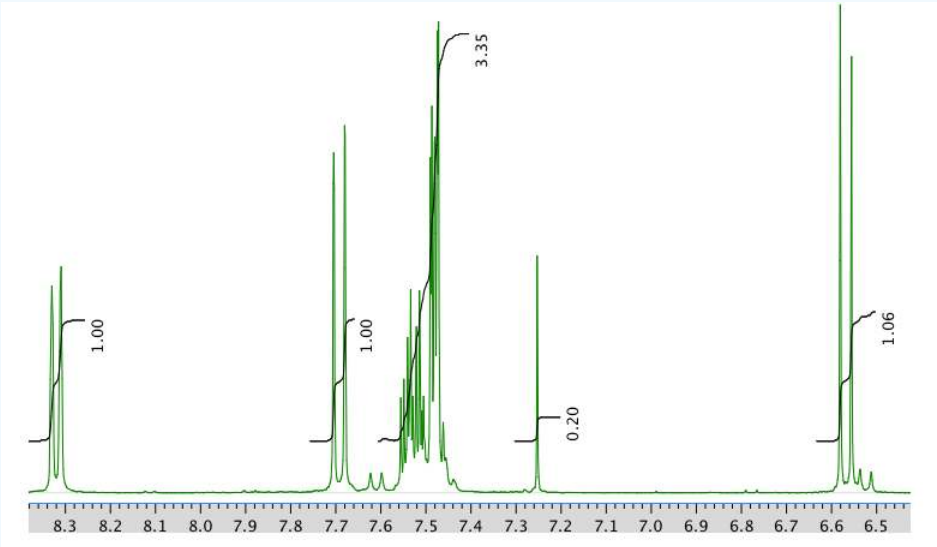
Present an analysis of the following data and propose a structure.

MW: 173 amu

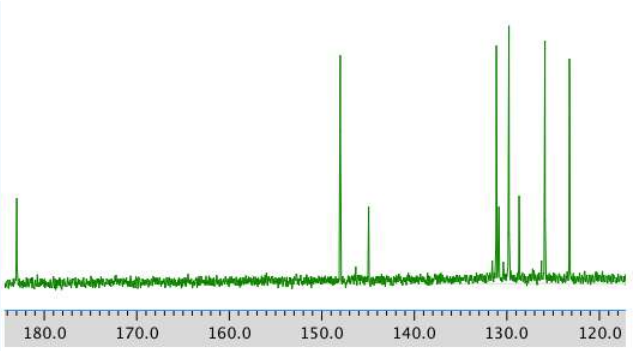
The full ^{1}H NMR spectrum in $CDCl_3$:



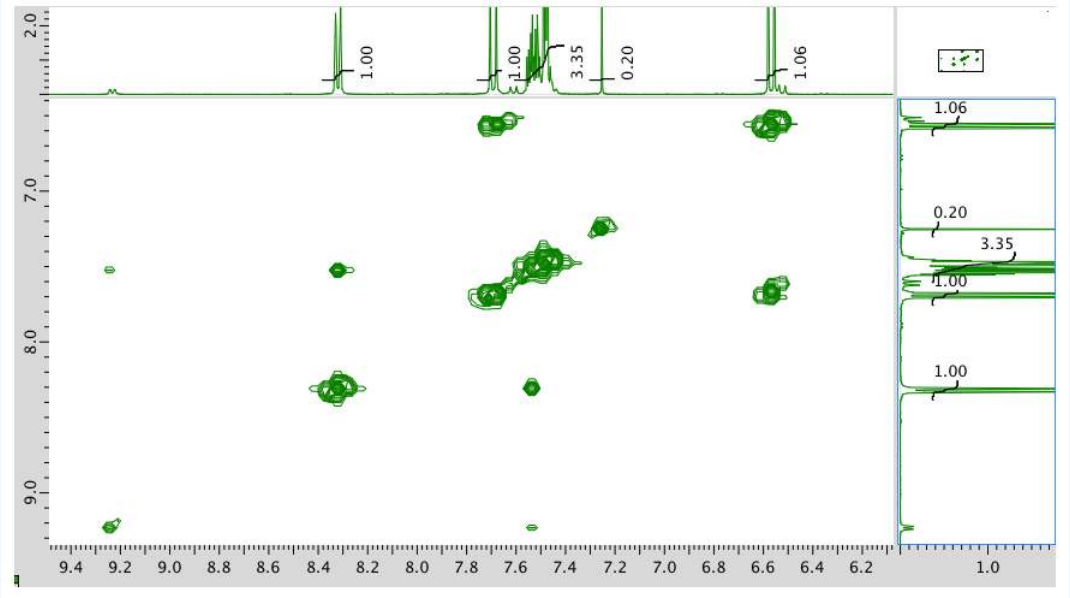
An expansion of the ^{1}H NMR spectrum:



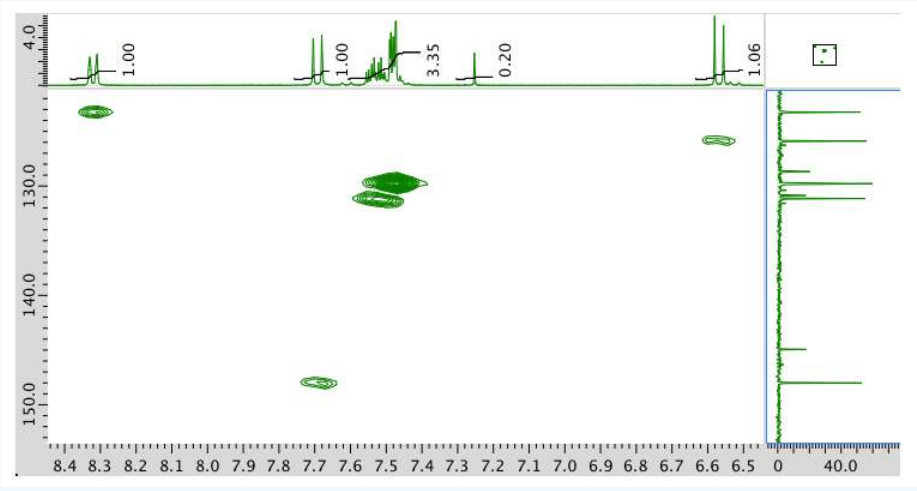
13C NMR spectrum:



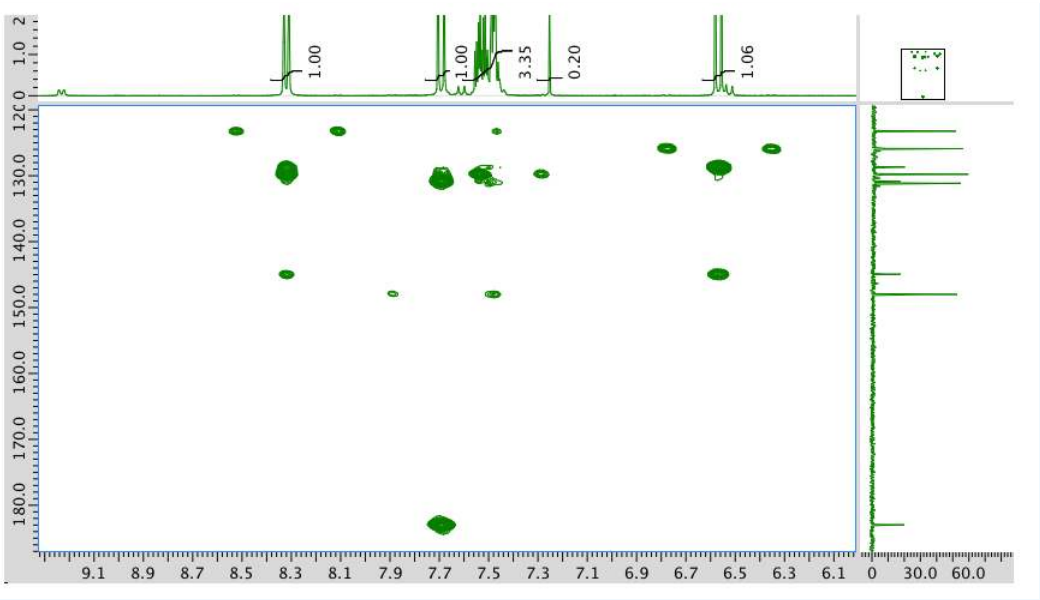
COSY:



HMQC:

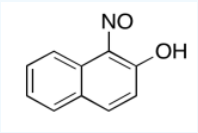


HMBC:



Answer

The data should be consistent with this structure:

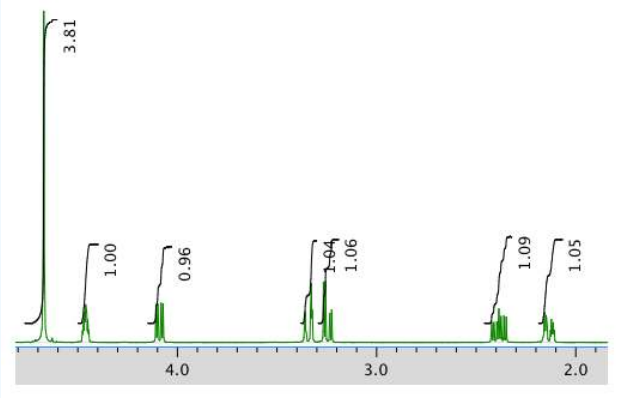


Exercise 3.17.5.9

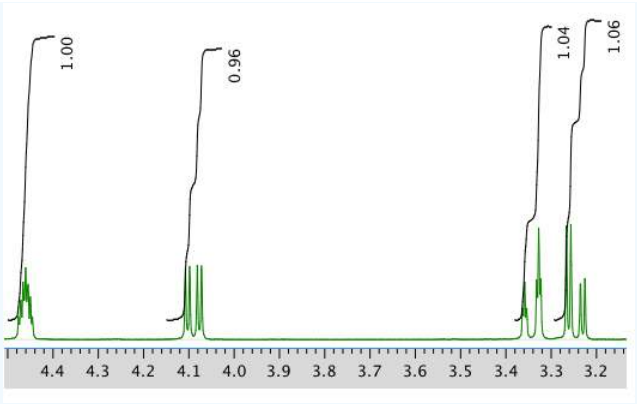
Present an analysis of the following data and propose a structure.

MW: 145 amu

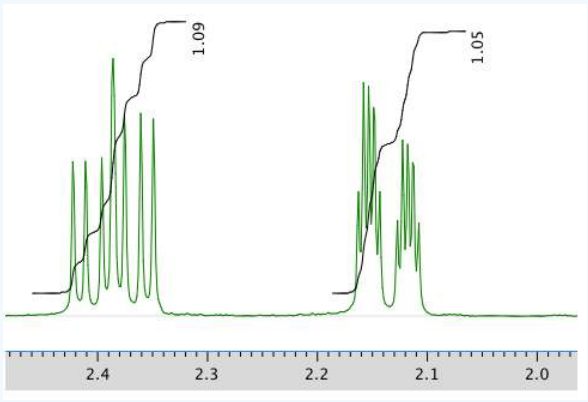
The full ^{1}H NMR spectrum in D_2O:



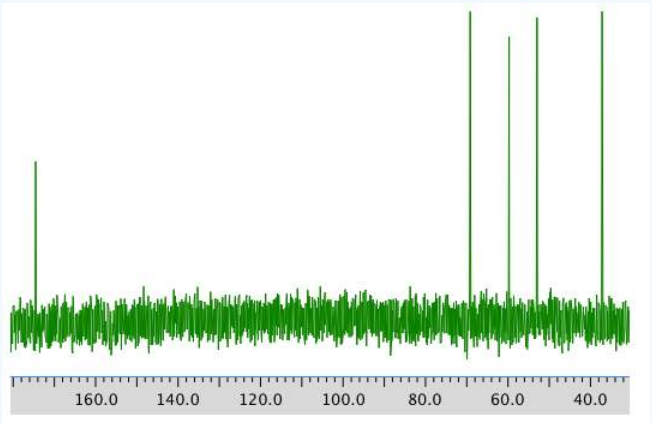
An expanded view of ^{1}H NMR spectrum:



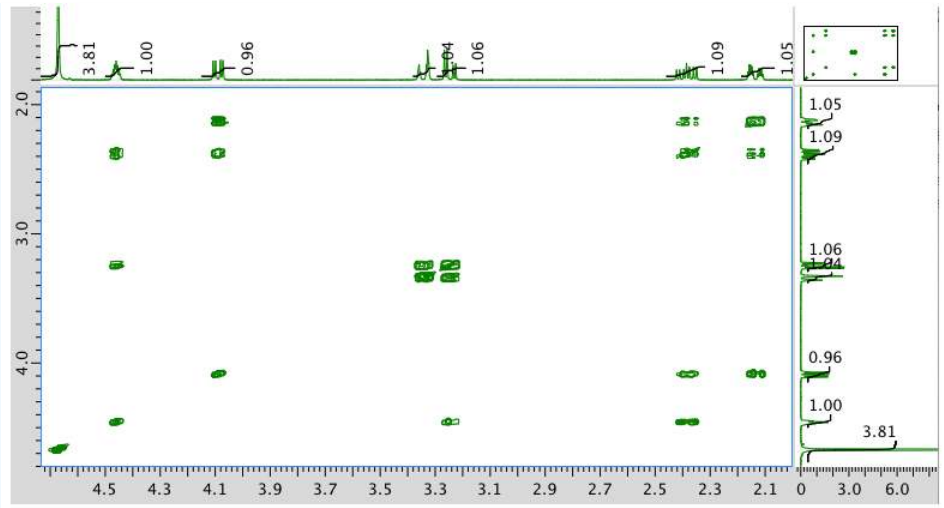
Another expanded view:



^{13}C NMR spectrum:

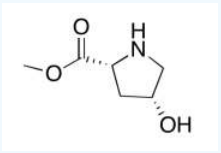


COSY spectrum:



Answer

The data should be consistent with this structure:

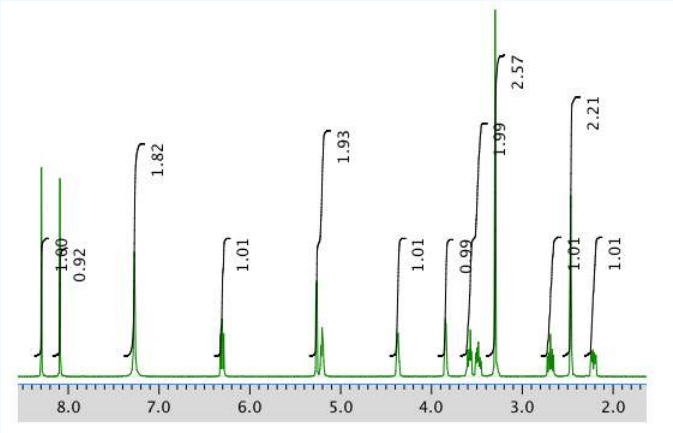


Exercise 3.17.5.10

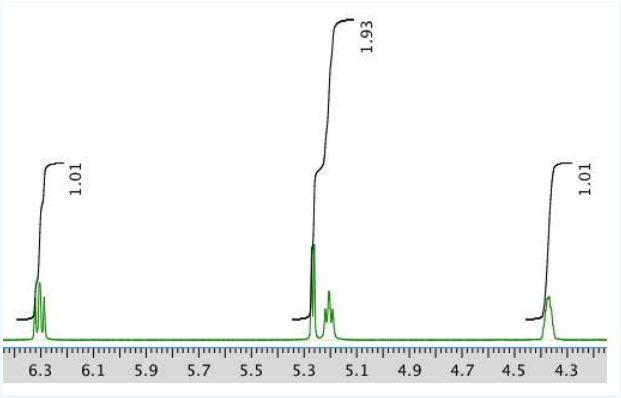
Present an analysis of the following data and propose a structure.

MW: 251 amu

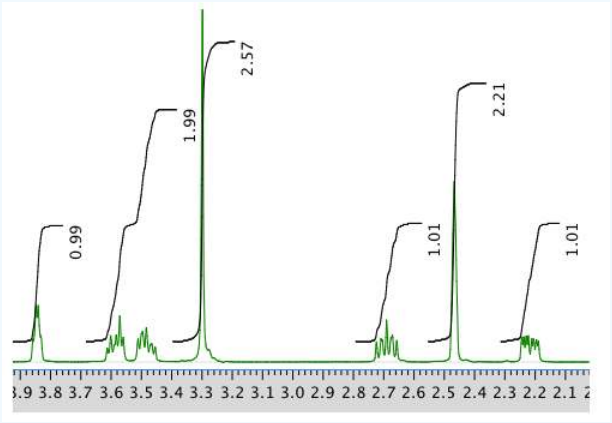
The full ^{1}H NMR spectrum in DMSO-d_6:



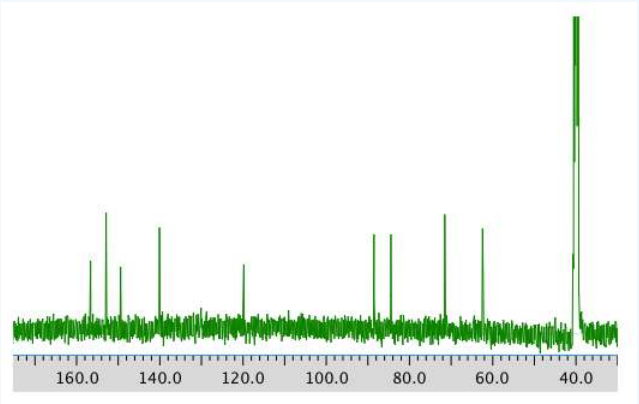
An expanded view of the ^{1}H NMR spectrum:



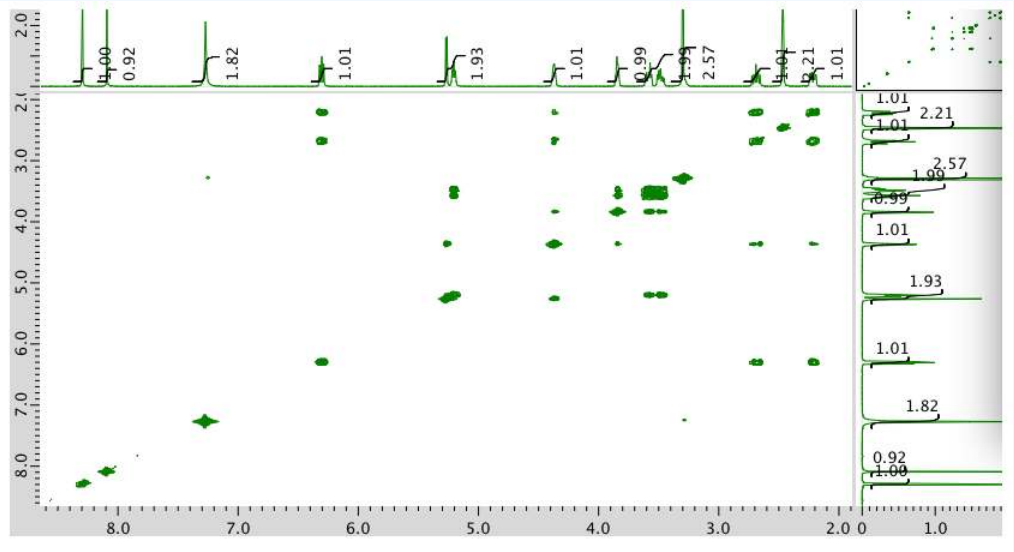
Another expansion:



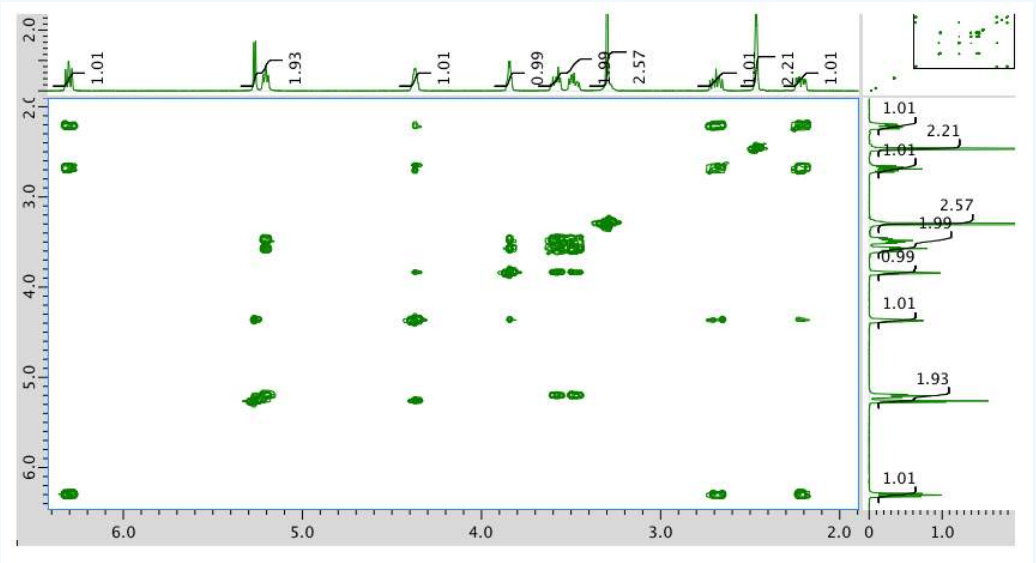
^{13}C NMR spectrum:



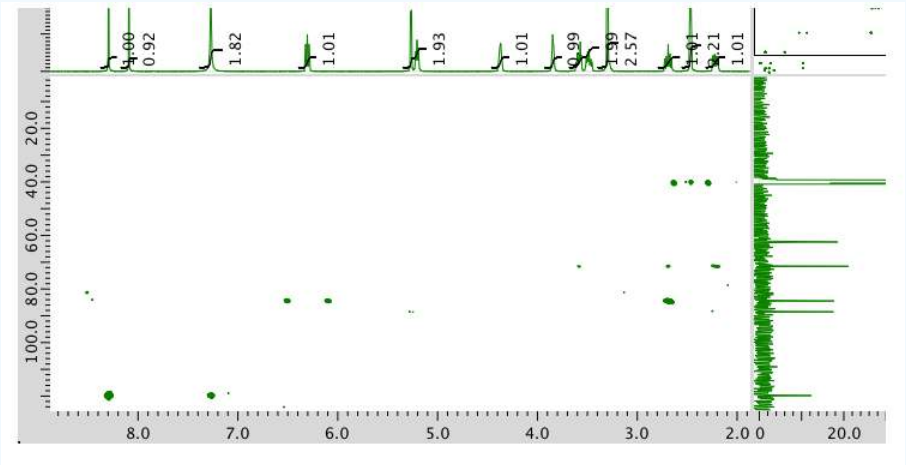
COSY spectrum:



Expansion of COSY:

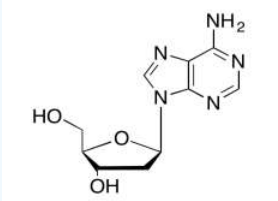


HMQC spectrum:



Answer

The data should be consistent with this structure:

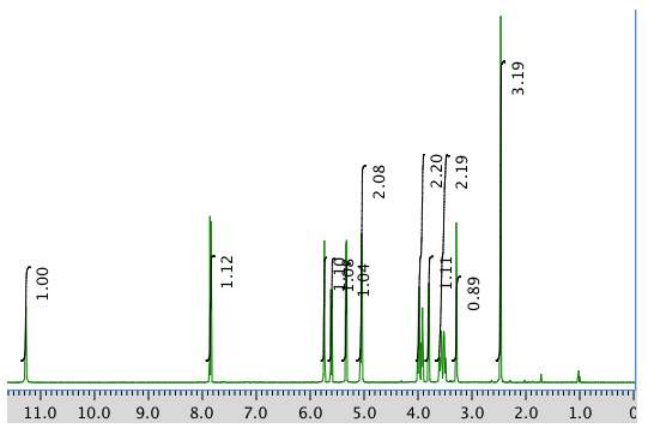


Exercise 3.17.5.11

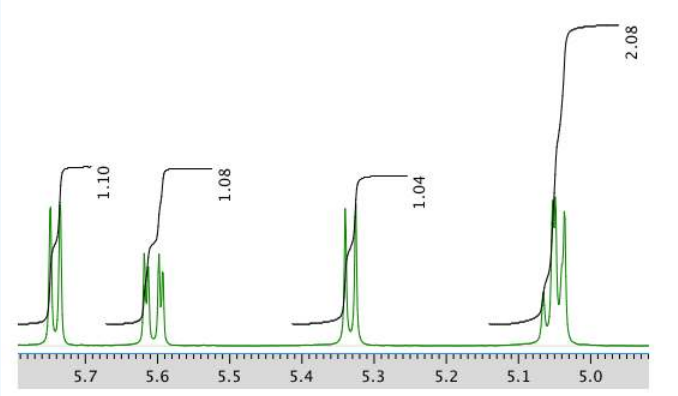
Present an analysis of the following data and propose a structure.

MW: 244 amu

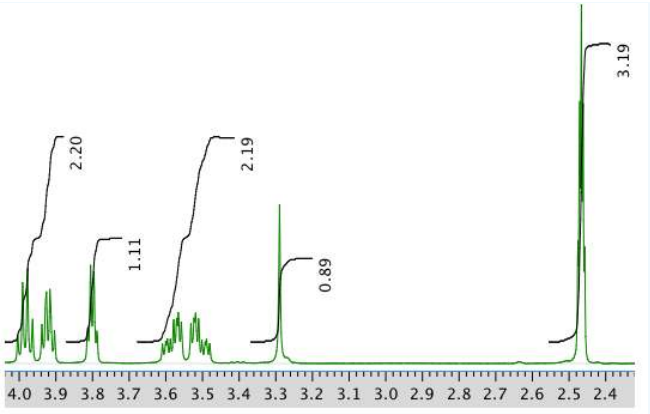
The full ^{1}H NMR spectrum in DMSO-d_6:



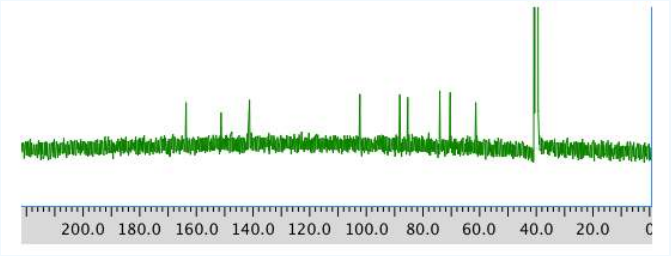
An expanded view of the ^{1}H NMR spectrum:



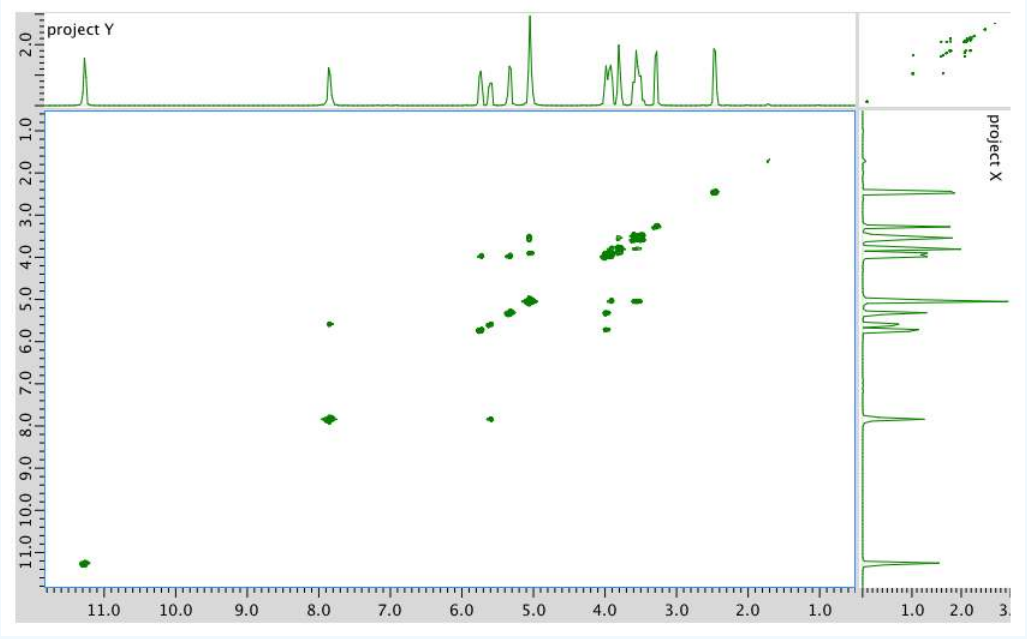
Another expansion of the 1H NMR spectrum:



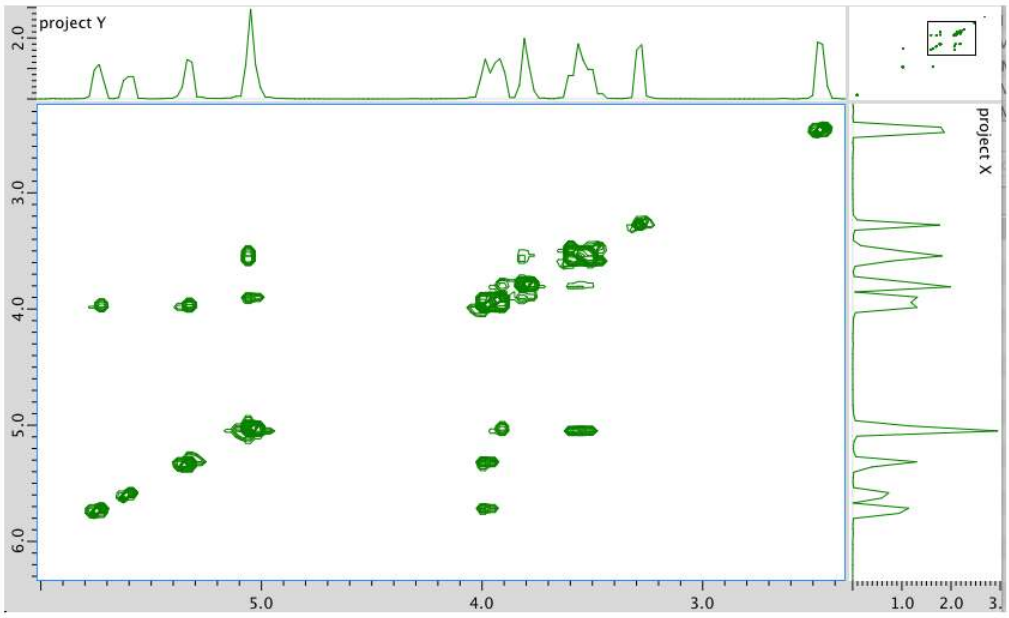
^{13}C NMR spectrum:



COSY:

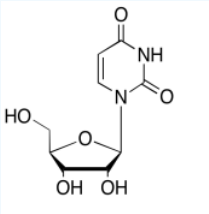


An expanded view of the COSY spectrum:



Answer

The data should be consistent with this structure:

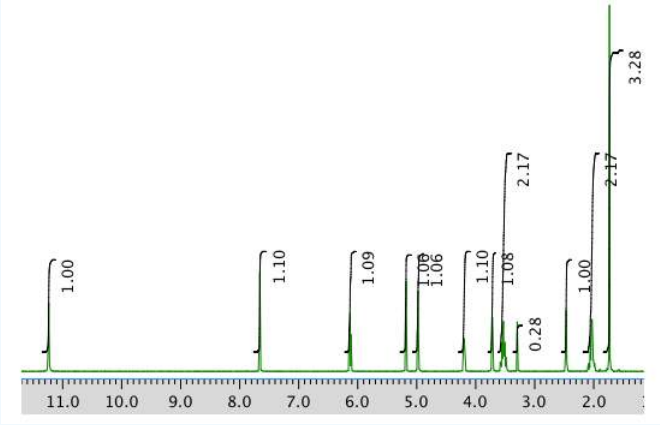


Exercise 3.17.5.12

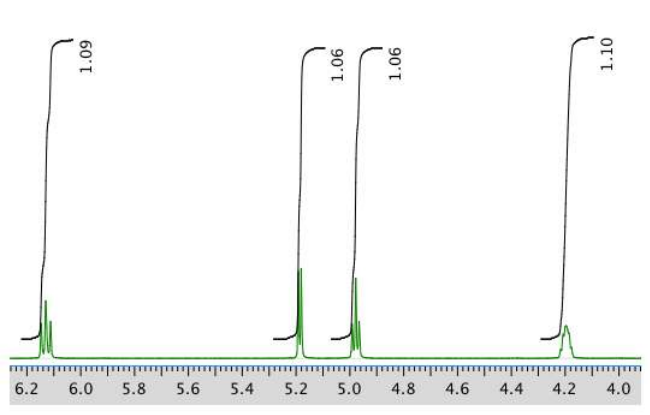
Present an analysis of the following data and propose a structure.

MW: 242 amu

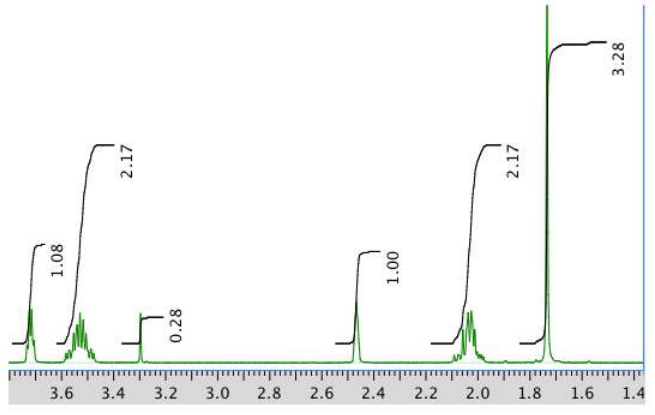
The full ^{1}H NMR spectrum in DMSO-d_6:



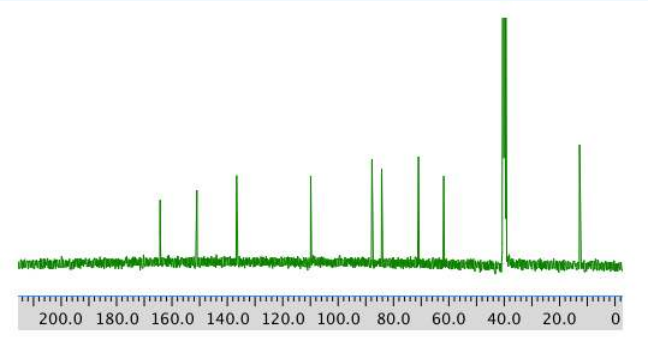
Expansion of the ^{1}H NMR spectrum:



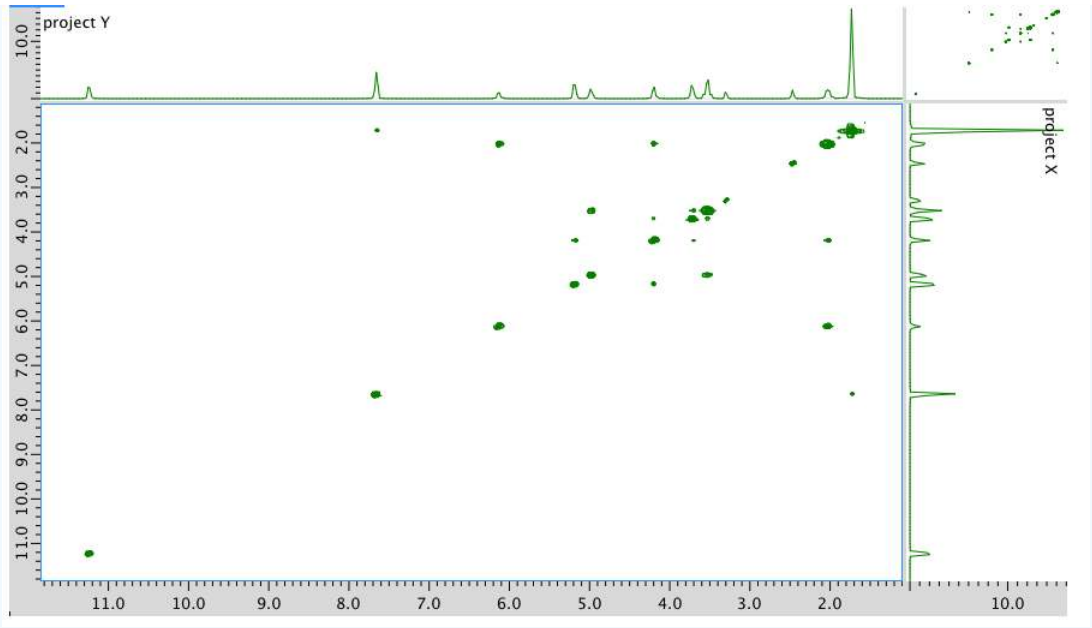
Another expansion:



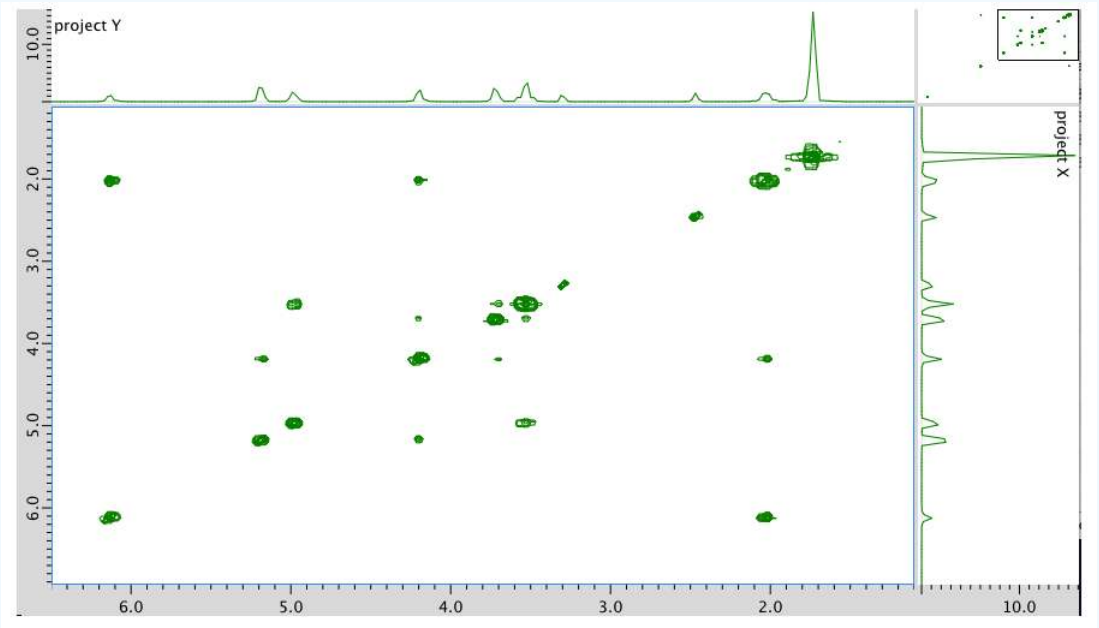
^{13}C NMR spectrum:



COSY:

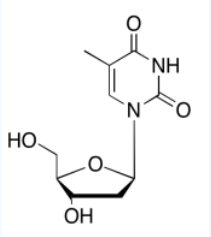


An expansion of the COSY spectrum:



Answer

The data should be consistent with this structure:

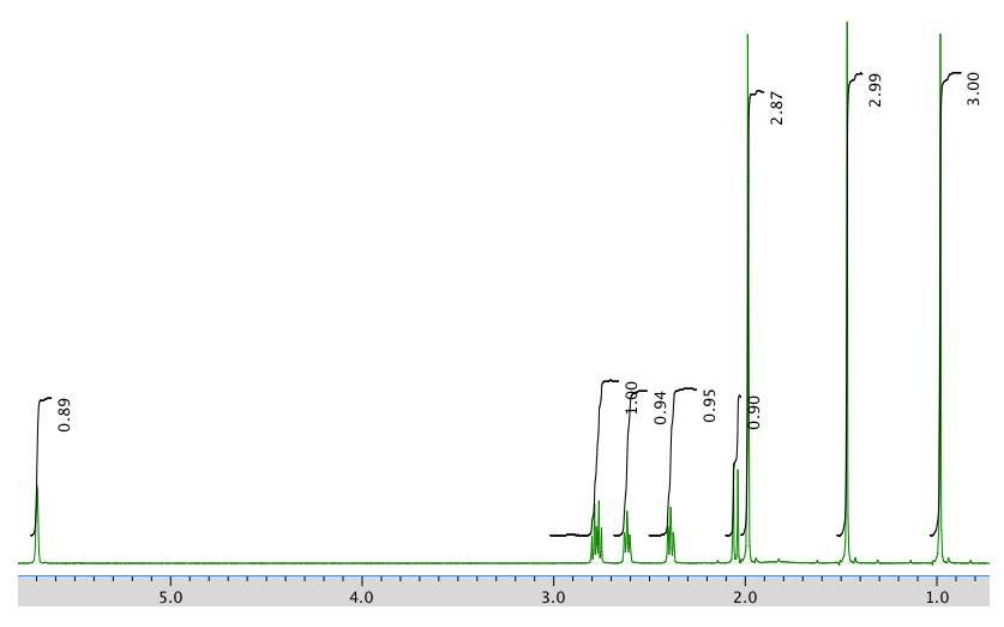


Exercise 3.17.5.13

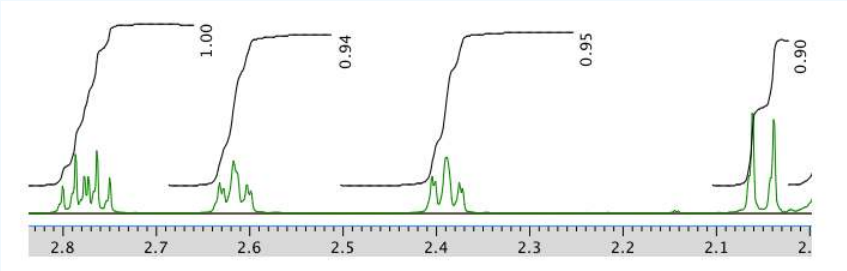
Present an analysis of the following data and propose a structure.

MW: 152 amu

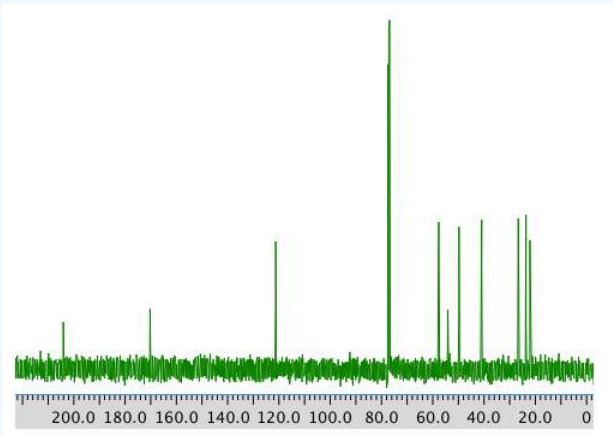
The full ^{1}H NMR spectrum in $CDCl_3$:



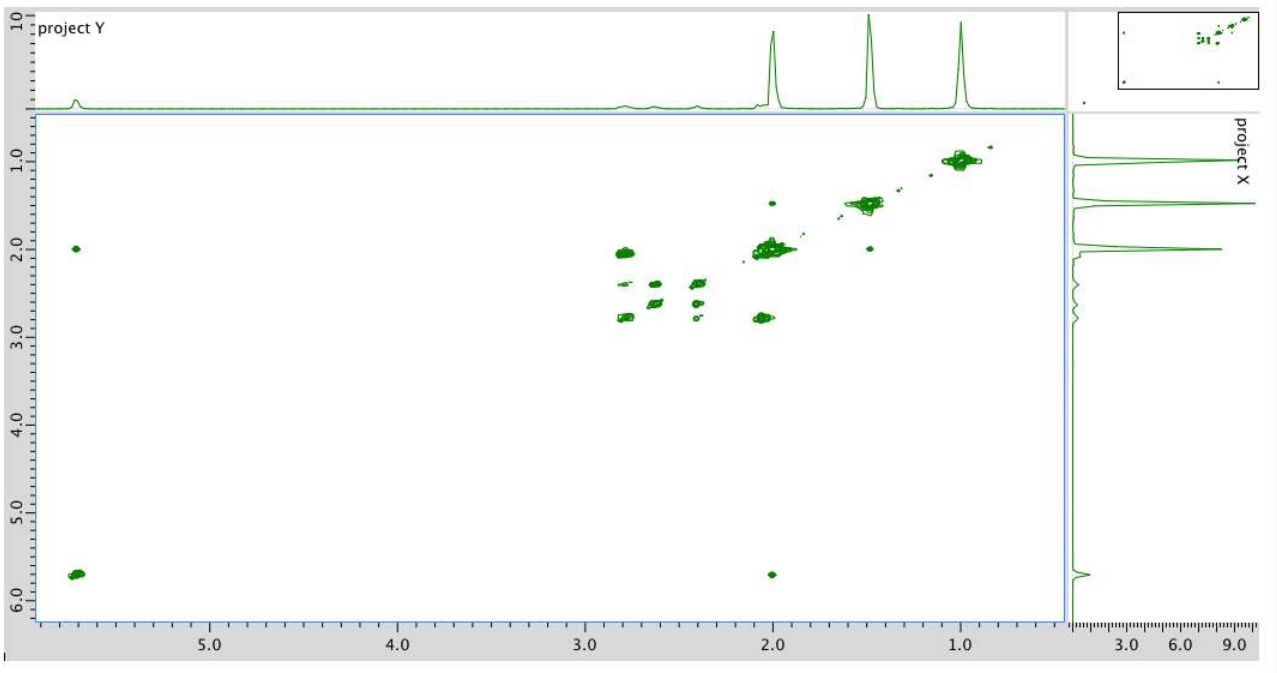
An expansion of the ^{1}H NMR spectrum:



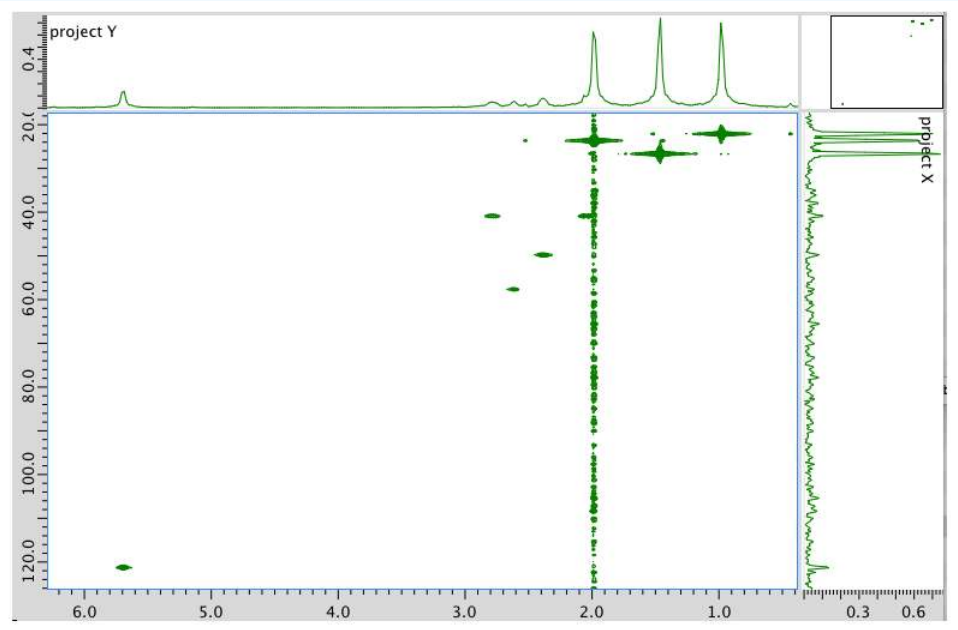
^{13}C NMR spectrum in CDCl3:



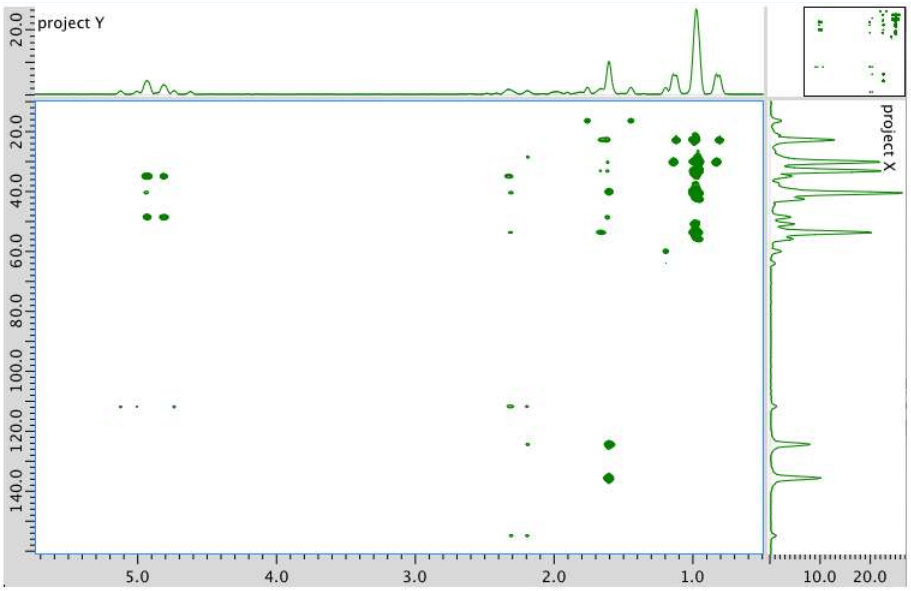
COSY spectrum:



HMQC spectrum:



HMBC spectrum:



Answer

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial structure
5.7	1H	singlet	C=C**H**-CO
2.77	1H	multiplet	CH_2-C**H**-CO
2.62	1H	multiplet	C-C**H**-C
2.39	1H	multiplet	C-C**H**-C
2.05	1H	doublet?	C-C**H**-CH?
1.96	3H	singlet	C-C**H**$_3$
1.48	3H	singlet	C-C**H**$_3$
0.98	3H	singlet	C-C**H**$_3$

^{13}C NMR:

Chemical shft (ppm)	Type of carbon
204	sp^2 C=O
170	sp^2
121	sp^2
59	sp^3
55	sp^3
50	sp^3
41	sp^3
28	sp^3
24	sp^3
22	sp^3

COSY:

Assignment	^{1}H	COSY
1	2.39	2.77, 2.62?
3	5.7	2.05?
5	2.62	2.62?
7a	2.77	2.05
7b	2.05	2.77
8	1.48	--
9	0.98	--
10	1.96	--

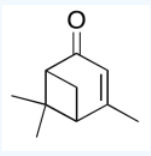
Formula:

$C_{10}H_{14}O$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $(10\times 12)+(14\times 1)+(1\times 16)=150$

Degrees of unsaturation = \(\frac{(2 \times 10) + 2 - 14}{2} = 4 units (e.g. 2 rings, 2 double bonds)

The data should be consistent with this structure:

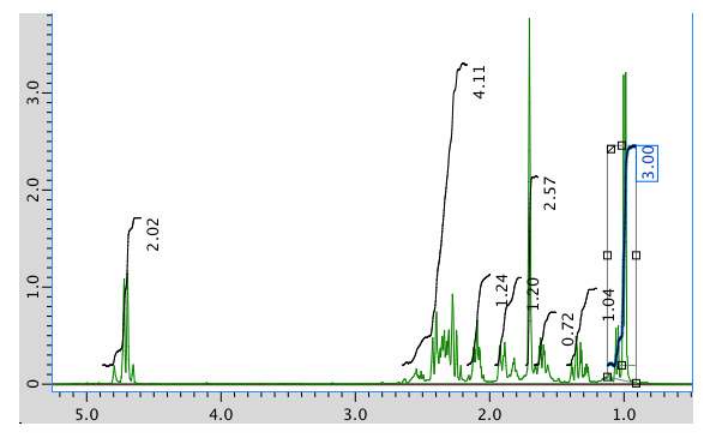


Exercise 3.17.5.14

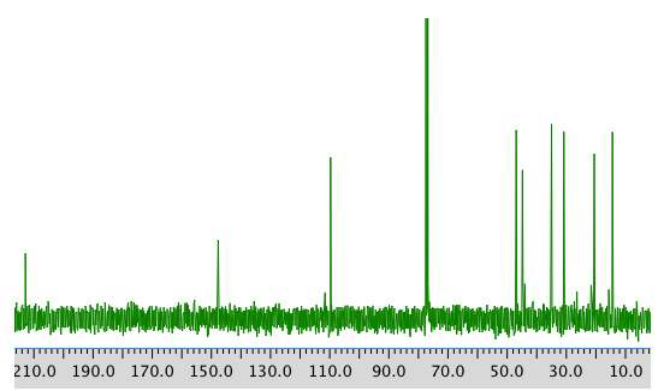
Present an analysis of the following data and propose a structure.

MW: 152 amu

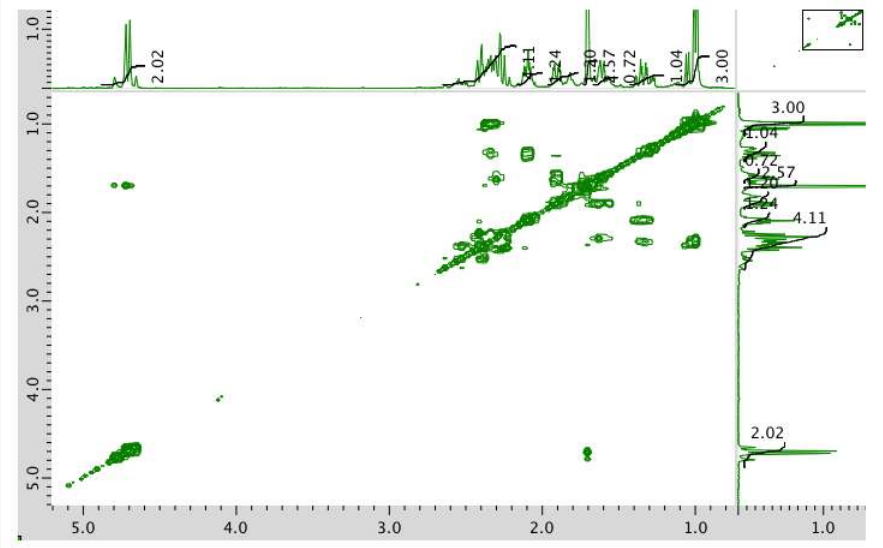
The full ^{1}H NMR spectrum in $CDCl_3$:



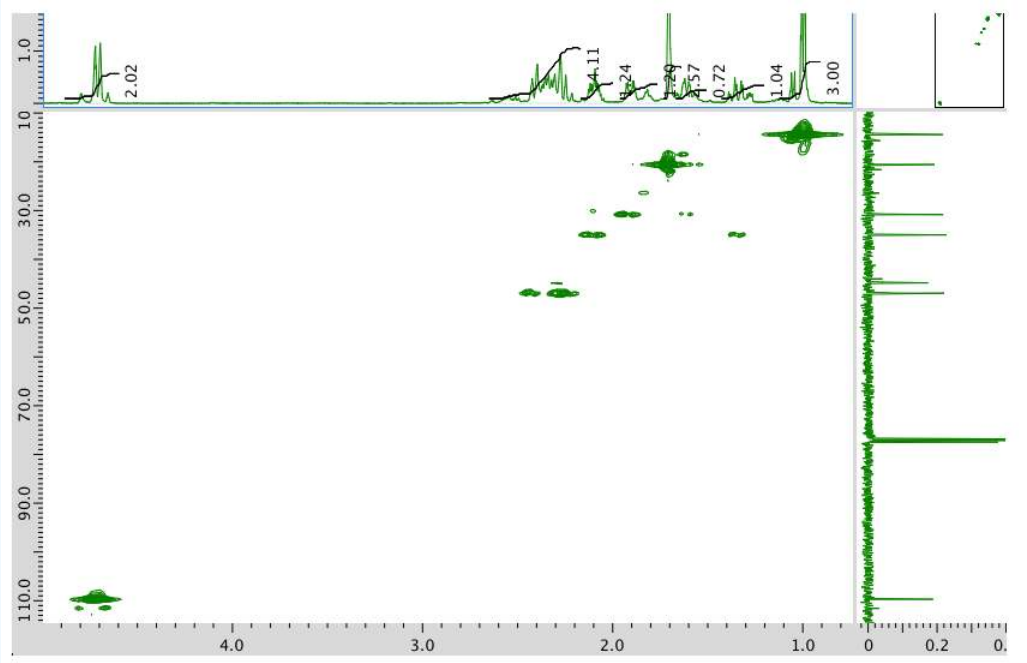
13C NMR spectrum:



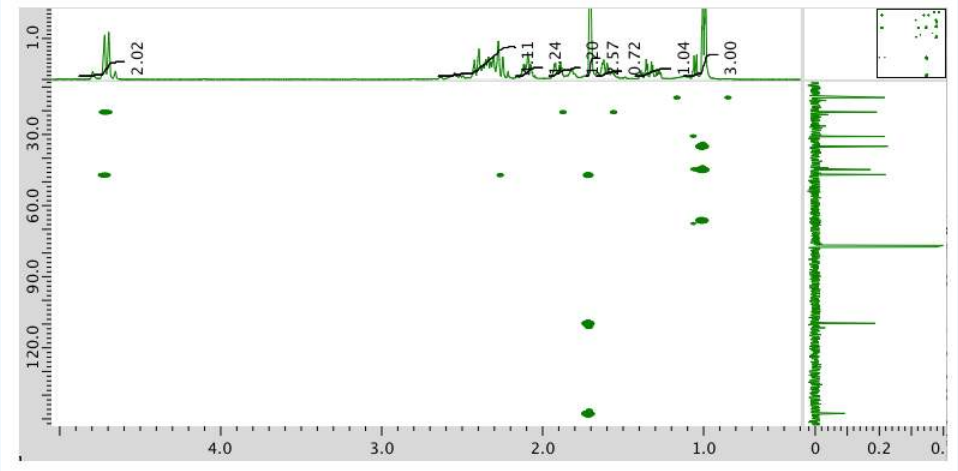
COSY spectrum:



HMQC spectrum:

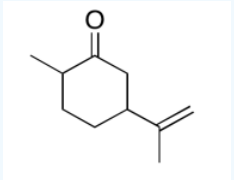


HMBC spectrum:



Answer

The data should be consistent with this structure:

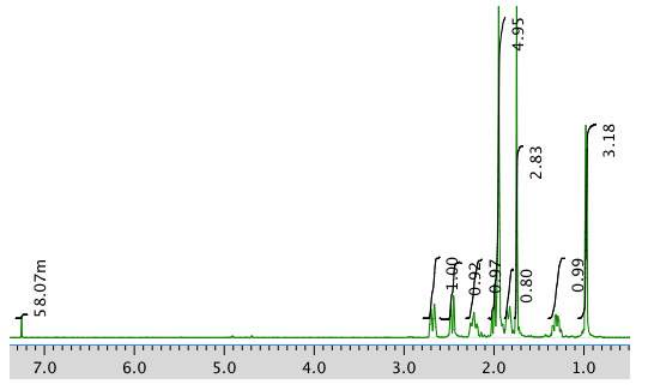


Exercise 3.17.5.15

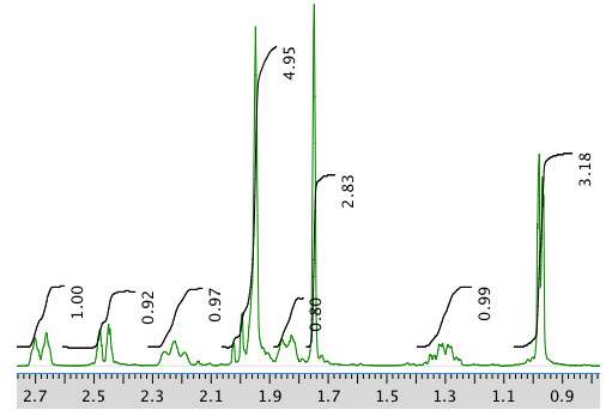
Present an analysis of the following data and propose a structure.

MW: 150 amu

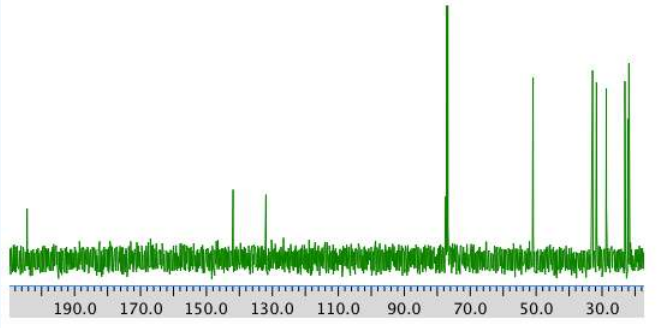
The full ^{1}H NMR spectrum in $CDCl_3$:



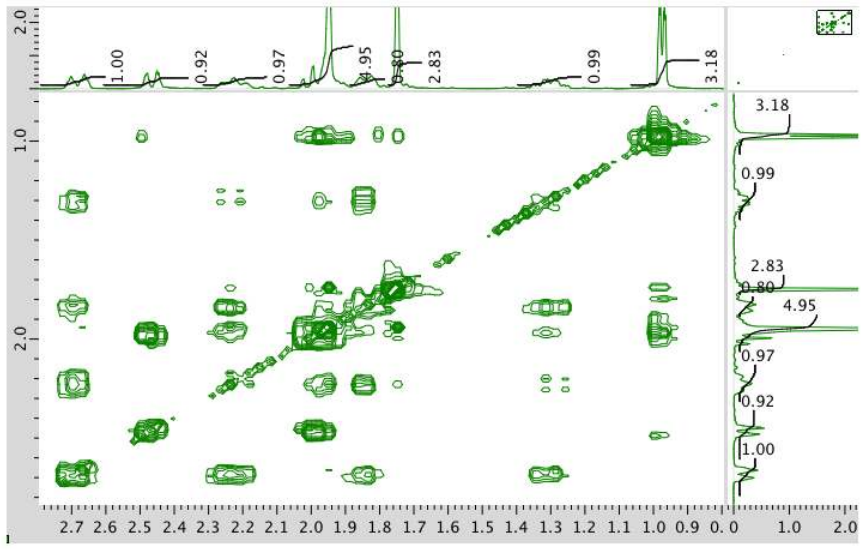
An expansion of the ^{1}H NMR spectrum:



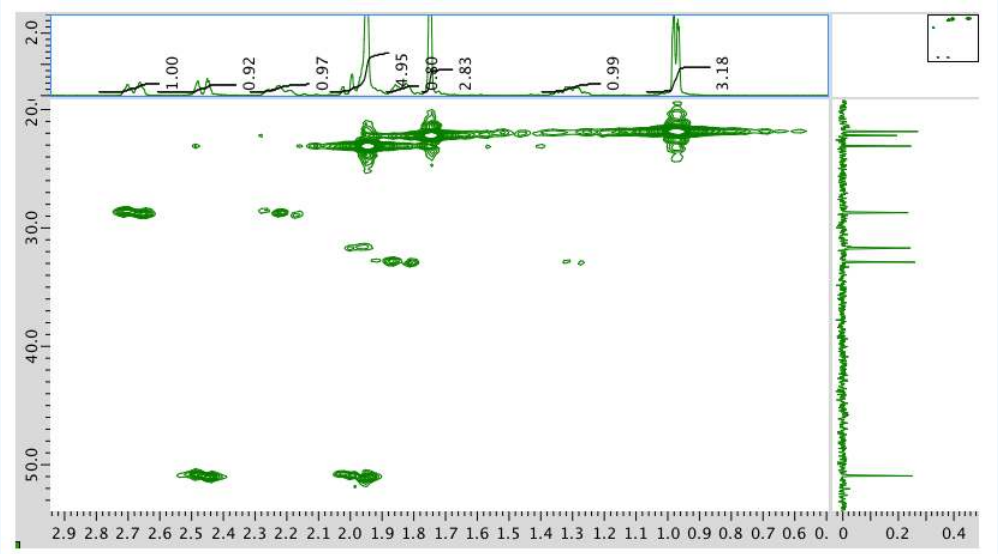
^{13}C NMR spectrum:



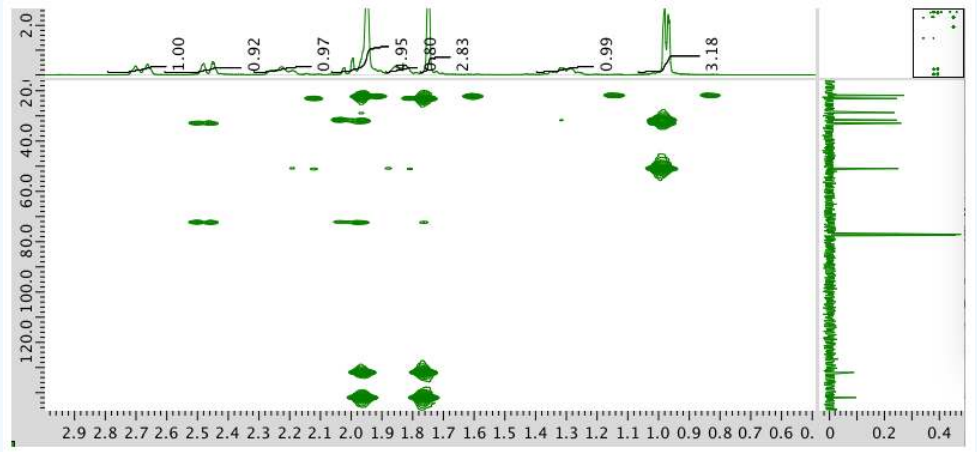
COSY spectrum:



HMQC spectrum:

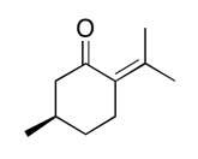


HMBC spectrum:



Answer

The data should be consistent with this structure:



NMR spectra obtained on a JEOL 400 MHz NMR spectrometer.

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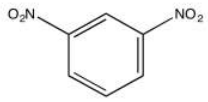
- **5.6: More Practice with 2D** by Chris Schaller is licensed CC BY-NC 3.0. Original source: https://employees.csbsju.edu/cschaller/ROBI2.htm.

3.17.6: 2D NMR Solutions

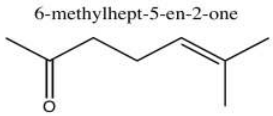
Exercise 5.1.1:

ethyl butanoate

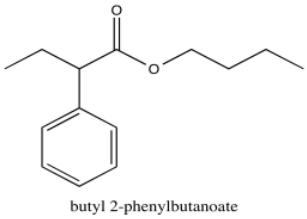
Exercise 5.1.2:



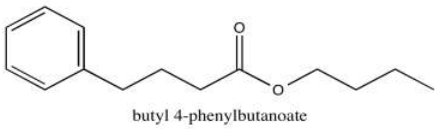
Exercise 5.1.3:



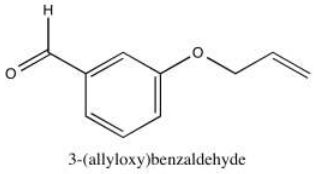
Exercise 5.1.4:



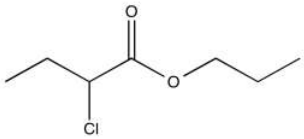
Exercise 5.1.5:



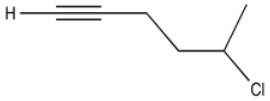
Exercise 5.1.6:



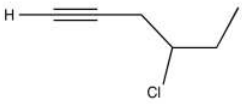
Exercise 5.1.7:



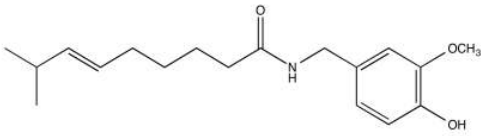
Exercise 5.1.8:



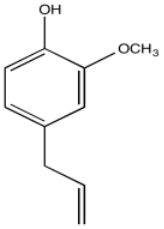
Exercise 5.1.9:



Exercise 5.1.10:

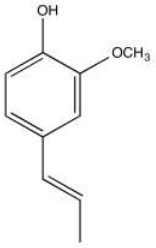


Exercise 5.1.11:



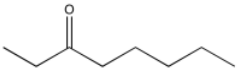
eugenol

Exercise 5.1.12:

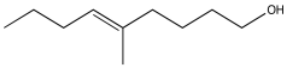


isoeugenol

Exercise 5.2.1:

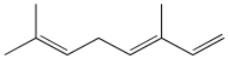


Exericse 5.2.2:

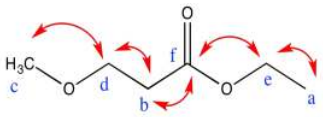


Exercise 5.2.3:

Ocimene

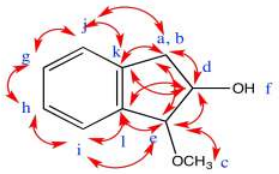


Exercise 5.3.1:



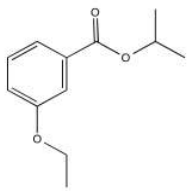
	^{1}H	^{13}C	HMBC
a	1.1	15	e
b	2.4	32	d, f
c	3.2	58	d
d	3.7	63	b, c
e	4.0	69	a, f
f	-	172	b, e

Exercise 5.3.2:

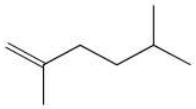


	^{1}H	^{13}C	HMBC
a	2.8	38	d, e, j, k
b	3.2		
c	3.2	57	e
d	4.4	78	a/b, e, k, l
e	4.7	92	a/b, c, d, i, l
f	5.0	-	-
g	7.1	127	h, i, j, k, l
h	7.2	127	g, i, j, k, l
i	7.3	126	e, g, h, j, k, l
j	7.4	129	a/b, g, h, i, k, l
k	-	140	a/b, d, g, h, i, j, l
l	-	142	d, e, g, h, i, j, k

Exercise 5.3.3:

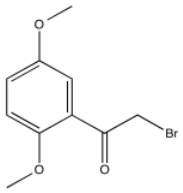


Exercise 5.3.4:

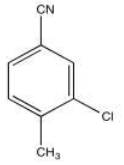


2,5-dimethylhex-1-ene

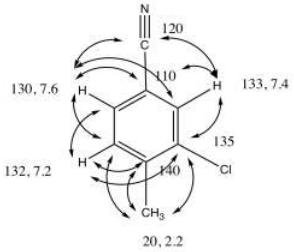
Exercise 5.3.5:



Exercise 5.3.6:

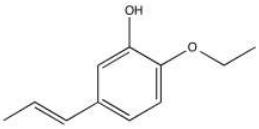


3-chloro-4-methylbenzonitrile



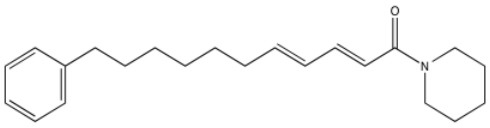
20, 2.2

Exercise 5.3.7:

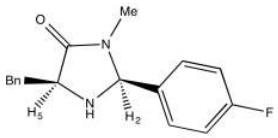


(*E*)-2-ethoxy-5-(prop-1-en-1-yl)phenol

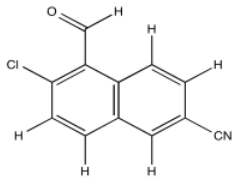
Exercise 5.3.8:



Exercise 5.4.1:

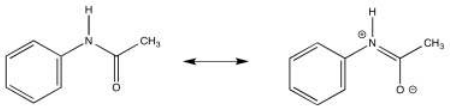


Exercise 5.4.2:

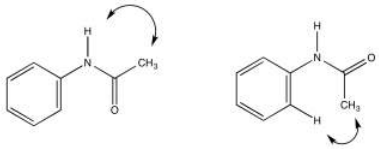


Exercise 5.4.3:

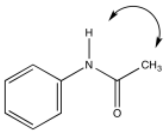
a) Due to resonance, there is substantial pi character to the amide bond which restricts free rotation around that bond.



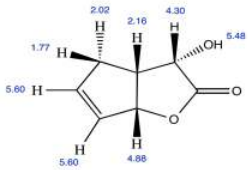
b)



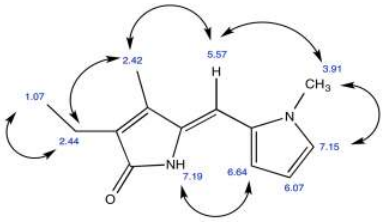
c)



Exercise 5.4.4:

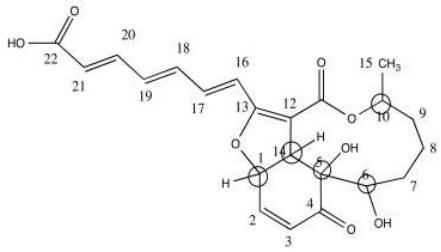


Exercise 5.4.5:

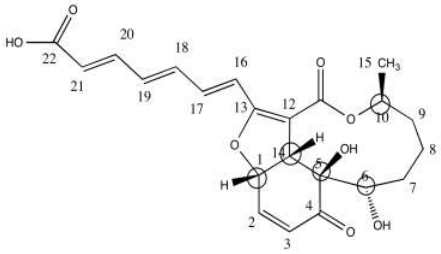


Exercise 5.4.6:

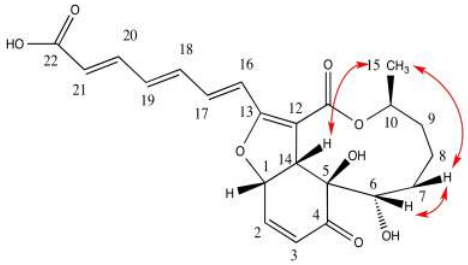
a)



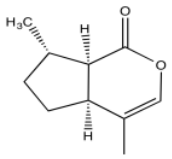
b)



c)

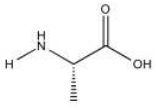


Exercise 5.4.7:



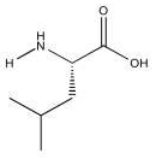
Catnip (nepetalactone)

Exercise 5.5.1:



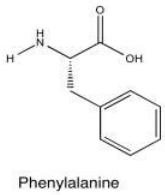
Alanine

Exercise 5.5.2:

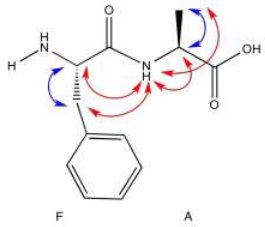


Leucine

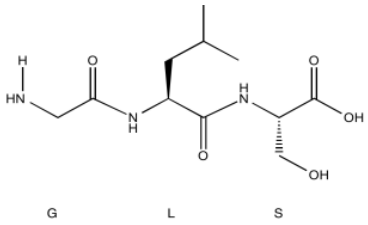
Exercise 5.5.3:



Exercise 5.5.4:



Exercise 5.5.5:



Exercise 5.6.1:

^{1}H NMR

Chemical shift (ppm)	Integration	Multiplicity	Partial Structure
5.54	2H	multiplet	C**H**=C (x 2)
4.17	2H	doublet	O-C**H**$_2$-CH
2.08	2H	quintet	CH-C**H**$_2$-CH$_3$
1.47	1H	boad singlet	OH
0.95	3H	triplet	CH$_2$-C**H**$_3$

* total # H: 10

^{13}C NMR

Chemical shift (ppm)	Type of carbon
134	sp^2
128	sp^2
58	sp^3-O
21	sp^3
14	sp^3

*total # C: 5

COSY

Assignment	^{1}H	COSY
A	0.95	2.08
B	2.08	0.95, 5.54
C	4.17	5.54
D	5.54	2.08
E	5.54	4.17

*HMQC indicates two hydrogens at 5.54 are in two different environments

HMQC

Assignment	^{13}C	^{1}H
A	14	0.95
B	21	2.08
C	58	4.17
D	128	5.54
E	134	5.54

Formula:

$C_5H_{10}O$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $\mathbf{5 \times 12) + (10 \times 1) + (1 \times 16) = 86}$

Compare C_5H_{10} ratio to C_5H_{12} in hydrocarbon

Degrees of unsaturation = \(\frac{(2 \times 5) + 2 - 10}{2} = 1 unit (1 double bond)

The data tables should be consitent with this structure:

pent-2-en-1-ol (could be *cis* or *trans* based on this analysis)

Exercise 5.6.2:

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial structure
4.7	5H	singlet	solvent
3.93	1H	triplet	CH_2-C**H**-N
2.40	2H	multiplet	CH_2-C$\mathbf{H}_2$?
2.09	2H	multiplet	C$\mathbf{H}_2$-CH_2?
1.4	9H	singlet	C(C$\mathbf{H}_3$)$_3$

*Total number of H: 19 H

^{13}C NMR:

Chemical shift (ppm)	Type of carbon
170	sp^2 (C=O)
80	sp^3 (C-O)
52	sp^3 (C-N)
32	sp^3
28	sp^3
26	sp^3

*Total number of C: 6 apparent, but two more suggested by symmetry (3 methyl groups in ^1H NMR) for 8 C; a third extra suggested by MW fit for 9 C

COSY:

Assignment	^1H	COSY
Solvent	4.7	--
B	3.93	2.40
D	2.40	2.09
C	2.09	2.40, 2.09
A	1.4	--

Formula:

$C_9H_{18}O_3N_2$ (extra O indicated from shift in ^{13}C, ^1H NMR; second O suggested by C=O in ^{13}C NMR; additional CO needed to fit MW)

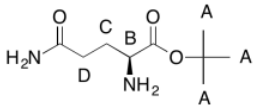
FW = $(9 \times 12) + (18 \times 1) + (3 \times 16) + (2 \times 14) = 202$

FW = ((9 \times 12) + (18 \times 1) + (3 \times 16) + (2 \times 14) = 202\)

Compare C_9H_{18} to C_9H_{22} for the corresponding hydrocarbon corrected for two nitrogens (therefore two extra hydrogens)

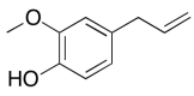
Degrees of unsaturation = $\frac{(2\times9)+2+2-10}{2} = 2$ units (2 double bonds)

The data tables should be consistent with this structure:



Exercise 5.6.3:

The data should be consistent with this structure:



Exercise 5.6.4:

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial Structure
4.71	--	singlet	solvent
4.17	1H	doublet?	CO-C**H**-N
3.75	3H	singlet	O-C**H**$_3$
2.25	1H	multiplet	CH-C**H**-(CH$_3$)$_2$
0.92	6H	triplet?	2 x C**H**$_3$

^{13}C NMR:

Chemical shift (ppm)	Type of carbon
170	sp^2 C=O
60	sp^3 C-N
52	sp^3 C-O
30	sp^3 C
19	sp^3 C

COSY:

Assignment	^{1}H	COSY
A	4.17	2.25
B	3.75	--
C	2.25	4.17
D	0.92	2.25

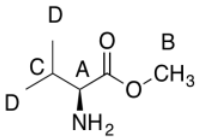
Formula:

$C_6H_{13}O_2N$ (1 O indicated from shift in ^{13}C, ^{1}H NMR)

FW = $(6 \times 120 + (13 \times 1) + (2 \times 16) + (1 \times 14) = 131$

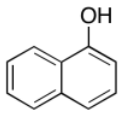
Degrees of unsaturation = $\frac{(2\times6)+2+1-13}{2} = 1$ unit (1 double bond)

The data should be consistent with this structure:



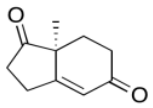
Exercise 5.6.5:

The data should be consistent with this structure:



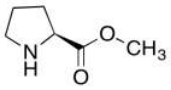
Exercise 5.6.6:

The data should be consistent with this structure:



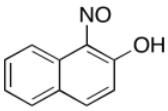
Exercise 5.6.7:

The data should be consistent with this structure:



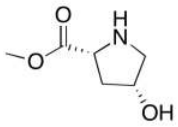
Exercise 5.6.8:

The data should be consistent with this structure:



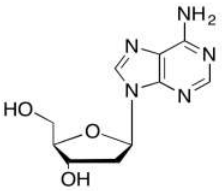
Exercise 5.6.9:

The data should be consistent with this structure:



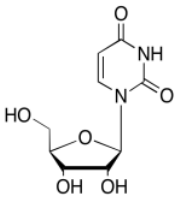
Exercise 5.6.10:

The data should be consistent with this structure:



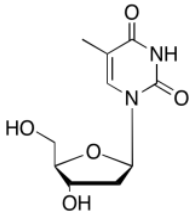
Exercise 5.6.11:

The data should be consistent with this structure:



Exercise 5.6.12:

The data should be consistent with this structure:



Exercise 5.6.13:

^{1}H NMR:

Chemical shift (ppm)	Integration	Multiplicity	Partial structure
5.7	1H	singlet	C=C**H**-CO
2.77	1H	multiplet	CH_2-C**H**-CO
2.62	1H	multiplet	C-C**H**-C
2.39	1H	multiplet	C-C**H**-C
2.05	1H	doublet?	C-C**H**-CH?
1.96	3H	singlet	C-C**H**$_3$
1.48	3H	singlet	C-C**H**$_3$
0.98	3H	singlet	C-C**H**$_3$

^{13}C NMR:

Chemical shft (ppm)	Type of carbon
204	sp^2 C=O
170	sp^2
121	sp^2
59	sp^3
55	sp^3
50	sp^3
41	sp^3
28	sp^3
24	sp^3
22	sp^3

COSY:

Assignment	^{1}H	COSY
1	2.39	2.77, 2.62?
3	5.7	2.05?
5	2.62	2.62?
7a	2.77	2.05
7b	2.05	2.77
8	1.48	--
9	0.98	--
10	1.96	--

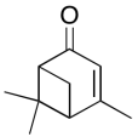
Formula:

$C_{10}H_{14}O$ (1 O indicated from shift in ^{13}C, ^1H NMR)

FW = $(10 \times 12) + (14 \times 1) + (1 \times 16) = 150$

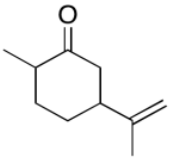
Degrees of unsaturation = \(\frac{(2 \times 10) + 2 - 14}{2} = 4 units (e.g. 2 rings, 2 double bonds)

The data should be consistent with this structure:



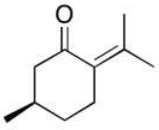
Exercise 5.6.14:

The data should be consistent with this structure:



Exercise 5.6.15:

The data should be consistent with this structure:



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3.18: Solutions to Selected Problems

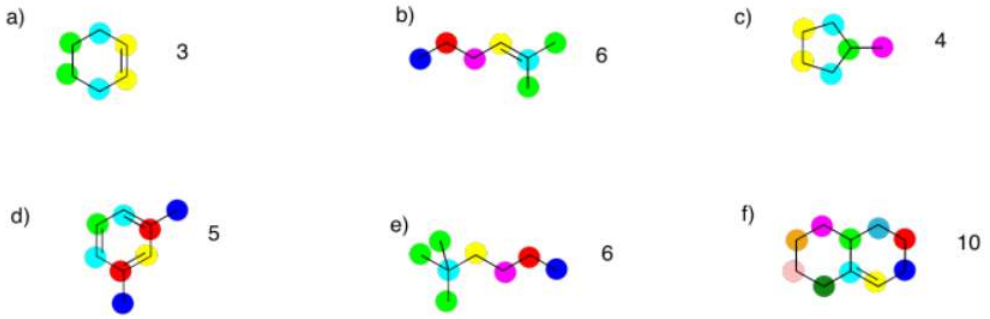
Exercise 4.2.1:

a) 10 ppm b) 64 ppm c) 158 ppm

Exercise 4.2.2:

a) 63 ppm b) 201 ppm c) 71 ppm

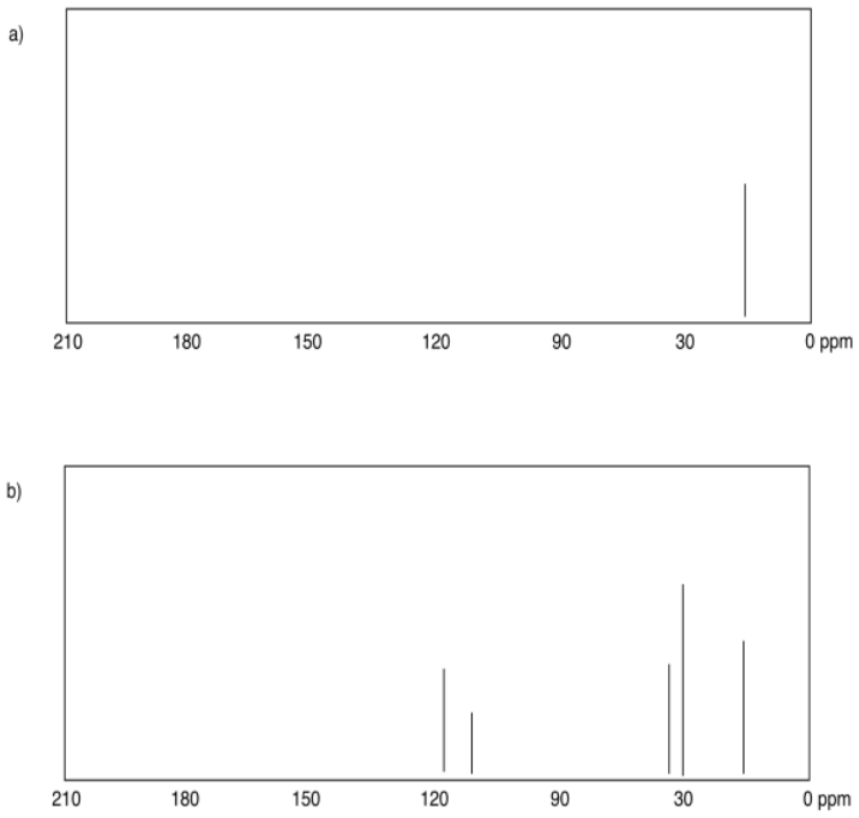
Exercise 4.3.1:



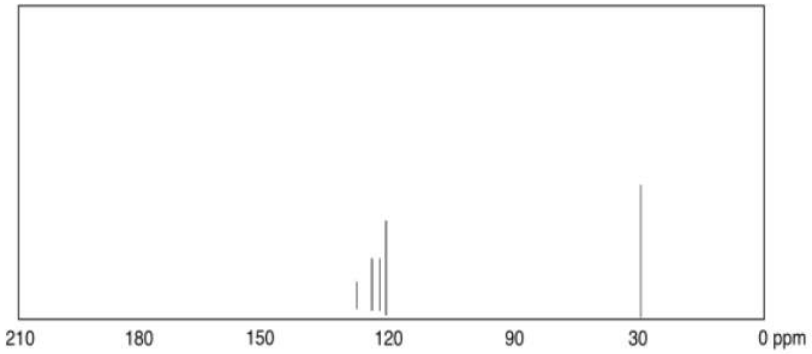
Exercise 4.3.2:

a. pentane, $CH_3CH_2CH_2CH_2CH_3$, or hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$
b. heptane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$, or octane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
c. nonane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, or decane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

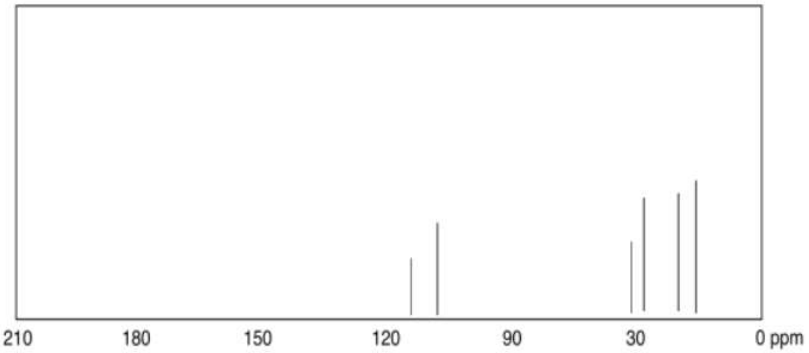
Exercise 4.4.1:



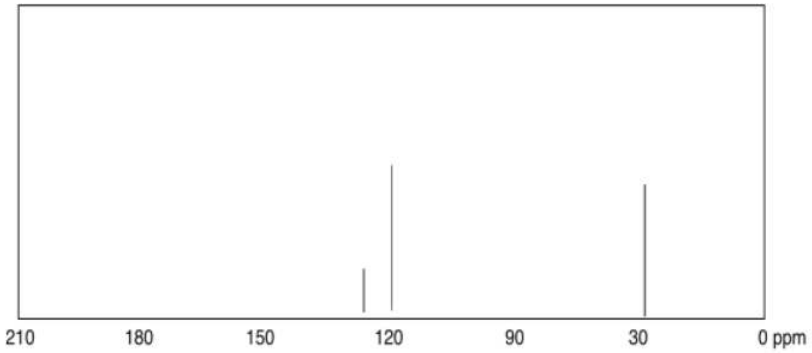
c)



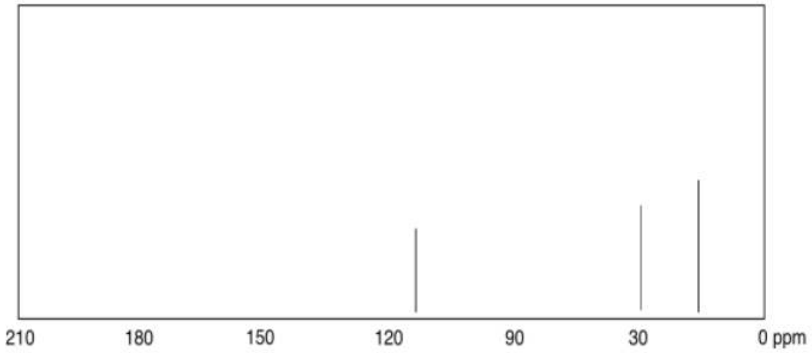
d)



e)



f)

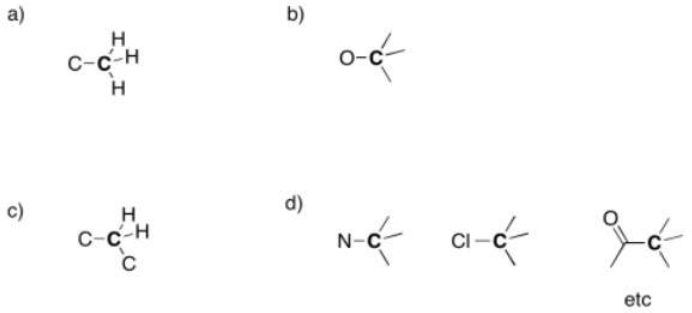


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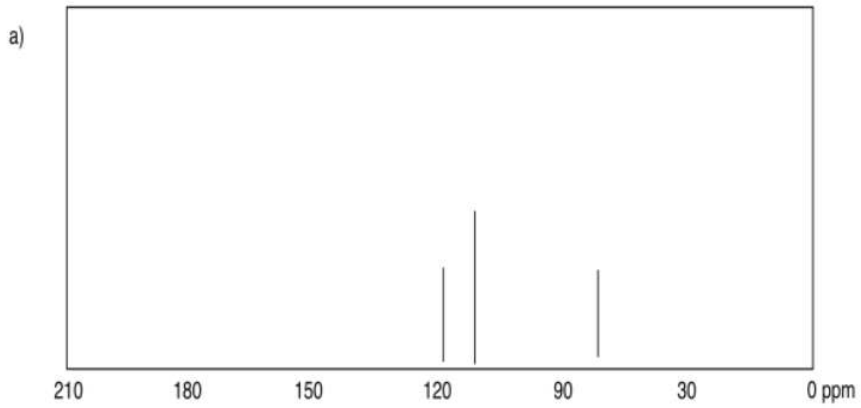
Exercise 4.4.2:

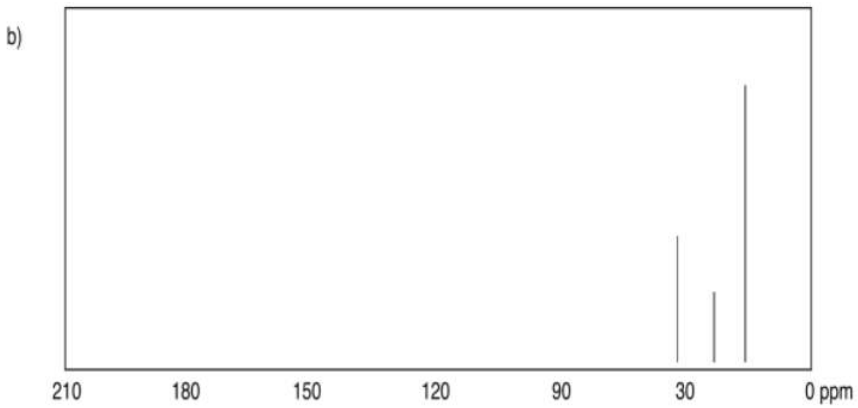
a) sp^3 b) sp^2 c) sp^2 d) sp^3 e) sp^3 f) sp^2

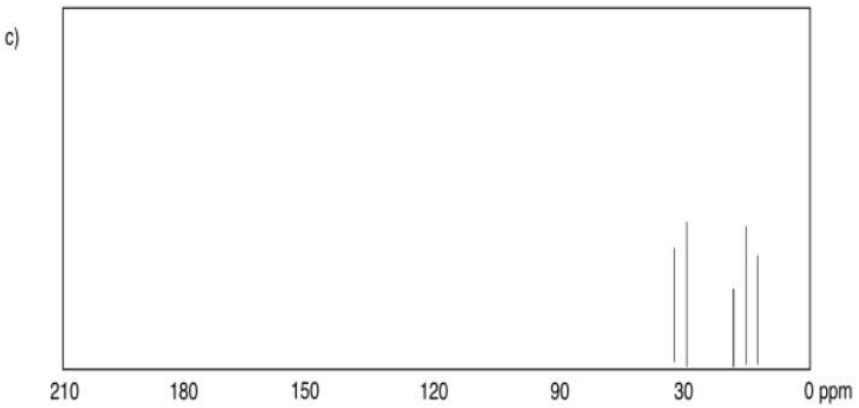
Exercise 4.5.1:



Exercise 4.5.2:







Exercise 4.6.1:

a) 127 ppm



Arom/Alkene

b) 11 ppm



probably Me

c) 196 ppm



ket/ald

d) 65 ppm



e) 111 ppm



f) 154 ppm



Arom

g) 210 ppm

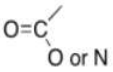


ket/ald

h) 28 ppm



i) 170 ppm

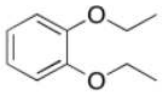


j) 42 ppm



Exercise 4.6.2:

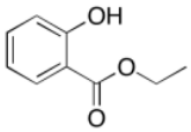
a)



b)



c)



Exercise 4.8.1:

a) H-$C_{sp}3$ b) H-$C_{sp}3$ c) H-$C_{sp}2$ d) H-$C_{sp}3$ e) H-$C_{sp}2$ f) H-$C_{sp}2$ g) H-$C_{sp}3$

Exercise 4.8.2:

a) carbon b) carbon c) nitrogen d) oxygen e) carbon f) oxygen g) nitrogen

Exercise 4.8.3:

a) aromatic b) aromatic c) alkene d) alkene e) alkene f) aromatic

Exercise 4.8.4:

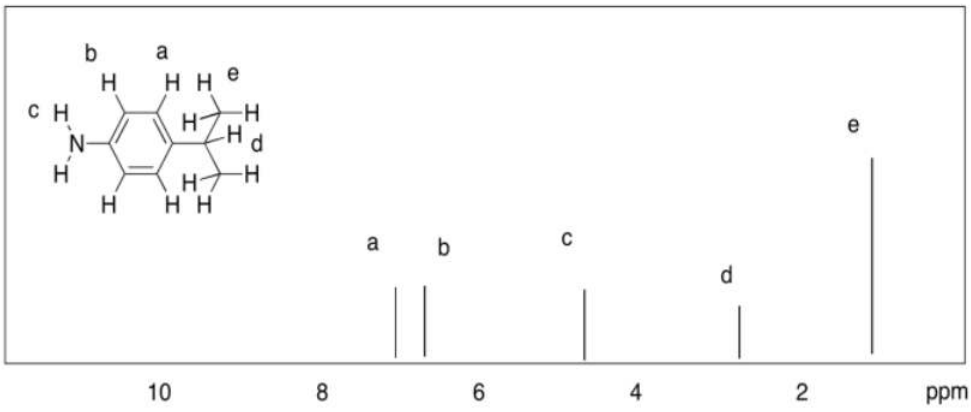
a) H-C_{Ar}-C b) H-C_{Ar}-C c) H-C_{Ar}-N d) C=O e) C=O f) H-C_{Ar}-N g) H-C_{Ar}-N

Exercise 4.8.5:

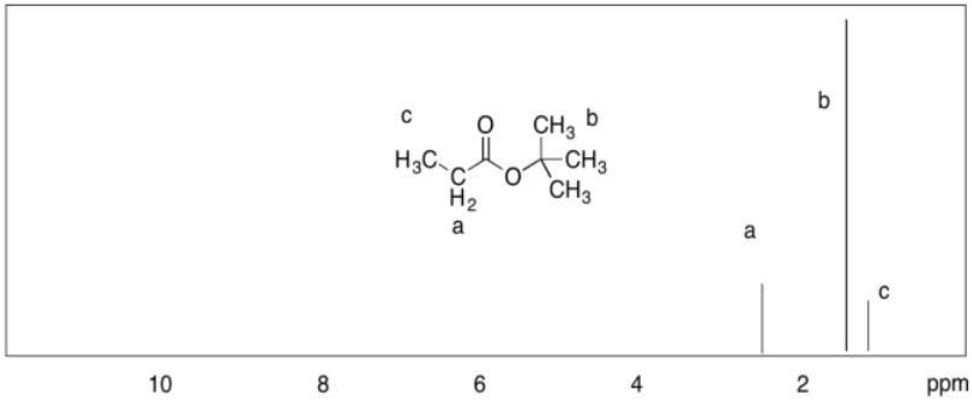
a. 3.4 ppm: H_a 1.5 ppm: H_b, H_c 0.9 ppm: H_d
b. 7.4 ppm: H_d 6.9 ppm: H_b, H_c 3.7 ppm: H_a
c. 10.1 ppm: H_a 7.9 ppm: H_b 7.6 ppm: H_d 7.5 ppm: H_c
d. 7.9 ppm: H_b 7.6 ppm: H_d 7.4 ppm: H_c 2.5 ppm: H_a

Exercise 4.8.6:

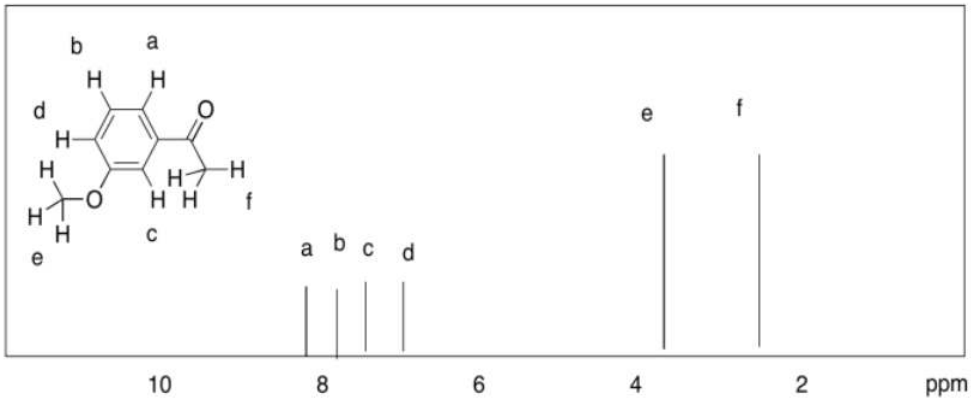
a)



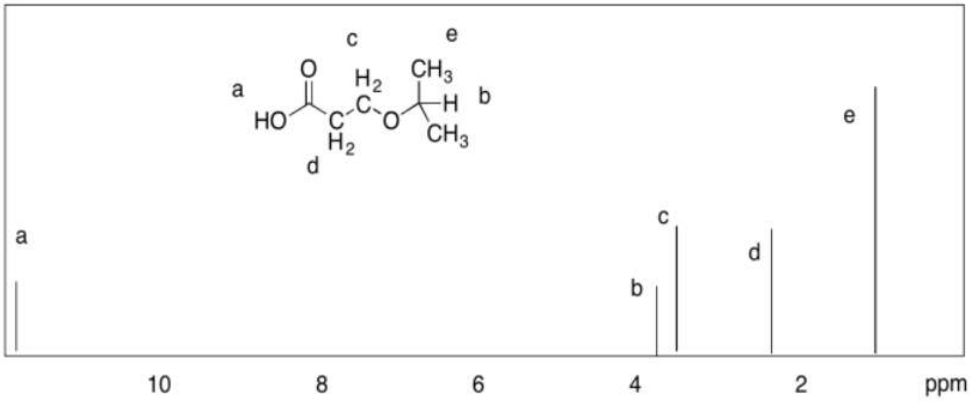
b)



c)



d)

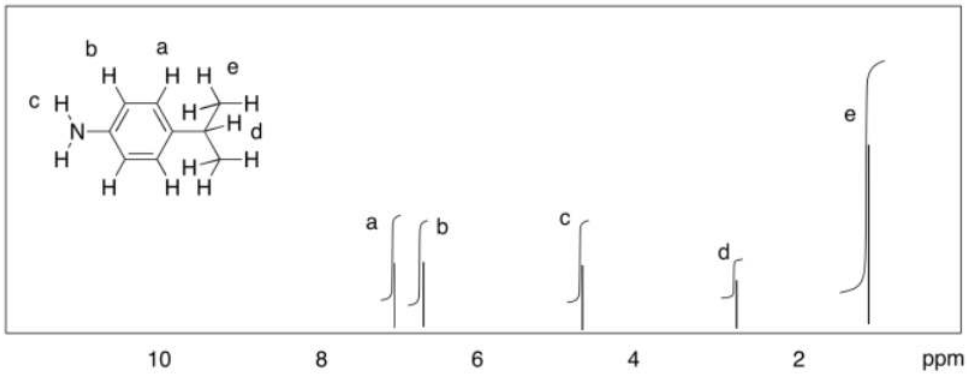


Exercise 4.9.1:

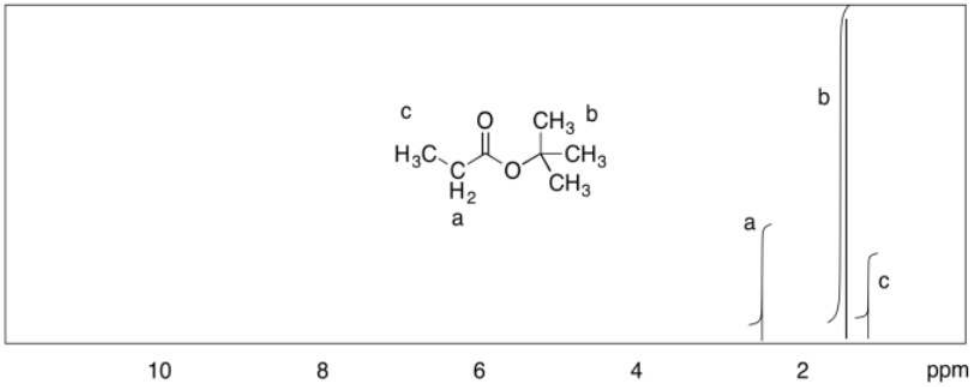
a. 0.9 ppm, 6H; 1.0 ppm, 6H (1:1 ratio)
b. 0.9 ppm, 6H; 1.0 ppm, 12H (1:2 ratio)
c. 0.9 ppm, 6H; 1.0 ppm, 16H (3:8 ratio)
d. 0.9 ppm, 6H; 1.0 ppm, 10H (3:5 ratio)
e. 0.9 ppm, 6H; 1.0 ppm, 8H (3:4 ratio)

Exercise 4.9.2:

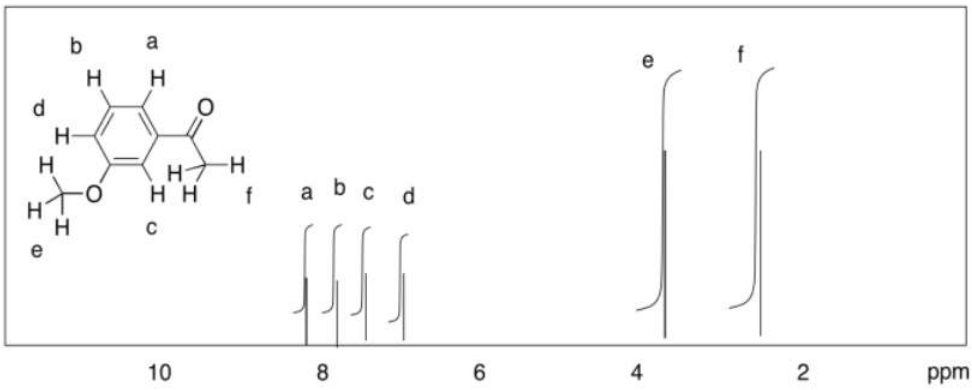
a)


b
a
e
c
H
N
H
d
a
b
c
d
e
10
8
6
4
2
ppm

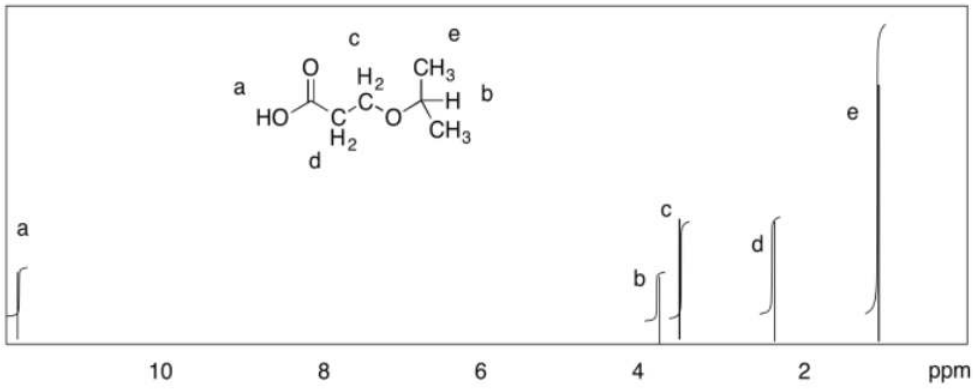
b)


c
O
CH3
b
H3C
C
O
CH3
H2
CH3
a
b
a
c
10
8
6
4
2
ppm

c)


b
a
H
H
d
O
H
H
H
H
H
f
O
H
H
H
c
e
a
b
c
d
e
f
10
8
6
4
2
ppm

d)



Exercise 4.9.3:

a) 5:2:3

Exericse 4.10.1:

(There will be some variation in the shift depending on the rest of the structure; this is just an estimate.)

a) 3.5 ppm, quartet, 2H b) 1.5 ppm, sextet, 2H c) 2.6 ppm, septet, 1H

d) 2.3 ppm, quintet, 1H e) 2.2 ppm, quartet, 2H f) 1.7 ppm, nonet, 1H

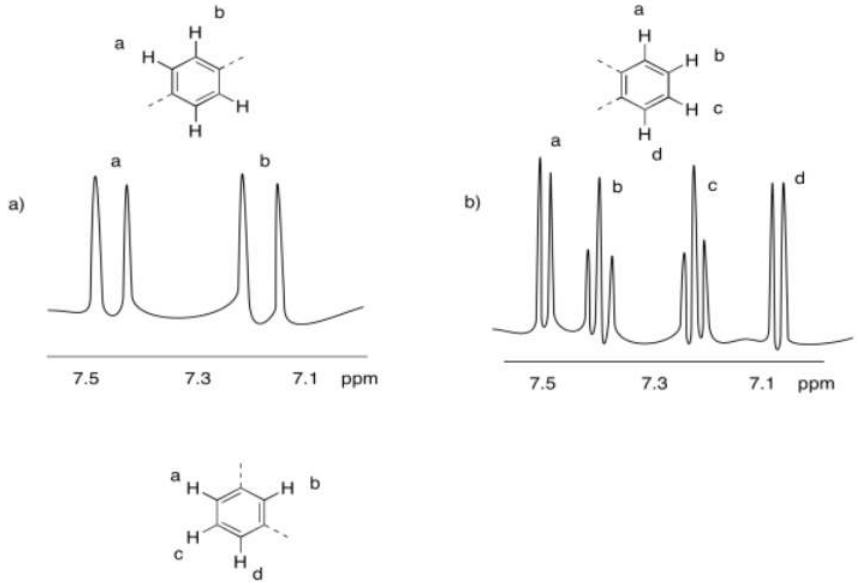
Exercise 4.10.2:

(There will be some variation in the shift depending on the rest of the structure; this is just an estimate.)

a) 7.8 ppm, doublet, 1H b) 8.4 ppm, singlet, 1H c) 6.7 ppm, singlet, 1H

d) 7.2 ppm, troplet, 1H e) 6.9 ppm, doublet, 1H

Exercise 4.10.3:



Exercise 4.10.4:

3.4 ppm, doublet: CH-C**H**$_2$-O

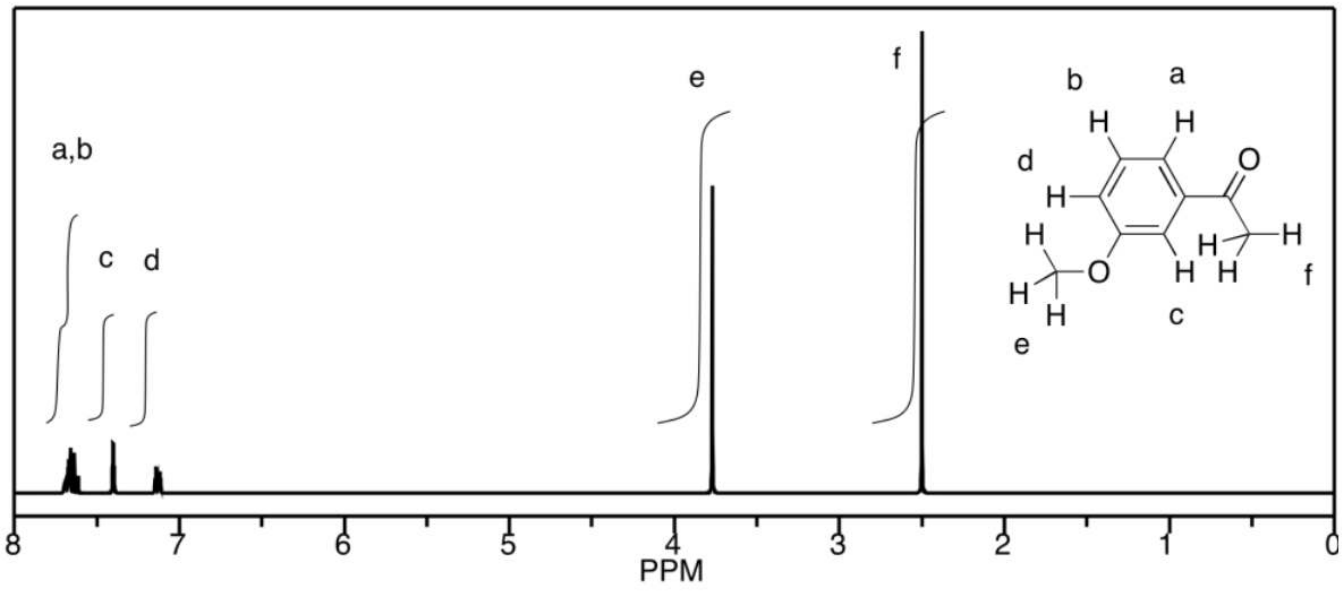
2.1 ppm, singlet: O**H**

1.7 ppm, nonet: $(CH_3)_2C\mathbf{H}CH_2$

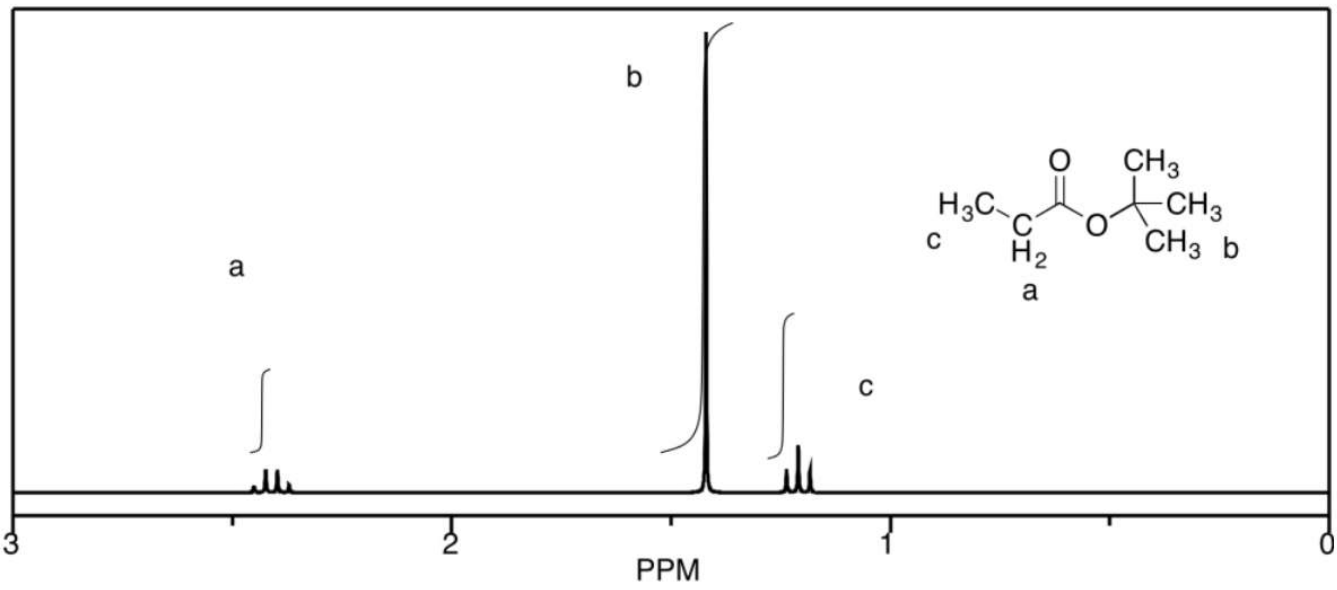
0.9 ppm, doublet: $CH(C\mathbf{H}_3)_2$

Exercise 4.10.5:

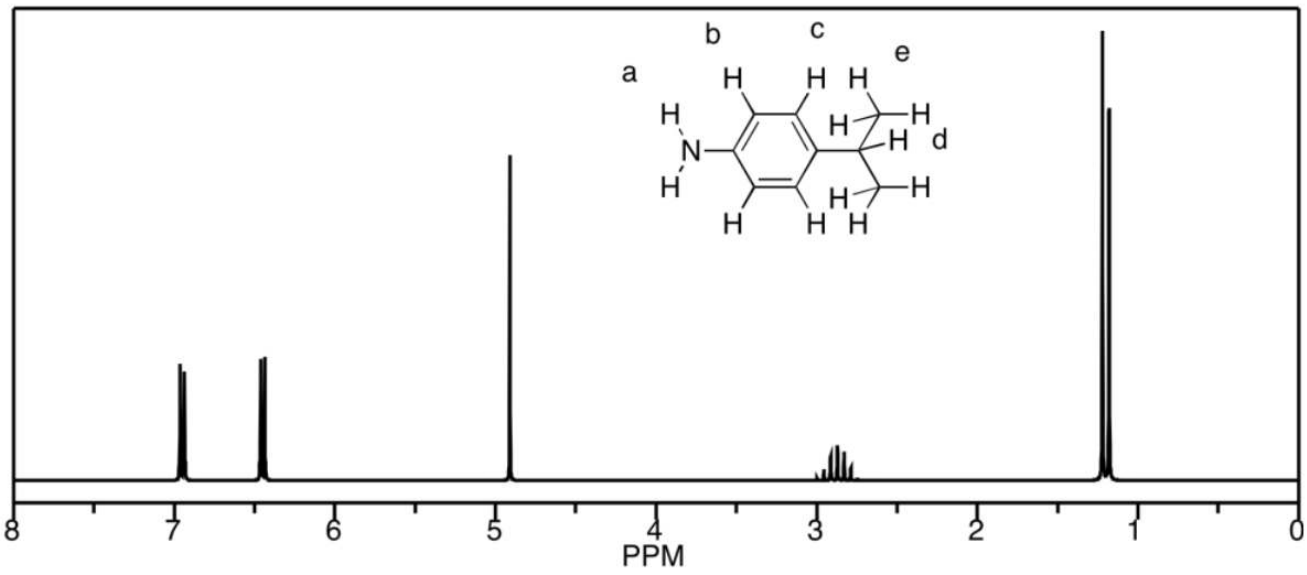
a) This is a simulated spectrum. The peaks at f, e, and c are singlets. The peak at d is a doublet. The peaks at a & b are unfortunately coincident, so their multiplicities are obscured, but they would be doublets & triplets, respectively.



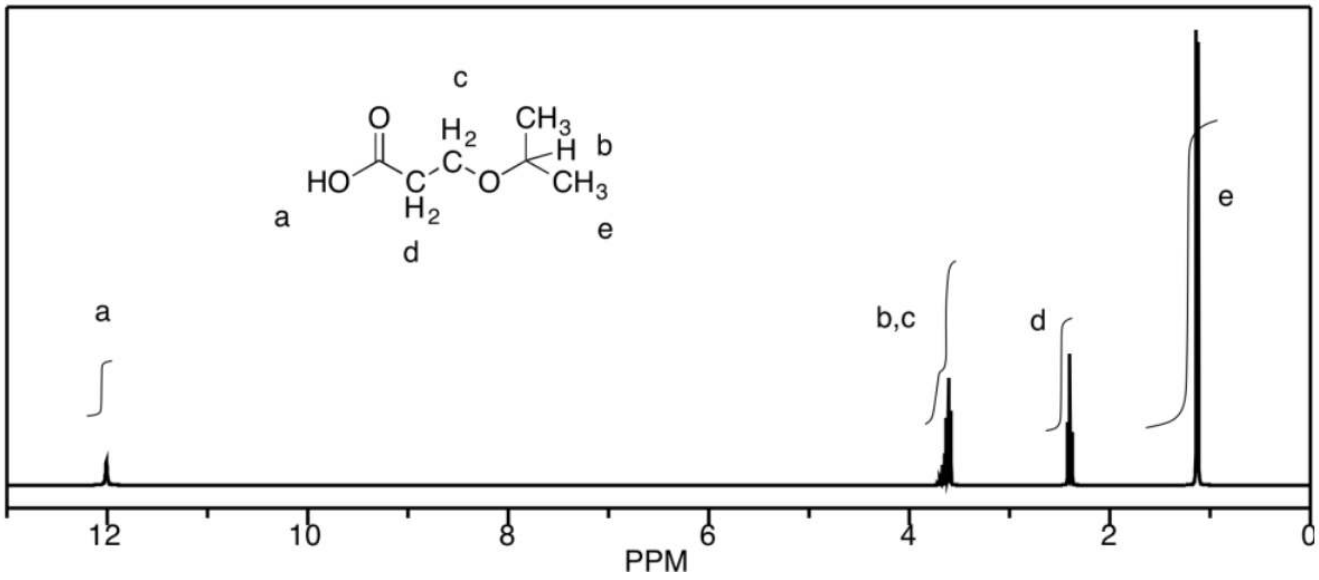
b)



c)



d) The peaks at b and c unfortunately coincide, but they would be a septet and a triplet, respectively. Otherwise, a is a singlet, d is a triplet, and e is a doublet.



Exercise 4.12.1:

Fill in partial structures for the following peaks.

Aromatic (benzene etc) peaks are labeled "Ar" to distinguish from alkene peaks that show up further upfield (lower shift). Also, some peaks may be in two symmetric positions and are labeled with "x2".

a) 10.1 ppm, 1H, triplet, CH_2-C**H**=O b) 3.4 ppm, 1H, septet, O-C**H**$(CH_3)_2$

c) 7.3 ppm, 2H, triplet, CH=C**H**-CH x 2 (Ar) d) 5.4 ppm, 1H, quartet, CH_3-C**H**=C

e) 1.4 ppm, 2H, sextet, CH_3-C**H**$_2$-CH_2 f) 8.0 ppm, 1H, singlet, C=C**H**-C (Ar)

g) 2.1 ppm, 3H, singlet, C**H**$_3$-C=C or C**H**$_3$-C=O or C**H**$_3$-N; need context to choose

h) 6.8 ppm, 2H, doublet, CH=C**H**-C x 2 (Ar) i) 0.9 ppm, 6H, doublet, CH-C**H**$_3$ x 2

Exercise 4.12.2:

Identify the errors in the following partial structures:

a) 3.6 ppm, 2H, triplet, C**H**$_2$-CH$_2$ the first carbon must be attached to O to have a shift at 3.6 ppm

b) 2.1 ppm, 2H, singlet, C**H**$_3$-C=C the integral says only 2H, not 3H

c) 7.4 ppm, 2H, doublet, CH=C**H**$_2$-C the shift implies aromatic, so there can only be one H per carbon; must be symmetry

d) 1.8 ppm, 2H, quintet, C**H**$_2$-CH$_4$ there can't be four hydrogens on one carbon; must be some hydrogens on each side

e) 7.8 ppm, 1H, triplet, -C**H**=CH$_2$ the shift implies aromatic, so there can only be one H per carbon; must be one one each side

f) 1.7 ppm, 1H, nonet, NH$_2$-C**H**(CH$_3$)$_2$ an attached nitrogen would shift this hydrogen past 2 ppm; also, coupling is rarely seen across O or N, so the two neighbouring H on the left are probably on a carbon

Exercise 4.13.1:

a) TBME b) acetone c) THF d) methanol e) ethyl acetate

Exercise 4.14.1:

a. appearance of CH-O near 3.5 ppm (multiplet, 1H)
b. appearance of CH$_2$-O near 3.5 ppm (triplet, 2H); disappearance of =CH near 5-6 ppm (mutiplets, total 3H)
c. appearance of HC=O near 10 ppm (triplet, 1H); disappearance of =CH near 5-6 ppm (mutiplets, total 3H)
d. appearance of HC=O near 10 ppm (triplet, 1H); disappearance of CH$_2$-O near 3.5 ppm (doublet, 2H)
e. appearance of CH$_2$-O near 3.5 ppm (triplet, 2H)
f. appearance of CH$_2$-O near 4 ppm (triplet, 2H)
g. appearance of =CH near 5-6 ppm (mutiplets, total 2H); disappearance of HC=O near 10 ppm (triplet, 1H);
h. disappearance of =CH near 5-6 ppm (mutiplets, total 2H); appearance of triplet:sextet:triplet pattern between 1-2 ppm

i) appearance of HC=O near 10 ppm (triplet, 1H); disappearance of CH$_2$-O near 3.5 ppm (doublet, 2H)

j) appearance of CH-O near 3 ppm (singlet, 3H) and 3.5 ppm (sextet, 1H); disappearance of =CH near 5-6 ppm (mutiplets, total 2H)

Exercise 4.15.1:

a) student 1: Let's use the H$_2$C-O peak of ethyl propanoate at 4 ppm and the acetonitrile methyl at 2 ppm. The ratio appears to be 2:1, but they represent 2 protons and 3 protons, respectively. That means the ratio of molecules is 2/2:1/3 = 3:1 ethyl propanoate : acetonitrile.

student 2: We'll use the H$_2$C-O peak of ethyl propanoate at 4 ppm and the H$_2$C-O peak of THF at 3.5 ppm. The ratio appears to be 3:2, but they represent 2 protons and 4 protons, respectively. That means the ratio of molecules is 3/2:2/4 = 12:4 = 3:1 ethyl propanoate : THF.

student 3: Look at the H$_2$CCl$_2$ peak of dichloromethane at 5 ppm and the H$_2$C-O peak of THF at 4 ppm. The ratio appears to be 1:2, and they both represent 2 protons, so the ratio of molecules is 1:2 dichloromethane : ethyl propanoate.

b) student 1: The sample is $\frac{1}{1+3} \times 100\% = 25\%$ acetonitrile.

student 2: The sample is $\frac{1}{1+3} \times 100\% = 25\%$ THF.

student 3: The sample is $\frac{1}{1+2} \times 100\% = 33\%$ acetonitrile.

Exercise 4.15.2:

The obvious NMR handles are the H-C=O aldehyde proton at 10 ppm for benzaldehyde and the alcohol-adjacent H-C-O proton at 4.5 ppm for 1-phenylpropanol.

Each of those peaks represents one proton, so the integral ratio of 1:2 suggests a ratio of bezaldehyde to 1-phenylpropanol of of 1:2. That translates into 33% benzaldehyde, 67% 1-phenylpropanol.

Exercise 4.15.3:

The NMR handles here are the H-C=O aldehyde proton at 10 ppm for benzaldehyde and the alcohol-adjacent H_2C-O protons near 5 ppm for benzyl alcohol.

In this case, we need to correct for the differing numbers of protons represented by each peak: 1H for the aldehyde peak but 2H for the alcohol one. The integral ratio of 1:6 therefore suggests a ratio of bezaldehyde to 1-phenylpropanol of of 1:3. That translates into 25% benzaldehyde, 75% 1-phenylpropanol.

Exercise 4.15.4:

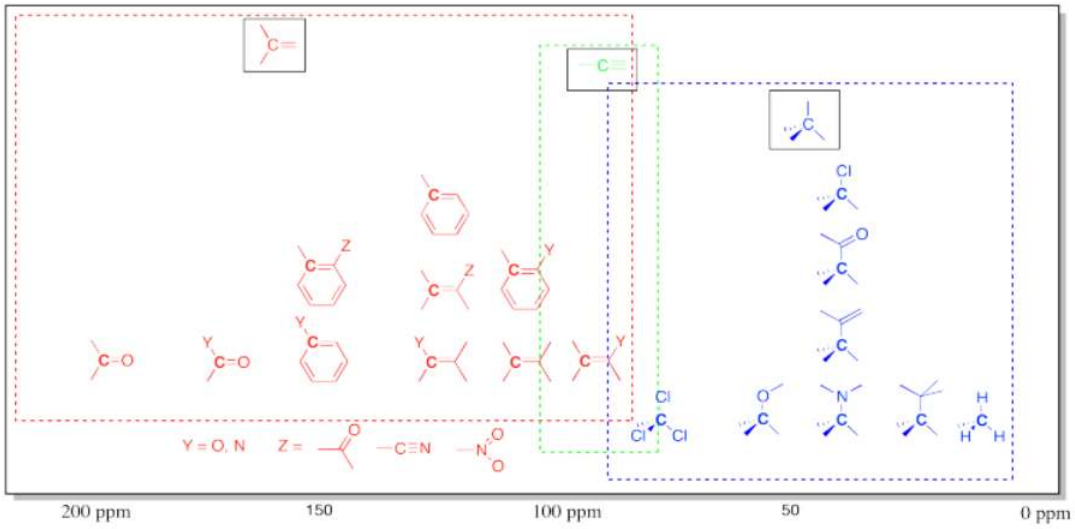
We could use the peak corresponding to the O-CH-C=O proton above 5 ppm for the repeat unit and the peak for the CH_2-O proton in the initiator/end group near 3.5 ppm. The integral ratio is 24:1, but they represent different numbers of hydrogens, so the repeat unit to end group ratio is really 24/1:1/2, or 48:1. The degree of polymerization is 48.

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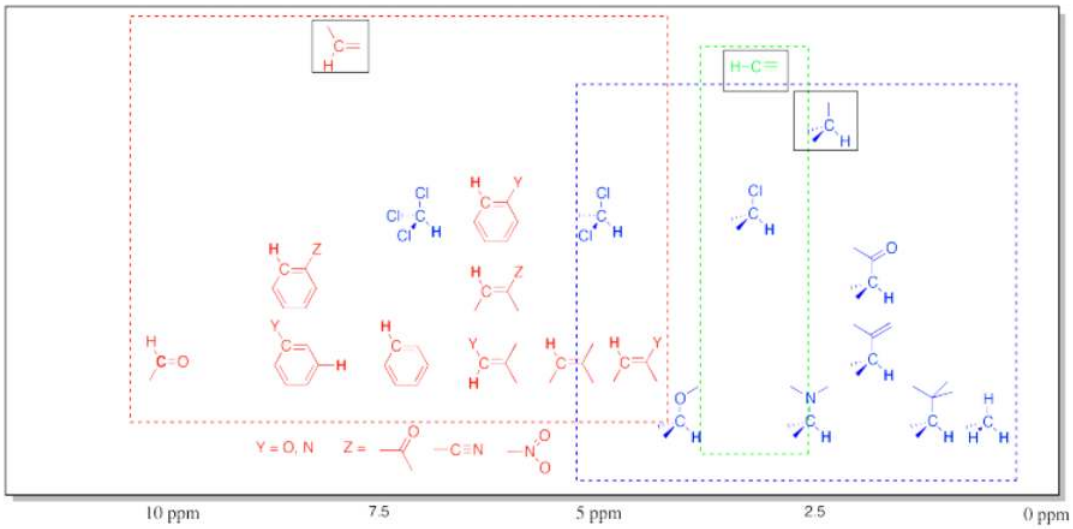
3.19: Appendix

Table of ^{13}C NMR Frequencies Common in Organic Compounds.



Note that effects are additive: two or more electron-withdrawing groups move the absorbance further to the left than just one group.

Table of ^{1}H NMR Frequencies Common in Organic Compounds.



This chart shows the frequancies of protons that are attached to carbons. In general, protons follow the trend seen in the carbon to which they are attached. Note again the additive effects of multiple attached groups.

This table does not include OH (or NH) protons. Protons attached to heteroatoms are more difficult to pinpoint because their locations in the spectrum are much less specific. Instead, they may be found across a very broad range.

Table of ^{1}H NMR Frequencies of OH Common in Organic Compounds.

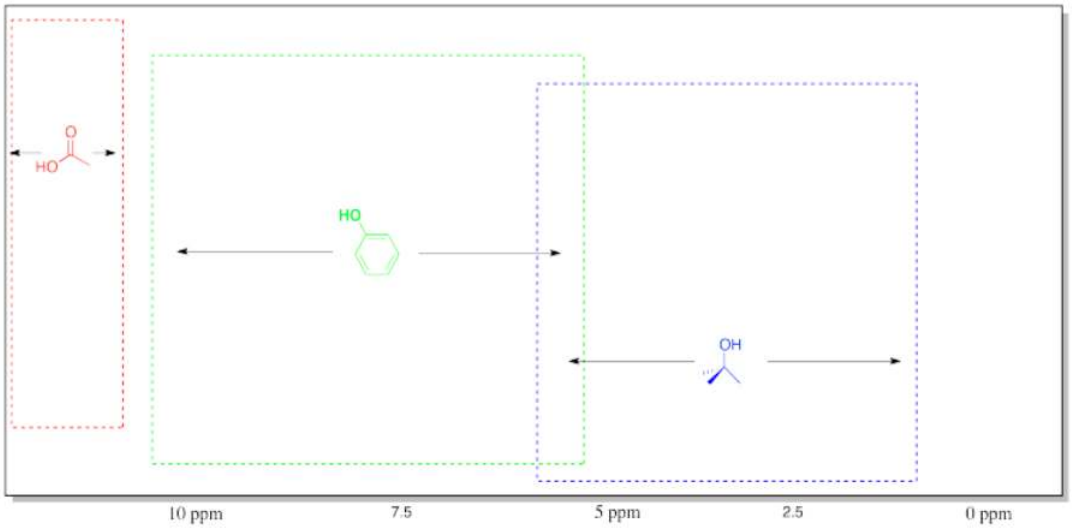


Table of Some Common Impurities in NMR Samples.

Minor impurities in the NMR spectrum are often the result of solvents used during a reaction or sample purification. A few examples are provided in the following table, showing the data you would see from common solvents in an NMR spectrum taken in chloroform.

solvent	number of peaks	shift	multiplicity	integral ratio	assignment
water	1	1.56	br. s	-	O-**H**
acetone	1	2.17	s	-	(C=O)C**H**$_3$
chloroform	1	7.26	s	-	Cl$_3$C-**H**
t-butyl methyl ether	2	1.19	s	3	C(C**H**$_3$)$_3$
		3.22	s	1	O-C**H**$_3$
ethyl acetate	3	1.26	t	3	CH$_2$C**H**$_3$
		2.05	s	3	(C=O)C**H**$_3$
		4.12	q	2	OC**H**$_2$CH$_3$
grease or alkanes	2	0.86	m	varies; smaller	CH$_2$C**H**$_3$
		1.26	m	varies; larger	CH$_2$C**H**$_2$CH$_2$ / CH$_2$C**H**$_2$CH$_3$

An excellent table, including shifts of a variety of impurities in different NMR solvents, can be found in the following article: Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem*. **1997**, *62*, 7512-7515.

Table of Solvent

Residual Peaks

Because an NMR sample is mostly solvent (with a small amount of dissolved solute that you are really interested in), there is usually a peak in the spectrum that comes from atoms in the solvent. Usually the use of deuterated solvents (enriched in ^{2}H instead

of ^{1}H) minimizes the size of solvent peaks in ^{1}H NMR. However, there is always a trace of ^{1}H left in the solvent, which shows up as a small peak in the spectrum. ^{13}C residual peaks are often much larger than the peaks arising from the solute.

Solvent	^{1}H Shift	Multiplicity	^{13}C Shift	Multiplicity*
Acetone-d_6	2.05	pent	206.68	sing
			29.92	sept
Acetonitrile-d_3	1.94	pent	118.69	sing
			1.39	sept
Benzene-d_6	7.16	sing	128.39	trip
Chloroform-*d*	7.27	sing	77.23	trip
D_2O	4.80		--	
Dichloromethane-d_2	5.32	trip	54.00	pent
DMF-d_7	8.03	sing	163.15	trip
	2.92	pent	34.89	sept
	2.75	pent	29.76	sept
DMSO-d_6	2.50	pent	39.51	sept
Methanol-d_4	4.87	sing	49.15	sept
	3.31	pent		
THF-d_8	3.58	sing	67.57	pent
	1.73	sing	25.37	sing

*Note that coupling to ^{2}H produces different patterns than coupling to ^{1}H.

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CHAPTER OVERVIEW

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Thumbnail: 3D depiction of electron density (blue) of a ligand (orange) bound to a binding site in a protein (yellow).[131] The electron density is obtained from experimental data, and the ligand is modeled into this electron density. (CC BY-SA 4.0; Theislikerice via Wikipedia)

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4.1: Background

X-ray Crystallography is a scientific method used to determine the arrangement of atoms of a crystalline solid in three dimensional space. This technique takes advantage of the interatomic spacing of most crystalline solids by employing them as a diffraction gradient for x-ray light, which has wavelengths on the order of 1 angstrom (10^{-8} cm).

Introduction

In 1895, Wilhelm Rontgen discovered X-rays. The nature of X-rays, whether they were particles or electromagnetic radiation, was a topic of debate until 1912. If the wave idea was correct, researchers knew that the wavelength of this light would need to be on the order of 1 Angstrom (Å) (10^{-8} cm). Diffraction and measurement of such small wavelengths would require a gradient with spacing on the same order of magnitude as the light.

In 1912, Max von Laue, at the University of Munich in Germany, postulated that atoms in a crystal lattice had a regular, periodic structure with interatomic distances on the order of 1 Å. Without having any evidence to support his claim on the periodic arrangements of atoms in a lattice, he further postulated that the crystalline structure can be used to diffract X-rays, much like a gradient in an infrared spectrometer can diffract infrared light. His postulate was based on the following assumptions: the atomic lattice of a crystal is periodic, X-rays are electromagnetic radiation, and the interatomic distance of a crystal are on the same order of magnitude as X-ray light. Laue's predictions were confirmed when two researchers: Friedrich and Knipping, successfully photographed the diffraction pattern associated with the X-ray radiation of crystalline $CuSO_4$ • 5 H_2O. The science of X-ray crystallography was born.

The arrangement of the atoms needs to be in an ordered, periodic structure in order for them to diffract the X-ray beams. A series of mathematical calculations is then used to produce a diffraction pattern that is characteristic to the particular arrangement of atoms in that crystal. X-ray crystallography remains to this day the primary tool used by researchers in characterizing the structure and bonding of organometallic compounds.

Diffraction

Diffraction is a phenomena that occurs when light encounters an obstacle. The waves of light can either bend around the obstacle, or in the case of a slit, can travel through the slits. The resulting diffraction pattern will show areas of constructive interference, where two waves interact in phase, and destructive interference, where two waves interact out of phase. Calculation of the phase difference can be explained by examining Figure 1 below.

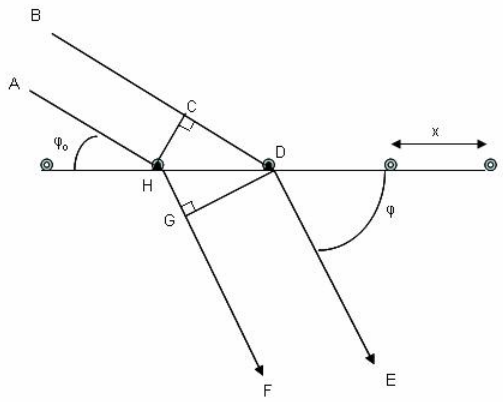


Figure 1: Scattering of light by a diffraction gratting

In the figure below, two parallel waves, BD and AH are striking a gradient at an angle θ_o. The incident wave BD travels farther than AH by a distance of CD before reaching the gradient. The scattered wave (depicted below the gradient) HF, travels father than the scattered wave DE by a distance of HG. So the total path difference between path AHGF and BCDE is CD - HG. To observe a wave of high intensity (one created through constructive interference), the difference CD - HG must equal to an integer number of

wavelengths to be observed at the angle psi, $CD - HG = n\lambda$, where λ is the wavelength of the light. Applying some basic trigonometric properties, the following two equations can be shown about the lines:

$$CD = x\cos(\theta o) \tag{4.1.1}$$

and

$$HG = x\cos(\theta) \tag{4.1.2}$$

where x is the distance between the points where the diffraction repeats. Combining the two equations,

$$x(\cos\theta_o - \cos\theta) = n\lambda \tag{4.1.3}$$

Bragg's Law

Diffraction of an X-ray beam, occurs when the light interacts with the electron cloud surrounding the atoms of the crystalline solid. Due to the periodic crystalline structure of a solid, it is possible to describe it as a series of planes with an equal interplaner distance. As an X-ray's beam hits the surface of the crystal at an angle, θ, some of the light will be diffracted at that same angle away from the solid (Figure 2). The remainder of the light will travel into the crystal and some of that light will interact with the second plane of atoms. Some of the light will be diffracted at an angle θ, and the remainder will travel deeper into the solid. This process will repeat for the many planes in the crystal. The X-ray beams travel different pathlengths before hitting the various planes of the crystal, so after diffraction, the beams will interact constructively only if the path length difference is equal to an integer number of wavelengths (just like in the normal diffraction case above). In the figure below, the difference in path lengths of the beam striking the first plane and the beam striking the second plane is equal to BG + GF. So, the two diffracted beams will constructively interfere (be in phase) only if $BG + GF = n\lambda$. Basic trigonometry will tell us that the two segments are equal to one another with the interplaner distance times the sine of the angle θ. So we get:

$$BG = BC = d\sin\theta \tag{4.1.4}$$

Thus,

$$2d\sin\theta = n\lambda \tag{4.1.5}$$

This equation is known as Bragg's Law, discovered in 1912. {C}{C}Bragg's Law relates the distance between two planes in a crystal and the angle of reflection to the X-ray wavelength. The X-rays that are diffracted off the crystal have to be in-phase in order to signal. Only certain angles that satisfy the following condition will register:

$$\sin\theta = \frac{n\lambda}{2d} \tag{4.1.6}$$

For historical reasons, the resulting diffraction spectrum is represented as intensity vs. 2θ.

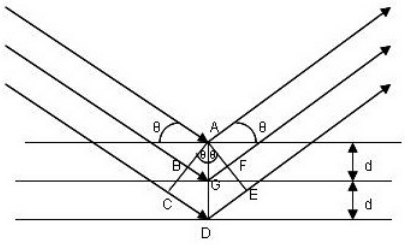


Figure 2: Incident X-ray strikes a set of planes (with an interplaner distance of d) at an angle of θ

Instrument Components

The main components of an X-ray instrument are similar to those of many optical spectroscopic instruments. These include a source, a device to select and restrict the wavelengths used for measurement, a holder for the sample, a detector, and a signal converter and readout. However, for X-ray diffraction; only a source, sample holder, and signal converter/readout are required.

The Source

X-ray tubes provides a means for generating X-ray radiation in most analytical instruments. An evacuated tube houses a tungsten filament which acts as a cathode opposite to a much larger, water cooled anode made of copper with a metal plate on it. The metal plate can be made of any of the following metals: chromium, tungsten, copper, rhodium, silver, cobalt, and iron. A high voltage is passed through the filament and high energy electrons are produced. The machine needs some way of controlling the intensity and wavelength of the resulting light. The intensity of the light can be controlled by adjusting the amount of current passing through the filament; essentially acting as a temperature control. The wavelength of the light is controlled by setting the proper accelerating voltage of the electrons. The voltage placed across the system will determine the energy of the electrons traveling towards the anode. X-rays are produced when the electrons hit the target metal. Because the energy of light is inversely proportional to wavelength ($E = hc = h(1/\lambda)$), controlling the energy, controls the wavelength of the X-ray beam.

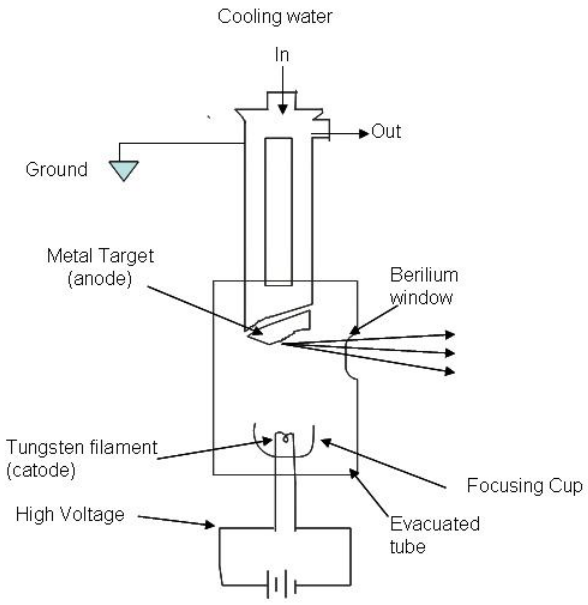


Figure 3: X-ray tube schematic

X-ray Filter

Monochromators and filters are used to produce monochromatic X-ray light. This narrow wavelength range is essential for diffraction calculations. For instance, a zirconium filter can be used to cut out unwanted wavelengths from a molybdenum metal target (see figure 4). The molybdenum target will produce X-rays with two wavelengths. A zirconium filter can be used to absorb the unwanted emission with wavelength $K\beta$, while allowing the desired wavelength, K_α to pass through.

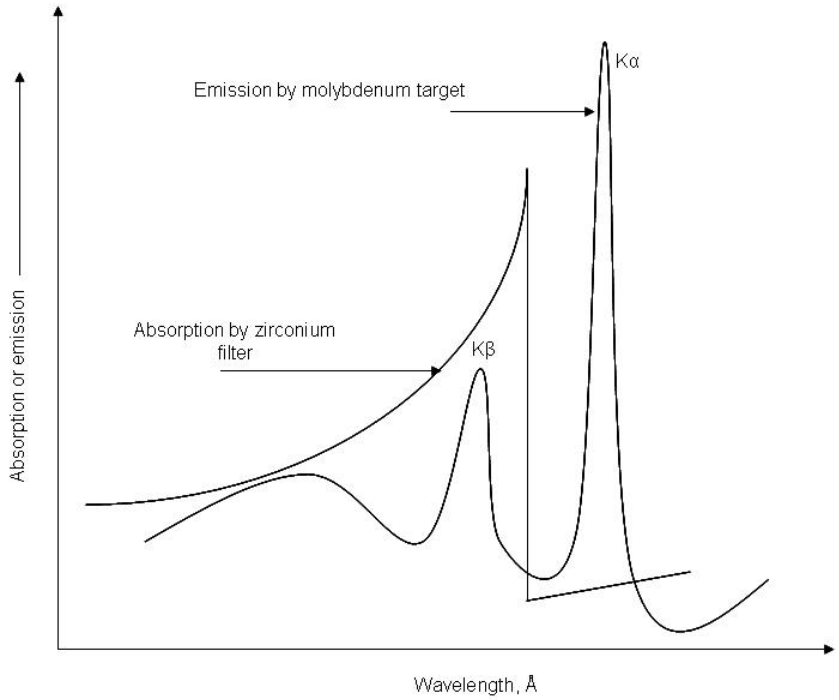


Figure 4: Monochromatic light produce by absorption of unwanted emissions.

Signal Converter

In x-ray diffraction, the detector is a transducer that counts the number of photons that collide into it. This photon counter gives a digital readout in number of photons per unit time.

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4.2: Unit Cells

Introduction

The construction of a simple powder diffractometer was first described by Hull in 1917[1] which was shortly after the discovery of X-rays by Wilhelm Conrad Röntgen in 1895[2]. Diffractometer measures the angles at which X-rays get reflected and thus get the structural information they contains. Nowadays resolution of this technique get significant improvement and it is widely used as a tool to analyze the phase information and solve crystal structures of solid-state materials.

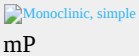
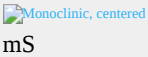
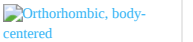
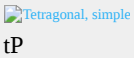
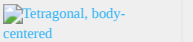
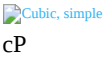
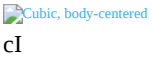
Since the wavelength of X-rays is similar to the distance between crystal layers, incident X-rays will be diffracted, interacting with certain crystalline layers and diffraction patterns containing important structural information about the crystal can be obtained. The diffraction pattern is considered the fingerprint of the crystal because each crystal structures produce unique diffraction patterns and every phase in a mixture produces its diffraction pattern independently. We can grind bulk samples into fine powders, which are typical under 10 μm,[2] as samples in powder X-ray Diffraction (XRD). Unlike single crystal X-ray diffraction (X-ray Crystallography) technique, the sample will distribute evenly at every possible orientation and powder XRD collects one-dimensional information, which is a diagram of diffracted beam intensity vs. Bragg angle θ, rather than three-dimensional information.

Unit cells

“Crystals are built up of regular arrangements of atoms in three dimensions; these arrangements can be represented by a repeat unit or motif called the unit cell.”[2] In crystallography, all the crystal unit cells can be classified into 230 space groups. Some basic knowledge about crystallography is necessary for a well understanding of powder XRD technique. In crystallography, the basic possible classifications are: 6 crystal families, 7 crystal systems, 5 centering position, 14 Bravais lattices and 32 crystal classes.

Based on the angles and the length of the axes sides, unit cell can be divided into 6 crystal families, which are cubic, tetragonal, hexagonal, orthorhombic, monoclinic and triclinic. As the hexagonal family can have two different appearances, we can divide it into two systems which are trigonal lattice and hexagonal lattice. That is how the 7 crystal systems generate. If forget the shape of lattice and just consider the atoms' positions, we can divide the lattices into primitive lattices and non-primitive ones. A primitive lattice (also defined as simple) is the lattice with the smallest possible atomic coordination number,[2] e.g. when eight atoms lie in the eight corners. And all the other lattices are called non-primitive lattice. Based on the three-dimension position of the atoms in the unit cell, we can divided the non-primitive lattice into three types: face centered (F), side centered (C), body centered (I) and based centered(R).

			14 Bravais lattices
Crystal family	Lattice system	Point group	

		Primitive (P)	Side-centered (C)	Body-centered (I)	Face-centered (F)
Triclinic (a)	C_i	 aP			
Monoclinic (m)	C_{2h}	 mP	 mS		
Orthorhombic (o)	D_{2h}	 oP	 oS	 oI	 oF
Tetragonal (t)	D_{4h}	 tP		 tI	
Hexagonal (h) Rhombohedral	D_{3d}	 hR			
Hexagonal	D_{6h}	 hP			
Cubic (c)	O_h	 cP		 cI	 cF

The 32 crystal classes refer to 32 crystallographic point group classified by the possible symmetric operations, which are rotation, reflection and inversion. You may wonder why only 32 possible point groups. The answer is crystallographic restriction, which means crystal systems can only have 5 kinds of rotation axes: 1-fold, 2-fold, 3-fold, 4-fold and 6-fold. Only the permissible rotation axes allow unit cells to grow uniformly without any openings among them.

The 230 space groups are combinations of 14 Bravais lattice and 32 crystal classes. Those space groups are generated from translations of related Bravais lattice and glide planes and/or screw axes of relative crystal classes. They are represented by Hermann-Mauguin notation. For example, space group 62, P_{nma} is derived from D_{2h} crystal class. P indicated it is primitive structure and n, m, a stand for a diagonal glide plane, a mirror plane and a axial glide planes. The space group belongs to orthorhombic crystal family.

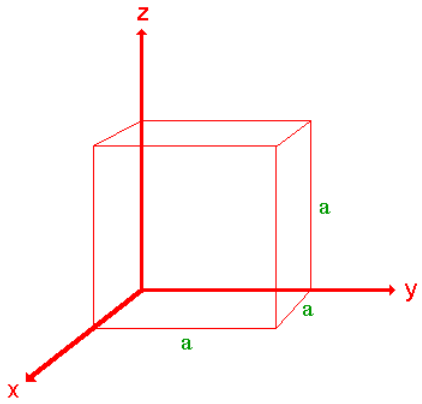
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4.3: Miller Indices (hkl)

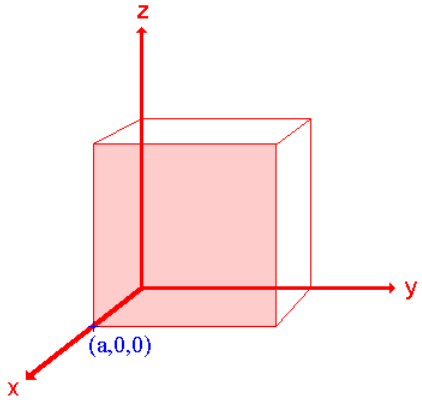
Miller indices

The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices (*hkl*), which are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

The following treatment of the procedure used to assign the Miller Indices is a simplified one and only a **cubic** crystal system (one having a cubic unit cell with dimensions a x a x a) will be considered.



The procedure is most easily illustrated using an example so we will first consider the following surface/plane:



Step 1: *Identify the intercepts on the* x- , y- *and* z- *axes.*

In this case the intercept on the x-axis is at x = a (at the point (a,0,0)), but the surface is parallel to the y- and z-axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the x- , y- and z-axes are thus **a , ∞ , ∞**.

Step 2: Specify the intercepts in fractional co-ordinates

Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (x,y,z) in a unit cell of dimensions a x b x c has fractional co-ordinates of (x/a , y/b , z/c). In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant, a. This gives

Fractional Intercepts = **a/a , ∞/a, ∞/a** i.e. **1 , ∞ , ∞**.

Step 3: Take the reciprocals of the fractional intercepts

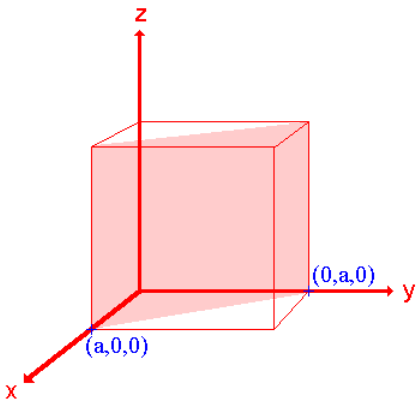
This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are also enclosed within standard brackets (….) when one is specifying a unique surface such as that being considered here.

The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding Miller Indices **(100)**.

So the surface/plane illustrated is the (100) plane of the cubic crystal.

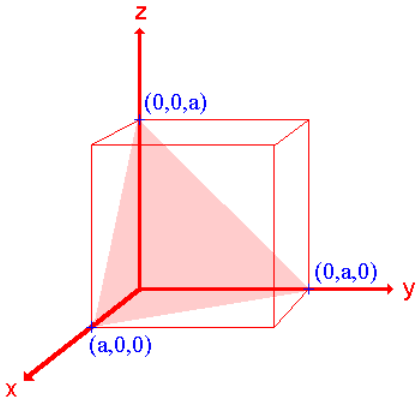
Other Examples

1. The (110) surface



Assignment
Intercepts: a , a , ∞
Fractional intercepts: 1 , 1 , ∞
Miller Indices: **(110)**

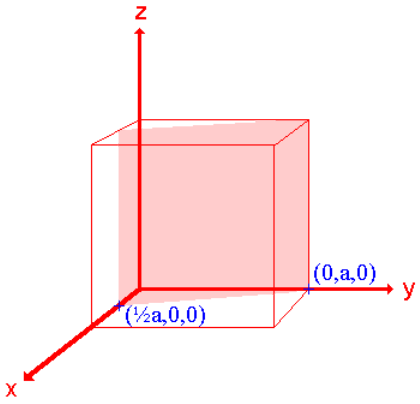
2. The (111) surface



Assignment
Intercepts: a , a , a
Fractional intercepts: 1 , 1 , 1
Miller Indices: **(111)**

The (100), (110) and (111) surfaces considered above are the so-called low index surfaces of a cubic crystal system (the "low" refers to the Miller indices being small numbers - 0 or 1 in this case). These surfaces have a particular importance but there an infinite number of other planes that may be defined using Miller index notation. We shall just look at one more …

3. The (210) surface



Assignment
Intercepts: ½ a , a , ∞
Fractional intercepts: ½ , 1 , ∞
Miller Indices: **(210)**

Structure factor

The diffraction pattern appears as dots in patterns. The circles in the diffraction patterns with smaller radii correspond to smaller h, k, l values. In certain types of unit cells, not all the lattice planes will have their diffraction observed, which is usually called a systematic absence, because the diffracted beam may happen to be out of phase by 180° and the overall intensity is zero. Structure factor, F_{hkl}, can decide the systematic absences and intensities. Systematic absences arise when F=0, so no diffraction is observed. For example:

For a fcc crystal, $F_{hkl}=f\{1+e^{\pi i(h+l)}+e^{\pi i(k+l)}+e^{\pi i(h+k)}\}$. When h, k, l are all odd or all even, F=4f. For the other situation, F=0 and thus diffraction intensity will also be zero. Structure factor is important in the structure determination step because it helps understand the Miller indices and intensities of diffraction peaks. The other common rules for reflection to be observed are as follows:

Lattice type	Rule for reflection to be observed
Primitive, P	None
Body centered, I	hkl: h+k+l=2n
Face centered, F	hkl: h, k, l either all odd or all even
Side centered, C	hkl: h+k=2n
Rhombohedral, R	hkl: -h+k+l=3n or (h-k+l=3n)

Further notes:

i. in some instances the Miller indices are best multiplied or divided through by a common number in order to simplify them by, for example, removing a common factor. This operation of multiplication simply generates a parallel plane which is at a different distance from the origin of the particular unit cell being considered. e.g. (200) is transformed to (100) by dividing through by 2 .
ii. if any of the intercepts are at negative values on the axes then the negative sign will carry through into the Miller indices; in such cases the negative sign is actually denoted by overstriking the relevant number. e.g. (00-1) is instead denoted by $(00\bar{1})$
iii. in the *hcp* crystal system there are four principal axes; this leads to four Miller Indices e.g. you may see articles referring to an *hcp* (0001) surface. It is worth noting, however, that the intercepts on the first three axes are necessarily related and not completely independent; consequently the values of the first three Miller indices are also linked by a simple mathematical relationship.

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- Roger Nix (Queen Mary, University of London)

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4.4: Sample and data collection

Crystallization

In order to run an X-ray diffraction experiment, one must first obtain a crystal. In organometallic chemistry, a reaction might work but when no crystals form, it is impossible to characterize the products. Crystals are grown by slowly cooling a supersaturated solution. Such a solution can be made by heating a solution to decrease the amount of solvent present and to increase the solubility of the desired compound in the solvent. Once made, the solution must be cooled gradually. Rapid temperature change will cause the compound to crash out of solution, trapping solvent and impurities within the newly formed matrix. Cooling continues as a seed crystal forms. This crystal is a point where solute can deposit out of the solution and into the solid phase. Solutions are generally placed into a freezer (-78 ºC) in order to ensure all of the compound has crystallized. One way to ensure gradual cooling in a -78 ºC freezer is to place the container housing the compound into a beaker of ethanol. The ethanol will act as a temperature buffer, ensuring a slow decrease in the temperature gradient between the flask and the freezer. Once crystals are grown, it is imperative that they remain cold as any addition of energy will cause a disruption of the crystal lattice, which will yield bad diffraction data. The result of an organometallic chromium compound crystallization can be seen below.

Mounting the Crystal

Due to the air-sensitivity of most organometallic compounds, crystals must be transported in a highly viscous organic compound called paratone oil. Crystals are abstracted from their respective container by dabbing the end of a spatula with the paratone oil and then sticking the crystal onto the oil. Although there might be some exposure of the compounds to air and water, crystals can withstand more exposure than solution can before degrading. On top of serving to protect the crystal, the paratone oil also serves as the glue to bind the crystal to the mount.

Rotating Crystal Method

To describe the periodic, three dimensional nature of crystals, the Laue equations are employed:

$$a(\cos\ \alpha_n - \cos\alpha_o) = h\lambda \tag{4.4.1}$$

$$b(\cos\ \beta_n - \cos\beta_o) = k\lambda \tag{4.4.2}$$

$$c(\cos\ \gamma_n - \cos\gamma_o) = l\lambda \tag{4.4.3}$$

where a, b, and c are the three axes of the unit cell, α_o, β_o, and γ_o are the angles of incident radiation, and α_n, β_n, and γ_n are the angles of the diffracted radiation. A diffraction signal (constructive interference) will arise when h, k, and l are integer values. The rotating crystal method employs these equations. A crystal is exposed to X-ray radiation as it rotates around one of its unit cell axis. The beam strikes the crystal at a 90 degree angle. Using Bragg's Law, we see that if θ_o is 90 degrees, then $\cos\theta_o = 0$. For the equation to hold true, we can set h=0, granted that \theta= 90. The above three equations will be satisfied at various points as the crystal rotates. This gives rise to a diffraction pattern.

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4.5: Crystallography quick reference

The branch of science devoted to the study of molecular and crystalline structure and properties, with far-reaching applications in mineralogy, chemistry, physics, mathematics, biology and materials science.

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4.5.1.1: Abelian group

An **abelian group**, also called a *commutative group*, is a group (G, *) such that

$$g_1 * g_2 = g_2 * g_1$$

for all g_1 and g_2 in G, where $*$ is a binary operation in G. This means that the order in which the binary operation is performed does not matter, and any two elements of the group commute.

Groups that are not commutative are called **non-abelian** (rather than non-commutative).

Abelian groups are named after Niels Henrik Abel.

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4.5.1.2: Absolute structure

The spatial arrangement of the atoms of a physically identified non-centrosymmetric crystal and its description by way of unit-cell dimensions, space group, and representative coordinates of all atoms.

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4.5.1.3: Affine Isomorphism

Each symmetry operation of crystallographic group in E^3 may be represented by a 3×3 matrix **W** (the *linear part*) and a vector **w**. Two crystallographic groups $G_1 = \{(\mathbf{W}_{1i},\mathbf{w}_{1i})\}$ and $G_2 = \{(\mathbf{W}_{2i},\mathbf{w}_{2i})\}$ are called **affine isomorphic** is there exists a non-singular 3×3 matrix **A** and a vector **a** such that:

$G_2 = \{(\mathbf{A},\mathbf{a})(\mathbf{W}_{1i},\mathbf{w}_{1i})(\mathbf{A},\mathbf{a})^{-1}\}$

Two crystallographic groups are affine isomorphic if and only if their arrangement of symmetry elements may be mapped onto each other by an affine mapping of E^3. Two affine isomorphic groups are always isomorphic.

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4.5.1.4: Affine mapping

An **affine mapping** is any mapping that preserves collinearity and ratios of distances: if three points belong to the same straight line, their images under an affine transformation also belong to the same line. Moreover, the middle point is also conserved under the affine mapping. By contrast, angles and lengths in general are not kept constant by an affine mapping.

Under an affine mapping:

- parallel lines remain parallel;
- concurrent lines remain concurrent (images of intersecting lines intersect);
- the ratio of length of segments of a given line remains constant;
- the ratio of areas of two triangles remains constant;
- ellipses, parabolas and hyperbolas remain ellipses, parabolas and hyperbolas respectively;
- barycenters of polygons map into the corresponding barycenters.

Geometric contraction, expansion, dilation, reflection, rotation, shear, similarity transformations, spiral similarities, and translation are all affine transformations, as are their combinations. Affine mappings that keep also distances and angles are called Euclidean mappings.

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4.5.1.5: Aperiodic crystal

A *periodic crystal* is a structure with, ideally, sharp diffraction peaks on the positions of a *reciprocal lattice*. The structure then is invariant under the translations of the *direct lattice*. Periodicity here means *lattice periodicity*. Any structure without this property is *aperiodic*. For example, an amorphous system is aperiodic. An *aperiodic crystal* is a structure with sharp diffraction peaks, but without lattice periodicity. Therefore, amorphous systems are not aperiodic crystals. The positions of the sharp diffraction peaks of an aperiodic crystal belong to a *vector module* of finite rank. This means that the diffraction wave vectors are of the form

$$\mathbf{k} = \sum_{i-1}^{n} h_i \mathbf{a}_i^*, (integer\ h_i)$$

The basis vectors a_i^* are supposed to be independent over the rational numbers, i.e. when a linear combination of them with rational coefficients is zero, all coefficients are zero. The minimum number of basis vectors is the *rank* of the vector module. If the rank *n* is larger than the space dimension, the structure is not periodic, but aperiodic.

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4.5.1.6: Aristotype

An aristotype is a high-symmetry structure type that can be viewed as an idealized version of a lower-symmetry structure. It was introduced by Helen Megaw in relation to perovskites, where it is still mostly used. The cubic perovskite structure (which is adopted at most by half a dozen compounds) is regarded as the aristotype for the vast array of other lower-symmetry perovskites. The lower-symmetry structure is called **hettotype**.

After Buerger, aristotypes are also known as **basic structures** and hettotypes as **derivative structures**.

Originally, an aristotype is a printing-out process using paper coated with silver chloride in gelatin; now, any such process using silver salts in either collodion or gelatin; also, a print so made.

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4.5.1.7: Arithmetic crystal class

The **arithmetic crystal classes** are obtained in an elementary fashion by combining the geometric crystal classes and the corresponding types of Bravais lattices. For instance, in the monoclinic system, there are three geometric crystal classes, 2, *m* and 2/*m*, and two types of Bravais lattices, *P* and *C*. There are therefore six monoclinic arithmetic crystal classes. Their symbols are obtained by juxtaposing the symbol of the geometric class and that of the Bravais lattice, in that order: 2*P*, 2*C*, *mP*, *mC*, 2/*mP*, 2/*mC* (note that in the space group symbol the order is inversed: *P*2, *C*2, etc...). In some cases, the centering vectors of the Bravais lattice and some symmetry elements of the crystal class may or may not be parallel; for instance, in the geometric crystal class *mm* with the Bravais lattice *C*, the centering vector and the two-fold axis may be perpendicular or coplanar, giving rise to two different arithmetic crystal classes, *mm*2*C* and 2*mmC* (or *mm*2*A*, since it is usual to orient the two-fold axis parallel to *c*), respectively. There are 13 two-dimensional arithmetic crystal classes and 73 three-dimensional arithmetic crystal classes that are listed in the attached **table**. Space groups belonging to the same geometric crystal class and with the same type of Bravais lattice belong to the same arithmetic crystal class; these are therefore in one to one correspondence with the symmorphic space groups.

The group-theoretical definition of the arithmetic crystal classes is given in Section 8.2.3 of *International Tables of Crystallography, Volume A.*

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4.5.1.8: Asymmetric Unit

An asymmetric unit of a space group is a simply connected smallest closed part of space from which, by application of all symmetry operations of the space group, the whole space is filled. This implies that:

- mirror planes must form boundary planes of the asymmetric unit;
- rotation axes must form boundary edges of the asymmetric unit;
- inversion centers must either form vertices of the asymmetric unit or be located at the midpoints of boundary planes or boundary edges.

These restrictions do not hold for screw axes and glide planes.

The term "asymmetric unit" does not mean that this region has an asymmetric shape. In mathematics it is called fundamental region or fundamental domain.

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4.5.1.9: Automorphism

An isomorphism from a group $(G,*)$ to itself is called an **automorphism** of this group. It is a bijection $f : G \rightarrow G$ such that

$$f(g) * f(h) = f(g * h)$$

An automorphism preserves the structural properties of a group, e.g.:

- The identity element of G is mapped to itself.
- Subgroups are mapped to subgroups, normal subgroups to normal subgroups.
- Conjugacy classes are mapped to conjugacy classes (the same or another).
- The image $f(g)$ of an element g has the same order as g.

The composition of two automorphisms is again an automorphism, and with composition as binary operation the set of all automorphisms of a group G, denoted by **Aut(*G*)**, forms itself a group, the *automorphism group* of G.

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4.5.1.10: Laue classes

The Laue classes correspond to the eleven centrosymmetric crystallographic point groups. When absorption is negligible and Friedel's law applies, it is impossible to distinguish by diffraction between a centrosymmetric point group and one of its non-centrosymmetric subgroups.

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Laue classes	Non-centrosymmetric groups having the same Laue class
$\bar{1}$	1
2/*m*	2, *m*
mmm	222, 2*mm*
$\bar{3}$	3
$\bar{3}m$	32, 3*m*
4/*m*	4, $\bar{4}$
4/*mmm*	422, $\bar{4}2m$, 42*m*
6/*m*	6, $\bar{6}$
6/*mmm*	622, $\bar{6}2m$, 62*m*
$m\bar{3}$	23
$m\bar{3}m$	432, $\bar{4}32$

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4.5.1.100: Friedel's law

Friedel's law, or rule, states that the intensities of the *h*, *k*, *l* and $\bar{h}, \bar{k}, \bar{l}$ reflections are equal. This is true either if the crystal is centrosymmetric or if no resonant scattering is present. It is in that case not possible to tell by diffraction whether an inversion center is present or not. The apparent symmetry of the crystal is then one of the eleven Laue classes.

The reason for Friedel's rule is that the diffracted intensity is proportional to the square of the modulus of the structure factor, $|F_h|^2$, according to the geometrical, or kinematical theory of diffraction. It depends similarly on the modulus of the structure factor according to the dynamical theory of diffraction. The structure factor is given by:

$$F_h = \Sigma_j f_j \exp -2\pi i \bold{h}.\bold{r}_j$$

where f_j is the atomic scattering factor of atom *j*, **h** the reflection vector and $\bold{r}_j$ the position vector of atom *j*. There comes:

$$|F_h|^2 = F_h F_h^* = F_h F_{\bar{h}} = |F_{\bar{h}}|^2$$

if the atomic scattering factor, f_j, is real. The intensities of the *h*, *k*, *l* and $\bar{h}, \bar{k}, \bar{l}$ reflections are then equal. If the crystal is absorbing, however, due to resonant scattering, the atomic scattering factor is complex and

$$F_{\bar{h}} \neq F_h^*$$

The reflections *h*, *k*, *l* and $\bar{h}, \bar{k}, \bar{l}$ are called a Friedel pair. They are used in the resolution of the phase problem for the solution of crystal structures and in the determination of absolute structure.

History

Friedel's law was stated by G. Friedel (1865-1933) in 1913 (Friedel G., 1913, *Sur les symétries cristallines que peut révéler la diffraction des rayons X.*, *C.R. Acad. Sci. Paris*, **157**, 1533-1536.

See also

Absolute structure

Section 3.1 of *International Tables of crystallography, Volume A*

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4.5.1.101: Geometric crystal class

Geometric crystal classes (or simply 'crystal classes') classify the symmetry groups of the external shape of macroscopic crystals, namely according to the morphological symmetry. There are 10 two-dimensional geometric crystal classes and 32 three-dimensional geometric crystal classes, in one to one correspondence with the 10 and 32 types of point groups in E^2 and E^3, respectively.

See also

- Section 8.2.4 of *International Tables for Crystallography, Volume A*

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4.5.1.102: Geometric element

A **geometric element** is an element in space (plane, line, point, or a combination of these) about which asymmetry operation is performed. Geometric elements are classified on the basis of the dimensionality N of the space on which they act, the upper limit on the dimensionality of the symmetry element being N-1.

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4.5.1.103: Voronoi domain

The Voronoi domain (or 'cell', or 'region') is the name given in mathematics to the Wigner-Seitz cell. Voronoi domains are in the form of polyhedra and are classified according to their topological properties ; one distinguishes five types of Voronoi polyhedra (see Section 9.1.6 of *International Tables of Crystallography, Volume A*.

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4.5.1.104: Group

A set *G* equipped with a binary operation *: *G x G* → *G*, assigning to a pair *(g,h)* the product *g*h* is called a **group** if:

1. The operation is *associative*, i.e. *(a*b)*c = a*(b*c)*.
2. *G* contains an *identity element* (*neutral element*) *e*: *g*e = e*g = g* for all *g* in *G*
3. Every *g* in *G* has an *inverse element h* for which *g*h = h*g = e*. The inverse element of *g* is written as g^{-1}.

Often, the symbol for the binary operation is omitted, the product of the elements *g* and *h* is then denoted by the concatenation *gh*.

The binary operation need not be commutative, i.e. in general one will have *g*h ≠ h*g*. In the case that *g*h = h*g* holds for all *g,h* in *G*, the group is an Abelian group.

A group *G* may have a finite or infinite number of elements. In the first case, the number of elements of *G* is the **order** of *G*, in the latter case, *G* is called an **infinite group**. Examples of infinite groups are space groups and their translation subgroups, whereas point groups are finite groups.

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4.5.1.105: Weissenberg complex

A **Weissenberg complex** is a lattice complex for which the multiplicity does not decrease for any special values of the coordinates. Weissenberg complexes can simulate invariant lattice complexes as limiting complexes.

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4.5.1.106: Group homomorphism

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4.5.1.107: Wigner-Seitz cell

The Wigner-Seitz cell is a a polyhedron obtained by connecting a lattice point *P* to all other lattice points and drawing the planes perpendicular to these connecting lines and passing through their midpoints (Figure 1). The polyhedron enclosed by these planes is the Wigner-Seitz cell. This construction is called the *Dirichlet* construction. The cell thus obtained is a primitive cell and it is possible to fill up the whole space by translation of that cell.

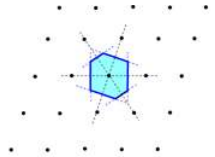


Figure 1 Wigner-Seitz cell.
Shaded: domain of influence.

The Wigner-Seitz cell of a body-centered cubic lattice *I* is a cuboctahedron (Figure 2) and the Wigner-Seitz cell of a face-centered cubic lattice *F* is a rhomb-dodecahedron (Figure 3). In reciprocal space this cell is the first Brillouin zone. Since the reciprocal lattice of body-centered lattice is a face-centered lattice and reciprocally, the first Brillouin zone of a body-centered cubic lattice is a rhomb-dodecahedron and that of a face-centered cubic lattice is a cuboctahedron.

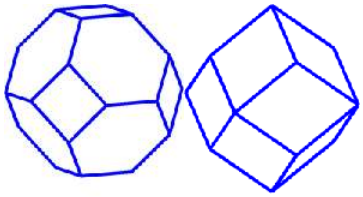


Figure 2. Figure 3.

The inside of the Wigner-Seitz cell has been called domain of influence by Delaunay (1933). It is also called Dirichlet domain or Voronoi domain. The domain of influence of lattice point *P* thus consists of all points *Q* in space that are closer to this lattice point than to any other lattice point or at most equidistant to it (such that $\mathbf{OP} \leq |\mathbf{t} - \mathbf{OP}|$ for any vector $\mathbf{t} \in L$).

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4.5.1.108: Group isomorphism

A **group isomorphism** is a special type of group homomorphism. It is a mapping between two groups that sets up a one-to-one correspondence between the elements of the groups in a way that respects the respective group operations. If there exists an isomorphism between two groups, then the groups are called **isomorphic**. Isomorphic groups have the same properties and the same structure of their multiplication table.

Let $(G, *)$ and $(H, \#)$ be two groups, where "*" and "#" are the binary operations in G and H, respectively. A *group isomorphism* from $(G, *)$ to $(H, \#)$ is a bijection from G to H, *i.e.* a bijective mapping $f : G \to H$ such that for all u and v in G one has

$$f(u * v) = f(u) \# f(v).$$

Two groups $(G, *)$ and $(H, \#)$ are isomorphic if an isomorphism between them exists. This is written:

$$(G, *) \cong (H, \#)$$

If $H = G$ and the binary operations # and * coincide, the bijection is an automorphism.

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4.5.1.109: Wyckoff position

A **Wyckoff position** of a space group G consists of all points *X* for which the site-symmetry groups are conjugate subgroups of G.

Each Wyckoff positon of a space group is labeled by a letter which is called the *Wyckoff letter*.

The number of different Wyckoff positions of each space group is finite, the maximal numbers being 9 for plane groups (realized in *p*2*mm*) and 27 for space groups (realized in *Pmmm*).

There is a total of 72 Wyckoff positions in plane groups and 1731 Wyckoff positions in space groups.

The transfer of Wyckoff positions from individual space groups to space-group types is not unique because Wyckoff positions with the same type of site-symmetry group may be exchanged in different space groups of the same type. This is no longer true when one makes use of Wyckoff sets.

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4.5.1.11: Local symmetry

A motion of E^n mapping onto itself a subdomain of a crystal pattern but not the whole crystal pattern is called a **local symmetry operation**. It may be crystallographic or noncrystallographic depending on whether or not it is possible to extend the subdomain to an *n*-dimensional crystal pattern invariant under the motion.

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4.5.1.110: H centered cell

The **H centered cell** (**triple hexagonal cell**) is an alternative description of the hexagonal Bravais lattice. From the conventional *hP* cell one obtains the *hH* cell by taking the new basis vectors by means of one of the following transformation matrices, which give three possible orientations of the *hH* cell with respect to the *hP* cell:

$$H_1: 110/\text{-}120/001\ H_2: 2\text{-}10/110/001\ H_3: 1\text{-}20/2\text{-}10/001$$

The resulting *hH* cell has centering nodes at 1/3,2/3,0 and 2/3,1/3,0.

Secondary and tertiary elements in the *hP* cell are exchanged in the *hH* cell. For example, the space-group symbol *P*3*m*1 become *H*31*m* when the triple cell is used.

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4.5.1.111: Wyckoff set

A *Wyckoff set* with respect to a space group *G* is the set of all points *X* for which the site-symmetry groups are conjugate subgroups of the normalizer *N* of *G* in the group of all affine mappings.

Any Wyckoff position of *G* is transformed onto itself by all elements of *G*, but not necessarily by the elements of *N*. Any Wyckoff set of *G* is instead transformed onto itself also by those elements of *N* that are contained in *G*.

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4.5.1.112: Image

Let X and Y be sets, f be the function $f : X \rightarrow Y$, and x be some member of X. Then the **image** of x under f, denoted $f(x)$, is the unique member y of Y that f associates with x.

The **image** of a subset $A \subseteq X$ under f is the subset of Y defined by $f[A] = \{y \in Y \mid y = f(x) \text{ for some } x \in A\}$.

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4.5.1.113: Lattice

A **lattice** in the vector space $\mathbf{V^n}$ is the set of all integral linear combinations $\mathbf{t} = u_1\mathbf{a_1} + u_2\mathbf{a_2} + ... + u_k\mathbf{a_k}$ of a system ($\mathbf{a_1}$, $\mathbf{a_2}$, ... , $\mathbf{a_k}$) of linearly independent vectors in $\mathbf{V^n}$.

If $k = n$, i.e. if the linearly independent system is a **basis** of $\mathbf{V^n}$, the lattice is often called a **full lattice**. In crystallography, lattices are almost always full lattices, therefore the attribute "full" is usually suppressed.

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4.5.1.114: Lattice system

A **lattice system** of space groups contains complete Bravais flocks. All those Bravais flocks which intersect exactly the same set of geometric crystal classes belong to the same lattice system.

All those Bravais flocks belong to the same lattice system for which the Bravais classes belong to the same (holohedral) geometric crystal class.

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4.5.1.115: Bravais flock

Space groups that are assigned to the same Bravais class belong to the same **Bravais flock of space groups**.

The introduction of the concept of Bravais flock is necessary in order to classify space groups on the basis of their Bravais type of lattice, independently from any accidental metric of the lattice.

An orthorhombic crystal may have accidentally $a = b$ have a tetragonal lattice not because of symmetry restrictions but just by accident. If the Bravais types of lattices were used directly to classify space group, such a crystal would be go in another category with respect to an orthorhombic crystal without specialized metric. The concept of Bravais flock solves this ambiguity.

A space group G is *assigned* to a Bravais class on the basis of the corresponding point group P and the arithmetic crystal class associated with it:

- If the arithmetic crystal class of G is a Bravais class, then G is assigned to that Bravais class;
- if the arithmetic crystal class of G is not a Bravais class, then the Bravais class to which G is assigned is obtained as follows:
  - those Bravais classes are retained whose point group B is such that P is a subgroup of B;
  - G is assigned to that Bravais class, among those selected above, for which the ratio of the order of the point groups of B and of P is minimal.

For example, a space group of type $I4_1$ belongs to the arithmetic crystal class $4I$, to which two Bravais class can be associated, $4/mmmI$ and $\boldsymbol{m\bar{3}mI}$. The second condition uniquely assigns G to the Bravais flock of $4/mmmI$, despite the fact that the Bravais class of the lattice may be $\boldsymbol{m\bar{3}mI}$ as a result of accidental symmetry.

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4.5.1.12: Brillouin zones

A *Brillouin Zone* is a particular choice of the unit cell of the reciprocal lattice. It is defined as the Wigner-Seitz cell (also called *Dirichlet* or *Voronoi Domain*) of the reciprocal lattice. It is constructed as the set of points enclosed by the *Bragg planes*, the planes perpendicular to a connection line from the origin to each lattice point and passing through the midpoint. Alternatively, it is defined as the set of points closer to the origin than to any other reciprocal lattice point. The whole reciprocal space may be covered without overlap with copies of such a Brillouin Zone.

For high-symmetry lattices one introduces sometimes the notion of *n-th Brillouin Zone*. This is the set of points one reaches with a straight line from the origin and passing through *n*-1 Bragg Planes. In this terminology, the Brillouin Zone defined above is the first Brillouin Zone. The *n*-th Brillouin Zone is a shell around lower Brillouin Zones and its shape becomes for higher values of *n* rapidly rather complicated.

Vectors in the Brillouin Zone or on its boundary characterize states in a system with lattice periodicity, e.g. phonon or electron states. States are non-equivalent if they belong to different vectors in a unit cell of the reciprocal lattice. This is not necessarily the Brillouin Zone. Especially, for low-symmetry systems Brillouin Zones are sometimes difficult to visualize, and another choice of unit cell may be useful, e.g. the parallelepiped spanned by the basis vectors.

The Brillouin Zone boundary consists of pieces of Bragg planes. Since two points on the boundary may differ by a reciprocal lattice vector, only a part of the boundary may be used for characterization of states. There is no simple rule for that choice. Dispersion curves at the zone boundary have either a maximum or minimum there or they merge with other curves giving rise to a change of degeneracy.

See also

Section 2.2 of *International Tables of Crystallography, Volume D*

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4.5.1.13: Mapping

The term **mapping** is often used in mathematics as a synonym of *function*. In crystallography it is particularly used to indicate a *transformation*.

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4.5.1.14: Center

The **center** (or **centre**) of a group *G* is the set *Z(G)* = { *a* in *G* : *a*g* = *g*a* for all *g* in *G* } of elements commuting with all elements of *G*. The center is an Abelian group.

The center of a group *G* is always a normal subgroup of *G*, namely the kernel of the homomorphism mapping an element *a* of *G* to the inner automorphism f_a: $g \rightarrow aga^{-1}$.

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4.5.1.15: Centralizer

The **centralizer** $C_G(g)$ of an element g of a group G is the set of elements of G which commute with g:

$$C_G(g) = \{x \in G : xg = gx\}.$$

If H is a subgroup of G, then $C_H(g) = C_G(g) \cap H$.

More generally, if S is any subset of G (not necessarily a subgroup), the centralizer of S in G is defined as

$$C_G(S) = \{x \in G : \forall\ s \in S, xs = sx\}.$$

If $S = \{g\}$, then $C(S) = C(g)$.

C(S) is a subgroup of G; in fact, if x, y are in C(S), then $xy^{-1}s = xsy^{-1} = sxy^{-1}$.

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4.5.1.16: Complex

A **complex** is a subset obtained from a group by choosing part of its elements in such a way that the closure property of groups is not respected. Therefore, a complex is not a group itself.

A typical example of complexes is that of cosets. In fact, a coset does not contain the identity and therefore it is not a group.

A subgroup is a particular case of complex that obeys the closure property and is a group itself.

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4.5.1.17: Conjugacy class

If g_1 and g_2 are two elements of a group G, they are called **conjugate** if there exists an element g_3 in G such that:

$$g_3 g_1 g_3^{-1} = g_2.$$

Conjugacy is an equivalence relation and therefore partitions G into equivalence classes: every element of the group belongs to precisely one conjugacy class

The equivalence class that contains the element g_1 in G is

$$Cl(g_1) = \{ g_3 g_1 g_3^{-1} | \, g_3 \in G\}$$

and is called the **conjugacy class** of g_1. The **class number** of G is the number of conjugacy classes.

The classes $Cl(g_1)$ and $Cl(g_2)$ are equal if and only if g_1 and g_2 are conjugate, and disjoint otherwise.

For Abelian groups the concept is trivial, since each element forms a class on its own.

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4.5.1.18: Coset

If G is a group, H a subgroup of G, and g an element of G, then

gH = { gh : h ∈ H } is a **left coset of H** in *G*

Hg = { hg : h ∈ H } is a **right coset of H** in *G*.

The decomposition of a group into cosets is unique. Left coset and right cosets however in general do not coincide, unless H is a normal subgroup of G.

Any two left cosets are either identical or disjoint: the left cosets form a partition of G, because every element of G belongs to one and only one left coset. In particular the identity is only in one coset, and that coset is H itself; this is also the only coset that is a subgroup. The same holds for right cosets.

All left cosets and all right cosets have the same order (number of elements, or cardinality), equal to the order of H, because H is itself a coset. Furthermore, the number of left cosets is equal to the number of right cosets and is known as the **index** of H in G, written as [G : H] and given by Lagrange's theorem:

|G|/|H| = [G : H].

Cosets are also sometimes called *associate complexes*.

Example

The coset decomposition of the twin lattice point group with respect to the point group of the individual gives the different possible twin laws. Each element in a coset is a possible twin operation.

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4.5.1.19: Crystallographic orbit

In mathematics , an *orbit* is a general group-theoretical term describing any set of objects that are mapped onto each other by the action of a group. In crystallography, the concept of orbit is used to indicate a point configuration in association with its generating group.

From any point of the three-dimensional Euclidean space the symmetry operations of a given space group *G* generate an infinite set of points, called a **crystallographic orbit**. The space group *G* is called the **generating space group** of the orbit. Two crystallographic orbits are said configuration-equivalent if and only if their sets of points are identical.

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4.5.1.20: Hemihedry

The point group of a crystal is called hemihedry if it is a subgroup of index 2 of the point group of its lattice.

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4.5.1.21: Displacive modulation

For a *displacively modulated crystal phase*, the positions of the atoms are displaced from those of a basis structure with space group symmetry (an ordinary crystal). The displacements are given by the *atomic modulation function* $\mathbf{u}_j(\mathbf{r})$, where *j* indicates the *j*th atom in the unit cell of the basic structure.

$$r(n,j) \;=\; n + r_j + u_j(n + r_j).$$

The modulation function has a Fourier expansion

$$u_j(r) \;=\; \sum_k \hat{u}(k) \exp(2\pi i k.r), \;\; with \;\; k = \sum_{i=1}^{n} h_i a_i^*,$$

with finite value of *n*. If *n*=1, the modulated structure is one-dimensionally modulated. A special case of a one-dimensionally modulated structure is

$$r(n,j)_\alpha \;=\; n_\alpha + r_{j\alpha} + A_{j\alpha} \sin\left(2\pi i q.n + r_j\right) + \phi_{j\alpha}\right), (\alpha = x, y, z).$$

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4.5.1.22: Domain of influence

The domain of influence of a lattice point *P* (Delaunay 1933), or Dirichlet domain or Voronoi domain, consists of all points *Q* in space that are closer to this lattice point than to any other lattice point or at most equidistant to it, namely such that **OP** ≤|**t** - **OP**| for any vector **t** belonging to the vector lattice *L*. It is the inside of the Wigner-Seitz cell.

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4.5.1.23: Double coset

Let G be a group, and H and K be two subgroups of G. One says that the two elements $g_1 \in G$ and $g_2 \in G$ belong to the same **double coset** of G relative to H and K if there exist elements $h_i \in H$ and $k_j \in K$ such that:

$g_2 = h_i g_1 k_j$

The complex Hg_1K is called a **double coset**

The partition of G into double cosets relative to H and K is a classification, *i.e.* each $g_i \in G$ belongs to exactly one double coset. It is also a generalization of the coset decomposition, because the double coset Hg_1K contains complete left cosets of K and complete right cosets of H.

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4.5.1.24: Flack parameter

The Flack parameter is the molar fraction x in the defining equation $C = (1 - x)X + x\bar{X}$, where C represents an oriented two-domain-structure crystal, twinned by inversion, consisting of an oriented domain structure X and an oriented inverted domain structure $\bar{X}$. In reciprocal space, the Flack parameter x is defined by the structure-amplitude equation

$$G^2(h,k,l,x) = (1-x)|F(h,k,l)|^2 + x\left|F(\bar{h},\bar{k},\bar{l})\right|^2.$$

For a multidomain-structure twin of a chiral crystal structure, an equivalent Flack parameter may be calculated according to the method of Flack and Bernardinelli (1999).

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4.5.1.25: Form

For a point group P a **form** is a set of all symmetrically equivalent "elements", namely:

- in vector space, a ***crystal form*** or ***face form*** is a set of all symmetrically equivalent faces;
- in point space, a ***point form*** is a set of all symmetrically equivalent points.

The polyhedron or polygon of a point form is dual to the polyhedron of the corresponding face form, where "dual" means that they have the same number of edges but the number of faces and vertices is interchanged. The inherent symmetry of a form is a point group C which either coincides with the generating point group P or is a supergroup of it.

Forms in point groups correspond to crystallographic orbits in space groups.

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4.5.1.26: Groupoid

A **groupoid** (G,*) is a set G with a law of composition * mapping of a subset of G x G into G. The properties of a groupoid are:

- if x, y, z ∈ G and if one of the compositions (x*y)*z or x*(y*z) is defined, so is the other and they are equal; (associativity);
- if x, x' and y ∈ G are such that x*y and x'*y are defined and equal, then x = x'; (cancellation property)
- for all x ∈ G there exist elements e_x (left unit of x), e_x' (right unit of x) and x^{-1} ("inverse" of x) such that:
  - $e_x*x = x$
  - $x* e_x' = x$
  - $x^{-1}*x = e_x'$.

From these properties it follows that:

- $x* x^{-1} = e_x$, *i.e.* that that e_x is right unit for x^{-1},
- e_x' is left unit for x^{-1}
- e_x and e_x' are idempotents, *i.e.* $e_x* e_x = e_x$ and $e_x'* e_x' = e_x'$.

The concept of groupoid as defined here was introduced by Brandt (1927). An alternative meaning of groupoid was introduced by Hausmann & Ore (1937) as a set on which binary operations act but neither the identity nor the inversion are included. For this second meaning nowadays the term **magma** is used instead (Bourbaki, 1998).

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4.5.1.27: Holohedry

The point group of a crystal is called holohedry if it is identical to the point group of its lattice. In the three-dimensional space, there are seven holohedral geometric crystal classes: $\bar{1}, 2/m, mmm, \bar{3}m, 4/mmm, 6/mmm, m\bar{3}m$

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4.5.1.28: Incommensurate composite crystal

An *incommensurate composite crystal* is a compound with two or more (*N*) subsystems that are themselves modulated structures, with basis structures that are mutually incommensurate. Each subsystem (numbered by ν) has a reciprocal lattice for its basic structure with three basis vectors $\boldsymbol{a}_i^{*\nu}$. There is a basis of the vector module of diffraction spots that has at most 3*N* basis vectors $\boldsymbol{A}_j^*$ such that

$$a_i^{*\nu} = \sum_{j=1}^{n} Z_{ij}^{\nu} A_j^* \quad (i = 1, 2, 3),$$

where $\boldsymbol{Z}_{ij}^{\nu}$ are integer coefficients. If *n* is larger than the dimension of space (three), the composite crystal is an aperiodic crystal. *n* is the rank of the vector module.

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4.5.1.29: Incommensurate magnetic structure

An *incommensurate magnetic structure* is a structure in which the magnetic moments are ordered, but without periodicity that is commensurate with that of the nuclear structure of the crystal. In particular, the magnetic moments have a spin density with wave vectors that have at least one irrational component with respect to the reciprocal lattice of the atoms. Or, in the case of localized moments, the spin function $\mathbf{S}(\mathbf{n}+\mathbf{r}_j)$ (where the jth atom has position $\mathbf{r}_j$ in the unit cell) has Fourier components with irrational indices with respect to the reciprocal lattice of the crystal.

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4.5.1.30: Incommensurate modulated structure

An *incommensurate modulated crystal structure* is a modulated crystal structure, for which the modulation function has a Fourier transform of sharp peaks at wave vectors that cannot all be expressed by rational coefficients in a basis of the reciprocal lattice of the basic structure. At least one of the components of the wave vectors of the modulation with respect to the basis structure should be irrational.

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4.5.1.31: Merohedral

Merohedral is the adjectival form of merohedry and indicates a crystal that does not possess the full point symmetry of its lattice.

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4.5.1.32: Miller Indices

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4.5.1.33: Lattice complex

A *lattice complex* is the set of all point configurations that may be generated within one type of Wyckoff set. All Wyckoff positions, Wyckoff sets and types of Wyckoff sets that generate the same set of point configurations are assigned to the same lattice complex.

Concretely, two Wyckoff positions are assigned to the same lattice complex if there is a suitable transformation that maps the point configurations of the two Wyckoff positions onto each other and if their space groups belong to the same crystal family. The 72 (in E^2) or 1731 (in E^3) Wyckoff positions are classified in 51 (E^2) or 1128 (E^3) types of Wyckoff sets. They are assigned to 30 (E^2) or 402 (E^3) lattice complexes.

The name *lattice complex* comes from the fact that an assemblage of points that are equivalent with respect to a group of symmetry operations including lattice translations can be visualized as a set of equivalent lattices.

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4.5.1.34: Limiting complex

A **limiting complex** is a lattice complex L1 which forms a true subset of a second lattice complex L2. Each point configuration of L1 also belongs to L2.

L2 is called a **comprehensive complex** of L1.

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4.5.1.35: Merohedry

The point group of a crystal is called merohedry if it is a subgroup of the point group of its lattice.

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4.5.1.36: Order

If G is a group consisting of a finite number of elements, this number of elements is the **order** of G. For example, the point group m3m has order 48.

For an element g of a (not necessarily finite) group G, the **order** of g is the smallest integer n such that g^n is the identity element of G. If no such integer exists, g is of **infinite order**. For example, the rotoinversion $\bar{3}$ has order 6 and a translation has infinite order. An element of order 2 is called an **involution**.

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4.5.1.37: Mesh

In a two-dimensional pattern possessing rotational symmetry, the rotation points constitute the nodes of a net and divide the plane into regions that are called **meshes**. The number of meshes meeting at any rotation point equals twice the order of the rotation at that point.

N.B. The term **mesh** is sometimes *improperly* used to indicate a two-dimensional cell.

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4.5.1.38: Patterson methods

The family of methods employed in structure determination to derive relationships between the scattering centers in a crystal lattice when the diffraction phases are unknown. They depend upon interpretation of the *Patterson function*

$$P(uvw) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)|^2 \cos[2\pi(hu + kv + lw)]$$

to reveal interatomic vectors within the unit cell.

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4.5.1.39: Patterson vector

A real-space vector representing the difference between two position vectors locating scattering centers in a diffracting crystal lattice .

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4.5.1.40: Modulated crystal structure

A *modulated crystal structure* is a density (or atom arrangement) that may be obtained from a density (or atom arrangement) with space-group symmetry by a finite density change (or finite displacement of each atom, respectively) that is (quasi)periodic. A function or a displacement field is periodic if it is invariant under a lattice of translations. Then its Fourier transform consists of δ-peaks on a reciprocal lattice that spans the space and is nowhere dense. A quasiperiodic function has a Fourier transform consisting of δ-peaks on a vector module of finite rank. This means that the peaks may be indexed with integers using a finite number of basis vectors . If the modulation consists of deviations from the basic structure in the positions, the modulation is *displacive* (displacive modulation). When the probability distribution deviates from that in the basic structure the modulation is occupational.

See also

Model for a displacively modulated crystal structure . The basic structure is two-dimensional rectangular, with lattice constants *a* and *b*, the modulation wave vector is in the *b*-direction, the wavelength of the periodic modulation is λ such that λ/*b* is an irrational number.

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4.5.1.41: Point configuration

The concept of *point configuration* is closely related to that of crystallographic orbit, but differs from it by the fact that point configurations are detached from their generating space groups. The concept of point configuration is the basis for the definition of lattice complexes.

Two crystallographic orbits are said *configuration-equivalent* if and only if their sets of points are identical. A **point configuration** is the set of all points that is common to a class of configuration-equivalent crystallographic orbits.

This definition uniquely assigns crystallographic orbits to point configurations but not *vice versa*.

The *inherent* symmetry of a point configuration is the most comprehensive space group that maps the point configuration onto itself. One crystallographic orbit out of each class of configuration-equivalent ones stands out because its generating space group coincides with the inherent symmetry of its point configuration.

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4.5.1.42: Normalizer

Given a group G and one of its supergroups S, they are uniquely related to a third, intermediated group $N_S(G)$, called the **normalizer of G with respect to S**. $N_S(G)$ is defined as the set of all elements $\mathbf{S} \in S$ that map G onto itself by conjugation:

$$N_S(G) := \{\mathbf{S} \in S \mid \mathbf{S}^{-1}GS = G\}$$

The normalizer $N_S(G)$ may coincide either with G or with S or it may be a proper intermediate group. In any case, G is a normal subgroup of its normalizer.

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4.5.1.43: Point group

A **point group** is a group of symmetry operations all of which leave at least one point unmoved. A *crystallographic* point group is a point group that maps a point lattice onto itself: in three dimensions rotations and rotoinversions are restricted to 1, 2, 3, 4, 6 and $\bar{1}$, $\bar{2}$ (= *m*), $\bar{3}$, $\bar{4}$, $\bar{6}$ respectively.

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4.5.1.44: Normal subgroup

A subgroup H of a group G is **normal** in G (H ◃ G) if gH = Hg for any g ∈G. Equivalently, H ⊂ G is normal if and only if gHg^{-1}= H for any g ∈G, i.e., if and only if each conjugacy class of G is either entirely inside H or entirely outside H. This is equivalent to say that H is invariant under all inner automorphisms of G.

The property gH = Hg means that left and rights cosets of H in G coincide. From this one sees that the cosets form a group with the operation $g_1H * g_2H = g_1g_2H$ which is called the factor group or **quotient group** of *G* by *H*, denoted by *G/H*.

In the special case that a subgroup *H* has only two cosets in *G* (namely *H* and *gH* for some *g* not contained in *H*), the subgroup *H* is always normal in *G*.

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4.5.1.45: Point space

A mathematical model of the space in which we live is the **point space**. Its elements are points. Objects in point space may be single points; finite sets of points like the centers of the atoms of a molecule; infinite discontinuous point sets like the centers of the atoms of an ideal crystal pattern; continuous point sets like straight lines, curves, planes, curved surfaces, etc.

Objects in point space are described by means of a coordinate system referred to point chosen as the origin O. An arbitrary point P is then described by its coordinates x, y, z.

The point space used in crystallography is a Euclidean space, *i.e.* an affine space where the scalar product is defined.

Crystal structures are described in point space. The vector space is a dual of the point space because to each pair of points in point space a vector in vector space can be associated.

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4.5.1.46: OD structure

OD structures consist of slabs with their own symmetry, containing coincidence operations constituting a diperiodic group(layer group) only within individual slabs. For the entire structure these coincidence operations are only local (partial), i.e. they are valid only in a subspace of the crystal space. The ambiguity (= existence of more than one equivalent possibilities) in the stacking of slabs arises from the existence of this local symmetry, which does not appear in the space group of the structure. The resulting structure can be "ordered" (*periodic*) or "disordered" (*non-periodic*), depending on the sequence of local symmetry operations relating pairs of slabs. The set of all the operations valid in the whole crystal space constitutes a space group; by adding the set of all the operations valid in a subspace of it, one obtains a space groupoid.

In the OD theory, a central role is played by the **vicinity condition** (**VC**), which states the geometrical equivalence of layer pairs. The vicinity condition consists of three parts:

- **VC α**: VC layers are either geometrically equivalent or, if not, they are relatively few in kind
- **VC β**: translation groups of all VC layers are either identical or they have a common subgroup
- **VC γ**: equivalent sides of equivalent layers are faced by equivalent sides of adjacent layers so that the resulting pairs are equivalent.

If the position of a layer is uniquely defined by the position of the adjacent layers and by the VC, the resulting structure is fully ordered. If, on the other hand, more than one position is possible that obeys the VC, the resulting structure is an **OD structure** and the layers are **OD layers**. VC structures may thus be either fully ordered structures or OD structures. All OD structures are polytypic; the reverse may or may not be true. Equivalency depends on the choice of OD layers and also on the definition of polytypism.

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4.5.1.47: Primitive cell

A primitive cell is a unit cell built on the basis vectors of a primitive basis of the direct lattice, namely a crystallographic basis of the vector lattice **L** such that every lattice vector **t** of **L** may be obtained as an integral linear combination of the basis vectors, **a**, **b**, **c**.

It contains only one lattice point and its volume is equal to the triple scalar product (**a**, **b**, **c**).

Non-primitive bases are used conventionally to describe *centered lattices*. In that case, the unit cell is a multiple cell and it contains more than one lattice point. The multiplicity of the cell is given by the ratio of its volume to the volume of a primitive cell.

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4.5.1.48: Ogdohedry

The point group of a crystal is called ogdohedry if it is a subgroup of index 8 of the point group of its lattice.

In the three dimensional space there is only one ogdohedry: it corresponds to the geometric crystal class 3 of crystals belonging to the hexagonal lattice system (in case rhombohedral crystals, it corresponds instead to a tetartohedry).

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4.5.1.49: Priority rule

When more than one kind of symmetry element occurs for a given symmetry direction, the choice for defining the appropriate Hermann–Mauguin symbol for the space group is made in order of descending priority:

- *m*, *e*, *a*, *b*, *c*, *n*, *d*;
- rotation axes before screw axes.

There are a few exceptions to this choice:

1. For glide planes in centered monoclinic space groups, the priority rule is purposely not followed in order to bring out the relations between the three ‘cell choices’ given for each setting.
2. For orthorhombic space groups, the priority rule is applied only to the ‘standard symbol’. The symbols for the other five settings are obtained from the standard symbol by the appropriate transformations, without invoking the priority rule again.
3. Space-group types *I*222 and $I2_12_12_1$ are two distinct types. Both contain parallel twofold rotation and screw axes and thus would receive the same symbol according to the priority rule. In *I*222, the three rotation axes and the three screw axes intersect, whereas in $I2_12_12_1$ neither the three rotation axes nor the three screw axes intersect.
4. For space groups of type No. 73, the standard symbol *Ibca* was adopted, instead of *Ibaa* according to the rule, because Ibca displays the equivalence of the three symmetry directions clearly.
5. In tetragonal space groups with both *a* and *b* glide planes containing the [001] direction, the preference was given to *b*, as in *P4bm*.
6. In cubic space groups where tertiary symmetry planes with glide components 1/2, 0, 0; 0, 1/2, 0; 0, 0, 1/2 and 1/2, 1/2 , 1/2 coexist, the tertiary symmetry element was called *n* in *P* groups (instead of *a*, *b* or *c*) but *c* in *F* groups, because these symmetry elements intersect the origin.
7. Space groups of type *I*23 and $I2_13$ (199) are two distinct types of space groups. For this pair, the same arguments apply as given above for *I*222 and $I2_12_12_1$.

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4.5.1.50: Pseudo symmetry

A crystal space can in general be divided in N components S_1 to S_N. When a coincidence operation $\varphi(S_i) \rightarrow S_j$ brings the i-th component S_i to coincide with the j-th component S_j, for any i and j, φ is a symmetry operation of the space group.

Sometimes, φ brings S_i close to, but not exactly on, the position and orientation of S_j: in this case the operation mapping S_i onto S_j is not crystallographic but the linear and/or rotational deviation from a space group operation is limited. For this reason, it is preferable to describe the crystallographic operation φ as a **pseudo symmetry operation**.

Pseudo symmetry operations for the lattice play an important role in twinning, namely in the case of twinning by pseudomerohedry and twinning by reticular pseudomerohedry.

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4.5.1.51: Point symmetry

The point symmetry of a position is its site symmetry. The point symmetry, or point group of a lattice is the group of linear mappings (symmetry operations, isometries) that map the vector lattice **L** onto itself. Those geometric crystal classes to which point symmetries of lattices belong are called holohedries.

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4.5.1.52: Reciprocal lattice

The reciprocal lattice is constituted by the set of all possible linear combinations of the basis vectors **a***, **b***, **c*** of the reciprocal space. A point (*node*), *H*, of the reciprocal lattice is defined by its position vector:

$$\mathbf{OH} = \mathbf{r_{hkl}}^* = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^*.$$

If *H* is the *n*th node on the row *OH*, one has:

$$\mathbf{OH} = n\,\mathbf{OH_1} = n\,(h_1\,\mathbf{a}^* + k_1\,\mathbf{b}^* + l_1\,\mathbf{c}^*),$$

where H_1 is the first node on the row *OH* and h_1 , k_1 , l_1 are relatively prime.

The generalization of the reciprocal lattice in a four-dimensional space for incommensurate structures is described in Section 9.8 of *International Tables of Crystallography, Volume C*.

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4.5.1.53: Partial symmetry

The symmetry operations of a space group are isometries operating on the whole crystal pattern and are also called **total operations** or **global operations**. More generally, the crystal space can be divided in N components S_1 to S_N, and a coincidence operation $\varphi(S_i) \rightarrow S_j$ can act on just the i-th component S_i to bring it to coincide with the j-th component S_j. Such an operation is not one of the operations of the space group of the crystal because it is not a coincidence operation of the whole crystal space; it is not even defined, in general, for any component k different from i. It is called a **partial operation**: from the mathematical viewpoint, partial operations are space-groupoid operations.

When $i = j$, *i.e.* when the operation is $\varphi(S_i) \rightarrow S_i$ and brings a component to coincide with itself, the partial operation is of special type and is called **local**. A local operation is in fact a symmetry operation, which is defined only on a part of the crystal space: local operations may constitute a subperiodic group.

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4.5.1.54: Reciprocal Space

The basis vectors **a***, **b***, **c*** of the reciprocal space are related to the basis vectors **a**, **b**, **c** of the direct space (or crystal space) through either of the following two equivalent sets of relations:

(1)

a*. **a** = 1; **b***. **b** = 1; **c***. **c** = 1;

a*. **b** = 0; **a***. **c** = 0; **b***. **a** = 0; **b***. **c** = 0; **c***. **a** = 0; **c***. **b** = 0.

(2)

a* = (**b** × **c**)/ (**a**, **b**, **c**);

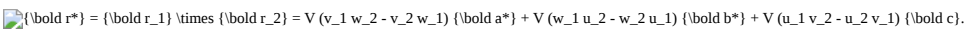
b* = (**c** × **a**)/ (**a**, **b**, **c**);

c* = (**b** × **c**)/ (**a**, **b**, **c**);

where (**b** × **c**) is the vector product of basis vectors **b** and **c** and (**a**, **b**, **c**) = *V* is the triple scalar product of basis vectors **a**, **b**and **c** and is equal to the volume *V* of the cell constructed on the vectors **a**, **b** and **c**.

The reciprocal and direct spaces are reciprocal of one another, that is the reciprocal space associated to the reciprocal space is the direct space. They are related by a Fourier transform and the reciprocal space is also called *Fourier space* or *phase space*.

The **vector product** of two direct space vectors, $\bold{r}_1 = u_1\bold{a} + v_1\bold{b} + w_1\bold{c}$ and $\bold{r}_2 = u_2\bold{a} + v_2\bold{b} + w_2\bold{c}$ is a reciprocal space vector,



Reciprocally, the vector product of two reciprocal vectors is a direct space vector.

As a consequence of the set of definitions (1), the **scalar product** of a direct space vector **r** = *u* **a** + *v* **b** + *w* **c** by a reciprocal space vector **r*** = *h* **a*** + *k* **b*** + *l* **c*** is simply:

r . **r*** = *uh* + *vk* +*wl*.

In a **change of coordinate system**, The coordinates of a vector in reciprocal space transform like the basis vectors in direct space and are called for that reason *covariant*. The vectors in reciprocal transform like the coordinates in direct space and are called *contravariant*.

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4.5.1.55: Site symmetry

The site-symmetry group (often called point symmetry) of a point is the finite group formed by the set of all symmetry operations of the space group of the crystal that leave that point invariant. It is isomorphic to a (proper or improper)subgroup of the point group to which the space group under consideration belongs. In general, the origin is a point of highest site symmetry.

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4.5.1.56: Space group

The symmetry group of a three-dimensional crystal pattern is called its **space group**. In E^2, the symmetry group of a two-dimensional crystal pattern is called its **plane group**. In E^1, the symmetry group of a one-dimensional crystal pattern is called its **line group**.

To each crystal pattern belongs an infinite set of translations **T**, which are symmetry operations of that pattern. The set of all **T** forms a group known as the **translation subgroup** T of the space group G of the crystal pattern. T is an Abelian group.

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4.5.1.57: Symmetry element

A **symmetry element** (of a given crystal structure or object) is defined as a concept with a double meaning, namely the combination of a geometric element with the set of symmetry operations having this geometric element in common (termed its *element set*). Together with the identity and the translations, for which a geometric element is not defined, the element sets cover all symmetry operations.

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4.5.1.58: Symmetry operation

A **symmetry operation** is an **isometry**, *i.e.* a transformation under which two objects, or two configurations or an object, are brought to coincide. A symmetry operation is a Euclidean mapping: to each point of the first configuration there corresponds a point of the second configuration, the distances between two points are kept by the transformation, as are the angles.

The two configurations/objects can be either congruent or enantiomorphous. Correspondingly, the symmetry operations are classed into two kinds:

- **symmetry operations of first kind**: they relate congruent objects and consist of translations, rotations and screw rotations;
- **symmetry operations of second kind**: they relate enantiomorphous objects and consist of inversion, reflections, rotoinversions, and glide reflections. There exist a 1:1 correspondence between rotoinversion and rotoreflections: the latter are more used in Schoenflies notation, whereas rotoinversions are preferred in Hermann-Mauguin notation.

A symmetry operation is performed about a symmetry element.

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4.5.1.59: Unit cell

The **unit cell** is the parallelepiped built on the vectors, **a**, **b**, **c**, of a crystallographic basis of the direct lattice. Its volume is given by the scalar triple product, $V = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ and corresponds to the square root of the determinant of the metric tensor.

If the basis is primitive, the unit cell is called the primitive cell. It contains only one lattice point. If the basis is non-primitive, the unit cell is a multiple cell and it contains more than one lattice point. The multiplicity of the cell is given by the ratio of its volume to the volume of a primitive cell.

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4.5.1.60: Polytypism

An element or compound is **polytypic** if it occurs in several structural modifications, each of which can be regarded as built up by stacking layers of (nearly) identical structure and composition, and if the modifications differ only in their stacking sequence. Polytypism is a special case of polymorphism: the two-dimensional translations within the layers are essentially preserved.

The complete definition is given in the Report of the International Union of Crystallography Ad-Hoc Committee on the Nomenclature of Disordered, Modulated and Polytype Structures: *Acta Cryst.* A**40**, 399-404(1984), "Nomenclature of Polytype Structures".

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4.5.1.61: Vector module

A *vector module* is the set of vectors spanned by a number n of basis vectors with integer coefficients. The basis vectors should be independent over the integers, which means that any linear combination

$$\sum_i m_i a_i$$

with m_i integers is equal to zero if, and only if, all coefficients m_i are zero. The term Z-module is sometimes used to underline the condition that the coefficients are integers. The number of basis vectors is the *rank* of the vector module.

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4.5.1.62: Primitive basis

A primitive basis is a crystallographic basis of the vector lattice **L** such that every lattice vector **t** of **L** may be obtained as an integral linear combination of the basis vectors, **a**, **b**, **c**.

In mathematics, a primitive basis is often called a *lattice basis*, whereas in crystallography the latter has a more general meaning and corresponds to a crystallographic basis.

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4.5.1.63: Vector space

For each pair of points X and Y in point space one can draw a vector **r** from X to Y. The set of all vectors forms a **vector space**. The vector space has no origin but instead there is the *zero vector* which is obtained by connecting any point X with itself. The vector **r** has a *length* which is designed by |**r**| = r, where r is a non–negative real number. This number is also called the *absolute value* of the vector. The maximal number of linearly independent vectors in a vector space is called the *dimension of the space*.

An essential difference between the behavior of vectors and points is provided by the changes in their coefficients and coordinates if a different origin in point space is chosen. The coordinates of the points change when moving from an origin to the other one. However, the coefficients of the vector **r** do not change.

The point space is a dual of the vector space because to each vector in vector space a pair of points in point space can be associated.

Face normals, translation vectors, Patterson vectors and reciprocal lattice vectors are elements of vector space.

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4.5.1.64: Bragg's Law

Bragg's law provides the condition for a plane wave to be diffracted by a family of lattice planes:

$$2d\sin\theta = n\lambda.$$

where d is the **lattice** spacing, θ the angle between the wavevector of the incident plane wave, $\mathbf{k_0}$, and the lattice planes, λ its wave length and n is an integer, the order of the reflection. It is equivalent to the diffraction condition in reciprocal space and to the Laue equations.

Direct Derivation of Bragg's Law

- **Reflection from the first plane:** The scattered waves will be in phase whatever the distribution of the point scatterers in the first plane if the angle of the reflected wave vector, $\mathbf{k_h}$, is also equal to θ. This is Snell-Descartes' law of reflection.
- **Reflection from the second plane:** Since the phase of the reflected waves is independent of the position of the point scatterer in the plane, the phase difference between the waves reflected by two successive lattice planes is obtained by choosing arbitrarily a scattering point, *A*, on the first plane and a scattering point, *b* on the second plane such that *AB* is normal to the planes. If *C* and *d* are the projections of *A* on the incident and reflected wave vectors passing through *B*, it is clear from Figure 1 that the path difference between the waves reflected at *A* and *B*, respectively, is:

  $$CB + BD = 2d\sin\theta$$

  and that the two waves will be in phase if this path difference is equal to n λ where n is an integer.
- **Reflection from the third, etc., planes:** If Bragg's relation is satisfied for the first two planes, the waves reflected with wave vector $\mathbf{k_h}$ will be in phase fo all the planes of the family.

Order of the Reflection

Bragg's law may also be written:

$$2(d/n)sin\theta = \lambda.$$

One may then say that a Bragg reflection of order n on a family of lattice planes or order n is equivalent to reflection of order 1 on a family of fictitious, or imaginary, planes of lattice spacing:

$$d_{hkl} = \frac{d}{n}$$

This fictitious family is associated to the reciprocal lattice vector **OH** where $OH = n/d = 1/d_{hkl}$. The indices of the reflection are:hkl. For instance, the dashed blue lines in Figure 1 correspond to the fistitious planes associated to the second order, n = 2.

Extinctions or Systematic Absences

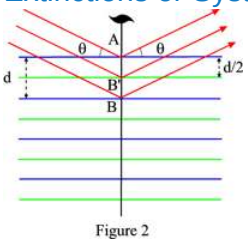


Figure 2

If there is a glide plane or a screw axis normal to the lattice planes, the spacing of the actual reflecting planes is d/2 for a glide plane and (d p/q) for a q_p screw axis. Bragg's law should then be written:

$$2\left(\frac{d}{2}\right)\sin\theta = n\lambda$$

$$2d\sin\theta = 2n\lambda$$

for a glide plane and

$$2(dp/q)\sin\theta = n\lambda \Rightarrow 2d\sin\theta = (q/p)n\lambda$$

for a screw axis q_p.

The reflections of odd order for a glide plane and of order different from $(q/p)n$ for a screw axis are then absent. One speaks of extinctions or systematic absences related to the presence of glide or screw components.

As an example, Figure 2 shows the case of a 2_1 screw axis: the reflecting planes are the blue planes and the green planes deduced from the latter by the action of the screw axis. Reflections of odd order will be sytematically absent.

Influence of deformation

A deformation that leaves a family of lattice planes (*hkl*) undistorted and its lattice spacing *d* unchanged will not affect the Bragg angle of *kkl* reflections, *e.g.* lattice planes parallel to a screw dislocations.

History

Bragg (1890-1971) presented his derivation of the reflection condition at a meeting of the Cambridge Philosophical Society on 11 November 1912. His paper was published in 1913 (Bragg W.L., 1913, *The Diffraction of Short Electromagnetic Waves by a Crystal*, *Proc. Cambridge Phil. Soc.*, **17**, 43-57. For details, see P. P. Ewald, 1962, IUCr, 50 Years of X-ray Diffraction, Section 5, page 64.

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4.5.1.65: Bravais-Miller indices

The Bravais-Miller indices are used in the case of hexagonal lattices. In that case, one uses four axes, $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$, $\mathbf{c}$ and four Miller indices, (*hkil*), where *h*, *k*, *i*, *l* are prime integers inversely proportional to the intercepts *OP*, *OQ*, *OS*, *OR* of a plane of the family with the four axes. The indices *h*, *k*, *i* are cyclically permutable and related by $h + k + i = 0$

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4.5.1.66: Bravais class

An arithmetic crystal class with matrix group of lattices is called a *Bravais arithmetic crystal class*, or **Bravais class** for short.

Each lattice is associated with a Bravais class, and each matrix group of a Bravais class represents the point group of a lattice referred to an appropriate primitive basis.

There exist 5 Bravais classes in two dimensions:

- 2*p*
- 2*mmp*
- 2*mmc*
- 4*mmp*
- 6*mmh*

There exist 14 Bravais classes in three dimensions:

- $\bar{1}P$
- 2/*mP*
- 2/*mS*
- *mmmP*
- *mmmS*
- *mmmI*
- *mmmF*
- 4/*mmmP*
- 4/*mmmI*
- $\bar{3}mR$
- 6/*mmmP*
- $m\bar{3}mP$
- $m\bar{3}mI$
- $m\bar{3}mF$

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4.5.1.67: Bravais lattice

The current nomenclature adopted by the IUCr prefers to use the expression **Bravais types of lattices** to emphasize that **Bravais lattices** are not individual lattices but types or classes of all lattices with certain common properties .

All vector lattices whose matrix groups belong to the same Bravais class correspond to the same **Bravais type of lattice**.

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4.5.1.68: Cartesian product

The **Cartesian product** is a direct product of sets.

The Cartesian product of two sets X and Y, denoted $X \times Y$, is the set of all possible ordered pairs whose first component is a member of X and whose second component is a member of Y:

$$X \times Y = \{(x, y) | x \in X \text{ and } y \in Y\}.$$

A Cartesian product of two finite sets can be represented by a table, with one set as the rows and the other as the columns, and forming the ordered pairs, the cells of the table, by choosing the element of the set from the row and the column.

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4.5.1.69: Centered lattices

When the unit cell does not reflect the symmetry of the lattice, it is usual in crystallography to refer to a 'conventional', non-primitive, crystallographic basis, $\mathbf{a_c}$, $\mathbf{b_c}$, $\mathbf{c_c}$ instead of a primitive basis, **a**, **b**, **c**. This is done by adding lattice nodes at the center of the unit cell or at one or three faces. The vectors joining the origin of the unit cell to these additional nodes are called 'centering vectors'. In such a lattice $\mathbf{a_c}$, $\mathbf{b_c}$ and $\mathbf{c_c}$ with all their integral linear combinations are lattice vectors again, but there exist other lattice vectors $\mathbf{t} \in \mathbf{L}$, $\mathbf{t} = t_1\,\mathbf{a_c} + t_2\,\mathbf{b_c} + t_3\,\mathbf{c_c}$; with at least two of the coefficients t_1, t_2, t_3 being fractional. The table below gives the various types of centering vectors and the corresponding types of centering. Each one is described by a letter, called the Bravais letter, which is to be found in the Hermann-Mauguin symbol of a space group.

The 'multiplicity', *m*, of the centered cell is the number of lattice nodes per unit cell (see table).

The volume of the unit cell, $V_c = (\mathbf{a_c}, \mathbf{b_c}, \mathbf{c_c})$ is given in terms of the volume of the primitive cell, $V = (\mathbf{a}, \mathbf{b}, \mathbf{c})$, by:

$V_c = m\,V$

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4.5.1.70: Semidirect product

In group theory, a **semidirect product** describes a particular way in which a group can be put together from two subgroups, one of which is normal.

Let G be a group, N a normal subgroup of G (i.e., $N \lhd G$) and H a subgroup of G. G is a **semidirect product** of N and H if there exists a homomorphism $G \to H$ which is the identity on H and whose kernel is N. This is equivalent to say that:

- $G = NH$ and $N \cap H = \{1\}$ (where "1" is identity element of G)
- $G = HN$ and $N \cap H = \{1\}$
- Every element of G can be written as a unique product of an element of N and an element of H
- Every element of G can be written as a unique product of an element of H and an element of N

One also says that "G *splits* over N".

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4.5.1.71: Conventional cell

For each lattice, the **conventional cell** is the cell obeying the following conditions:

- its basis vectors define a right-handed axial setting;
- its edges are along symmetry directions of the lattice;
- it is the smallest cell compatible with the above condition.

Crystals having the same type of conventional cell belong to the same crystal family.

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4.5.1.72: Crystal

Those solids in which atoms, ions or molecules are arranged in a definite three dimensional pattern are called crystalline solids. A material is a crystal if it has **essentially** a sharp diffraction pattern. The word **essentially** means that most of the intensity of the diffraction is concentrated in relatively sharp **Bragg peaks**, besides the always present diffuse scattering. In all cases, the positions of the diffraction peaks can be expressed by

$$H = \sum_{i=1}^{n} h_i a_i^* \ (n \geq 3)$$

Here $\mathbf{a}_i^*$ and h_i are the basis vectors of the reciprocal lattice and integer coefficients respectively and the number $n \backslash 0 is the minimum for which the positions of the peaks can be described with integer coefficient \(h_i$. The conventional crystals are a special class, though very large, for which $n = 3$.

See also

Acta Cryst. (1992), **A48**, 928 where the definition of a crystal appears in the **Terms of reference** of the IUCr commission on aperiodic crystals

- Online Dictionary of Crystallography

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4.5.1.73: Subperiodic group

A **subperiodic group** is a group of Euclidean mappings such that its translations form a lattice in a proper subspace of the space on which it acts.

A **crystallographic subperiodic group** in n-dimensional space is a subperiodic group for which the group of linear parts is a crystallographic point group of n-dimensional space. The crystallographic subperiodic groups in two and three-dimensional space are classified in:

- **frieze groups**: 7 two-dimensional groups with one-dimensional translations;
- **rod groups**: 75 three-dimensional groups with one-dimensional translations;
- **layer groups**: 80 three-dimensional groups with two-dimensional translations.

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4.5.1.74: Crystallographic basis

A basis of n vectors $\mathbf{e_1}$, $\mathbf{e_2}$, ... , $\mathbf{e_n}$ of the vector space $\mathbf{V^n}$ is a *crystallographic basis* of the vector lattice **L** if *every* integral linear combination $\mathbf{t} = u^1\mathbf{e_1} + u^2\mathbf{e_2} + ... + u^n\mathbf{e_n}$ is a lattice vector of **L**. It may or may not be a primitive basis.

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4.5.1.75: Crystallographic symmetry

A motion is called a **crystallographic symmetry operation** if a crystal pattern exists for which it is a symmetry operation.

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4.5.1.76: Stabilizer

Let G be a group which acts on a set A by a composition law *, and let a be a given element of A. Then the set: $G_a = \{g \in G \mid a*g = a\}$ is called the **stabilizer** of A. G_a is the set of all elements of G which leave a unchanged or 'stable'. G_a is a subgroup of G.

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4.5.1.77: Crystal family

A **crystal family** is the smallest set of space groups containing, for any of its members, all space groups of the Bravais flock and all space groups of the geometric crystal class to which this member belongs.

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4.5.1.78: Statistical descriptors

A separate online document Statistical Descriptors in Crystallography prepared for the International Union of Crystallography provides an authoritative statement on some aspects of the use of statistics and statistical techniques in crystallography, principally that of least-squares refinement of diffraction data against an atomic model. The following topics are treated:

- Glossary
- Basic notions
- Uncertainty of measurement
- Refinement
- Refinement on I, $|F|^2$ or $|F|$?
- Defects in the model
- Weighting schemes
- **Recommendations**

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4.5.1.79: Crystal pattern

An object in the n-dimensional point space E^n is called an n-dimensional **crystallographic pattern** or, for short, **crystal pattern** if among its symmetry operations:

1. there are *n* translations, the translation vectors $\mathbf{t}_1$, ... , $\mathbf{t}_n$ of which are linearly independent;
2. all translation vectors, except the zero vector **0**, have a length of at least d > 0.

When the crystal pattern consists of atoms, it takes the name of **crystal structure**. The crystal pattern is thus the generalization of a crystal structure to any pattern, concrete of abstract, in any dimension, which obeys the conditions of periodicity and discreteness expressed above.

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4.5.1.80: Subcell

A cell C' obtained from a cell C by adding one or more translation vectors of fractional periodicity in C is called a **subcell** of C. The translation subgroup **T'** of the lattice **L'** built on C' is a supergroup of the translation subgroup **T** of the lattice **L** built on C and corresponds therefore to superlattice of **L**.

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4.5.1.81: Crystal system

A crystal-class system , or **crystal system** for short, contains complete geometric crystal classes of space groups . All those geometric crystal classes belong to the the same crystal system which intersect exactly the same set of Bravais flocks.

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4.5.1.82: Subgroup

Let G be a group and H a non-empty subset of G. Then H is called a **subgroup** of G if the elements of H obey the group postulates, i.e. if

1. the identity element 1_G of G is contained in H;
2. H is closed under the group operation (inherited from G);
3. H is closed under taking inverses.

The subgroup H is called a **proper subgroup** of G if there are elements of G not contained in H.

A subgroup H of G is called a **maximal subgroup** of G if there is no proper subgroup M of G such that H is a proper subgroup of M.

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4.5.1.83: Direct Lattice

The direct lattice represents the triple periodicity of the ideal infinite perfect periodic structure that can be associated to the structure of a finite real crystal. To express this periodicity one calls *crystal pattern* an object in point space E^n (direct space) that is invariant with respect to three linearly independent translations, $\mathbf{t_1}$, $\mathbf{t_2}$ and $\mathbf{t_3}$. One distinguishes two kinds of lattices, the *vector lattices* and the *point lattices*.

Any translation $\mathbf{t} = u^i\ \mathbf{t_i}$ (u^i arbitrary integers) is also a translation of the pattern and the infinite set of all translation vectors of a crystal pattern is the **vector lattice L** of this crystal pattern.

Given an arbitrary point P in point space, the set of all the points P_i deduced from one of them by a translation $\mathbf{PP_i} = \mathbf{t_i}$ of the vector lattice **L** is called the **point lattice**.

A basis **a**, **b**, **c** of the vector space $\mathbf{V^n}$ is a *crystallographic basis* of the vector lattice **L** if *every* integral linear combination $\mathbf{t} = u\ \mathbf{a} + v\ \mathbf{b} + w\ \mathbf{c}$ is a lattice vector of **L**. It is called a *primitive basis* if *every* lattice vector **t** of **L** may be obtained as an integral linear combination of the basis vectors, **a**, **b**, **c**. Referred to any crystallographic basis the coefficients of each lattice vector are either integral or rational, while in the case of a primitive basis they are integral. *Non-primitive* bases are used conventionally to describe *centered lattices*.

The parallelepiped built on the basis vectors is the *unit cell*. Its volume is given by the triple scalar product, $V = (\mathbf{a}, \mathbf{b}, \mathbf{c})$.

If the basis is primitive, the unit cell is called the *primitive cell*. It contains only one lattice point. If the basis is non-primitive, the unit cell is a *multiple cell* and it contains more than one lattice point. The multiplicity of the cell is given by the ratio of its volume to the volume of a primitive cell.

The generalization of the notion of point and vector lattices to n-dimensional space is given in Section 8.1 of *International Tables of Crystallography, Volume A*

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4.5.1.84: Sublattice

A lattice **L'** obtained by another lattice **L** by removing one or more sets of nodes is called a **sublattice of L**. The translation subgroup **T'** of **L'** is a subgroup of the translation subgroup **T** of **L**. The unit cell of **L'** is larger than the unit cell of **L** and is therefore called a supercell.

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4.5.1.85: Direct product

In group theory, **direct product** of two groups (G, *) and (H, o), denoted by $G \times H$ is the as set of the elements obtained by taking the cartesian product of the sets of elements of G and H: {(g, h): g in G, h in H};

For abelian groups which are written additively, it may also be called the *direct sum* of two groups, denoted by $\boldsymbol{G \oplus H}$.

The group obtained in this way has a normal subgroup isomorphic to G (given by the elements of the form (g, 1)), and one isomorphic to H (comprising the elements (1, h)).

The reverse also holds: if a group K contains two normal subgroups G and H, such that $K = GH$ and the intersection of G and H contains only the identity, then $K = G$ x H. A relaxation of these conditions gives the semidirect product.

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4.5.1.86: Supercell

A cell C' obtained from a cell C by removing one or more translation vectors is called a **supercell** of C. The translation subgroup **T'** of the lattice **L'** built on C' is a subgroup of the translation subgroup **T** of the lattice **L** built on C and corresponds therefore to sublattice of **L**.

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4.5.1.87: Direct space

The direct space (or *crystal space*) is the *point space*, E^n, in which the structures of finite real crystals are idealized as infinite perfect three-dimensional structures. To this space one associates the *vector space*, V^n, of which lattice and translation vectors are elements. It is a *Euclidean* space where the scalar product of two vectors is defined. The two spaces are connected through the following relations:

(i) To any two points P and Q of the point space E^n a vector **PQ** = **r** of the vector space V^n is attached

(ii) For each point P of E^n and for each vector **r** of V^n there is exactly one point Q of E^n for which **PQ** = **r** holds

(iii) If R is a third point of the point space, **PQ** + **QR** = **PR**

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4.5.1.88: Supergroup

If *G* is a group and *H* is a subgroup of *G*, then *G* is a **supergroup** of *H*.

If *H* is a maximal subgroup of *G*, then *G* is a **minimal supergroup** of *H*.

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4.5.1.89: Dual basis

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4.5.1.90: Superlattice

A lattice **L'** obtained by another lattice **L** by adding one or more sets of nodes is called a **superlattice of L**. The translation subgroup **T'** of **L'** is a supergroup of the translation subgroup **T** of **L**. The unit cell of **L'** is smaller than the unit cell of **L** and is therefore called a subcell.

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4.5.1.91: D centered cell

The **D centered cell** is the used for the rhombohedral description of the hexagonal lattice. Six right-handed *D* cell with basis vectors of equal length are obtained from the *hP* cell by means of one of the following transformation matrices:

D_1: 10-1/01-1/111 D_2: -101/0-11/111

the other four *D* cells are obtained by cyclic permutation of the basis vectors.

The resulting *hD* cell has centering nodes at 1/3,1/3,1/3 and 2/3,2/3,2/3

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4.5.1.92: Eigensymmetry

The *eigensymmetry*, or *inherent symmetry*, of a crystal is the point group or space group of a crystal, irrespective of its orientation and location in space. For instance, all individuals of a twinned crystal have the same (or the enantiomorphic) eigensymmetry but may exhibit different orientations. The orientations of each of two twin components are related by a twin operation which cannot be part of the eigensymmetry.

In morphology, the eigensymmetry is the full symmetry of a crystalline form, considered as a polyhedron by itself. The eigensymmetry point group is either the generating point group itself or a supergroup of it.

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4.5.1.93: Euclidean mapping

The **Euclidean mapping** or **isometry** is a special case of affine mapping that, besides collinearity and ratios of distances, keeps also *distances* and *angles*. Because of this, a Euclidean mapping is also called a *rigid motion*.

Euclidean mappings are of three types:

- translations
- rotations
- reflections.

A special case of Euclidean mapping is a symmetry operation.

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4.5.1.94: Symmorphic space groups

A space group is called ‘symmorphic’ if, apart from the lattice translations, all generating symmetry operations leave one common point fixed. Permitted as generators are thus only the point-group operations: rotations, reflections, inversions and rotoinversions. The symmorphic space groups may be easily identified because their Hermann-Mauguin symbol does not contain a glide or screw operation. The combination of the Bravais lattices with symmetry elements with no translational components yields the 73 symmorphic space groups, *e.g.* *P*2, *Cm*, *P*2/*m*, *P*222, *P*32, *P*23. They are in one to one correspondence with the arithmetic crystal classes.

A characteristic feature of a symmorphic space group is the existence of a special position, the site-symmetry group of which is isomorphic to the point group to which the space group belongs. Symmorphic space groups have no zonal or serial reflection conditions, but may have integral reflection conditions (*e.g.* *C*2, *Fmmm*).

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4.5.1.95: Factor group

Let N be a normal subgroup of a group G. The **factor group** or **quotient group** G/N is the set of all left cosets of N in G, i.e.:

$$G/N = \{aN : a \in G\}.$$

For each aN and bN in G/N, the product of aN and bN is (aN)(bN), which is still a left coset. In fact, because N is normal:

(aN)(bN) = a(Nb)N = a(bN)N = (ab)NN = (ab)N.

The inverse of an element aN of G/N is $a^{-1}N$.

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4.5.1.96: Tetartohedry

The point group of a crystal is called tetartohedry if it is a subgroup of index 4 of the point group of its lattice.

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4.5.1.97: Family structure

By superposing two or more identical copies of the same polytype translated by a superposition vector (*i.e*. a vector corresponding to a submultiple of a translation period) a fictitious structure is obtained, which is termed a *superposition structure*. Among the infinitely possible superposition structures, that structure having all the possible positions of each OD layers is termed a **family structure**: it exists only if the shifts between adjacent layers are rational, i.e. if they correspond to a submultiple of lattice translations.

The family structure is common to all polytypes of the same family. From a group-theoretical viewpoint, building the family structure corresponds to transforming (“completing”) all the local symmetry operations of a space groupoid into the global symmetry operations of a space-group.

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4.5.1.98: Fixed-point-free space groups

Space groups with no special Wyckoff positions (*i.e.* with no special crystallographic orbits) are called **fixed-point-free space groups** or **torsion-free space groups** or **Bieberbach groups**. In fixed-point-free space groups group every element other than the identity has infinite order.

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4.5.1.99: Binary Operation

A **binary operation** on a set *S* is a mapping *f* from the Cartesian product $S \times S$ to *S*. A mapping from *K x S* to *S*, where *K* need not be *S*, is called an **external binary operation**.

Many binary operations are commutative (i.e. *f(a,b) = f(b,a)* holds for all *a*, *b* in *S*) or associative (i.e. *f(f(a,b), c) = f(a, f(b,c))* holds for all *a,b,c* in *S*). Many also have identity elements and inverse elements. Typical examples of binary operations are the addition (+) and multiplication (*) of numbers and matrices as well as composition of functions or symmetry operations.

Examples of binary operations that are not commutative are subtraction (-), division (/), exponentiation(^), super-exponentiation(@), and composition.

Binary operations are often written using infix notation such as $a * b$, $a + b$, or $a \cdot b$ rather than by functional notation of the form *f(a,b)*. Sometimes they are even written just by concatenation: *ab*.

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SECTION OVERVIEW

4.5.2: Structure Determination

Topic hierarchy

4.5.2.1: Bragg R factor

4.5.2.2: Constrained refinement

4.5.2.3: Direct methods

4.5.2.4: Free R factor

4.5.2.5: Harker section

4.5.2.6: Heavy-Atom Method

4.5.2.7: Phase problem

4.5.2.8: Refinement

4.5.2.9: Restrained refinement

4.5.2.10: Rietveld method

4.5.2.11: R factor

4.5.2.12: Sharpened Patterson function

4.5.2.13: Structure-factor coefficient

4.5.2.14: Structure amplitude

4.5.2.15: Structure determination

4.5.2.16: Superposition methods

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4.5.2.1: Bragg R factor

The *R* factor measuring the agreement between the reflection intensities calculated from a crystallographic model and those measured experimentally.

\(R_B =

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\).

In the Rietveld method R_B is useful because it depends on the fit of the structural parameters and not on the profile parameters.

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4.5.2.2: Constrained refinement

A refinement is said to be constrained if one or more parameters in the refinement are held fixed or are determined by the value of one or more refined parameters. Constraints related to space group symmetry are not usually counted among the constraints applied to a given refinement as they are always present where applicable.

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4.5.2.3: Direct methods

The family of methods for solving the phase problem in crystal structure determination. The phases of scattered diffraction beams cannot be directly observed. However, they can be estimated from probability relationships applied to the phases of the most intense diffraction peaks. The facts that scattering centers in a crystal are discrete atoms (*i.e.* sources of electron density) and that the electron density must be non-negative are the types of constraints that restrict the possible values of the phases, and allow initial estimates of some of them.

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4.5.2.4: Free R factor

A residual function calculated during structure refinement in the same way as the conventional *R* factor, but applied to a small subset of reflections that are not used in the refinement of the structural model. The purpose is to monitor the progress of refinement and to check that the *R* factor is not being artificially reduced by the introduction of too many parameters.

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4.5.2.5: Harker section

In Patterson methods of structure solution, relationships between symmetrically related atoms produce peaks in the Patterson function on certain planes or along certain lines determined by the known crystallographic symmetries. **Harker sections** are portions of the Patterson map that contain a large proportion of the readily interpretable information because they contain many such **Harker peaks** (vectors between space-group equivalent atoms).

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4.5.2.6: Heavy-Atom Method

An application of Patterson methods in crystal structure determination. For a compound containing a heavy atom (*i.e.* one with a significantly higher atomic scattering factor than the others present) the diffraction phases calculated from the position of the heavy atom are used to compute a first approximate electron density map. Further portions of the structure are recognizable as additional peaks in the map. Successive approximate electron density maps may then be calculated to solve the entire structure.

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4.5.2.7: Phase problem

Waves diffracted from a primitive lattice of simple scatterers obey Bragg's law, which allows ready determination of interplanar distances and thus the easy recovery of a description of the crystal lattice. Where the scattering objects are complex (*e.g.* in molecular crystals) the diffracted radiation suffers a phase shift arising from the spatial distribution of individual scatterers. The amplitudes of the resulting structure factors are directly derivable from the experimental measured intensities of the diffracted beams, but the phases are not. Without a knowledge of the phases, it is not possible to reconstruct the individual atomic positions. Estimating the phases is an essential step in successful structure determination.

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4.5.2.8: Refinement

In structure determination, the process of improving the parameters of an approximate (trial) structure until the best fit is achieved between an observed diffraction pattern and that calculated by Fourier transformation from the numerically parameterized trial structure.

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4.5.2.9: Restrained refinement

A refinement is said to be restrained if the refinement is based on additional observations or pseudo-observations besides the observed structure factors.

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4.5.2.10: Rietveld method

Method of analyzing powder diffraction data in which the crystal structure is refined by fitting the entire profile of the diffraction pattern to a calculated profile using a least-squares approach. There is no intermediate step of extracting structure factors, and so patterns containing many overlapping Bragg peaks can be analyzed.

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4.5.2.11: R factor

The term ***R* factor** in crystallography is commonly taken to refer to the 'conventional' *R* factor

\(R =

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\),

a measure of agreement between the amplitudes of the structure factors calculated from a crystallographic model and those from the original X-ray diffraction data. The *R* factor is calculated during each cycle of least-squares structure refinement to assess progress. The final *R* factor is one measure of model quality.

More generally, a variety of *R* factors may be determined to measure analogous residuals during least-squares optimization procedures. Where the refinement attempts to minimize the deviates of the squares of the structure factors (refinement against F^2), the *R* factor based on F^2 is used to monitor the progress of refinement:

\(R(F^2) =

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\).

Likewise, refinement against *I* can be tracked using the Bragg *R* factor

\(R_B =

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\).

Even for refinement against F^2 or *I*, the 'conventional' *R* factor may be calculated and quoted as a measure of model quality, in order to compare the resulting quality of models calculated at different times and with different refinement strategies.

The *R* factor is sometimes described as the **discrepancy index**.

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4.5.2.12: Sharpened Patterson function

Patterson methods of structure determination use the Patterson function

$P(uvw) = (1 / V)$	$\sum$	$\sum$	$\sum$	$\{ \mid F(hkl) \mid ^2 \cos[2\pi(hu + kv + lw)]\}$
	h	k	l	

to generate a map of interatomic vectors within the unit cell. Better results can be obtained by artificially sharpening the peaks in the Patterson function, thereby enhancing the resolution of individual peaks.

One technique for doing so, introduced by Patterson in 1935, considers the effect of thermal motion on the broadening of electron-density peaks and consequently their Patterson peaks. The F^2 coefficients can be corrected for thermal effects by simulating the atoms as point scatterers and using a modified set of coefficients $|\mathbf{F}_{\mathbf{h},\mathrm{sharp}}|^2 = |\mathbf{F}_{\mathbf{h}}|^2/\bar{f}^2$, where $\bar{f}$, the average scattering factor per electron, is given by

$$\bar{f} = \sum_{i=1}^{N} f_i / \sum_{i=1}^{N} Z_i.$$

A common formulation for this type of sharpening expresses the atomic scattering factors at a given angle in terms of an overall isotropic thermal parameter B as $f(s) = f_0 \exp(-Bs^2)$. The Patterson coefficients then become

\(\mathbf{F}_{\mathbf{h}, \, \mathrm{sharp}} =

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\).

More often nowadays normalized structure factors $\mid E^2 \mid - 1$ are used in place of $\mid F^2 \mid$. Normalized structure factors are used in direct methods techniques of structure solution. They are defined as

$$|E_{\mathbf{h}}|^2 = |F_{\mathbf{h}}|^2 / \langle |F_{\mathbf{h}}|^2 \rangle,$$

where the squared observed structure-factor magnitudes on an absolute scale are divided by their expected values. Their use gives much greater weight to higher-resolution data and resolves some peaks in the vector map that would otherwise be continuous. On the other hand, they are less accurately known and are adjacent to data that have not been measured; they may therefore introduce spurious definition into the map.

A compromise that is often helpful is to use $\mid EF \mid$ as the Patterson coefficients.

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4.5.2.13: Structure-factor coefficient

The quantity F, F^2 or I that is used in place of Y in the function $\sum w(Y_o - Y_c)^2$ minimized during least-squares refinement of a crystal structure determination.

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4.5.2.14: Structure amplitude

The magnitude of the structure factor.

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4.5.2.15: Structure determination

Structure determination in crystallography refers to the process of elaborating the three-dimensional positional coordinates (and also, usually, the three-dimensional anisotropic displacement parameters) of the scattering centers in an ordered crystal lattice. Where a crystal is composed of a molecular compound, the term generally includes the three-dimensional description of the *chemical* structures of each molecular compound present.

Experimental techniques

Owing to the highly ordered arrangement of atoms as scattering centers in a crystal lattice, most structure determination techniques involve the diffraction of electromagnetic or matter waves of wavelengths comparable to atomic dimensions. Bragg's law specifies the condition for plane waves to be diffracted from lattice planes. The diffracted radiation passing through a crystal emerges with intensity varying as a function of scattering angle. This variation arises from constructive and destructive interference of scattered beams from the planes associated with the different atoms present in the lattice. The result is seen by an imaging detector as a pattern of diffraction spots or rings.

Among diffraction-based techniques are:

- single-crystal X-ray diffraction
- X-ray powder diffraction
- X-ray fiber diffraction
- neutron powder diffraction
- neutron single-crystal diffraction
- polymer electron diffraction

Other techniques for three-dimensional structure determination that are complementary to diffraction methods include

- electron microscopy
- nuclear magnetic resonance spectroscopy (used largely for biological macromolecules in solution)

Methodology

The following summary applies to single-crystal X-ray diffraction. A crystal, mounted on a goniometer, is illuminated by a collimated monochromatic X-ray beam, and the positions and intensities of diffracted beams are measured. The measured intensities I_{hkl} (corresponding to scattering from a lattice plane with Miller indices h,k,l) are reduced to structure amplitudes F_{hkl} by the application of a number of experimental corrections:

$$F_{hkl}^2 = I_{hkl}(k\mathrm{Lp}A)^{-1}$$

where k is a scale factor, Lp the Lorentz–polarization correction, and A the transmission factor representing the absorption of X-rays by the crystal. The structure amplitude represents the amplitude of the diffracted wave measured relative to the scattering amplitude of a single electron.

However, the diffracted wave is completely described by the structure factor $\mathbf{F}_{hkl}$:



where the sum is over all atoms in the unit cell, x_j,y_j,z_j are the positional coordinates of the jth atom, f_j is the scattering factor of the jth atom, and α_{hkl} is the phase of the diffracted beam.

The atomic scattering factor can be worked out from the physical properties of the atom species, but the phase cannot be determined by direct experimental observation. If the phases can be derived in some way, then the positional coordinates can be calculated from the expression above. The phase problem represents the major obstacle to constructing an initial structural model, and is addressed through a number of techniques, such as direct methods, Patterson synthesis, heavy-atom method, isomorphous replacement *etc.*

Once an initial structural model has been calculated, it is usually necessary to conduct an iterative refinement procedure to improve the agreement between the structural model and the experimental diffraction intensities. The most common approach is to perform a least-squares minimization between the experimental structure factors and those calculated by varying the adjustable parameters of the structural model. These normally include atomic positions, anisotropic displacement parameters, occupancies, chemical bond lengths and angles, and other geometric characteristics of a molecule. Some metric, such as the residual R factor

\(R =

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\),

is used to indicate improvements or reductions in the quality of fit between model and observation. In the expression above (the 'conventional' R factor), F_{obs} and F_{calc} are the observed and calculated structure amplitudes, and the deviations are summed over all experimentally recorded intensities. There is considerable discussion on the most appropriate statistical metric to use for this purpose.

Other refinement techniques, such as maximum likelihood and maximum entropy, are also used.

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4.5.2.16: Superposition methods

A subset of Patterson methods of structure solution that involve analyzing the Patterson map, transforming the origin of the map in turn on to the known positions of certain atoms, and suitably combining the superposed maps. The degree of coincidence between the peaks of the superposing maps is assessed by optimizing one of a number of image-seeking functions, of which the symmetry minimum function is perhaps most often used.

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SECTION OVERVIEW

4.5.3: Twinning

Crystal twinning occurs when two separate crystals share some of the same crystal lattice points in a symmetrical manner. The result is an intergrowth of two separate crystals in a variety of specific configurations.

Topic hierarchy

https://chem.libretexts.org/@go/page/364998

4.5.3.1: Allotwin

4.5.3.2: Corresponding Twins

4.5.3.3: Hybrid twin

4.5.3.4: Inversion twin

4.5.3.5: Mallard's Law

4.5.3.6: Reflection twin

4.5.3.7: Rotation Twin

4.5.3.8: Selective merohedry

4.5.3.9: TLQS twinning

4.5.3.10: TLS twinning

4.5.3.11: Twinning

4.5.3.12: Twinning(effects of)

4.5.3.13: Twinning (consequences of)

4.5.3.14: Twinning (endemic conditions of)

4.5.3.15: Twinning by inversion

4.5.3.16: Twinning by merohedry

4.5.3.17: Twinning by metric merohedry

4.5.3.18: Twinning by psuedomerohedry

4.5.3.19: Twinning by reticular merohedry

4.5.3.20: Twinning by reticular polyholohedry

4.5.3.21: Twinning by reticular pseudomerohedry

4.5.3.22: Twin element

4.5.3.23: Twin index

4.5.3.24: Twin lattice

4.5.3.25: Twin law

4.5.3.26: Twin obliquity

4.5.3.27: Twin operation

Thumbnail: Twinned pyrite crystal group. (Public Domain; Vassil).

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4.5.3.1: Allotwin

An **allotwin** is a twin whose individuals are different polytypes of the same compound.

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4.5.3.2: Corresponding Twins

In case of twinning by merohedry, when the twin element is twofold and the crystal is centrosymmetric, the twin operation can be described either as a rotation or as a reflection (the two operations being equivalent under the action of the center).

In case of twinning by pseudomerohedry, instead, the two twin operations are no longer equivalent even in centrosymmetric crystals but produce different twins, which are called **reciprocal twins** (Mügge, 1898) or **corresponding twins** (Friedel, 1904, 1926). One of the most classical examples is that of albite vs. pericline twins in feldspars.

Pairs of corresponding twins normally do not have the same frequency of occurrence, as one would be tempted to assume from the identical value of their twin obliquity.

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4.5.3.3: Hybrid twin

A twin in which more than one concurrent sublattice is necessary to explain the restoration of lattice nodes by the twin operation is called a **hybrid twin**.

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4.5.3.4: Inversion twin

Two domains of one crystal form an *inversion twin* when the twin operation is an inversion through a center (*twin center*).

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4.5.3.5: Mallard's Law

The **law of Mallard** was introduced by Georges Friedel (*Leçons de Cristallographie* 1926, page 436) to explain, on reticular basis, twinning by pseudomerohedry.

The law of Mallard states that twin elements are always rational (i.e. direct lattice elements): therefore, a twin plane is a lattice plane, and a twin axis is a lattice row. These twin elements are pseudosymmetry elements for the lattice of the individual. The twin operations produce now slightly different orientations of the lattice of the individual, which are only quasi-equivalent, and no longer equivalent, as in the case of twinning by merohedry.

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4.5.3.6: Reflection twin

Two domains of one crystal form a *reflection twin* when the twin operation is a reflection across a lattice plane (*twin plane*).

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4.5.3.7: Rotation Twin

Two domains of one crystal form a *rotation twin* when the twin operation is a rotation about a lattice row (*twin axis*).

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4.5.3.8: Selective merohedry

In twinning by merohedry, the twin operations belong to the point group of the crystal lattice. When twinning concerns an OD structure, the definition of merohedry should take into account not only the point group of the crystal and that of the lattice, but also the point group of the family structure. If the latter is a subgroup of the twin point group, some of the twin laws restore only a part of the reciprocal lattice nodes corresponding to the family reflections (the reflections common to all the OD structures of a family). This kind of twinning is called **twinning by selective merohedry**: it can occur when the Laue point group of the crystal is lower than the twin point group, *i.e.* in the so-called “class II twins”.

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4.5.3.9: TLQS twinning

TLQS (Twin Lattice Quasi-Symmetry) twinning is a term employed to indicate twinning where the twin lattice is close to a higher holohedry. The degree of quasi-symmetry is commonly measure by the twin obliquity, which depends on the perpendicularity of lattice row / lattice plane [*uvw*] / (*hkl*) defining the cell of the twin lattice.

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4.5.3.10: TLS twinning

TLS (Twin Lattice Symmetry) twinning is a term employed to indicate twinning where the twin lattice does not possess a pseudo-symmetry, differently from what happens in TLQS twinning.

In TLS twinning, the lattice row / lattice plane [*uvw*] / (*hkl*) defining the cell of the twin lattice are mutually perpendicular. When this perpendicularity is imposed by the symmetry of the lattice, one speaks of *intrinsic-TLS* (*i-TLS*). In all other cases, the conditions of perpendicularity, depend on one or more metric parameters: one then speaks of *extrinsic-TLS* (*e-TLS*).

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4.5.3.11: Twinning

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4.5.3.12: Twinning(effects of)

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4.5.3.13: Twinning (consequences of)

By effect of a twinning operation, both the direct and reciprocal lattice of the individuals forming a twin are overlapped. Overlapping (restoration) of nodes belonging to different individuals can be: (i) exact and total (twinning by merohedry); (ii) exact but partial (i.e. only a fraction of the nodes of an individual lattice is restored; twinning by reticular merohedry); (iii) total but approximate (twinning by pseudomerohedry), approximate and partial (twinning by reticular pseudomerohedry).

- **twin index**

The reciprocal *n* of the fraction 1/*n* of (quasi)restored nodes is called *twin index*

- **twin lattice**

The lattice that is formed by the (quasi)restored nodes is the *twin lattice*. It corresponds to the crystal lattice in twins by (pseudo)merohedry and to a sublattice of the crystal (individual) in twins by reticular (pseudo)merohedry.

- **twin obliquity**

The *twin obliquity* is a measure of the distortion of a (sub)lattice in twins by (reticular) pseudomerohedry.

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4.5.3.14: Twinning (endemic conditions of)

When a lattice necessarily contains at least one sublattice that supports either twinning by reticular merohedry or twinning by reticular pseudomerohedry, it is said that an endemic condition of twinning does exist. The following cases are known.

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4.5.3.15: Twinning by inversion

The symmetry operation relating pairs of domain structures twinned by inversion may be represented by inversion through a point or by some other isometry equivalent to inversion under the point symmetry group of the domain structure. A two-domain-structure twin that is twinned by inversion is called an *inversion twin*, but this term is not appropriate when there are more than two domain structures. Twinning by inversion can only occur in non-centrosymmetric structures.

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4.5.3.16: Twinning by merohedry

The twin operation belongs to to the point group of the lattice but not to the point group of the crystal. Therefore, the point group of the crystal must be a subgroup of the point group of the lattice, i.e. the crystal shows only a part (*merohedry*) of the symmetry elements belonging to the its lattice which, instead, shows *holohedry* (complete symmetry). The twinning element of symmetry may (*Class I of twins by merohedry*) or may not belong to the Laue class of the crystal (*Class II of twins by merohedry*): Examples - Class I: in crystals with point group 2 (Laue group 2/*m*) the mirror plane *m* acts as twinning operator . Class II: in crystals with point group 4 (Laue group 4/*m*) a mirror plane *m* parallel to the foufold axis 4 acts as twinning operator.

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4.5.3.17: Twinning by metric merohedry

Twinning by metric merohedry is a special case of twinning by merohedry which occurs when:

- the lattice of the individual has accidentally a specialized metric which corresponds to a higher holohedry
- the twin operation belongs to this higher holohedry only

If H is the individual point group, D(H) the corresponding holohedry and D(L) the point group of the lattice, twinning by metric merohedry corresponds to $D(L) \supset D(H) \supseteq H$

Twinning by metric merohedry can be seen as the degeneration of twinning by reticular merohedry to twin index 1, or of twinning by pseudomerohedry to twin obliquity zero.

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4.5.3.18: Twinning by psuedomerohedry

A lattice is said to be pseudosymmetric if at least a lattice row or/and a lattice plane approximately correspond to elements of symmetry; these elements can act as twinning operators (e.g., a monoclinic lattice with its oblique angle *close* to 90° is pseudo-orthorhombic and thus shows two pseudo twofold axes and two pseudo mirror planes).

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4.5.3.19: Twinning by reticular merohedry

In the presence of a sublattice whose oriented point group D($\mathbf{L}_T$) differs from that of the crystal (individual) lattice D($\mathbf{L}_{ind}$), a symmetry element belonging to D($\mathbf{L}_T$) but not to D($\mathbf{L}_{ind}$) can act as twin element.

If lattice and sublattice have the same point group but (some of) their symmetry elements are differently oriented, *twinning by reticular polyholohedry* can occur.

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4.5.3.20: Twinning by reticular polyholohedry

Twinning by **reticular polyholohedry** is a special case of twinning by reticular merohedry that occurs when the twin lattice has the same point group as the lattice of the individual but at least one of its symmetry elements is differently oriented in space.

When the point group of the twin lattice is only close to that of the individual lattice one speaks of **twinning by reticular pseudopolyholohedry**, which corresponds to non-zero twin obliquity.

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4.5.3.21: Twinning by reticular pseudomerohedry

In the presence of a sublattice displaying pseudosymmetry, a pseudosymmetry element belonging to the sublattice can act as twinning operator. See twinning by pseudomerohedry and twinning by reticular merohedry.

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4.5.3.22: Twin element

The direct lattice element about which a twin operation is performed.

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4.5.3.23: Twin index

A twin operation overlaps both the direct and reciprocal lattices of the individuals that form a twin; consequently, the nodes of the individual lattices are overlapped (restored) to some extent (twinning). The reciprocal n of the fraction $1/n$ of (quasi)restored nodes is called *twin index*

Let (hkl) be the twin plane and [uvw] the lattice direction (quasi)-normal to it. alternatively, let [uvw] be the twin axis and (hkl) the lattice plane (quasi)-normal to it. For *twofold operations*(180º rotations or reflections) the twin index is:

$n = X/\mathrm{f}$, $X = |uh+vk+wl|$

where f depends on the lattice type and on the parities of X, h, k, l, u, v and w, as in the following table

Lattice type	condition on *hkl*	condition on *uvw*	condition on *X*	*n*
P	none	none	X odd	$n = X$
			X even	$n = X/2$
C	$h+k$ odd	none	none	$n = X$
	$h+k$ even	$u+v$ and w not both even	X odd	$n = X$
			X even	$n = X/2$
		$u+v$ and w both even	$X/2$ odd	$n = X/2$
			$X/2$ even	$n = X/4$
B	$h+l$ odd	none	none	$n = X$
	$h+l$ even	$u+w$ and v not both even	X odd	$n = X$
			X even	$n = X/2$
		$u+w$ and v both even	$X/2$ odd	$n = X/2$
			$X/2$ even	$n = X/4$
A	$k+l$ odd	none	none	$n = X$
	$k+l$ even	$v+w$ and u not both even	X odd	$n = X$
			X even	$n = X/2$
		$v+w$ and u both even	$X/2$ odd	$n = X/2$
			$X/2$ even	$n = X/4$
I	$h+k+l$ odd	none	none	$n = X$
	$h+k+l$ even	u, v and w not all odd	X odd	$n = X$
			X even	$n = X/2$
		u, v and w all odd	$X/2$ odd	$n = X/2$
			$X/2$ even	$n = X/4$
F	none	$u+v+w$ odd	none	$n = X$
h, k, l not all odd	u+v+w even	X odd	$n = X$	
		X even	$n = X/2$	
h, k, l all odd	u+v+w even	$X/2$ odd	$n = X/2$	
		$X/2$ even	$n = X/4$	

When the twin operation is a rotation of higher degree about [*uvw*], in general the rotational symmetry of the two-dimensional mesh in the (*hkl*) plane does no longer coincide with that of the twin operation. The degree of restoration of lattice nodes must now take into account the two-dimensional coincidence index Ξ for a plane of the family (*hkl*), which defines a super mesh in the twin lattice. Moreover, such a super mesh may exist in ξ planes out of *N*, depending on where is located the intersection of the [*uvw*] twin axis with the plane. The twin index *n* is finally given by:

$n = N\Xi/\xi$

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4.5.3.24: Twin lattice

A twin operation overlaps both the direct and reciprocal lattices of the individuals that form a twin; consequently, the nodes of the individual lattices are overlapped (restored) to some extent. The (sub)lattice that is formed by the (quasi)restored nodes is the *twin lattice*. In case of non-zero twin obliquity the twin lattice suffers a slight deviation at the composition surface.

Let $H^* = \cap_i H_i$ be the intersection group of the individuals in their respective orientations, $D(H^*)$ the holohedral supergroup (proper or trivial) of H^*, $D(\mathbf{L}_T)$ the point group of the twin lattice and $D(\mathbf{L}_{ind})$ the point group of the individual lattice. $D(\mathbf{L}_T)$ either coincides with $D(H^*)$ (case of zero twin obliquity) or is a proper supergroup of it (case of non-zero twin obliquity): it can be higher, equal or lower than $D(\mathbf{L}_{ind})$.

- When $D(\mathbf{L}_T) = D(\mathbf{L}_{ind})$ and the two lattices have the same orientation, twinning is by merohedry (twin index = 1). When at least some of the symmetry elements of $D(\mathbf{L}_T)$ are differently oriented from the corresponding ones of $D(\mathbf{L}_{ind})$, twinning is by reticular polyholohedry (twin index > 1, twin obliquity = 0) or reticular pseudopolyholohedry (twin index > 1, twin obliquity > 0).
- When $D(\mathbf{L}_T) \neq D(\mathbf{L}_{ind})$ twinning is by pseudomerohedry (twin index = 1, twin obliquity > 0),reticular merohedry (twin index > 1, twin obliquity = 0) or reticular pseudomerohedry (twin index > 1, twin obliquity > 0).

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4.5.3.25: Twin law

The **twin law** is the set of twin operations mapping two individuals of a twin. It is obtained by coset decomposition of the point group of the twin lattice with respect to the intersection group of the point groups of the individuals in their respective orientations. Each operation in the same coset is a possible twin operation that, from the lattice viewpoint, is equivalent to any other operation in the same coset. Any of these can be taken as **coset representative** and indicated by the symbol of the twin element: $\bar{1}$, [*uvw*] and (*hkl*) for the centre (*inversion twin*), direction of the rotation axis (*rotation twin*) and Miller indices of the mirror plane (*reflection twin*), in the order. Except when one refers to a specific plane or direction, the symbols {*hkl*} or <*uvw*> have to be be used to indicate all the planes or directions which belong to the same coset and are therefore equivalent under the point group of the individual.

In case of TLQS twinning the equivalence of the operations in a coset is only approximate.

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4.5.3.26: Twin obliquity

The concept of obliquity was introduced by Friedel in 1920 as a measure of the overlap of the lattices on the individuals forming a twin.

Let us indicate with [*u* ' *v* ' *w* '] the direction exactly perpendicular to a twin plane (*hkl*), and with (*h*' *k* ' *l* ') the plane perpendicular to a twin axis [uvw]. [*u* ' *v* ' *w* '] is parallel to the reciprocal lattice vector [*hkl*]* and (*h* ' *k* ' *l* ') is parallel to the reciprocal lattice plane (*uvw*)*. The angle between [*uvw*] and [*u* ' *v* ' *w* '] or, which is the same, between (*hkl*) and (*h* ' *k* ' *l* '), is called the **obliquity ω**.

The vector in direct space [*uvw*] has length L(*uvw*); the reciprocal lattice vector [*hkl*]* has length L*(*hkl*). The obliquity ω is thus the angle between the vectors [*uvw*] and [*hkl*]*; the scalar product between these two vectors is

$L(uvw)\, L^*(hkl) \cos\omega = \langle uvw|hkl\rangle = uh + vk + wl$

where <| stands for a 1x3 row matrix and |> for a 3x1 column matrix.

It follows that

$\cos\omega = (uh + vk + wl)/L(uvw)L^*(hkl)$

where $L(uvw) = \langle uvw|\mathbf{G}|uvw\rangle^{1/2}$ and $L^*(hkl) = \langle hkl|\mathbf{G}^*|hkl\rangle^{1/2}$, **G** and **G*** being the metric tensors in direct and reciprocal space, respectively.

Notice that $\mathbf{G}^* = \mathbf{G}^{-1}$ (and thus $\mathbf{G} = \mathbf{G}^{*-1}$) and that the matrix representation of the metric tensor is symmetric and coincides thus with its transpose ($\mathbf{G} = \mathbf{G}^T$, $\mathbf{G}^* = \mathbf{G}^{*T}$).

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4.5.3.27: Twin operation

The operation (action) of an element of symmetry that generates a *twin*.

Let H_i be the oriented point group of the i-th individual of a twin. The intersection group of the oriented vector point groups H_i of the individuals is indicated as $H^* = \cap_i H_i$. The symmetry of a twin is identified in vector space by a point group K which is a supergroup of H*. The coset decomposition of K with respect to H* gives the possible twin laws, each coset representing a twin law, and each operation in a coset representing a twin operation; the operations in a coset are equivalent under the operations of H*.

Operations in H describe the vector point symmetry of the individuals, whereas those in the cosets obtained by decomposing K in terms of H* connect the different individuals. To underline their different nature, the twin operations are often associated with a "color" and K is a thus a chromatic vector point group, known as *twin point group*.

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SECTION OVERVIEW

4.5.4: X-rays

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4.5.4.1: Absorption edge

An absorption edge is a sharp discontinuity in the absorption spectrum of X-rays by an element that occurs when the energy of the photon corresponds to the energy of a shell of the atom (K, L_I, L_{II}, L_{III}, etc.).

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4.5.4.2: Anomalous absorption

Anomalous absorption takes place when radiation is dynamically diffracted by a perfect or nearly perfect crystal. The optical field in the crystal is then made up by several components, called wavefields, two in the two beam case (neglecting polarization in the X-ray case). One of them is absorbed more than normal and the other one less than normal. In the transmission, or Laue geometry, both wavefields propagate inside the crystal; one then speaks of anomalous transmission for the less absorbed wavefield (Borrmann effect). In the reflection, or Bragg geometry, one wavefield only propagates in the crystal, the more absorbed one for angles of incidence corresponding to one side of the total reflection rocking curve and the less absorbed one for the other side. This results in an asymmetry of the rocking curve that is calculated using dynamical theory.

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4.5.4.3: Anomalous dispersion

The 'anomalous' dispersion corrections, which are not in fact anomalous, take into account the effect of absorption in the scattering of phonons by electrons. In the classic picture the electron is approximated by a damped harmonic oscillator. The scattering factor of the electron is then complex and the atomic scattering factor, or atomic form factor, is given by:

$f + f' + \mathrm{i}\, f''$

where f' and f'' are the real and imaginary parts of the anomalous dispersion correction. Their importance increases as one gets closer to an absorption edge (resonant scattering). Numerical calculations usually follow the Hartree-Fock approximations. For details on the non-relativistic and relativistic approaches, see Section 4.2.6 of *International Tables of Crystallography, Volume C*.

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4.5.4.4: Anomalous scattering

The history of the description of the scattering of an atom when illuminated with X-rays is that initially wavelength dependencies were ignored. This was initially referred to as 'normal scattering'. The wavelength dependencies were then corrections to the normal scattering and also called anomalous. These had to describe changes in amplitude and phase, respectively initially given the symbols $\Delta f'$ and $\Delta f''$. Thus the X-ray scattering factor of an atom is described by the equation:-

$$f = f_o + \Delta f' + i\Delta f''$$

The nomenclature changed when tunable synchrotron sources became available and whereby the Δ prefixes were removed because changes between two wavlengths would then have required a double Δ label, which is cumbersome. Thus the $\Delta f'$ now means the change in f'between two wavelengths. The Δ prefix to f'' is dropped for consistency even though its use is based on its value at a single wavelength.

The values of f' and f'' change most at the absorption edge of the element in question. Thus this resonance effect sometimes leads to the term being refererred to as 'resonant scattering'. However, since the off resonance f'' effect is extensively used in crystal structure determination of the hand of a molecule (its chirality) 'anomalous scattering' is the best *i.e.* most widely embracing term. Another commonly used term is Multiple-wavelength Anomalous Dispersion ('MAD'), which involves measurements made at the resonance condition and at more than one wavelength obviously.

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4.5.4.5: Borrmann Effect

Due to anomalous absorption, type 1 wavefields propagate in a perfect or nearly perfect crystal with a less than normal absorption. For details and the physical interpretation, see anomalous absorption.

Super-Borrmann effect

It is the enhancement of the Borrmann effect in a three-beam case, *e.g.* when the \(111\) and $\overline{111}$ reflections are simultaneously excited in a silicon or germanium crystal.

History

The Borrmann effect was first discovered in quartz (Borrmann G., 1941, *Über Extinktionsdiagramme der Röntgenstrahlen von Quarz*. *Physik Z.*, **42**, 157-162) and then in calcite crystals (Borrmann G., 1950, *Die Absorption von Röntgenstrahlen in Fall der Interferenz*. *Z. Phys.*, **127**, 297-323), and interpreted by Laue (Laue, M. von, 1949, *Die Absorption der Röntgenstrahlen in Kristallen im Interferenzfall*. *Acta Crystallogr*. **2**, 106-113).

The super-Borrmann effect was first observed by Borrmann G. and Hartwig W. (1965), *Die Absorption der Röntgenstrahlen im Dreistrahlfall der Interferenz*. *Z. Krist.*, **121**, 401-409.

See also

- Section 5.1 of *International Tables of Crystallography, Volume B* for X-rays
- Section 5.2 of *International Tables of Crystallography, Volume B* for electrons
- Section 5.3 of *International Tables of Crystallography, Volume B* for neutrons

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4.5.4.6: Bragg's law

Bragg's law provides the condition for a plane wave to be diffracted by a family of lattice planes:

$$2d\sin\theta = n\lambda.$$

where d is the **lattice** spacing, θ the angle between the wavevector of the incident plane wave, $\mathbf{k_o}$, and the lattice planes, λ its wave length and n is an integer, the order of the reflection. It is equivalent to the diffraction condition in reciprocal space and to the Laue equations.

Direct derivation of Bragg's law

- **Reflection from the first plane**

The scattered waves will be in phase whatever the distribution of the point scatterers in the first plane if the angle of the reflected wave vector, $\mathbf{k_h}$, is also equal to θ. This is Snell-Descartes' law of reflection.

- **Reflection from the second plane**

Since the phase of the reflected waves is independent of the position of the point scatterer in the plane, the phase difference between the waves reflected by two successive lattice planes is obtained by choosing arbitrarily a scattering point, A, on the first plane and a scattering point,b on the second plane such that AB is normal to the planes. If C and d are the projections of A on the incident and reflected wave vectors passing through B, it is clear from figure 1 that the path difference between the waves reflected at A and B, respectively, is:

$$CB + BD = 2d\sin\theta$$

and that the two waves will be in phase if this path difference is equal to n λ where n is an integer.

- **Reflection from the third, etc., planes**

If Bragg's relation is satisfied for the first two planes, the waves reflected with wave vector $\mathbf{k_h}$ will be in phase fo all the planes of the family.

Order of the reflection

Bragg's law may also be written:

$$2\left(\frac{d}{n}\right)\sin\theta = \lambda.$$

One may then say that a Bragg reflection of order n on a family of lattice planes or order n is equivalent to reflection of order 1 on a family of fictitious, or imaginary, planes of lattice spacing:

$$d_{hkl} = \frac{d}{n}$$

This fictitious family is associated to the reciprocal lattice vector **OH** where $OH = n/d = 1/d_{hkl}$. The indices of the reflection are: hkl. For instance, the dashed blue lines in Figure 1 correspond to the fistitious planes associated to the second order, $n = 2$.

Extinctions, or systematic absences

If there is a glide plane or a screw axis normal to the lattice planes, the spacing of the actual reflecting planes is$d/2$ for a glide plane and (d p/q) for a q_p screw axis. Bragg's law should then be written:

2 ($d/2$) sin θ = n λ ⇒ 2 d sin θ = 2n λ

for a glide plane and

2 (d p/q) sin θ = n λ ⇒ 2 d sin θ = (q/p)n λ

for a screw axis q_p.

The reflections of odd order for a glide plane and of order different from (q/p)n for a screw axis are then absent. One speaks of extinctions or systematic absences related to the presence of glide or screw components.

As an example, the case of a 2_1 screw axis. Reflections of odd order will be systematically absent.

Influence of deformation

A deformation that leaves a family of lattice planes (*hkl*) undistorted and its lattice spacing *d* unchanged will not affect the Bragg angle of *kkl*reflections, *e.g.* lattice planes parallel to a screw dislocations.

History

A deformation that leaves a family of lattice planes (*hkl*) undistorted and its lattice spacing *d* unchanged will not affect the Bragg angle of *kkl* reflections, *e.g.* lattice planes parallel to a screw dislocations.

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4.5.4.7: Bragg angle

In Bragg's law describing the condition for a plane wave to be diffracted from a family of lattice planes, the angle θ between the wavevector of the incident plane wave, $\mathbf{k_0}$, and the lattice planes.

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4.5.4.8: Cromer–Mann coefficients

The set of nine coefficients $a_i, b_i, c\ (i = 1, \ldots, 4)$ in a parameterization of the non-dispersive part of the atomic scattering factor for neutral atoms as a function of (sinθ) / λ:

$$f^0(\sin\theta/\lambda) = \sum_{i=1}^{4} a_i \exp[-b_i(\sin\theta/\lambda)^2] + c$$

for $0 < (\sin\theta)/\lambda < 2.0\,\text{Å}^{-1}$.

This expression is convenient for calculation in crystal structure software suites.

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4.5.4.9: Dynamical diffraction

When a crystal is perfect or nearly perfect, the usual geometrical, or kinematical theory of diffraction is an insufficient approximation and the dynamical theory of diffraction must be used to describe the diffracted intensities.

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4.5.4.10: Dynamical theory of Scattering

In the geometrical, or kinematical theory, the amplitudes diffracted by a three-dimensional periodic assembly of atoms (Laue) or by a stack of planes (Darwin) is derived by adding the amplitudes of the waves diffracted by each atom or by each plane, simply taking into account the optical path differences between them, but neglecting the interaction of the propagating waves and matter. This approximation is not compatible with the law of conservation of energy and is only valid for very small or highly imperfect crystals. The purpose of the dynamical theory is to take this interaction into account. There are three forms of the dynamical theory:

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4.5.4.11: Electron density map

A three-dimensional description of the electron density in a crystal structure, determined from X-ray diffraction experiments. X-rays scatter from the electron clouds of atoms in the crystal lattice; the diffracted waves from scattering planes *h*,*k*,*l* are described by structure factors $\mathbf{F}_{hkl}$. The electron density as a function of position *x*,*y*,*z* is the Fourier transform of the structure factors:

$\rho(xyz) = \frac{1}{V} \sum_{hkl} F(hkl) \exp[-2\pi i(hx + ky + lz)]$.

The electron density map describes the contents of the unit cells averaged over the whole crystal and not the contents of a single unit cell (a distinction that is important where structural disorder is present).

Three-dimensional maps are often evaluated as parallel two-dimensional contoured sections at different heights in the unit cell.

Units

Electron density is measured in electrons per cubic ångström, e $Å^{-3}$.

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4.5.4.12: Ewald sphere

The Ewald sphere, or sphere of reflection, is a sphere of radius 1/λ passing through the origin *O* of the reciprocal lattice. The incident direction is along a radius of the sphere, **IO** (Figure 1). A reflected direction, of unit vector $\mathbf{s_h}$, will satisfy the diffraction condition if the diffraction vector **OH** = **IH** – **IO** = $\mathbf{s_h}/\lambda - \mathbf{s_o}/\lambda$ ($\mathbf{s_o}$ unit vector in the direction **IO**) is a reciprocal lattice vector, namely if *H* is a node of the reciprocal lattice (see Diffraction condition in reciprocal space) . If other reciprocal lattice nodes, such as *G*, lie also on the sphere, there will be reflected beams along **IG**, etc. This construction is known as the Ewald construction. When the wavelength is large, there are seldom more than two nodes, *O* and *H*, of the reciprocal lattice simultaneously on the Ewald sphere. When there are three or more, one speaks of multiple diffraction, multiple scattering or *n*-beam diffraction. This situation becomes increasingly frequent as the wavelength decreases and is practically routine for very short wavelengths such as those of γ-rays and electrons. The curvature of Ewald sphere then becomes negligible and it can often be approximated by a plane. Many reflections must then be taken into account at the same time.

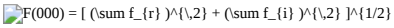
When the wavelength changes, the radius of the Ewald sphere changes. If the incident beam is a white beam, with a wavelength range $\lambda_{min} \leq \lambda \leq \lambda_{max}$, there will be a nest of Ewald spheres of radii $1/\lambda_{max} \leq 1/\lambda \leq 1/\lambda_{min}$.

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4.5.4.13: F(000)

The expression for a structure factor evaluated in the zeroth-order case $h = k = l = 0$ yields the result



where f_r is the real part of the scattering factors at $\theta = 0°$, f_i is the imaginary part of the scattering factors at $\theta = 0°$, θ is the Bragg angle, and the sum is taken over each atom in the unit cell.

F(000) is computed without dispersion effects in electron-density calculation by Fourier inversion. In all cases, non-dispersive *F*(000) is a structure factor and not a structure amplitude: it has both magnitude and a sign.

For X-rays non-dispersive *F*(000) is positive definite and in many cases an integer (but it is not an integer for non-stoichiometric compounds). It counts the number of electrons in the cell.

For neutrons non-dispersive *F*(000) is either positive or negative and counts the total nuclear scattering power in the cell.

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4.5.4.14: Friedel's Law

Friedel's law states that the intensities of the h, k, l and $\bar{h}$, $\bar{k}$, $\bar{l}$ reflections are equal. This is true either if the crystal is centrosymmetric or if no resonant scattering is present. It is in that case not possible to tell by diffraction whether an inversion center is present or not. The apparent symmetry of the crystal is then one of the eleven **Laue classes**.

The reason for Friedel's rule is that the diffracted intensity is proportional to the square of the modulus of the structure factor, $|F_h|^2$, according to the geometrical, or kinematical theory of diffraction. It depends similarly on the modulus of the structure factor according to the dynamical theory of diffraction. The structure factor is given by:

'_' allowed only in math mode

where f_j is the atomic scattering factor of atom j, $\mathbf{h}$ the reflection vector and '_' allowed only in math mode the position vector of atom j. There comes:

$$|F_h|^2 = F_h F_h^* = F_h F_{\bar{h}} = |F_{\bar{h}}|^2$$

if the atomic scattering factor, f_j, is real. The intensities of the h, k, l and $\bar{h}$, $\bar{k}$, $\bar{l}$ reflections are then equal. If the crystal is absorbing, however, due to resonant scattering, the atomic scattering factor is complex and

$$F_{\bar{h}} \neq F_h^*$$

The reflections h, k, l and $\bar{h}$, $\bar{k}$, $\bar{l}$ are called a *Friedel pair*. They are used in the resolution of the phase problem for the solution of crystal structures and in the determination of absolute structure.

History

Friedel's law was stated by G. Friedel (1865-1933) in 1913 (Friedel G., 1913, *Sur les symétries cristallines que peut révéler la diffraction des rayons X.*, *C.R. Acad. Sci. Paris*, **157**, 1533-1536.

See also

Section 3.1 of *International Tables of crystallography, Volume A*

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4.5.4.15: Friedel pair

The couple of reflections h, k, l and $\bar{h}, \bar{k}, \bar{l}$ is called a Friedel pair, or Bijvoet pair. Their intensities are equal either if the crystal structure is centrosymmetric or if there is no resonant scattering, but differ otherwise. Friedel's law then does not hold. For crystals with a non-centrosymmetric structure and significant resonant scattering, equivalent reflections generated by the symmetry operations of the point group of the crystal have intensities different from those of equivalent reflections generated by the introduction of an additional inversion centre in normal scattering. Friedel, or Bijvoet pairs are used in the resolution of the phase problem for the solution of crystal structures and in the determination of absolute structure.

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4.5.4.16: Integral reflection conditions

The integral reflections are the general reflection conditions due to the centering of cells. They are given in the table below:

Integral reflection conditions for centered lattices.

Reflection condition	Centering type of cell	Centering symbol
None	Primitive	*P* *R* (rhombohedral axes)
$h + k = 2n$	*C*-face centered	*C*
$k + l = 2n$	*A*-face centered	*A*
$l + h = 2n$	*B*-face centered	*B*
$h + k + l = 2n$	body centered	*I*
$h + k$, $h + l$ and $k + l = 2n$ or: h, k, l all odd or all even ('unmixed')	all-face centered	*F*
$-h + k + l = 3n$	rhombohedrally centered, reverse setting	*R* (hexagonal axes)
$h - k + l = 3n$	rhombohedrally centered, obverse setting (standard)	
$h - k = 3n$	hexagonally centered	*H*

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4.5.4.17: Kinematical theory

In the **kinematical** or **geometrical** theory, the amplitudes diffracted by a three-dimensional periodic assembly of atoms (Laue) or by a stack of planes (Darwin) is derived by adding the amplitudes of the waves diffracted by each atom or by each plane, simply taking into account the optical path differences between them, but neglecting the interaction of the propagating waves and matter. This approximation is not compatible with the law of conservation of energy and is only valid for very small or highly imperfect crystals. The purpose of the dynamical theory is to take this interaction into account .

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4.5.4.18: Laue equations

The three Laue equations give the conditions to be satisfied by an incident wave to be diffracted by a crystal. Consider the three basis vectors, **OA** = **a**, **OB** = **b** , **OC** = **c** of the crystal and let $\vec{s}_o$ and $\vec{s}_h$ be unit vectors along the incident and reflected directions, respectively. The conditions that the waves scattered by *O* and *A*, *O* and *B*,*O* and *C*, respectively, be in phase are that

$$\vec{a} \cdot (\mathbf{s}_h - \vec{s}_o) = h\lambda$$

$$\vec{b} \cdot (\vec{s}_h - \vec{s}_o) = k\lambda$$

$$\vec{c} \cdot (\vec{s}_h - \vec{s}_o) = l\lambda$$

If these three conditions are simultaneously satisfied, the incoming wave is reflected on the set of lattice planes of Miller indices *h/n*, *k/n*, *l/n*. *h*, *k*, *l* are the indices of the reflection.

The three Laue equations can be generalized by saying that the diffraction condition is satisfied if the scalar product

$$\vec{r} \cdot (\vec{s}_h/\lambda - \vec{s}_o/\lambda)$$

is an integer for any vector

$$\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$$

where (u, v, w integers) of the direct lattice. This is the case if

$$(\mathbf{s_h}/\lambda - \mathbf{s_0}/\lambda) = h\,\mathbf{a^*} + k\,\mathbf{b^*} + l\,\mathbf{c^*},$$

where *h*, *k*, *l* are integers, namely if the diffraction vector **OH** = $\mathbf{s_h}$/λ - $\mathbf{s_0}$/λ is a vector of the reciprocal lattice. This is the diffraction condition in reciprocal space.

History

The three Laue conditions for diffraction were first given in Laue, M. (1912). *Eine quantitative Prüfung der Theorie für die Interferenz-Erscheinungen bei Röntgenstrahlen*. *Sitzungsberichte der Kgl. Bayer. Akad. der Wiss* 363--373, reprinted in *Ann. Phys.* (1913), **41**, 989-1002 where he interpreted and indexed the first diffraction diagram (Friedrich, W., Knipping, P., and Laue, M. (1912). *Interferenz-Erscheinungen bei Röntgenstrahlen*, *Sitzungsberichte der Kgl. Bayer. Akad. der Wiss*, 303--322, reprinted in *Ann. Phys.*, (1913), **41**, 971-988, taken with zinc-blende, ZnS. For details, see P. P. Ewald, 1962, IUCr, 50 Years of X-ray Diffraction, Section 4, page 52.

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4.5.4.19: Lorentz–polarization correction

A multiplicative factor involved in converting diffracted radiation intensities to structure factors during the process of structure determination for X-ray diffraction experiments involving moving crystals.

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4.5.4.20: Mosaic crystal

The **mosaic crystal** is a simplified model of real crystals proposed by C. G. Darwin. In this model, a real crystal is described as a mosaic of crystalline blocks with dimensions of 10^{-5} cm, tilted to each other by fractions of a minute of arc. Each block is separated from the surrounding blocks by faults and cracks.

In a diffraction experiment, interference between waves only occurs inside a block, whose dimensions satisfy the theoretical conditions of applicability of the kinematical theory. Because of the loss of coherence between the waves diffracted from different blocks, the diffracted intensity from the whole crystal is equal to the sum of the intensities diffracted by every block.

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4.5.4.21: Primary extinction

The **primary extinction** is responsible for the loss of intensity due to dynamic effect inside every block of a mosaic crystal. At the Bragg angle, each incident wave can undergo multiple reflections from different atomic planes; each scattering introduced causes a phase difference of $\lambda/4 = \pi/2$ so that along each direction waves differing by an even number of scattering, *i.e.* by $n\pi$ in phase, interfere , whose intensity decreasing rapidly with the number of scatterings. Because of the decrease in intensity of waves multiply scattered, the effect of waves differing by more than two scatterings can normally be neglected: in each direction one observes then the destructive interference between waves having a significant difference in intensity and an overall reduction of the intensity with respect to the intensity given by the kinematical theory.

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4.5.4.22: Reflection conditions

The reflection conditions describe the conditions of occurrence of a reflection (structure factor not systematically zero). There are two types of systematic reflection conditions for diffraction of crystals by radiation:

(1) *General conditions*. They apply to all Wyckoff positions of a space group, *i.e.* they are always obeyed, irrespective of which Wyckoff positions are occupied by atoms in a particular crystal structure. They are due to one of three effects:

- *Centered cells*.

The resulting conditions apply to the whole three-dimensional set of reflections hkl. Accordingly, they are called *integral reflection conditions*. They are given in Table 1.

- *Glide planes*.

The resulting conditions apply only to two-dimensional sets of reflections, *i.e.* to reciprocal-lattice nets containing the origin (such as *hk*0, *h*0*l*, 0*kl*, *hhl*). For this reason, they are called *zonal reflection conditions*. For instance, for a glide plane parallel to (001):

type of reflection	reflection condition	glide vector	glide plane
0*kl*	$k = 2n$	**b**/2	*b*
	$l = 2n$	**c**/2	*c*
	$k + l = 2n$	**b**/2 + **c**/2	*n*
	$k + l = 4n$ $k, l = 2n$	**b**/4 ± **c**/4	*d*

The zonal reflection conditions are listed in Table 2.2.13.2 of *International Tables of Crystallography, Volume A*.

- *Screw axes*.

The resulting conditions apply only to one-dimensional sets of reflections, *i.e.* reciprocal-lattice rows containing the origin (such as *h*00, 0*k*0, 00*l*). They are called *serial reflection conditions*. For instance, for a screw axis parallel to [001], the reflection conditions are:

type of reflection	reflection condition	screw vector	screw axis
00*l*	$l = 2n$	**c**/2	2_1; 4_2
	$l = 4n$	**c**/4	4_1; 4_3
000*l*	$l = 2n$	**c**/2	6_3
	$l = 3n$	**c**/3	4_1; 3_1; 3_2; 6_2; 6_4
	$l = 6n$	**c**/6	6_1;6_5

The serial reflection conditions are listed in Table 2.2.13.2 of *International Tables of Crystallography, Volume A*.

(2) *Special conditions* ('extra' conditions). They apply only to special Wyckoff positions and occur always in addition to the general conditions of the space group.

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4.5.4.23: Resolution

In crystal structure determination, the term **resolution** is used to describe the ability to distinguish between neighboring features in an electron density map. By convention, it is defined as the minimum plane spacing given by Bragg's law for a particular set of X-ray diffraction intensities. The resolution improves with an increase in the maximum value of $(\sin\theta)/\lambda$ at which reflections are measured.

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4.5.4.24: Resonant scattering

The elementary theory of the scattering of X-rays by atoms, leading to the real atomic scattering factor f_o, applies only for X-radiation whose wavelength is far removed from that of any natural (resonant) frequency of the atom. When this condition does not hold, one needs to use as physical model for the scattering that of a forced damped harmonic oscillator. This leads to resonant-scattering terms in the full, now complex, scattering factor of an atom, represented by:-

$f = f_o + f' + if''$.

The real and imaginary terms, f', f'', in the atomic scattering factor are independent of sin(θ)/λ and in general small compared to f_o. The values of f' and f'' change most at the absorption edge of the element in question.

In the older literature the term *anomalous dispersion* was used for resonant scattering. In macromolecular crystallography the term *anomalous scattering* is used widely in place of resonant scattering.

History

The resonant scattering of X-rays was theoretically predicted by Waller (Waller, I., 1928, *Über eine verallgemeinerte Streuungsformel*. *Z. Phys.* **51**, 213-231.) and first calculated by Hönl (Hönl, H., 1933, *Zur Dispersionstheorie der Röntgenstrahlen. Z. Phys.* **84**, 1-16; Hönl, H., 1933, *Atomfactor für Röntgenstrahlen als Problem der Dispersionstheorie (K-Schale)*. *Ann. Phys.* (Leipzig), **18**, 625-657.

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4.5.4.25: Secondary extinction

The **secondary extinction** is responsible for the loss of intensity occurring when the incident beam crosses a crystal. Each plane of a family (*hkl*) satisfying Laue equations (or Bragg's law) diffracts the incident beam, and thus subtracts part of the intensity to the incident beam. Successive planes of the same family will then experience a weakening of the incident beam and as a consequence the diffracted beams will result from the positive interference of waves not having the same intensities, as it is instead considered by the kinematical theory.

Secondary extinction is equivalent to an increase of the linear absorption coefficient and is negligible for sufficiently small crystals.

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4.5.4.26: Serial reflection conditions

The serial reflection conditions are the general reflection conditions due to the presence of screw axes. The resulting conditions apply only to one-dimensional sets of reflections, *i.e.* reciprocal-lattice rows containing the origin (such as *h*00, 0*k*0, 00*l*). For instance, for a screw axis parallel to [001], the reflection conditions are:

type of reflection	reflection condition	screw vector	screw axis
00*l*	$l = 2n$	**c**/2	2_1; 4_2
	$l = 4n$	**c**/4	4_1; 4_3
000*l*	$l = 2n$	**c**/2	6_3
	$l = 3n$	**c**/3	4_1; 3_1; 3_2; 6_2; 6_4
	$l = 6n$	**c**/6	6_1;6_5

The serial reflection conditions are listed in Table 2.2.13.2 of *International Tables of Crystallography, Volume A*.

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4.5.4.27: Structure Factor

The **structure factor** $\mathbf{F}_{hkl}$ is a mathematical function describing the amplitude and phase of a wave diffracted from crystal lattice planes characterized by Miller indices *h*,*k*,*l*.

The structure factor may be expressed as

$$\mathbf{F}_{hkl} = F_{hkl}\exp(i\alpha_{hkl}) = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (4.5.4.27.1)$$

$$= \sum_j f_j \cos[2\pi(hx_j + ky_j + lz_j)] + i\sum_j f_j \sin[2\pi(hx_j + ky_j + lz_j)] \quad (4.5.4.27.2)$$

$$= A_{hkl} + iB_{hkl} \quad (4.5.4.27.3)$$

where the sum is over all atoms in the unit cell, x_j,y_j,z_j are the positional coordinates of the *j*th atom, f_j is the scattering factor of the *j*th atom, and α_{hkl} is the phase of the diffracted beam.

The intensity of a diffracted beam is directly related to the amplitude of the structure factor, but the phase must normally be deduced by indirect means. In structure determination, phases are estimated and an initial description of the positions and anisotropic displacements of the scattering atoms is deduced. From this initial model, structure factors are calculated and compared with those experimentally observed. Iterative refinement procedures attempt to minimize the difference between calculation and experiment, until a satisfactory fit has been obtained.

Derivation

Consider Bragg's law for an array of atom scatterers in a primitive lattice with just one atom at each lattice point. An incident X-ray wave of wavelength λ diffracts strongly through an angle 2θ where the perpendicular distance between two lattice planes d_{hkl} satisfies the relation

$$2d_{hkl}\sin\theta = n\lambda$$

It is seen that the path difference between waves diffracted from the two planes shown differs by just one wave cycle.

Now consider a second atom added to the unit cell. Each original atom is now accompanied by a companion atom of the new type, offset by a displacement vector $\mathbf{r}_1$. The incident X-ray beam will also diffract from these new scatterers (since they occupy planes parallel to those originally drawn). But now there is a phase difference φ_1 between the waves scattered from the first and the new sets of atoms.

The amplitudes of the waves are proportional to the atomic scattering factors f_0 and f_1. The phases differ by the angle φ_1 . The resultant vector represents the two-atom structure factor with amplitude F_{hkl}. Note that there is a net phase φ arising from the phase difference due to the offset in position between the two sets of diffracting atoms.

As in the case of two atoms, the resultant diffracted wave is obtained from the linear superposition of the wave vectors scattered from each different atom.

Units

The units of the structure-factor amplitude depend on the incident radiation. For X-ray crystallography they are multiples of the unit of scattering by a single electron ($2.82 \times 10^{-15}\ m$); for neutron scattering by atomic nuclei the unit of scattering length of $10^{-14}\ m$ is commonly used.

See also

The structure factor. P. Coppens. *International Tables for Crystallography* (2006). Vol. B, ch. 1.2, pp. 10-24

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4.5.4.28: Systematic absences

One speaks of *systematic absences* or *extinctions* when the structure factor is zero, due either to the centering of the lattice or to the presence of glide or screw symmetry elements. Conversely, the conditions for a reflection to exist and not to be systematically absent, are called reflection conditions.

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4.5.4.29: Zonal reflection conditions

The zonal reflection conditions are the general reflection conditions due to the presence of glide planes. The resulting conditions apply only to two dimensional sets of reflections, *i.e.* to reciprocal-lattice nets containing the origin (such as *hk*0, *h*0*l*, 0*kl*, *hhl*). For instance, for a glide plane parallel to (001):

type of reflection	reflection condition	glide vector	glide plane
0*kl*	$k = 2\,n$	**b**/2	*b*
	$l = 2\,n$	**c**/2	*c*
	$k + l = 2\,n$	**b**/2 + **c**/2	*n*
	$k + l = 4\,n$ $k, l = 2n$	**b**/4 ± **c**/4	*d*

The zonal reflection conditions are listed in Table 2.2.13.2 of *International Tables of Crystallography, Volume A*.

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