

FUNDAMENTAL ORGANIC ALA MECH



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Fundamental Organic ala Mech

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This text was compiled on 03/11/2026

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CHAPTER OVERVIEW

1: Atomic Structure

1.1: Atomic Structure - The Nucleus

1.2: Atomic Structure - Orbitals

1.3: Atomic Structure - Electron Configurations

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1.1: Atomic Structure - The Nucleus

As you might remember from your general chemistry course, an atom consists of a dense, positively charged nucleus surrounded at a relatively large distance by negatively charged electrons (Figure 1.1.1). The nucleus consists of subatomic particles called *neutrons*, which are electrically neutral, and *protons*, which are positively charged. Because an atom is neutral overall, the number of positive protons in the nucleus and the number of negative electrons surrounding the nucleus are the same.

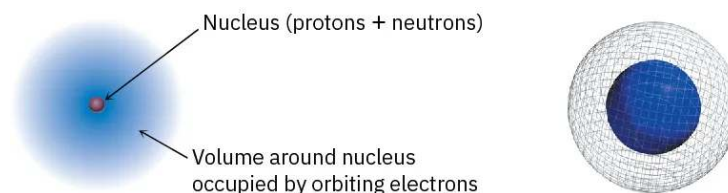


Figure 1.1.1: A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three-dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the **blue solid surface** than at the **gray mesh surface**.

Although extremely small—about 10^{-14} to 10^{-15} meter (m) in diameter—the nucleus nevertheless contains essentially all the mass of the atom. Electrons have negligible mass and circulate around the nucleus at a distance of approximately 10^{-10} m. Thus, the diameter of a typical atom is about 2×10^{-10} m, or 200 picometers (pm), where $1 \text{ pm} = 10^{-12} \text{ m}$. To give you an idea of how small this is, a thin pencil line is about 3 million carbon atoms wide. Although most chemists throughout the world use the International System (SI) of units and describe small distances in picometers, many organic chemists and biochemists in the United States still use the unit angstrom (Å) to express atomic distances, where $1 \text{ Å} = 100 \text{ pm} = 10^{-10} \text{ m}$. As you probably did in your general chemistry course, however, we'll stay with SI units in this book.

A specific atom is described by its atomic number (Z), which gives the number of protons (or electrons) it contains, and its mass number (A), which gives the total number of protons and neutrons in its nucleus. All the atoms of a given element have the same atomic number: 1 for hydrogen, 6 for carbon, 15 for phosphorus, and so on; but they can have different mass numbers depending on how many neutrons they contain. Atoms with the same atomic number but different mass numbers are called isotopes. The element carbon, for instance, has three isotopes that occur naturally, with mass numbers of 12, 13, and 14. Carbon-12 has a natural abundance of 98.89%, carbon-13 has a natural abundance of 1.11%, and carbon-14 has only a negligible natural abundance.

The weighted-average of an element's naturally occurring isotopes is called **atomic weight** and is given in unified atomic mass units (u) or daltons (Da) where 1 u or 1 Da is defined as one twelfth the mass of one atom of carbon-12. Thus, the atomic weight is 1.008 u for hydrogen, 12.011 u for carbon, 30.974 u for phosphorus, and so on. Atomic weights of all elements are given in the periodic table in Appendix D.

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1.2: Atomic Structure - Orbitals

How are the electrons distributed in an atom? You might recall from your general chemistry course that, according to the *quantum mechanical model*, the behavior of a specific electron in an atom can be described by a mathematical expression called a *wave equation*—the same type of expression used to describe the motion of waves in a fluid. The solution to a wave equation is called a *wave function*, or orbital, and is denoted by the lowercase Greek letter psi (ψ).

When the square of the wave function, ψ^2 , is plotted in three-dimensional space, an orbital describes the volume of space around a nucleus that an electron is most likely to occupy. You might therefore think of an orbital as looking like a photograph of the electron taken at a slow shutter speed. In such a photo, the orbital would appear as a blurry cloud, indicating the region of space where the electron has been. This electron cloud doesn't have a sharp boundary, but for practical purposes we can set the limits by saying that an orbital represents the space where an electron spends 90% to 95% of its time.

What do orbitals look like? There are four different kinds of orbitals, denoted *s*, *p*, *d*, and *f*, each with a different shape. Of the four, we'll be concerned primarily with *s* and *p* orbitals because these are the most common in organic and biological chemistry. An *s* orbital has a spherical shape, with the nucleus at its center; a *p* orbital has a dumbbell shape with two parts, or *lobes*; and four of the five *d* orbitals have a cloverleaf shape with four lobes, as shown in Figure 1.2.1. The fifth *d* orbital is shaped like an elongated dumbbell with a doughnut around its middle.

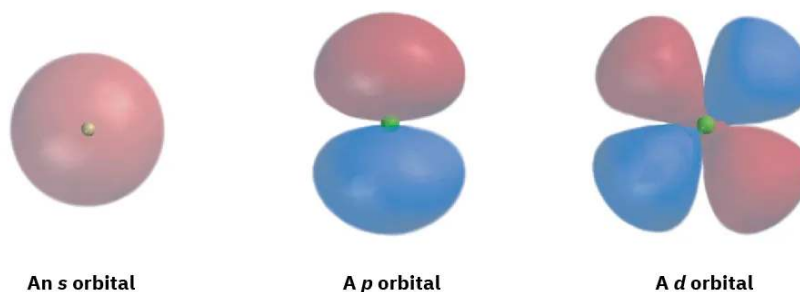


Figure 1.2.1: Representations of *s*, *p*, and *d* orbitals. An *s* orbital is spherical, a *p* orbital is dumbbell-shaped, and four of the five *d* orbitals are cloverleaf-shaped. Different lobes of *p* orbitals are often drawn for convenience as teardrops, but their actual shape is more like that of a doorknob, as indicated.

The orbitals in an atom are organized into different layers around the nucleus called electron shells, which are centered around the nucleus and have successively larger size and energy. Different shells contain different numbers and kinds of orbitals, and each orbital within a shell can be occupied by two electrons. The first shell contains only a single *s* orbital, denoted *1s*, and thus holds only 2 electrons. The second shell contains one *2s* orbital and three *2p* orbitals and thus holds a total of 8 electrons. The third shell contains a *3s* orbital, three *3p* orbitals, and five *3d* orbitals, for a total capacity of 18 electrons. These orbital groupings and their energy levels are shown in Figure 1.2.2.

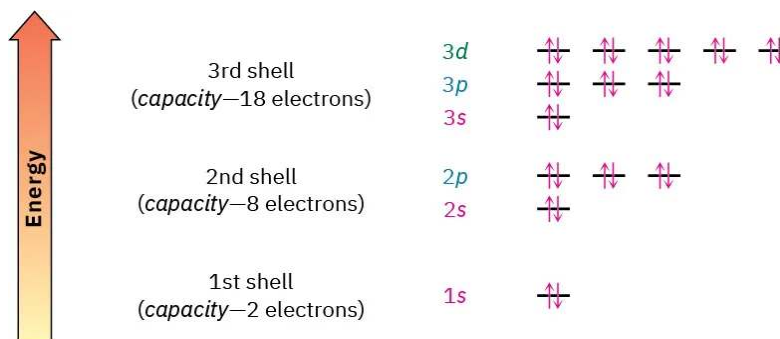


Figure 1.2.2: Energy levels of electrons in an atom. The first shell holds a maximum of 2 electrons in one *1s*

orbital; the second shell holds a maximum of 8 electrons in one *2s* and three *2p* orbitals; the third shell holds a maximum of 18 electrons in one *3s*, three *3p*, and *3d* orbitals; and so on. The two electrons in each orbital are represented by five up and down arrows, $\uparrow\downarrow$. Although not shown, the energy level of the *4s* orbital falls between *3p* and *3d*.

The three different p orbitals within a given shell are oriented in space along mutually perpendicular directions, denoted p_x , p_y , and p_z . As shown in Figure 1.2.3, the two lobes of each p orbital are separated by a region of zero electron density called a node. Furthermore, the two orbital regions separated by the node have different algebraic signs, $+$ and $-$, in the wave function, as represented by the different colors in Figure 1.2.1 and Figure 1.2.3. As we'll see in **Section 1.12**, these algebraic signs for different orbital lobes have important consequences with respect to chemical bonding and chemical reactivity.

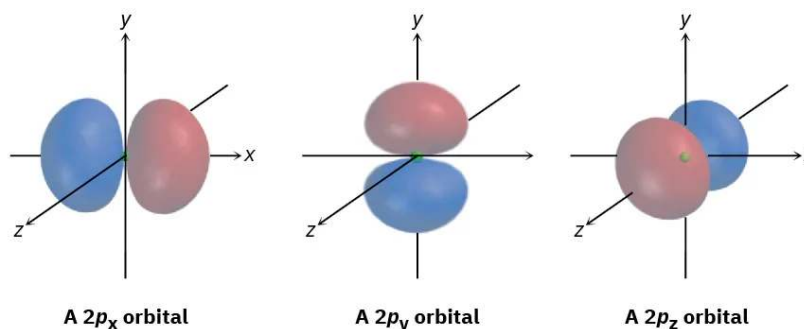


Figure 1.2.3: Shapes of the $2p$ orbitals. Each of the three mutually perpendicular, dumbbell-shaped orbitals has two lobes separated by a node. The two lobes have different algebraic signs in the corresponding wave function, as indicated by the different colors.

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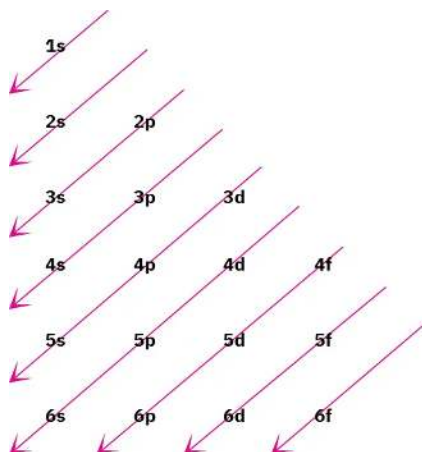
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1.3: Atomic Structure - Electron Configurations

The lowest-energy arrangement, or ground-state electron configuration, of an atom is a list of the orbitals occupied by its electrons. We can predict this arrangement by following three rules.

RULE 1

The lowest-energy orbitals fill up first, $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$, according to the following graphic, a statement called the *Aufbau principle*. Note that the 4s orbital lies between the 3p and 3d orbitals in energy.



RULE 2

Electrons act in some ways as if they were spinning around an axis, somewhat as the earth spins. This spin can have two orientations, denoted as up ($\uparrow$) and down ($\downarrow$). Only two electrons can occupy an orbital, and they must have opposite spins, a statement called the *Pauli exclusion principle*.

RULE 3

If two or more empty orbitals of equal energy are available, one electron occupies each with spins parallel until all orbitals are half-full, a statement called *Hund's rule*.

Some examples of how these rules apply are shown in Table 1.3.1. Hydrogen, for instance, has only one electron, which must occupy the lowest-energy orbital. Thus, hydrogen has a 1s ground-state configuration. Carbon has six electrons and the ground-state configuration $1s^2 2s^2 2p_x^1 2p_y^1$, and so forth. Note that a superscript is used to represent the number of electrons in a particular orbital.

Table 1.3.1: Ground-State Electron Configurations of Some Elements

Element	Atomic number	Configuration
Hydrogen	1	1s $\uparrow$
Carbon	6	1s $\uparrow\downarrow$ 2s $\uparrow\downarrow$ 2p $\uparrow \uparrow \text{—}$
Phosphorus	15	1s $\uparrow\downarrow$ 2s $\uparrow\downarrow$ 2p $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$ 3s $\uparrow\downarrow$ 3p $\uparrow \uparrow \uparrow$

? Exercise 1.3.1

What is the ground-state electron configuration of each of the following elements:

- a. Oxygen
- b. Nitrogen
- c. Sulfur

Answer

- a. $1s^2 2s^2 2p^4$
- b. $1s^2 2s^2 2p^3$
- c. $1s^2 2s^2 2p^6 3s^2 3p^4$

? Exercise 1.3.2

How many electrons does each of the following biological trace elements have in its outermost electron shell?

- a. Magnesium
- b. Cobalt
- c. Selenium

Answer

- a. 2
- b. 2
- c. 6

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CHAPTER OVERVIEW

2: Molecular Structure

- 2.1: Development of Chemical Bonding Theory
- 2.2: Describing Chemical Bonds - Valence Bond Theory
- 2.3: Drawing Chemical Structures
- 2.4: sp^3 Hybrid Orbitals and the Structure of Methane
- 2.5: sp^3 Hybrid Orbitals and the Structure of Ethane
- 2.6: sp^2 Hybrid Orbitals and the Structure of Ethylene
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2.1: Development of Chemical Bonding Theory

By the mid-1800s, the new science of chemistry was developing rapidly, especially in Europe, and chemists had begun to probe the forces holding compounds together. In 1858, the German chemist August Kekulé and the Scottish chemist Archibald Couper independently proposed that, in all organic compounds, carbon is *tetravalent*—it always forms four bonds when it joins other elements to form stable compounds. Furthermore, said Kekulé, carbon atoms can bond to one another to form extended chains of linked atoms. In 1865, Kekulé provided another major advance when he suggested that carbon chains can double back on themselves to form *rings* of atoms.

Although Kekulé and Couper were correct in describing the tetravalent nature of carbon, chemistry was still viewed in a two-dimensional way until 1874. In that year, the Dutch chemist Jacobus van 't Hoff and French chemist Joseph Le Bel added a third dimension to our ideas about organic compounds when they proposed that the four bonds of carbon are not oriented randomly but have specific spatial directions. Van't Hoff went even further and suggested that the four atoms to which carbon is bonded sit at the corners of a regular tetrahedron, with carbon in the center.

A representation of a tetrahedral carbon atom is shown in Figure 2.1.1. Note the conventions used to show three-dimensionality: solid lines represent bonds in the plane of the page, the heavy wedged line represents a bond coming out of the page toward the viewer, and the dashed line represents a bond receding back behind the page, away from the viewer. Get used to them; these representations will be used throughout the text.

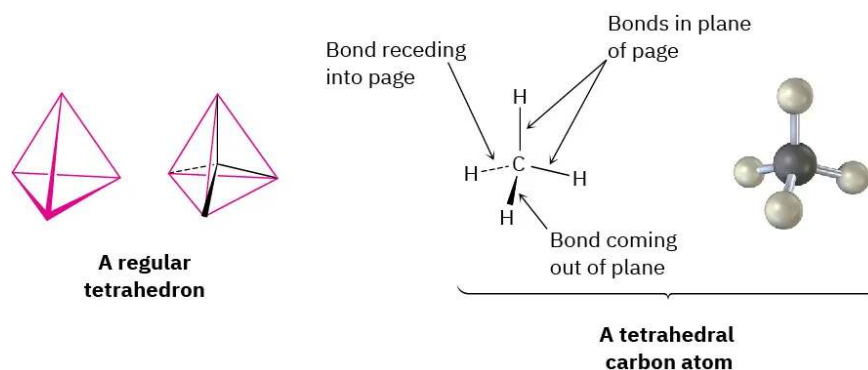


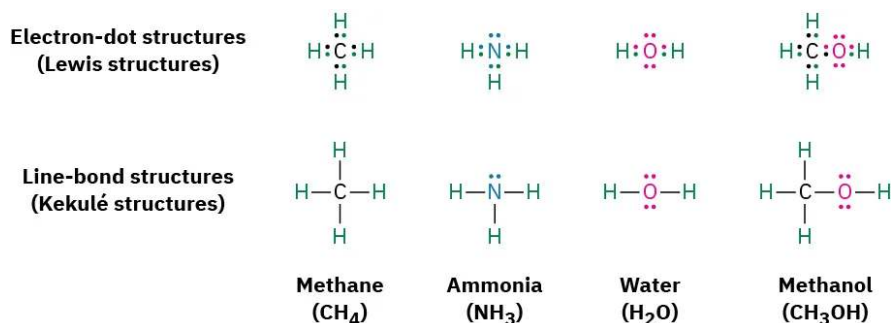
Figure 2.1.1: A representation of van't Hoff's tetrahedral carbon atom. The solid lines represent bonds in the plane of the paper, the heavy wedged line represents a bond coming out of the plane of the page toward the viewer, and the dashed line represents a bond going back behind the plane of the page away from the viewer.

Why, though, do atoms bond together, and how can chemical bonds be described electronically? The *why* question is relatively easy to answer: atoms bond together because the compound that results is more stable and lower in energy than the separate atoms. Energy—usually as heat—is always released and flows out of the chemical system when a bond forms. Conversely, energy is added to the chemical system when a bond breaks. Making bonds always releases energy, and breaking bonds always absorbs energy. The *how* question is more difficult. To answer it, we need to know more about the electronic properties of atoms.

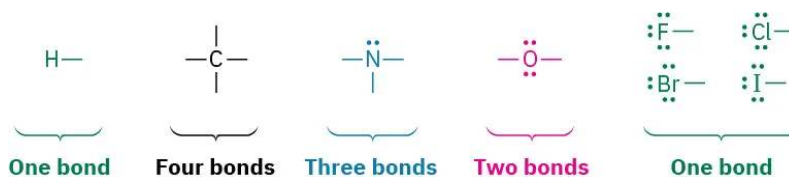
We know through observation that eight electrons (an electron *octet*) in an atom's outermost shell, or valence shell, impart special stability to the noble-gas elements in group 8A of the periodic table: Ne (2 + 8); Ar (2 + 8 + 8); Kr (2 + 8 + 18 + 8). We also know that the chemistry of the main-group elements on the left and right sides of the periodic table is governed by their tendency to take on the electron configuration of the nearest noble gas. The alkali metals such as sodium in group 1A, for example, achieve a noble-gas configuration by losing the single *s* electron from their valence shell to form a cation, while the halogens such as chlorine in group 7A achieve a noble-gas configuration by gaining a *p* electron to fill their valence shell and form an anion. The resultant ions are held together in compounds like $\text{Na}^+ \text{Cl}^-$ by the electrical attraction of unlike charges that we call an ionic bond.

But how do elements closer to the middle of the periodic table form bonds? Look at methane, CH_4 , the main constituent of natural gas, for example. The bonding in methane is not ionic because it would take too much energy for carbon ($1s^2 2s^2 2p^2$) either to gain or lose four electrons to achieve a noble-gas configuration. Instead, carbon bonds to other atoms, not by gaining or losing electrons, but by *sharing* them. Such a shared-electron bond, first proposed in 1916 by the American chemist G. N. Lewis, is called a covalent bond. The neutral collection of atoms held together by covalent bonds is called a molecule. Ionic compounds such as sodium chloride, however, are not called molecules.

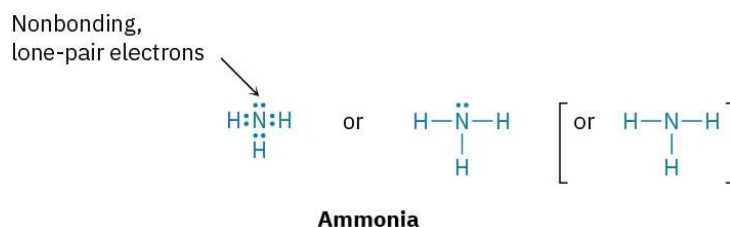
A simple way of indicating the covalent bonds in molecules is to use what are called Lewis structures, or electron-dot structures, in which the valence-shell electrons of an atom are represented as dots. Thus, hydrogen has one dot representing its $1s$ electron, carbon has four dots ($2s^2 2p^2$), oxygen has six dots ($2s^2 2p^4$), and so on. A stable molecule results whenever a noble-gas configuration of eight dots (an octet) is achieved for all main-group atoms or two dots for hydrogen. Even simpler than Lewis structures is the use of Kekulé structures, or line-bond structures, in which the two-electron covalent bonds are indicated as lines drawn between atoms.



The number of covalent bonds an atom forms depends on how many additional valence electrons it needs to reach a noble-gas configuration. Hydrogen has one valence electron ($1s$) and needs only one more to reach the helium configuration ($1s^2$), so it forms one bond. Carbon has four valence electrons ($2s^2 2p^2$) and needs four more to reach the neon configuration ($2s^2 2p^6$), so it forms four bonds. Nitrogen has five valence electrons ($2s^2 2p^3$), needs three more, and forms three bonds; oxygen has six valence electrons ($2s^2 2p^4$), needs two more, and forms two bonds; and the halogens have seven valence electrons, need one more, and form one bond.



Valence electrons that are not used for bonding remain as dots in structures and are called lone-pair electrons, or nonbonding electrons. The nitrogen atom in ammonia, NH₃, for instance, shares six valence electrons in three covalent bonds and has its remaining two valence electrons as two dots in a nonbonding lone pair. As a time-saving shorthand, nonbonding electrons are often omitted when drawing line-bond structures, but you still have to keep them in mind since they're often crucial in chemical reactions.



✓ Worked Example 2.1.1: Predicting the Number of Bonds Formed by Atoms in Molecules

How many hydrogen atoms does phosphorus bond to in forming phosphine, PH₃?

Strategy

Identify the periodic group of phosphorus, and find from that how many electrons (bonds) are needed to make an octet.

Solution

Phosphorus is in group 5A of the periodic table and has five valence electrons. It thus needs to share three more electrons to make an octet and therefore bonds to three hydrogen atoms, giving PH₃.

✓ Worked Example 2.1.2: Drawing Electron-Dot and Line-Bond Structures

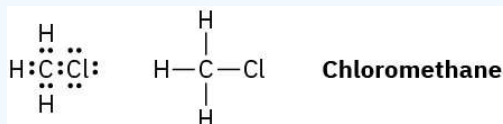
Draw both electron-dot and line-bond structures for chloromethane, CH_3Cl .

Strategy

Remember that a covalent bond—that is, a pair of shared electrons—is represented as a line between atoms.

Solution

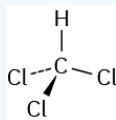
Hydrogen has one valence electron, carbon has four valence electrons, and chlorine has seven valence electrons. Thus, chloromethane is represented as



? Exercise 2.1.1

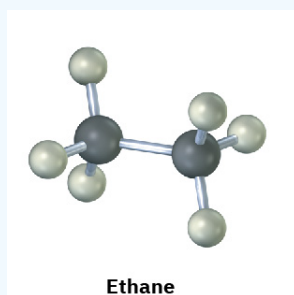
Draw a molecule of chloroform, CHCl_3 , using solid, wedged, and dashed lines to show its tetrahedral geometry.

Answer

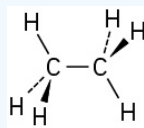


? Exercise 2.1.2

Convert the following representation of ethane, C_2H_6 , into a conventional drawing that uses solid, wedged, and dashed lines to indicate tetrahedral geometry around each carbon (black = C, gray = H).



Answer



? Exercise 2.1.3

What are likely formulas for the following substances?

(a) CCl_7 (b) AlH_7 (c) CH_7Cl_2 (d) SiF_7 (e) CH_3NH_7

Answer

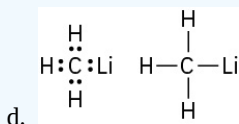
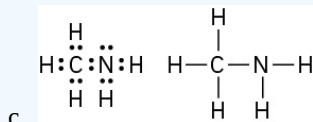
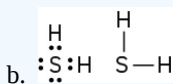
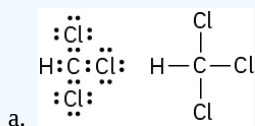
(a) CCl_4 (b) AlH_3 (c) CH_2Cl_2 (d) SiF_4 (e) CH_3NH_2

? Exercise 2.1.4

Write line-bond structures for the following substances, showing all nonbonding electrons:

- CHCl_3 , chloroform
- H_2S , hydrogen sulfide
- CH_3NH_2 , methylamine
- CH_3Li , methyllithium

Answer



? Exercise 2.1.5

Why can't an organic molecule have the formula C_2H_7 ?

Answer

C_2H_7 has too many hydrogens for a compound with two carbons.

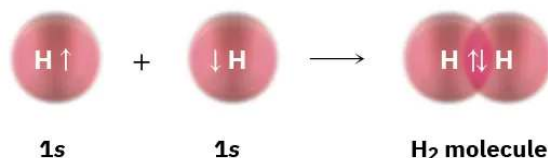
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2.2: Describing Chemical Bonds - Valence Bond Theory

How does electron sharing lead to bonding between atoms? Two models have been developed to describe covalent bonding: *valence bond theory* and *molecular orbital theory*. Each model has its strengths and weaknesses, and chemists tend to use them interchangeably depending on the circumstances. Valence bond theory is the more easily visualized of the two, so most of the descriptions we'll use in this book derive from that approach.

According to valence bond (VB) theory, a covalent bond forms when two atoms approach each other closely and a singly occupied orbital on one atom *overlaps* a singly occupied orbital on the other atom. The electrons are now paired in the overlapping orbitals and are attracted to the nuclei of both atoms, thus bonding the atoms together. In the H_2 molecule, for instance, the H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals.



The overlapping orbitals in the H_2 molecule have the elongated egg shape we might get by pressing two spheres together. If a plane were to pass through the middle of the bond, the intersection of the plane and the overlapping orbitals would be a circle. In other words, the H–H bond is cylindrically symmetrical, as shown in Figure 2.2.1. Such bonds, which are formed by the head-on overlap of two atomic orbitals along a line drawn between the nuclei, are called sigma (σ) bonds.

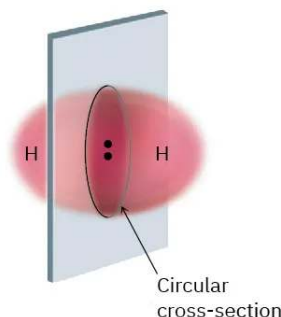


Figure 2.2.1: The cylindrical symmetry of the H–H σ bond in an H_2 molecule. The intersection of a plane cutting through the σ bond is a circle.

During the bond-forming reaction $2\text{H}\cdot \rightarrow \text{H}_2$, 436 kJ/mol (104 kcal/mol) of energy is released. Because the product H_2 molecule has 436 kJ/mol less energy than the starting 2 $\text{H}\cdot$ atoms, the product is more stable than the reactant and we say that the H–H bond has a bond strength of 436 kJ/mol. In other words, we would have to put 436 kJ/mol of energy into the H–H bond to break the H_2 molecule apart into two H atoms (Figure 2.2.2). For convenience, we'll generally give energies in both kilocalories (kcal) and the SI unit kilojoules (kJ): 1 kJ = 0.2390 kcal; 1 kcal = 4.184 kJ.

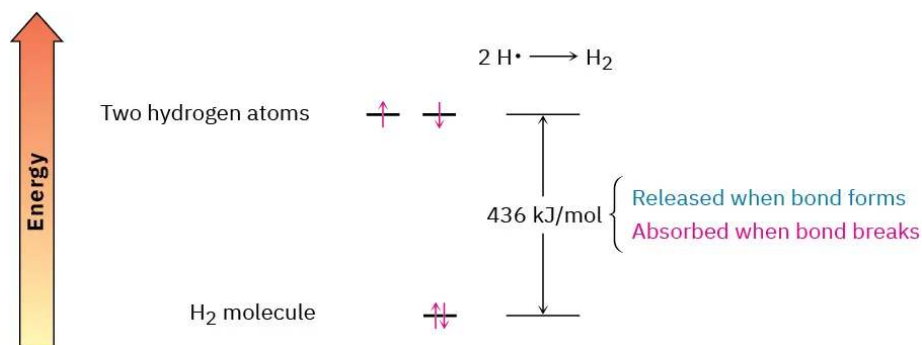


Figure 2.2.2: Relative energy levels of two H atoms and the H_2 molecule. The H_2 molecule has 436 kJ/mol (104 kcal/mol) less energy than the two separate H atoms, so 436 kJ/mol of energy is **released when the H–H bond forms**. Conversely, 436 kJ/mol is **absorbed when the H–H bond breaks**.

How close are the two nuclei in the H_2 molecule? If they are too close, they will repel each other because both are positively charged. Yet if they're too far apart, they won't be able to share the bonding electrons. Thus, there is an optimum distance between nuclei that leads to maximum stability (Figure 2.2.3). Called the bond length, this distance is 74 pm in the $\text{H}-\text{H}$ molecule. Every covalent bond has both a characteristic bond strength and bond length.

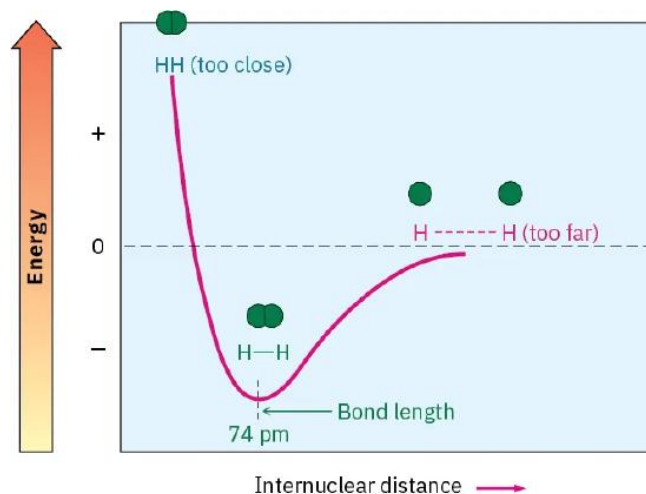


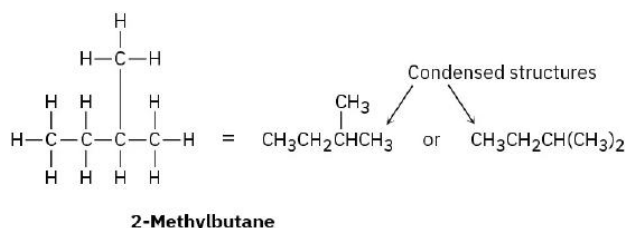
Figure 2.2.3: A plot of energy versus internuclear distance for two hydrogen atoms. The distance between nuclei at the minimum energy point is the **bond length**.

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2.3: Drawing Chemical Structures

Let's cover just one more point before ending this introductory chapter. In the structures we've been drawing until now, a line between atoms has represented the two electrons in a covalent bond. Drawing every bond and every atom is tedious, however, so chemists have devised several shorthand ways for writing structures. In condensed structures, carbon–hydrogen and carbon–carbon single bonds aren't shown; instead, they're understood. If a carbon has three hydrogens bonded to it, we write CH_3 ; if a carbon has two hydrogens bonded to it, we write CH_2 ; and so on. The compound called 2-methylbutane, for example, is written as follows:



Note that the horizontal bonds between carbons aren't shown in condensed structures—the CH_3 , CH_2 , and CH units are simply placed next to each other—but vertical carbon–carbon bonds like that of the first of the condensed structures drawn above is shown for clarity. Notice also in the second of the condensed structures that the two CH_3 units attached to the CH carbon are grouped together as $(\text{CH}_3)_2$.

Even simpler than condensed structures are skeletal structures such as those shown in Table 2.3.1. The rules for drawing skeletal structures are straightforward.

RULE 1

Carbon atoms aren't usually shown. Instead, a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Occasionally, a carbon atom might be indicated for emphasis or clarity.

RULE 2

Hydrogen atoms bonded to carbon aren't shown. Because carbon always has a valence of 4, we mentally supply the correct number of hydrogen atoms for each carbon.

RULE 3

Atoms other than carbon and hydrogen *are* shown.

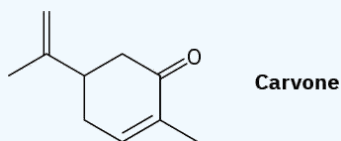
Table 2.3.1 Line-bond and Skeletal Structures for Some Compounds

Compound	Line-bond structure	Skeletal structure
Isoprene, C_5H_8		
Methylcyclohexane, C_7H_{14}		
Phenol, C_6H_6O		

One further comment: Although such groupings as $-CH_3$, $-OH$, and $-NH_2$ are usually written with the C, O, or N atom first and the H atom second, the order of writing is sometimes inverted to H_3C- , $HO-$, and H_2N- if needed to make the bonding connections clearer. Larger units such as $-CH_2CH_3$ are not inverted, though; we don't write H_3CH_2C- because it would be confusing. There are, however, no well-defined rules that cover all cases; it's largely a matter of preference.

✓ Worked Example 2.3.1: Interpreting a Line-Bond Structure

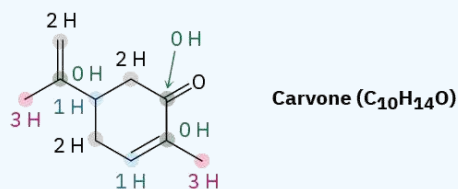
Carvone, a substance responsible for the odor of spearmint, has the following structure. Tell how many hydrogens are bonded to each carbon, and give the molecular formula of carvone.



Strategy

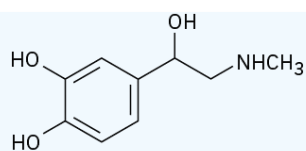
The end of a line represents a carbon atom with 3 hydrogens, CH_3 ; a two-way intersection is a carbon atom with 2 hydrogens, CH_2 ; a three-way intersection is a carbon atom with 1 hydrogen, CH ; and a four-way intersection is a carbon atom with no attached hydrogens.

Solution

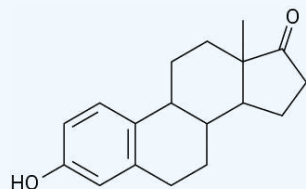


? Exercise 2.3.1

How many hydrogens are bonded to each carbon in the following compounds, and what is the molecular formula of each substance?

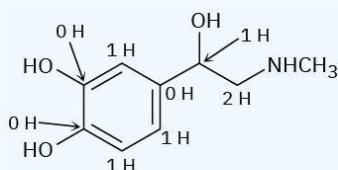


a. **Adrenaline**

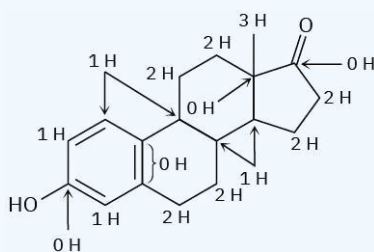


b. **Estrone (a hormone)**

Answer



a. **Adrenaline— $C_9H_{13}NO_3$**



b. **Estrone— $C_{18}H_{22}O_2$**

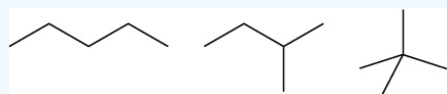
? Exercise 2.3.2

Propose skeletal structures for compounds that satisfy the following molecular formulas: There is more than one possibility in each case.

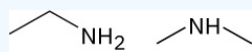
- C_5H_{12}
- C_2H_7N
- C_3H_6O
- C_4H_9Cl

Answer

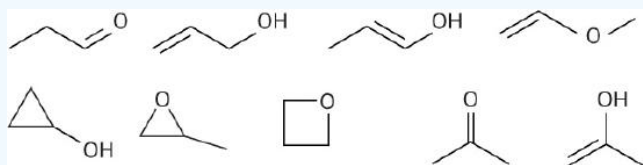
(a) There are numerous possibilities, such as:



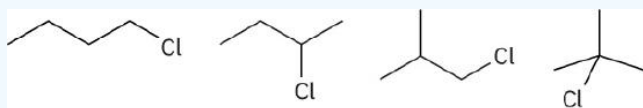
(b) There are numerous possibilities, such as:



(c) There are numerous possibilities, such as:

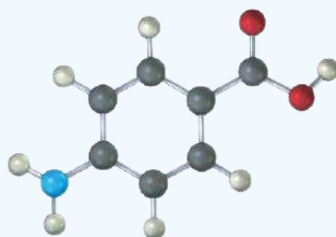


(d) There are numerous possibilities, such as:

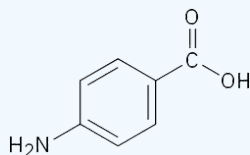


? Exercise 2.3.3

The following molecular model is a representation of *para*-aminobenzoic acid (PABA), the active ingredient in many sunscreens. Indicate the positions of the multiple bonds, and draw a skeletal structure (black = C, red = O, blue = N, gray = H).



Answer



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2.4: sp^3 Hybrid Orbitals and the Structure of Methane

The bonding in the hydrogen molecule is fairly straightforward, but the situation is more complicated in organic molecules with tetravalent carbon atoms. Take methane, CH_4 , for instance. As we've seen, carbon has four valence electrons ($2s^2 2p^2$) and forms four bonds. Because carbon uses two kinds of orbitals for bonding, $2s$ and $2p$, we might expect methane to have two kinds of C–H bonds. In fact, though, all four C–H bonds in methane are identical and are spatially oriented toward the corners of a regular tetrahedron. How can we explain this?

An answer was provided in 1931 by Linus Pauling, who showed mathematically how an s orbital and three p orbitals on an atom can combine, or *hybridize*, to form four equivalent atomic orbitals with tetrahedral orientation. Shown in Figure 2.4.1, these tetrahedrally oriented orbitals are called sp^3 hybrid orbitals. Note that the superscript 3 in the name sp^3 tells how many of each type of atomic orbital combine to form the hybrid, not how many electrons occupy it.

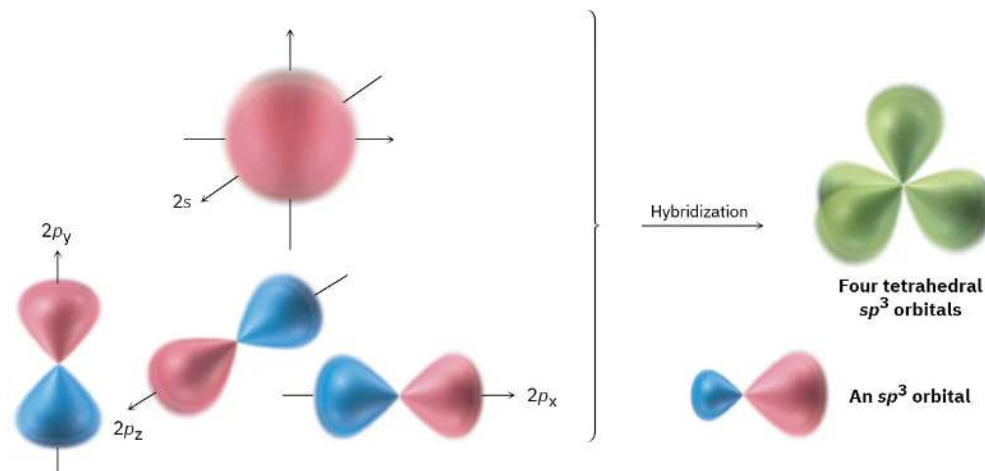


Figure 2.4.1: Four sp^3 hybrid orbitals, oriented toward the corners of a regular tetrahedron, are formed by the combination of an s orbital and three p orbitals (red/blue). The sp^3 hybrids have two lobes and are unsymmetrical about the nucleus, giving them a directionality and allowing them to form strong bonds to other atoms.

The concept of hybridization explains how carbon forms four equivalent tetrahedral bonds but not why it does so. The shape of the hybrid orbital suggests the answer to why. When an s orbital hybridizes with three p orbitals, the resultant sp^3 hybrid orbitals are unsymmetrical about the nucleus. One of the two lobes is larger than the other and can therefore overlap more effectively with an orbital from another atom to form a bond. As a result, sp^3 hybrid orbitals form stronger bonds than do unhybridized s or p orbitals.

The asymmetry of sp^3 orbitals arises because, as noted previously, the two lobes of a p orbital have different algebraic signs, $+$ and $-$, in the wave function. Thus, when a p orbital hybridizes with an s orbital, the positive p lobe adds to the s orbital but the negative p lobe subtracts from the s orbital. The resultant hybrid orbital is therefore unsymmetrical about the nucleus and is strongly oriented in one direction.

When each of the four identical sp^3 hybrid orbitals of a carbon atom overlaps with the $1s$ orbital of a hydrogen atom, four identical C–H bonds are formed and methane results. Each C–H bond in methane has a strength of 439 kJ/mol (105 kcal/mol) and a length of 109 pm. Because the four bonds have a specific geometry, we also can define a property called the bond angle. The angle formed by each H–C–H is 109.5° , the so-called tetrahedral angle. Methane thus has the structure shown in Figure 2.4.2.

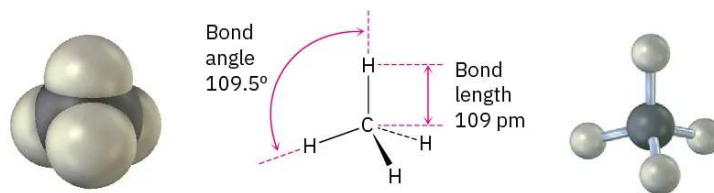


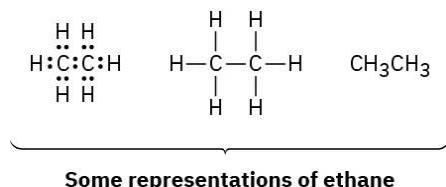
Figure 2.4.2: The structure of methane, showing its 109.5° bond angles.

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2.5: sp^3 Hybrid Orbitals and the Structure of Ethane

The same kind of orbital hybridization that accounts for the methane structure also accounts for the bonding together of carbon atoms into chains and rings to make possible many millions of organic compounds. Ethane, C_2H_6 , is the simplest molecule containing a carbon–carbon bond.



We can picture the ethane molecule by imagining that the two carbon atoms bond to each other by head-on sigma (σ) overlap of an sp^3 hybrid orbital from each (Figure 2.5.1). The remaining three sp^3 hybrid orbitals on each carbon overlap with the 1s orbitals of three hydrogens to form the six C–H bonds. The C–H bonds in ethane are similar to those in methane, although a bit weaker: 421 kJ/mol (101 kcal/mol) for ethane versus 439 kJ/mol for methane. The C–C bond is 153 pm in length and has a strength of 377 kJ/mol (90 kcal/mol). All the bond angles of ethane are near, although not exactly at, the tetrahedral value of 109.5° .

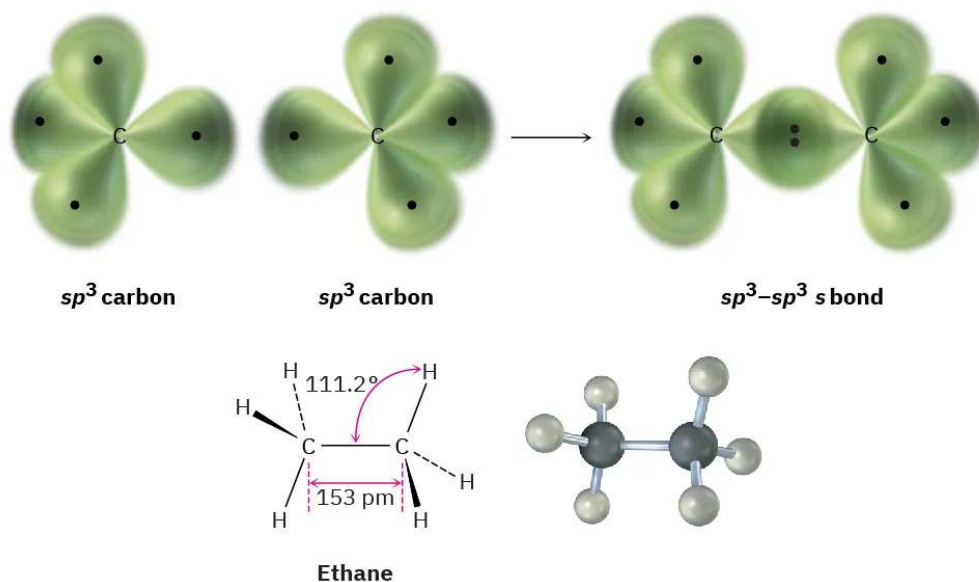
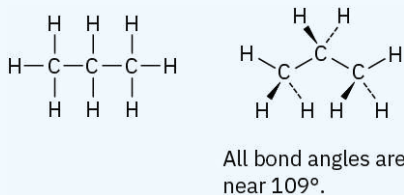


Figure 2.5.1: The structure of ethane. The carbon–carbon bond is formed by σ overlap of two sp^3 hybrid orbitals. For clarity, the smaller lobes of the sp^3 hybrid orbitals are not shown.

? Exercise 2.5.1

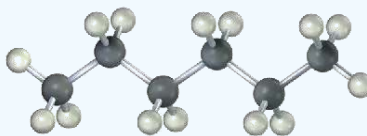
Draw a line-bond structure for propane, $CH_3CH_2CH_3$. Predict the value of each bond angle, and indicate the overall shape of the molecule.

Answer



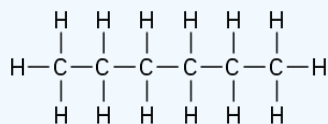
? Exercise 2.5.2

Convert the following molecular model of hexane, a component of gasoline, into a line-bond structure (black = C, gray = H).



Hexane

Answer



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2.6: sp^2 Hybrid Orbitals and the Structure of Ethylene

The bonds we've seen in methane and ethane are called *single bonds* because they result from the sharing of one electron pair between bonded atoms. It was recognized nearly 150 years ago, however, that carbon atoms can also form *double bonds* by sharing two electron pairs between atoms or *triple bonds* by sharing three electron pairs. Ethylene, for instance, has the structure $\text{H}_2\text{C}=\text{CH}_2$ and contains a carbon-carbon double bond, while acetylene has the structure $\text{HC}\equiv\text{CH}$ and contains a carbon-carbon triple bond.

How are multiple bonds described by valence bond theory? When we discussed sp^3 hybrid orbitals in Section 1.6, we said that the four valence-shell atomic orbitals of carbon combine to form four equivalent sp^3 hybrids. Imagine instead that the 2s orbital combines with only *two* of the three available 2p orbitals. Three sp^2 hybrid orbitals result, and one 2p orbital remains unchanged. Like sp^3 hybrids, sp^2 hybrid orbitals are unsymmetrical about the nucleus and are strongly oriented in a specific direction so they can form strong bonds. The three sp^2 orbitals lie in a plane at angles of 120° to one another, with the remaining p orbital perpendicular to the sp^2 plane, as shown in Figure 2.6.1.

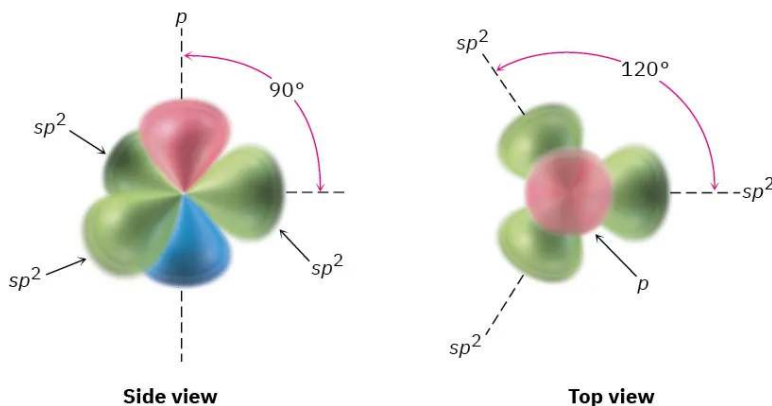


Figure 2.6.1: sp^2 Hybridization. The three equivalent sp^2 hybrid orbitals lie in a plane at angles of 120° to one another, and a single unhybridized p orbital (red/blue) is perpendicular to the sp^2 plane.

When two carbons with sp^2 hybridization approach each other, they form a strong σ bond by sp^2 - sp^2 head-on overlap. At the same time, the unhybridized p orbitals interact by sideways overlap to form what is called a pi (π) bond. The combination of an sp^2 - sp^2 σ bond and a $2p$ - $2p$ π bond results in the sharing of four electrons and the formation of a carbon-carbon double bond (Figure 2.6.2). Note that the electrons in the σ bond occupy the region centered between nuclei, while the electrons in the π bond occupy regions above and below a line drawn between nuclei.

To complete the structure of ethylene, four hydrogen atoms form σ bonds with the remaining four sp^2 orbitals. Ethylene thus has a planar structure, with H-C-H and H-C-C bond angles of approximately 120° . (The actual values are 117.4° for the H-C-H bond angle and 121.3° for the H-C-C bond angle.) Each C-H bond has a length of 108.7 pm and a strength of 464 kJ/mol (111 kcal/mol).

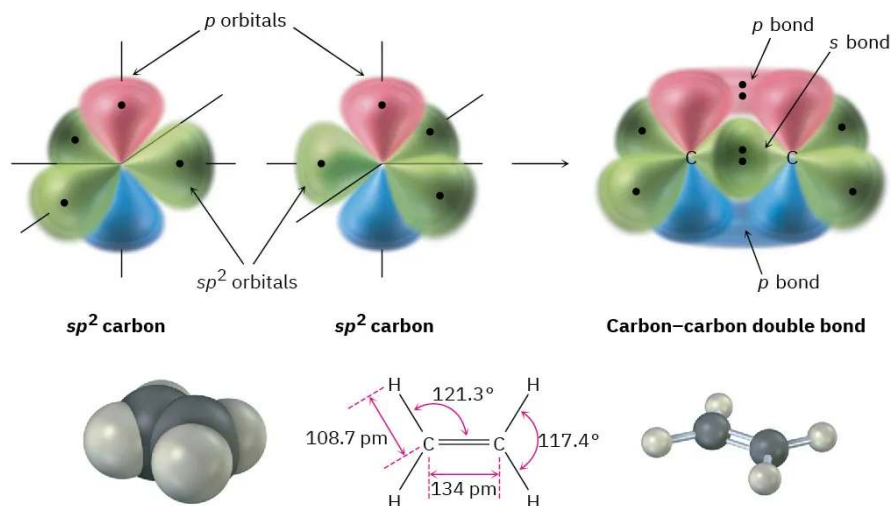


Figure 2.6.2: The structure of ethylene. One part of the double bond in ethylene results from σ (head-on) overlap of sp^2 hybrid orbitals, and the other part results from π (sideways) overlap of unhybridized p orbitals (red/blue). The π bond has regions of electron density above and below a line drawn between nuclei.

As you might expect, the carbon-carbon double bond in ethylene is both shorter and stronger than the single bond in ethane because it has four electrons bonding the nuclei together rather than two. Ethylene has a $\text{C}=\text{C}$ bond length of 134 pm and a strength of 728 kJ/mol (174 kcal/mol) versus a $\text{C}-\text{C}$ length of 153 pm and a strength of 377 kJ/mol for ethane. The carbon-carbon double bond is less than twice as strong as a single bond because the sideways overlap in the π part of the double bond is not as great as the head-on overlap in the σ part.

✓ Worked Example 2.6.1: Drawing Electron-Dot and Line-Bond Structures

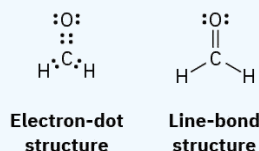
Commonly used in biology as a tissue preservative, formaldehyde, CH_2O , contains a carbon-oxygen double bond. Draw electron-dot and line-bond structures of formaldehyde, and indicate the hybridization of the carbon orbitals.

Strategy

We know that hydrogen forms one covalent bond, carbon forms four, and oxygen forms two. Trial and error, combined with intuition, is needed to fit the atoms together.

Solution

There is only one way that two hydrogens, one carbon, and one oxygen can combine:



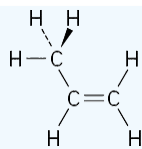
Like the carbon atoms in ethylene, the carbon atom in formaldehyde is in a double bond and its orbitals are therefore sp^2 -hybridized.

? Exercise 2.6.1

Draw a line-bond structure for propene, $\text{CH}_3\text{CH}=\text{CH}_2$. Indicate the hybridization of the orbitals on each carbon, and predict the value of each bond angle.

Answer

The CH_3 carbon is sp^3 ; the double-bond carbons are sp^2 ; the $\text{C}=\text{C}-\text{C}$ and $\text{C}=\text{C}-\text{H}$ bond angles are approximately 120° ; other bond angles are near 109° .

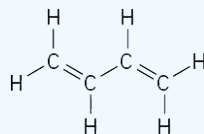


? Exercise 2.6.2

Draw a line-bond structure for 1,3-butadiene, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$. Indicate the hybridization of the orbitals on each carbon, and predict the value of each bond angle.

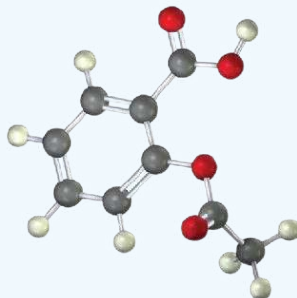
Answer

All carbons are sp^2 , and all bond angles are near 120° .



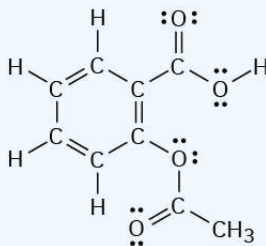
? Exercise 2.6.3

A molecular model of aspirin (acetylsalicylic acid) is shown. Identify the hybridization of the orbitals on each carbon atom in aspirin, and tell which atoms have lone pairs of electrons (black = C, red = O, gray = H).



Answer

All carbons except CH_3 are sp^2 .



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2.7: sp Hybrid Orbitals and the Structure of Acetylene

In addition to forming single and double bonds by sharing two and four electrons, respectively, carbon can also form a triple bond by sharing six electrons. To account for the triple bond in a molecule such as acetylene, $\text{H} - \text{C} \equiv \text{C} - \text{H}$, we need a third kind of hybrid orbital, an sp hybrid. Imagine that, instead of combining with two or three p orbitals, a carbon $2s$ orbital hybridizes with only a single p orbital. Two sp hybrid orbitals result, and two p orbitals remain unchanged. The two sp orbitals are oriented 180° apart on the right-left (x) axis, while the p orbitals are perpendicular on the up-down (y) axis and the in-out (z) axis, as shown in Figure 2.7.1.

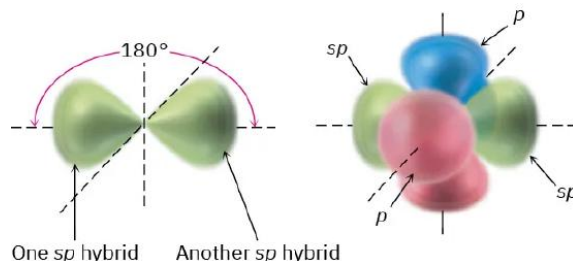


Figure 2.7.1: sp Hybridization. The two sp hybrid orbitals are oriented 180° away from each other, perpendicular to the two remaining p orbitals (red/blue).

When two sp -hybridized carbon atoms approach each other, sp hybrid orbitals on each carbon overlap head-on to form a strong $sp-sp$ σ bond. At the same time, the p_z orbitals from each carbon form a p_z-p_z π bond by sideways overlap, and the p_y orbitals overlap similarly to form a p_y-p_y π bond. The net effect is the sharing of six electrons and formation of a carbon-carbon triple bond. Each of the two remaining sp hybrid orbitals forms a σ bond with hydrogen to complete the acetylene molecule (Figure 2.7.2).

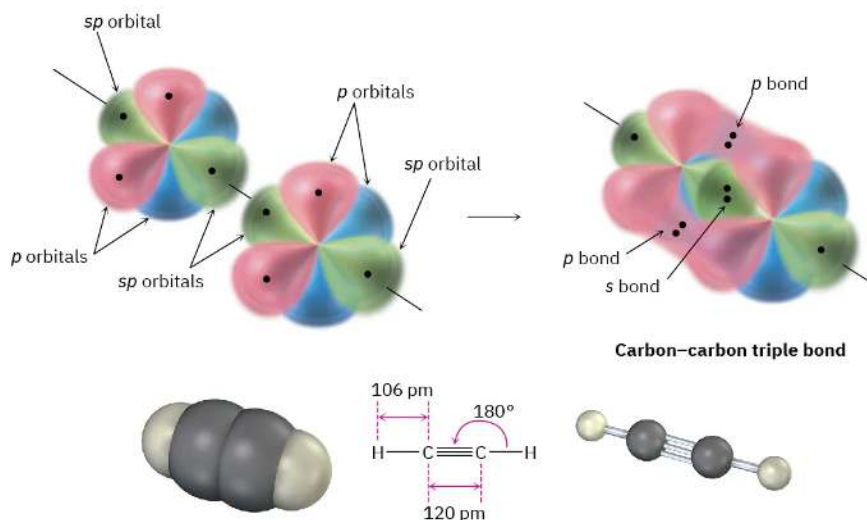


Figure 2.7.2: The structure of acetylene. The two carbon atoms are joined by one $sp-sp$ σ bond and two $p-p$ π bonds.

As suggested by sp hybridization, acetylene is a linear molecule with $\text{H}-\text{C}-\text{C}$ bond angles of 180° . The $\text{C}-\text{H}$ bonds have a length of 106 pm and a strength of 558 kJ/mol (133 kcal/mol). The $\text{C}-\text{C}$ bond length in acetylene is 120 pm, and its strength is about 965 kJ/mol (231 kcal/mol), making it the shortest and strongest of any carbon-carbon bond. A comparison of sp , sp^2 , and sp^3 hybridization is given in Table 2.7.1.

Table 2.7.1 Comparison of $\text{C}-\text{C}$ and $\text{C}-\text{H}$ Bonds in Methane, Ethane, Ethylene, and Acetylene

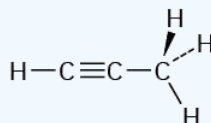
Molecule	Bond	Bond strength		Bond length (pm)
		(kJ/mol)	(kcal/mol)	
Methane, CH_4	$(sp^3) \text{C} - \text{H}$	439	105	109
Ethane, CH_3CH_3	$(sp^3) \text{C} - \text{C} (sp^3)$	377	90	153
	$(sp^3) \text{C} - \text{H}$	421	101	109
Ethylene, $\text{H}_2\text{C} = \text{CH}_2$	$(sp^2) \text{C} = \text{C} (sp^2)$	728	174	134
	$(sp^2) \text{C} - \text{H}$	464	111	109
Acetylene, $\text{HC} \equiv \text{CH}$	$(sp) \text{C} \equiv \text{C} (sp)$	965	231	120
	$(sp) \text{C} - \text{H}$	558	133	106

? Exercise 2.7.1

Draw a line-bond structure for propyne, $\text{CH}_3\text{C}\equiv\text{CH}$. Indicate the hybridization of the orbitals on each carbon, and predict a value for each bond angle.

Answer

The CH_3 carbon is sp^3 ; the triple-bond carbons are sp ; the $\text{C}\equiv\text{C}-\text{C}$ and $\text{H}-\text{C}\equiv\text{C}$ bond angles are approximately 180° .

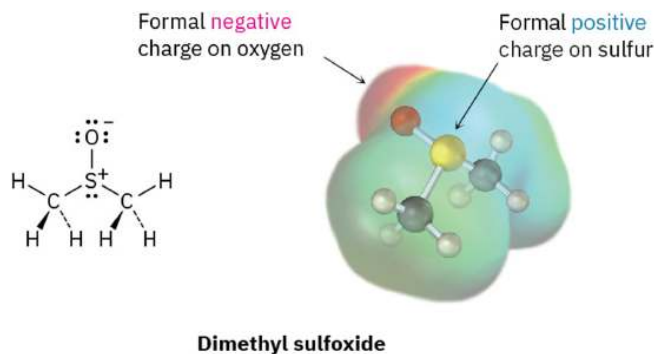


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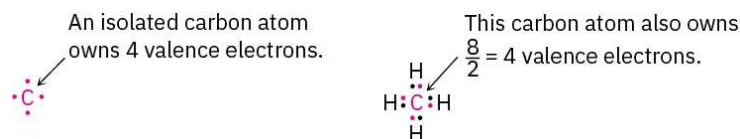
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2.8: Formal Charges

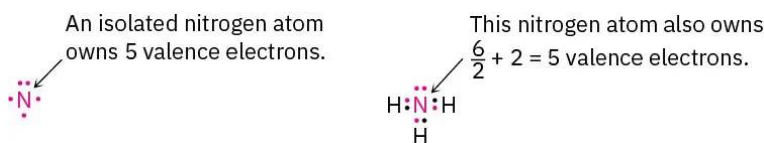
Closely related to the ideas of bond polarity and dipole moment is the assignment of *formal charges* to specific atoms within a molecule, particularly atoms that have an apparently “abnormal” number of bonds. Look at dimethyl sulfoxide (CH_3SOCH_3), for instance, a solvent commonly used for preserving biological cell lines at low temperature. The sulfur atom in dimethyl sulfoxide has three bonds rather than the usual two and has a formal positive charge. The oxygen atom, by contrast, has one bond rather than the usual two and has a formal negative charge. Note that an electrostatic potential map of dimethyl sulfoxide shows the oxygen as negative (red) and the sulfur as relatively positive (blue), in accordance with the formal charges.



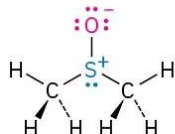
Formal charges, as the name suggests, are a formalism and don't imply the presence of actual ionic charges in a molecule. Instead, they're a device for electron “bookkeeping” and can be thought of in the following way: A typical covalent bond is formed when each atom donates one electron. Although the bonding electrons are shared by both atoms, each atom can still be considered to “own” one electron for bookkeeping purposes. In methane, for instance, the carbon atom owns one electron in each of the four C–H bonds. Because a neutral, isolated carbon atom has four valence electrons, and because the carbon atom in methane still owns four, the methane carbon atom is neutral and has no formal charge.



The same is true for the nitrogen atom in ammonia, which has three covalent N–H bonds and two nonbonding electrons (a lone pair). Atomic nitrogen has five valence electrons, and the ammonia nitrogen also has five—one in each of three shared N–H bonds plus two in the lone pair. Thus, the nitrogen atom in ammonia has no formal charge.



The situation is different in dimethyl sulfoxide. Atomic sulfur has six valence electrons, but the dimethyl sulfoxide sulfur owns only five—one in each of the two S–C single bonds, one in the S–O single bond, and two in a lone pair. Thus, the sulfur atom has formally lost an electron and therefore has a positive formal charge. A similar calculation for the oxygen atom shows that it has formally gained an electron and has a negative charge. Atomic oxygen has six valence electrons, but the oxygen in dimethyl sulfoxide has seven—one in the O–S bond and two in each of three lone pairs. Thus, the oxygen has formally gained an electron and has a negative formal charge.



For sulfur:

Sulfur valence electrons = 6
Sulfur bonding electrons = 6
Sulfur nonbonding electrons = 2

$$\text{Formal charge} = 6 - 6/2 - 2 = +1$$

For oxygen:

Oxygen valence electrons = 6
Oxygen bonding electrons = 2
Oxygen nonbonding electrons = 6

$$\text{Formal charge} = 6 - 2/2 - 6 = -1$$

To express the calculations in a general way, the formal charge on an atom is equal to the number of valence electrons in a neutral, isolated atom minus the number of electrons owned by that bonded atom in a molecule. The number of electrons in the bonded atom, in turn, is equal to half the number of bonding electrons plus the nonbonding, lone-pair electrons.

$$\begin{aligned} \text{Formal Charge} &= (\text{Number of valence electron in free atom}) \\ &\quad - (\text{Number of valence electrons in bonded atom}) \\ &= (\text{Number of valence electron in free atom}) \\ &\quad - \left(\frac{\text{Number of bonding electrons}}{2} + \text{Number of nonbonding electrons} \right) \end{aligned}$$

A summary of commonly encountered formal charges and the bonding situations in which they occur is given in Table 2.8.1. Although only a bookkeeping device, formal charges often give clues about chemical reactivity, so it's helpful to be able to identify and calculate them correctly.

Table 2.8.1: A Summary of Common Formal Charges

Atom	C			N		O		S		P
Structure										
Valence electrons	4	4	4	5	5	6	6	6	6	5
Number of bonds	3	3	3	4	2	3	1	3	1	4
Number of nonbonding electrons	1	0	2	0	4	2	6	2	6	0
Formal charge	0	+1	-1	+1	-1	+1	-1	+1	-1	+1

? Exercise 2.8.1

Calculate formal charges for the nonhydrogen atoms in the following molecules:

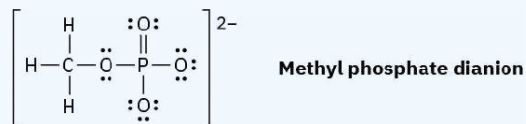
- Diazomethane, $\text{H}_2\text{C} = \text{N} = \text{N} :$
- Acetonitrile oxide, $\text{H}_3\text{C} - \text{C} \equiv \text{N} - \ddot{\text{O}} :$
- Methyl isocyanide, $\text{H}_3\text{C} - \text{N} \equiv \text{C} :$

Answer

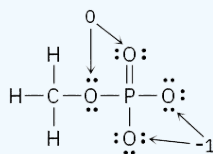
- a. For carbon: $FC = 4 - 8/2 - 0 = 0$ For the middle nitrogen: $FC = 5 - 8/2 - 0 = +1$ For the end nitrogen: $FC = 5 - 4/2 - 4 = -1$
- b. For nitrogen: $FC = 5 - 8/2 - 0 = +1$ For oxygen: $FC = 6 - 2/2 - 6 = -1$
- c. For nitrogen: $FC = 5 - 8/2 - 0 = +1$ For the triply bonded carbon: $FC = 4 - 6/2 - 2 = -1$

? Exercise 2.8.2

Organic phosphate groups occur commonly in biological molecules. Calculate formal charges on the four O atoms in the methyl phosphate dianion.



Answer

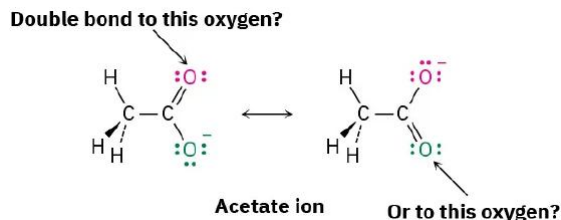


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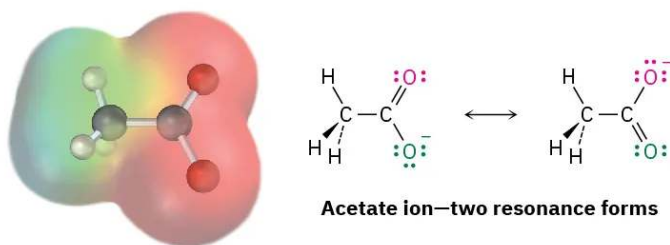
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2.9: Resonance

Most substances can be represented unambiguously by the Kekulé line-bond structures we've been using up to this point, but an interesting problem sometimes arises. Look at the acetate ion, for instance. When we draw a line-bond structure for acetate, we need to show a double bond to one oxygen and a single bond to the other. But which oxygen is which? Should we draw a double bond to the "top" oxygen and a single bond to the "bottom" oxygen, or vice versa?



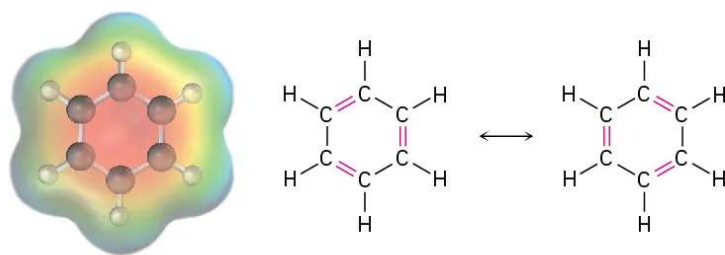
Although the two oxygen atoms in the acetate ion appear different in line-bond structures, experiments show that they are equivalent. Both carbon–oxygen bonds, for instance, are 127 pm in length, midway between the length of a typical C–O single bond (135 pm) and a typical C=O double bond (120 pm). In other words, neither of the two structures for acetate is correct by itself. The true structure is intermediate between the two, and an electrostatic potential map shows that both oxygen atoms share the negative charge and have equal electron densities (red).



The two individual line-bond structures for acetate ion are called resonance forms, and their special resonance relationship is indicated by the double-headed arrow between them. The only difference between the two resonance forms is the placement of the π and nonbonding valence electrons. The atoms themselves occupy exactly the same place in both resonance forms, the connections between atoms are the same, and the three-dimensional shapes of the resonance forms are the same.

A good way to think about resonance forms is to realize that a substance like the acetate ion is the same as any other. Acetate doesn't jump back and forth between two resonance forms, spending part of the time looking like one and part of the time looking like the other. Rather, acetate has a single unchanging structure that we say is a resonance hybrid of the two individual forms and has characteristics of both. The only "problem" with acetate is that we can't draw it accurately using a familiar line-bond structure—line-bond structures just don't work for resonance hybrids. The difficulty, however, is with the *representation* of acetate on paper, not with acetate itself.

Resonance is a very useful concept that we'll return to on numerous occasions throughout the rest of this book. We'll see in Chapter 15, for instance, that the six carbon–carbon bonds in aromatic compounds, such as benzene, are equivalent and that benzene is best represented as a hybrid of two resonance forms. Although each individual resonance form seems to imply that benzene has alternating single and double bonds, neither form is correct by itself. The true benzene structure is a hybrid of the two individual forms, and all six carbon–carbon bonds are equivalent. This symmetrical distribution of electrons around the molecule is evident in an electrostatic potential map.



Benzene (two resonance forms)

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2.10: Rules for Resonance Forms

When first dealing with resonance forms, it's useful to have a set of guidelines that describe how to draw and interpret them. The following rules should be helpful:

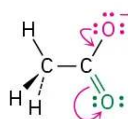
RULE 1

Individual resonance forms are imaginary, not real. The real structure is a composite, or resonance hybrid, of the different forms. Species such as the acetate ion and benzene are no different from any other. They have single, unchanging structures, and they don't switch back and forth between resonance forms. The only difference between these and other substances is in the way they are represented in drawings.

RULE 2

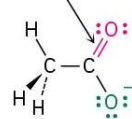
Resonance forms differ only in the placement of their π or nonbonding electrons. Neither the position nor the hybridization of any atom changes from one resonance form to another. In the acetate ion, for instance, the carbon atom is sp^2 -hybridized and the oxygen atoms remain in exactly the same place in both resonance forms. Only the positions of the π electrons in the $C=O$ bond and the lone-pair electrons on oxygen differ from one form to another. This movement of electrons from one resonance structure to another can be indicated with curved arrows. *A curved arrow always indicates the movement of electrons, not the movement of atoms.* An arrow shows that a pair of electrons moves *from* the atom or bond at the tail of the arrow *to* the atom or bond at the head of the arrow.

The red curved arrow indicates that a lone pair of electrons moves from the top oxygen atom to become part of a $C=O$ bond.



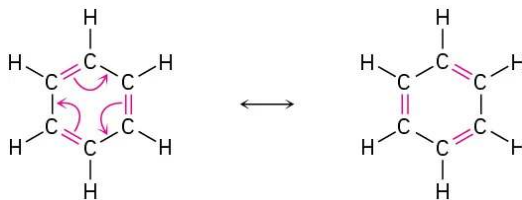
Simultaneously, two electrons from the $C=O$ bond move onto the bottom oxygen atom to become a lone pair.

The new resonance form has a double bond here...



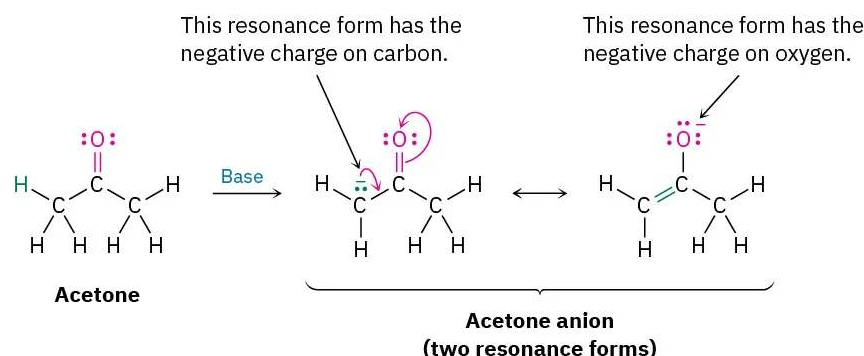
and has a lone pair of electrons here.

The situation with benzene is similar to that with acetate. The π electrons in the double bonds move, as shown with curved arrows, but the carbon and hydrogen atoms remain in place.



RULE 3

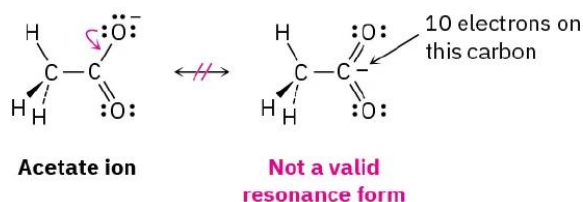
Different resonance forms of a substance don't have to be equivalent. As an example, we'll see in Chapter 22 that a compound such as acetone, which contains a $C=O$ bond, can be converted into its anion by reaction with a strong base. The resultant anion has two resonance forms. One form contains a carbon-oxygen double bond and has a negative charge on *carbon*; the other contains a carbon-carbon double bond and has a negative charge on *oxygen*. Even though the two resonance forms aren't equivalent, both contribute to the overall resonance hybrid.



When two resonance forms are nonequivalent, the actual structure of the resonance hybrid resembles the more stable form. Thus, we might expect the true structure of the acetone anion to be more like that of the form that places the negative charge on the electronegative oxygen atom rather than on the carbon.

RULE 4

Resonance forms obey normal rules of valency. A resonance form is like any other structure: the octet rule still applies to second-row, main-group atoms. For example, one of the following structures for the acetate ion is not a valid resonance form because the carbon atom has five bonds and ten valence electrons:



RULE 5

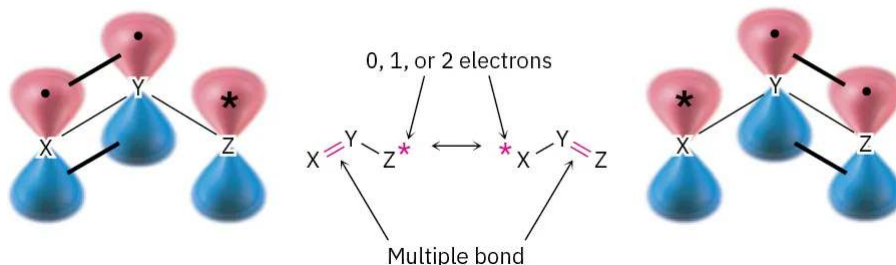
The resonance hybrid is more stable than any individual resonance form. In other words, resonance leads to stability. Generally speaking, the larger the number of resonance forms a substance has, the more stable the substance is, because its electrons are spread out over a larger part of the molecule and are closer to more nuclei. We'll see in Chapter 15, for instance, that a benzene ring is more stable because of resonance than might otherwise be expected.

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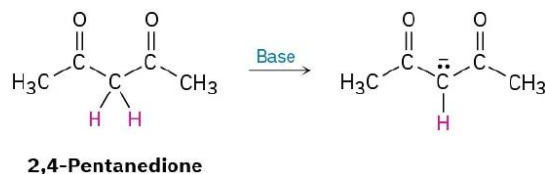
2.11: Drawing Resonance Forms

Look back at the resonance forms of the acetate ion and the acetone anion shown in the previous section. The pattern seen there is a common one that leads to a useful technique for drawing resonance forms. In general, any three-atom grouping with a p orbital on each atom has two resonance forms:

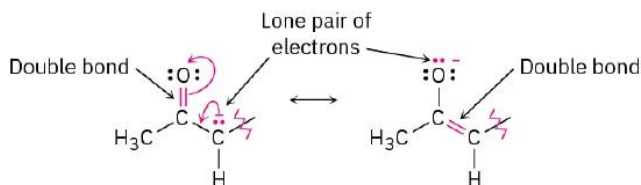


The atoms X, Y, and Z in the general structure might be C, N, O, P, S, or others, and the asterisk (*) might mean that the p orbital on atom Z is vacant, that it contains a single electron, or that it contains a lone pair of electrons. The two resonance forms differ simply by an exchange in position of the multiple bond and the asterisk from one end of the three-atom grouping to the other.

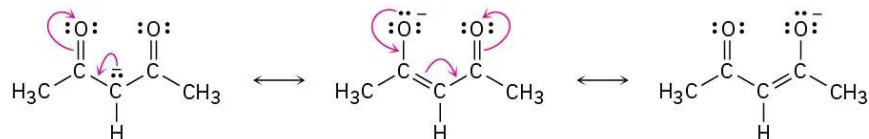
By learning to recognize such three-atom groupings within larger structures, resonance forms can be systematically generated. Look, for instance, at the anion produced when H^+ is removed from 2,4-pentanedione by reaction with a base. How many resonance structures does the resultant anion have?



The 2,4-pentanedione anion has a lone pair of electrons and a formal negative charge on the central carbon atom, next to a $\text{C}=\text{O}$ bond on the left. The $\text{O}=\text{C}-\text{C}^-$ grouping is a typical one for which two resonance structures can be drawn.

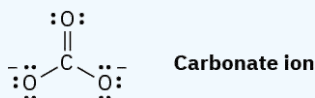


Just as there is a $\text{C}=\text{O}$ bond to the left of the lone pair, there is a second $\text{C}=\text{O}$ bond to the right. Thus, we can draw a total of three resonance structures for the 2,4-pentanedione anion.



✓ Worked Example 2.11.1: Drawing Resonance Forms for an Anion

Draw three resonance structures for the carbonate ion, CO_3^{2-} .

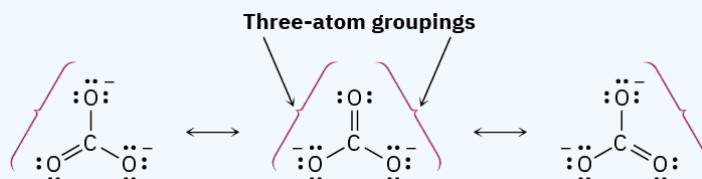


Strategy

Look for three-atom groupings that contain a multiple bond next to an atom with a p orbital. Then exchange the positions of the multiple bond and the electrons in the p orbital. In the carbonate ion, each singly bonded oxygen atom with three lone pairs and a negative charge is adjacent to the $C=O$ double bond, giving the grouping $\ddot{O}=C-\ddot{O}^-$.

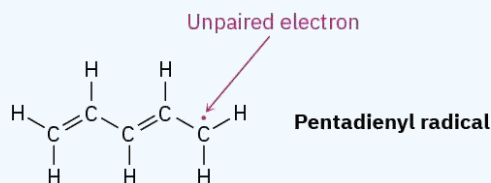
Solution

Exchanging the position of the double bond and an electron lone pair in each grouping generates three resonance structures.



✓ Worked Example 2.11.2: Drawing Resonance Forms for a Radical

Draw three resonance forms for the pentadienyl radical, where a **radical** is a substance that contains a single, unpaired electron in one of its orbitals, denoted by a dot ($\cdot$).

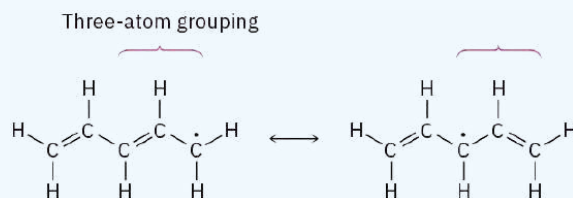


Strategy

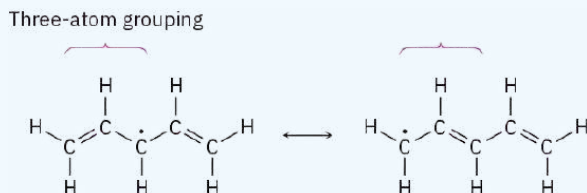
Find the three-atom groupings that contain a multiple bond next to an atom with a p orbital.

Solution

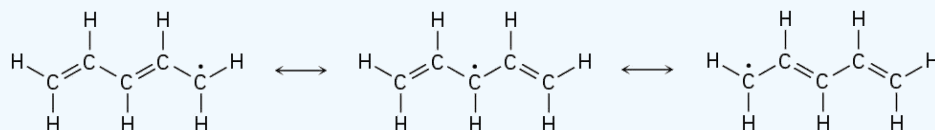
The unpaired electron is on a carbon atom next to a $C=C$ bond, giving a typical three-atom grouping that has two resonance forms.



In the second resonance form, the unpaired electron is next to another double bond, giving another three-atom grouping and leading to another resonance form.

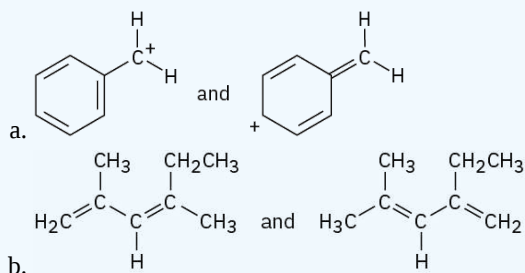


Thus, the three resonance forms for the pentadienyl radical are:



? Exercise 2.11.1

Which of the following pairs of structures represent resonance forms, and which do not? Explain.



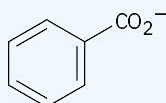
Answer

The structures in **(a)** are resonance forms.

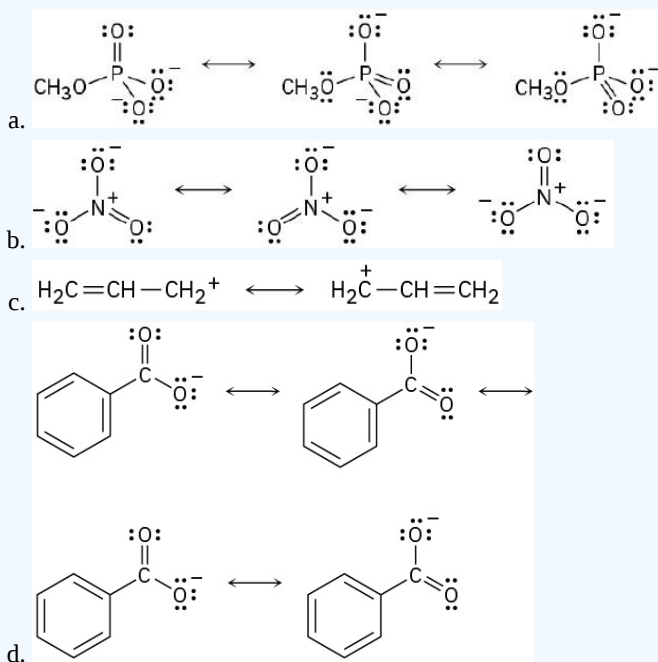
? Exercise 2.11.2

Draw the indicated number of resonance forms for each of the following substances:

- The methyl phosphate anion, $\text{CH}_3\text{OPO}_3^{2-}$ (3 resonance structures)
- The nitrate anion, NO_3^- (3)
- The allyl cation, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$ (2)
- The benzoate anion (2)



Answer



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CHAPTER OVERVIEW

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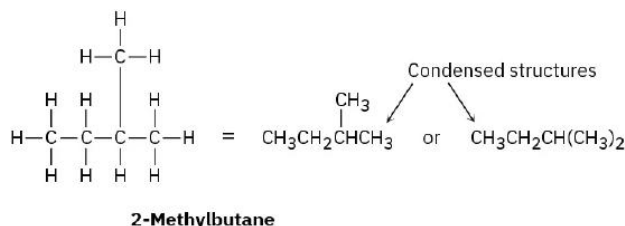
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3.1: Drawing Chemical Structures

Let's cover just one more point before ending this introductory chapter. In the structures we've been drawing until now, a line between atoms has represented the two electrons in a covalent bond. Drawing every bond and every atom is tedious, however, so chemists have devised several shorthand ways for writing structures. In condensed structures, carbon–hydrogen and carbon–carbon single bonds aren't shown; instead, they're understood. If a carbon has three hydrogens bonded to it, we write CH_3 ; if a carbon has two hydrogens bonded to it, we write CH_2 ; and so on. The compound called 2-methylbutane, for example, is written as follows:



Note that the horizontal bonds between carbons aren't shown in condensed structures—the CH_3 , CH_2 , and CH units are simply placed next to each other—but vertical carbon–carbon bonds like that of the first of the condensed structures drawn above is shown for clarity. Notice also in the second of the condensed structures that the two CH_3 units attached to the CH carbon are grouped together as $(\text{CH}_3)_2$.

Even simpler than condensed structures are skeletal structures such as those shown in Table 3.1.1. The rules for drawing skeletal structures are straightforward.

RULE 1

Carbon atoms aren't usually shown. Instead, a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Occasionally, a carbon atom might be indicated for emphasis or clarity.

RULE 2

Hydrogen atoms bonded to carbon aren't shown. Because carbon always has a valence of 4, we mentally supply the correct number of hydrogen atoms for each carbon.

RULE 3

Atoms other than carbon and hydrogen *are* shown.

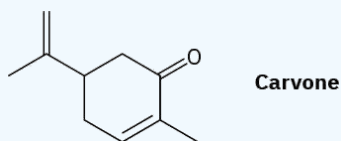
Table 3.1.1 Line-bond and Skeletal Structures for Some Compounds

Compound	Line-bond structure	Skeletal structure
Isoprene, C_5H_8		
Methylcyclohexane, C_7H_{14}		
Phenol, C_6H_6O		

One further comment: Although such groupings as $-CH_3$, $-OH$, and $-NH_2$ are usually written with the C, O, or N atom first and the H atom second, the order of writing is sometimes inverted to H_3C- , $HO-$, and H_2N- if needed to make the bonding connections clearer. Larger units such as $-CH_2CH_3$ are not inverted, though; we don't write H_3CH_2C- because it would be confusing. There are, however, no well-defined rules that cover all cases; it's largely a matter of preference.

✓ Worked Example 3.1.1: Interpreting a Line-Bond Structure

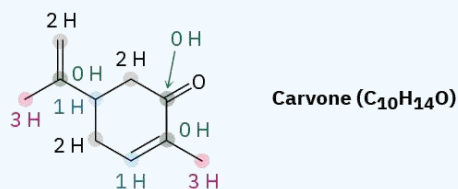
Carvone, a substance responsible for the odor of spearmint, has the following structure. Tell how many hydrogens are bonded to each carbon, and give the molecular formula of carvone.



Strategy

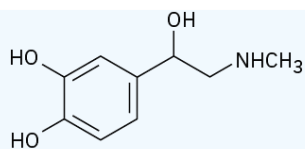
The end of a line represents a carbon atom with 3 hydrogens, CH_3 ; a two-way intersection is a carbon atom with 2 hydrogens, CH_2 ; a three-way intersection is a carbon atom with 1 hydrogen, CH ; and a four-way intersection is a carbon atom with no attached hydrogens.

Solution

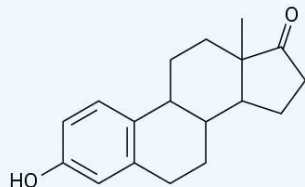


? Exercise 3.1.1

How many hydrogens are bonded to each carbon in the following compounds, and what is the molecular formula of each substance?

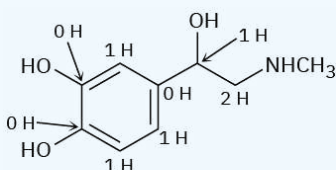


a. **Adrenaline**

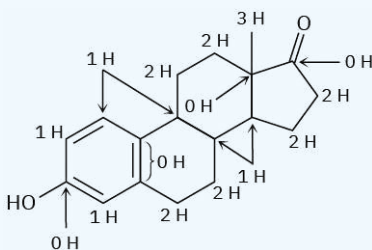


b. **Estrone (a hormone)**

Answer



a. **Adrenaline— $C_9H_{13}NO_3$**



b. **Estrone— $C_{18}H_{22}O_2$**

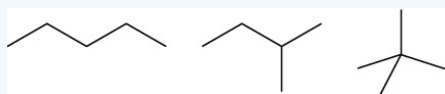
? Exercise 3.1.2

Propose skeletal structures for compounds that satisfy the following molecular formulas: There is more than one possibility in each case.

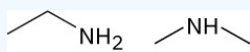
- C_5H_{12}
- C_2H_7N
- C_3H_6O
- C_4H_9Cl

Answer

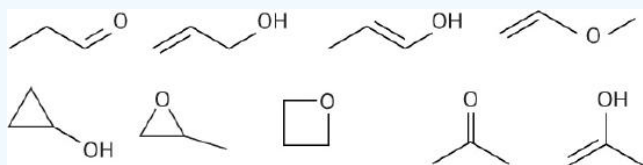
(a) There are numerous possibilities, such as:



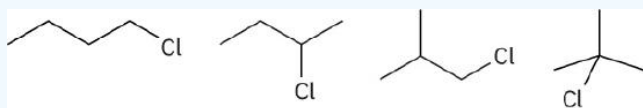
(b) There are numerous possibilities, such as:



(c) There are numerous possibilities, such as:

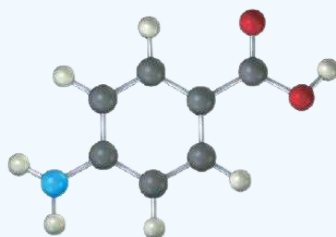


(d) There are numerous possibilities, such as:

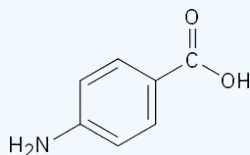


? Exercise 3.1.3

The following molecular model is a representation of *para*-aminobenzoic acid (PABA), the active ingredient in many sunscreens. Indicate the positions of the multiple bonds, and draw a skeletal structure (black = C, red = O, blue = N, gray = H).



Answer



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3.2: Conformations of Ethane

Up until now, we've viewed molecules primarily in a two-dimensional way and have given little thought to any consequences that might arise from the spatial arrangement of atoms in molecules. Now it's time to add a third dimension to our study. Stereochemistry is the branch of chemistry concerned with the three-dimensional aspects of molecules. We'll see on many occasions in future chapters that the exact three-dimensional structure of a molecule is often crucial to determining its properties and biological behavior.

We know from Section 1.6 that σ bonds are cylindrically symmetrical. In other words, the intersection of a plane cutting through a carbon-carbon single-bond orbital looks like a circle. Because of this cylindrical symmetry, rotation is possible around carbon-carbon bonds in open-chain molecules. In ethane, for instance, rotation around the C-C bond occurs freely, constantly changing the spatial relationships between the hydrogens on one carbon and those on the other (Figure 3.2.1).

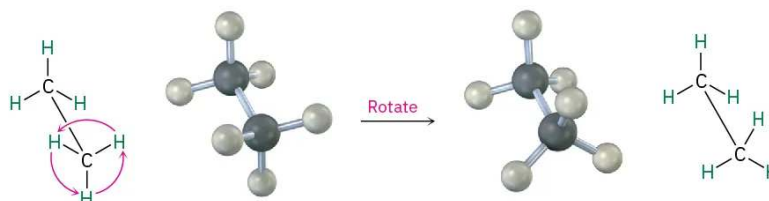


Figure 3.2.1: Rotation occurs around the carbon-carbon single bond in ethane because of σ bond cylindrical symmetry.

The different arrangements of atoms that result from bond rotation are called conformations, and molecules that have different arrangements are called conformational isomers, or conformers. Unlike constitutional isomers, however, different conformers often can't be isolated because they interconvert too rapidly.

Conformational isomers are represented in two ways, as shown in Figure 3.2.2. A sawhorse representation views the carbon-carbon bond from an oblique angle and indicates spatial orientation by showing all C-H bonds. A Newman projection views the carbon-carbon bond directly end-on and represents the two carbon atoms by a circle. Bonds attached to the front carbon are represented by lines to the center of the circle, and bonds attached to the rear carbon are represented by lines to the edge of the circle.

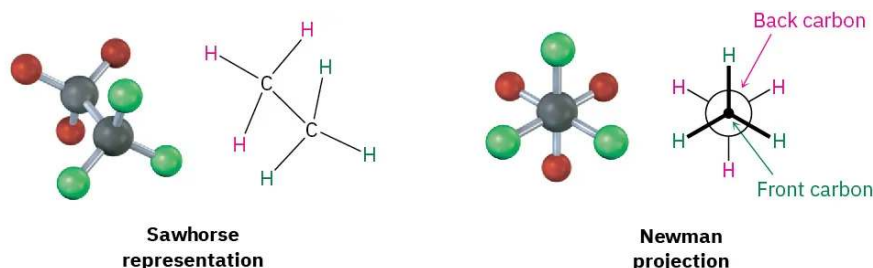
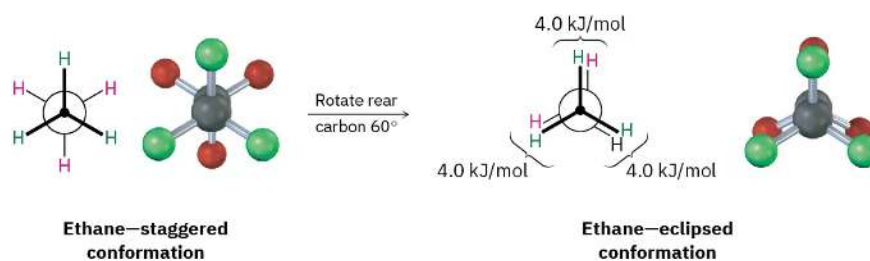


Figure 3.2.2: A sawhorse representation and a Newman projection of ethane. The sawhorse representation views the molecule from an oblique angle, while the Newman projection views the molecule end-on. Note that the molecular model of the Newman projection appears at first to have six atoms attached to a single carbon. Actually, the front carbon, with three attached **green atoms**, is directly in front of the rear carbon, with three attached **red atoms**.

Despite what we've just said, we actually don't observe perfectly free rotation in ethane. Experiments show that there is a small (12 kJ/mol; 2.9 kcal/mol) barrier to rotation and that some conformations are more stable than others. The lowest-energy, most stable conformation is the one in which all six C-H bonds are as far away from one another as possible—*staggered* when viewed end-on in a Newman projection. The highest-energy, least stable conformation is the one in which the six C-H bonds are as close as possible—*eclipsed* in a Newman projection. At any given instant, about 99% of ethane molecules have an approximately staggered conformation and only about 1% are near the eclipsed conformation.



The extra 12 kJ/mol of energy present in the eclipsed conformation of ethane is called torsional strain. Its cause has been the subject of controversy, but the major factor is an interaction between C–H bonding orbitals on one carbon and antibonding orbitals on the adjacent carbon, which stabilizes the staggered conformation relative to the eclipsed one. Because a total strain of 12 kJ/mol arises from three equal hydrogen–hydrogen eclipsing interactions, we can assign a value of approximately 4.0 kJ/mol (1.0 kcal/mol) to each single interaction. The barrier to rotation that results can be represented on a graph of potential energy versus degree of rotation, in which the angle between C–H bonds on the front and back carbons as viewed end-on (the *dihedral angle*) goes full circle from 0 to 360°. Energy minima occur at staggered conformations, and energy maxima occur at eclipsed conformations, as shown in Figure 3.2.3.

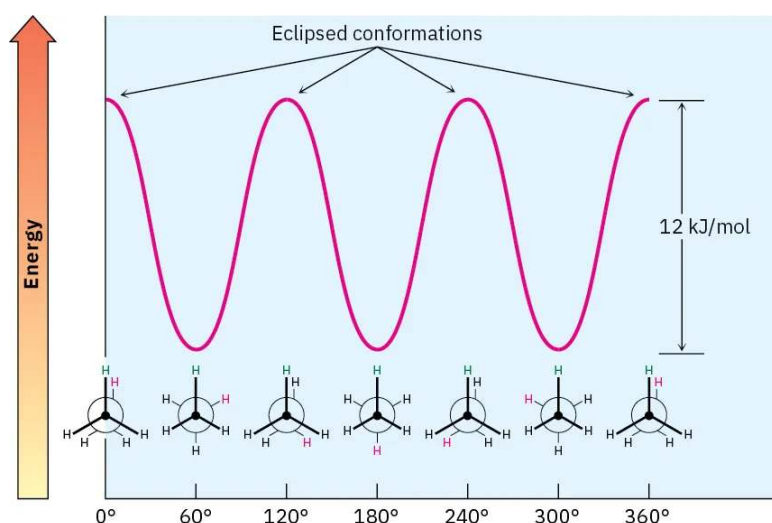


Figure 3.2.3: A graph of potential energy versus bond rotation in ethane. The staggered conformations are 12 kJ/mol lower in energy than the eclipsed conformations.

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3.3: Conformations of Other Alkanes

Propane, the next-higher member in the alkane series, also has a torsional barrier that results in hindered rotation around the carbon–carbon bonds. The barrier is slightly higher in propane than in ethane—a total of 14 kJ/mol (3.4 kcal/mol) versus 12 kJ/mol.

The eclipsed conformation of propane has three interactions—two ethane-type hydrogen–hydrogen interactions and one additional hydrogen–methyl interaction. Since each eclipsing $\text{H} \leftrightarrow \text{H}$ interaction is the same as that in ethane and thus has an energy “cost” of 4.0 kJ/mol, we can assign a value of $14 - (2 \times 4.0) = 6.0$ kJ/mol (1.4 kcal/mol) to the eclipsing $\text{H} \leftrightarrow \text{CH}_3$ interaction (Figure 3.3.1).

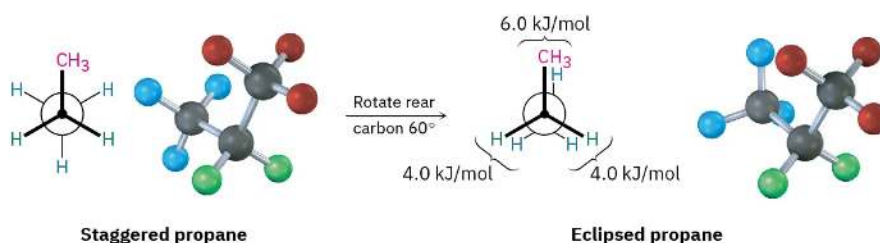
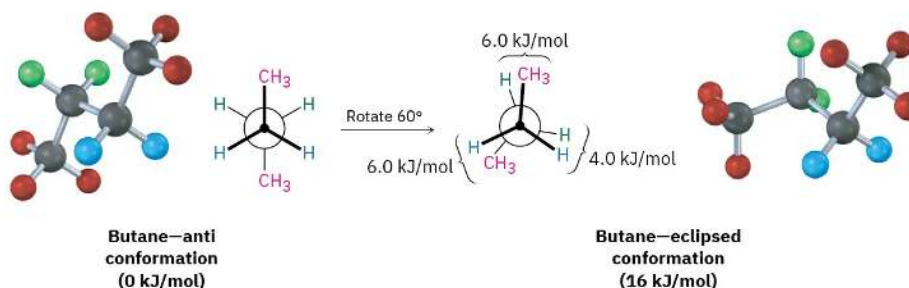
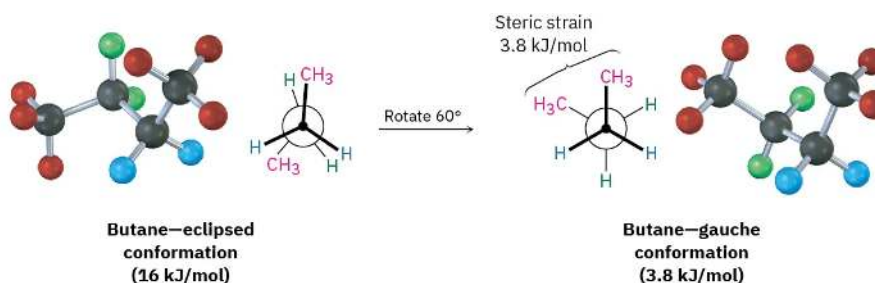


Figure 3.3.1: Newman projections of propane showing staggered and eclipsed conformations. The staggered conformer is lower in energy by 14 kJ/mol.

The conformational situation becomes more complex for larger alkanes because not all staggered conformations have the same energy and not all eclipsed conformations have the same energy. In butane, for instance, the lowest-energy arrangement, called the anti conformation, is the one in which the two methyl groups are as far apart as possible—180° away from each other. As rotation around the C2–C3 bond occurs, an eclipsed conformation is reached where there are two $\text{CH}_3 \leftrightarrow \text{H}$ interactions and one $\text{H} \leftrightarrow \text{H}$ interaction. Using the energy values derived previously from ethane and propane, this eclipsed conformation is more strained than the anti conformation by 2×6.0 kJ/mol + 4.0 kJ/mol (two $\text{CH}_3 \leftrightarrow \text{H}$ interactions plus one $\text{H} \leftrightarrow \text{H}$ interaction), for a total of 16 kJ/mol (3.8 kcal/mol).

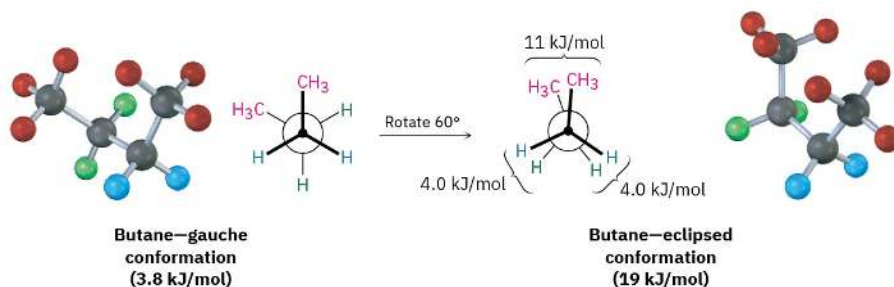


As bond rotation continues, an energy minimum is reached at the staggered conformation where the methyl groups are 60° apart. Called the **gauche conformation**, it lies 3.8 kJ/mol (0.9 kcal/mol) higher in energy than the anti conformation even though it has no eclipsing interactions. This energy difference occurs because the hydrogen atoms of the methyl groups are near one another in the gauche conformation, resulting in what is called **steric strain**. Steric strain is the repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow. It's the result of trying to force two atoms to occupy the same space.



As the dihedral angle between the methyl groups approaches zero, an energy maximum is reached at a second eclipsed conformation. Because the methyl groups are forced even closer together than in the gauche conformation, both torsional strain and

steric strain are present. A total strain energy of 19 kJ/mol (4.5 kcal/mol) has been estimated for this conformation, making it possible to calculate a value of 11 kJ/mol (2.6 kcal/mol) for the $\text{CH}_3 \leftrightarrow \text{CH}_3$ eclipsing interaction: total strain of 19 kJ/mol minus the strain of two $\text{H} \leftrightarrow \text{H}$ eclipsing interactions ($2 \times 4.0 \text{ kcal/mol}$) equals 11 kJ/mol.



After 0° , the rotation becomes a mirror image of what we've already seen: another gauche conformation is reached, another eclipsed conformation, and finally a return to the anti conformation. A plot of potential energy versus rotation about the C2–C3 bond is shown in Figure 3.3.2.

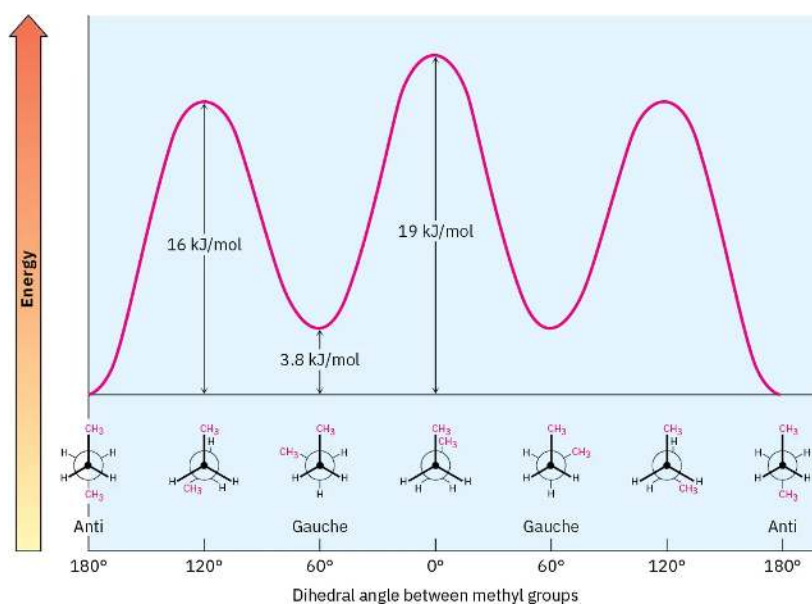


Figure 3.3.2: A plot of potential energy versus rotation for the C2–C3 bond in butane. The energy maximum occurs when the two methyl groups eclipse each other, and the energy minimum occurs when the two methyl groups are 180° apart (anti).

The notion of assigning definite energy values to specific interactions within a molecule is very useful, and we'll return to it in the next chapter. A summary of what we've seen thus far is given in Table 3.3.1.

Table 3.3.1: Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost	
		(kJ/mol)	(kcal/mol)
$\text{H} \leftrightarrow \text{H}$ eclipsed	Torsional strain	4.0	1.0
$\text{H} \leftrightarrow \text{CH}_3$ eclipsed	Mostly torsional strain	6.0	1.4
$\text{CH}_3 \leftrightarrow \text{CH}_3$ eclipsed	Torsional and steric strain	11.0	2.6
$\text{CH}_3 \leftrightarrow \text{CH}_3$ gauche	Steric strain	3.8	0.9

The same principles just developed for butane apply to pentane, hexane, and all higher alkanes. The most favorable conformation for any alkane has the carbon–carbon bonds in staggered arrangements, with large substituents arranged anti to one another. A generalized alkane structure is shown in Figure 3.3.3.

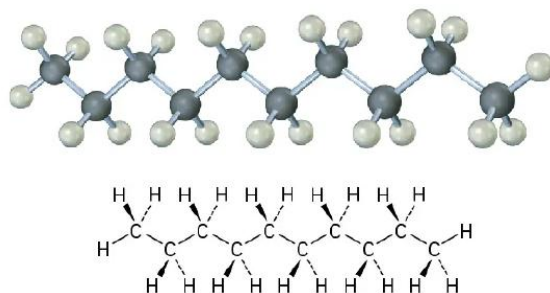


Figure 3.3.3: The most stable alkane conformation is the one in which all substituents are staggered and the carbon-carbon bonds are arranged anti, as shown in this model of decane.

One final point: saying that one particular conformer is “more stable” than another doesn’t mean the molecule adopts and maintains only the more stable conformation. At room temperature, rotations around σ bonds occur so rapidly that all conformers are in equilibrium. At any given instant, however, a larger percentage of molecules will be found in a more stable conformation than in a less stable one.

✓ Worked Example 3.3.1: Newman Projections

Sight along the C1–C2 bond of 1-chloropropane, and draw Newman projections of the most stable and least stable conformations.

Strategy

The most stable conformation of a substituted alkane is generally a staggered one in which large groups have an anti relationship. The least stable conformation is generally an eclipsed one in which large groups are as close as possible.

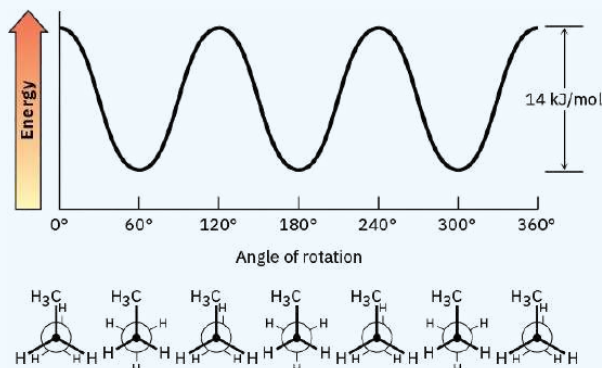
Solution



? Exercise 3.3.1

Make a graph of potential energy versus angle of bond rotation for propane, and assign values to the energy maxima.

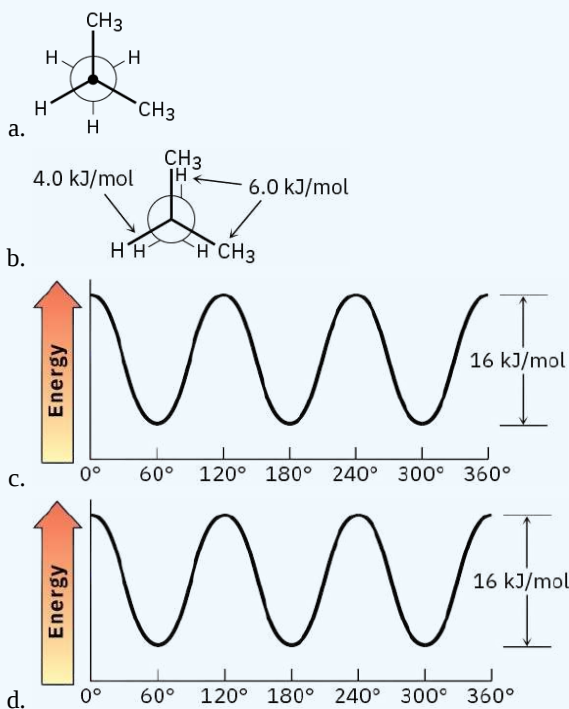
Answer



? Exercise 3.3.2

- Draw a Newman projection of the most stable conformation.
- Draw a Newman projection of the least stable conformation.
- Make a graph of energy versus angle of rotation around the C2–C1 bond.
- Assign relative values to the maxima and minima in your graph, given that an $\text{H} \leftrightarrow \text{H}$ eclipsing interaction costs 4.0 kJ/mol and an $\text{H} \leftrightarrow \text{CH}_3$ eclipsing interaction costs 6.0 kJ/mol.

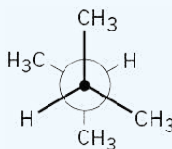
Answer



? Exercise 3.3.3

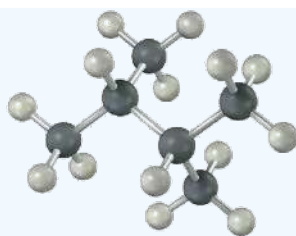
Sight along the C2–C3 bond of 2,3-dimethylbutane, and draw a Newman projection of the most stable conformation.

Answer

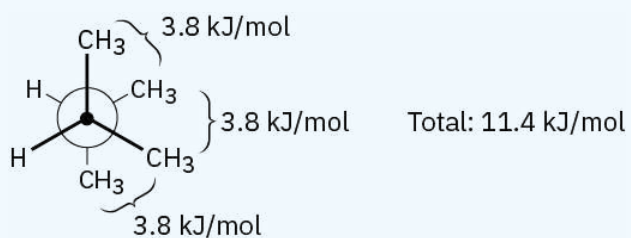


? Exercise 3.3.4

Draw a Newman projection along the C2–C3 bond of the following conformation of 2,3-dimethylbutane, and calculate a total strain energy:



Answer



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3.4: Conformations of Cycloalkanes

Cyclopropane

Cyclopropane is the most strained of all rings, primarily due to the angle strain caused by its 60° C–C–C bond angles. In addition, cyclopropane has considerable torsional strain because the C–H bonds on neighboring carbon atoms are eclipsed (Figure 3.4.1).

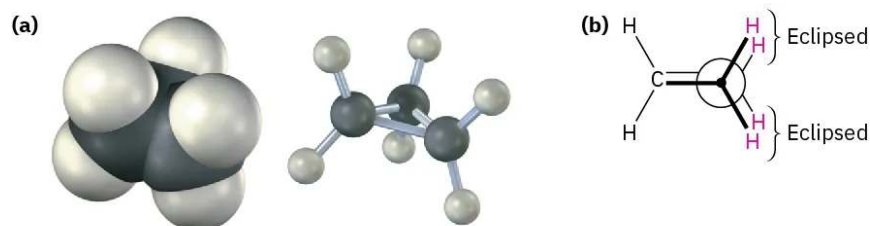
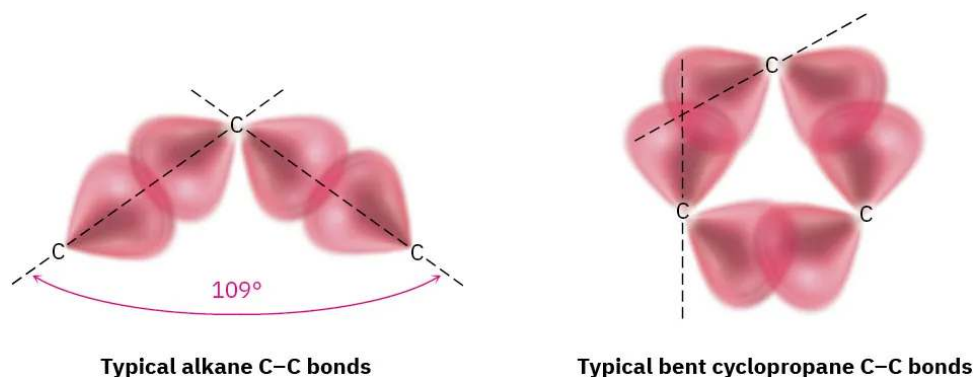


Figure 3.4.1: The structure of cyclopropane, showing the eclipsing of neighboring C–H bonds that gives rise to torsional strain. Part (b) is a Newman projection along a C–C bond.

How can the hybrid-orbital model of bonding account for the large distortion of bond angles from the normal 109° tetrahedral value to 60° in cyclopropane? The answer is that cyclopropane has *bent bonds*. In an unstrained alkane, maximum bonding is achieved when two atoms have their overlapping orbitals pointing directly toward each other. In cyclopropane, though, the orbitals can't point directly toward each other; instead, they overlap at a slight angle. The result is that cyclopropane bonds are weaker and more reactive than typical alkane bonds—255 kJ/mol (61 kcal/mol) for a C–C bond in cyclopropane versus 370 kJ/mol (88 kcal/mol) for a C–C bond in open-chain propane.



Cyclobutane

Cyclobutane has less angle strain than cyclopropane but has more torsional strain because of its larger number of ring hydrogens. As a result, the total strain for the two compounds is nearly the same—110 kJ/mol (26.4 kcal/mol) for cyclobutane versus 115 kJ/mol (27.5 kcal/mol) for cyclopropane. Cyclobutane is not quite flat but is slightly bent so that one carbon atom lies about 25° above the plane of the other three (Figure 3.4.2). The effect of this slight bend is to increase angle strain but to decrease torsional strain, until a minimum-energy balance between the two opposing effects is achieved.

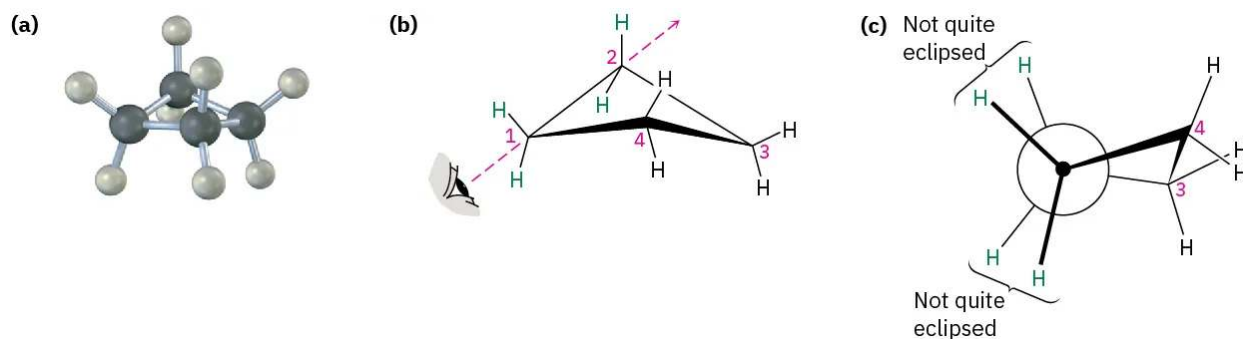


Figure 3.4.2: The conformation of cyclobutane. Part (c) is a Newman projection along a C-C bond, showing that neighboring C-H bonds are not quite eclipsed.

Cyclopentane

Cyclopentane was predicted by Baeyer to be nearly strain-free, but it actually has a total strain energy of 26 kJ/mol (6.2 kcal/mol). Although planar cyclopentane has practically no angle strain, it has a large torsional strain. Cyclopentane therefore twists to adopt a puckered, nonplanar conformation that strikes a balance between increased angle strain and decreased torsional strain. Four of the cyclopentane carbon atoms are in approximately the same plane, with the fifth carbon atom bent out of the plane. Most of the hydrogens are nearly staggered with respect to their neighbors (Figure 3.4.3).

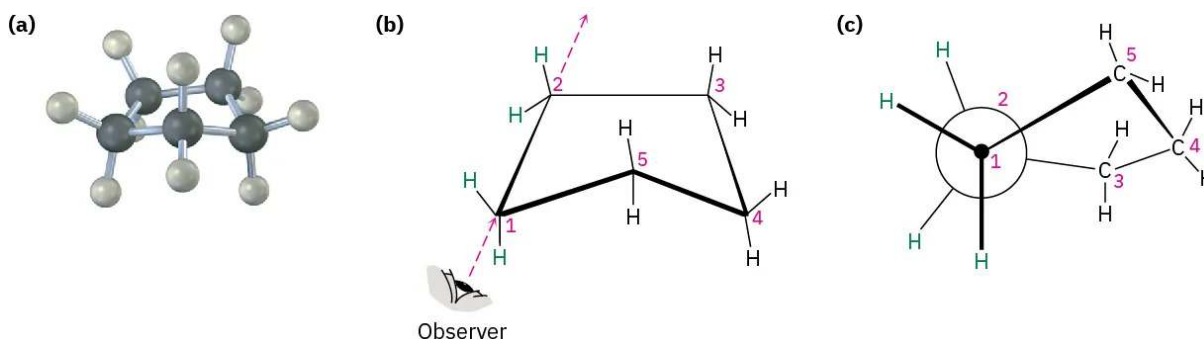


Figure 3.4.3: The conformation of cyclopentane. Carbons 1, 2, 3, and 4 are nearly coplanar, but carbon 5 is out of the plane. Part (c) is a Newman projection along the C1-C2 bond, showing that neighboring C-H bonds are nearly staggered.

? Exercise 3.4.1

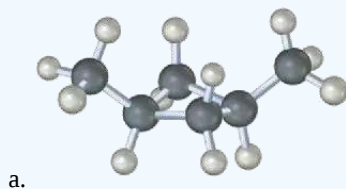
How many H ↔ H eclipsing interactions would be present if cyclopentane were planar? Assuming an energy cost of 4.0 kJ/mol for each eclipsing interaction, how much torsional strain would planar cyclopentane have? Since the measured total strain of cyclopentane is 26 kJ/mol, how much of the torsional strain is relieved by puckering?

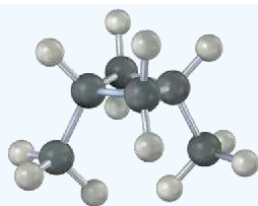
Answer

Ten eclipsing interactions; 40 kJ/mol; 35% is relieved.

? Exercise 3.4.1

Two conformations of *cis*-1,3-dimethylcyclobutane are shown. What is the difference between them, and which do you think is likely to be more stable?





b.

Answer

Conformation **(a)** is more stable because the methyl groups are farther apart.

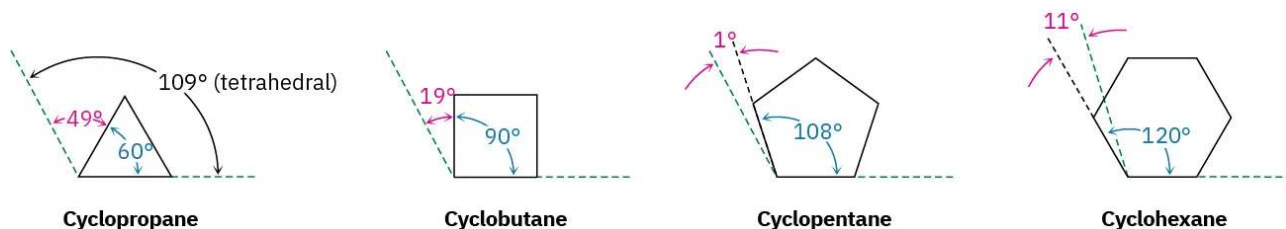
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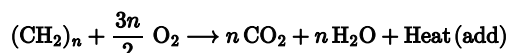
3.4.1: Stability of Cycloalkanes - Ring Strain

Chemists in the late 1800s knew that cyclic molecules existed, but the limitations on ring size were unclear. Although numerous compounds containing five-membered and six-membered rings were known, smaller and larger ring sizes had not been prepared, despite many attempts.

A theoretical interpretation of this observation was proposed in 1885 by Adolf von Baeyer, who suggested that small and large rings might be unstable due to angle strain—the strain induced in a molecule when bond angles are forced to deviate from the ideal 109° tetrahedral value. Baeyer based his suggestion on the simple geometric notion that a three-membered ring (cyclopropane) should be an equilateral triangle with bond angles of 60° rather than 109° , a four-membered ring (cyclobutane) should be a square with bond angles of 90° , a five-membered ring should be a regular pentagon with bond angles of 108° , and so on. Continuing this argument, large rings should be strained by having bond angles that are much greater than 109° .



What are the facts? To measure the amount of strain in a compound, we have to measure the total energy of the compound and then subtract the energy of a strain-free reference compound. The difference between the two values should represent the amount of extra energy in the molecule due to strain. The simplest experimental way to do this for a cycloalkane is to measure its *heat of combustion*, the amount of heat released when the compound burns completely with oxygen. The more energy (strain) the compound contains, the more energy (heat) is released by combustion.



Because the heat of combustion of a cycloalkane depends on size, we need to look at heats of combustion per CH_2 unit. Subtracting a reference value derived from a strain-free acyclic alkane and then multiplying by the number of CH_2 units in the ring gives the overall strain energy. Figure 3.4.1.1 shows the results.

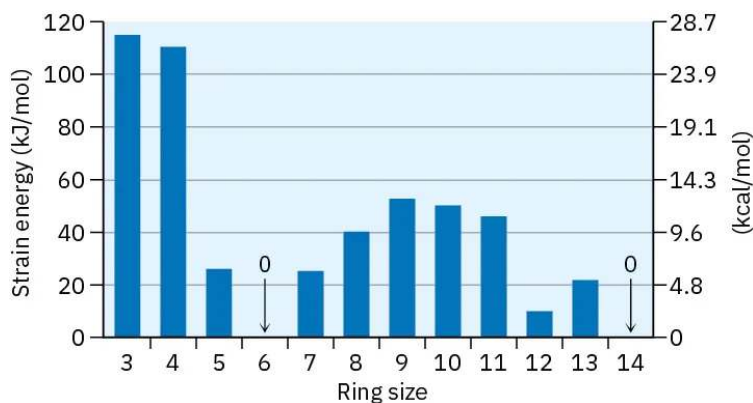


Figure 3.4.1.1: Cycloalkane strain energies, as calculated by taking the difference between cycloalkane heat of combustion per CH_2 and acyclic alkane heat of combustion per CH_2 , and multiplying by the number of CH_2 units in a ring. Small and medium rings are strained, but cyclohexane rings and very large rings are strain-free.

The data in Figure 3.4.1.1 show that Baeyer's theory is only partially correct. Cyclopropane and cyclobutane are indeed strained, just as predicted, but cyclopentane is more strained than predicted, and cyclohexane is strain-free. Cycloalkanes of intermediate size have only modest strain, and rings of 14 carbons or more are strain-free. Why is Baeyer's theory wrong?

Baeyer's theory is wrong for the simple reason that he assumed all cycloalkanes to be flat. In fact, as we'll see in the next section, most cycloalkanes are not flat; instead, they adopt puckered three-dimensional conformations that allow bond angles to be nearly tetrahedral. As a result, angle strain occurs only in three- and four-membered rings, which have little flexibility. For most ring sizes,

particularly the medium-ring (C_7 – C_{11}) cycloalkanes, torsional strain caused by $H \leftrightarrow H$ eclipsing interactions at adjacent carbons (Section 3.7) and steric strain caused by the repulsion between nonbonded atoms that approach too closely (Section 3.8) are the most important factors. Thus, three kinds of strain contribute to the overall energy of a cycloalkane.

- **Angle strain**—the strain due to expansion or compression of bond angles
- **Torsional strain**—the strain due to eclipsing of bonds between neighboring atoms
- **Steric strain**—the strain due to repulsive interactions when atoms approach each other too closely

? Exercise 3.4.1.1

Each $H \leftrightarrow H$ eclipsing interaction in ethane costs about 4.0 kJ/mol. How many such interactions are present in cyclopropane? What fraction of the overall 115 kJ/mol (27.5 kcal/mol) strain energy of cyclopropane is due to torsional strain?

Answer

Six interactions; 21% of strain

? Exercise 3.4.1.2

cis-1,2-Dimethylcyclopropane has more strain than *trans*-1,2-dimethylcyclopropane. How can you account for this difference? Which of the two compounds is more stable?

Answer

The *cis* isomer is less stable because the methyl groups nearly eclipse each other.

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3.4.2: Cis-Trans Isomerism in Cycloalkanes

In many respects, the chemistry of cycloalkanes is like that of open-chain alkanes: both are nonpolar and fairly inert. There are, however, some important differences. One difference is that cycloalkanes are less flexible than open-chain alkanes. In contrast with the relatively free rotation around single bonds in open-chain alkanes (Section 3.7 and Section 3.8), there is much less freedom in cycloalkanes. Cyclopropane, for example, must be a rigid, planar molecule because three points (the carbon atoms) define a plane. No bond rotation can take place around a cyclopropane carbon-carbon bond without breaking open the ring (Figure 3.4.2.1).

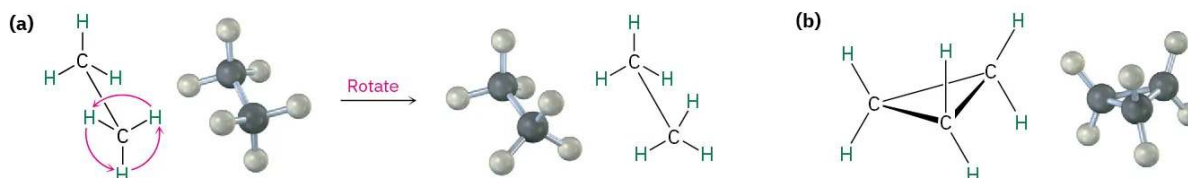


Figure 3.4.2.1: Bond rotation in ethane and cyclopropane. (a) Rotation occurs around the carbon-carbon bond in ethane, but (b) no rotation is possible around the carbon-carbon bonds in cyclopropane without breaking open the ring.

Larger cycloalkanes have increasing rotational freedom, and very large rings (C₂₅ and up) are so floppy that they are nearly indistinguishable from open-chain alkanes. The common ring sizes (C₃-C₇), however, are severely restricted in their molecular motions.

Because of their cyclic structures, cycloalkanes have two faces when viewed edge-on, a “top” face and a “bottom” face. As a result, isomerism is possible in substituted cycloalkanes. For example, there are two different 1,2-dimethylcyclopropane isomers, one with the two methyl groups on the same face of the ring and one with the methyl groups on opposite faces (Figure 3.4.2.2). Both isomers are stable compounds, and neither can be converted into the other without breaking and reforming chemical bonds.

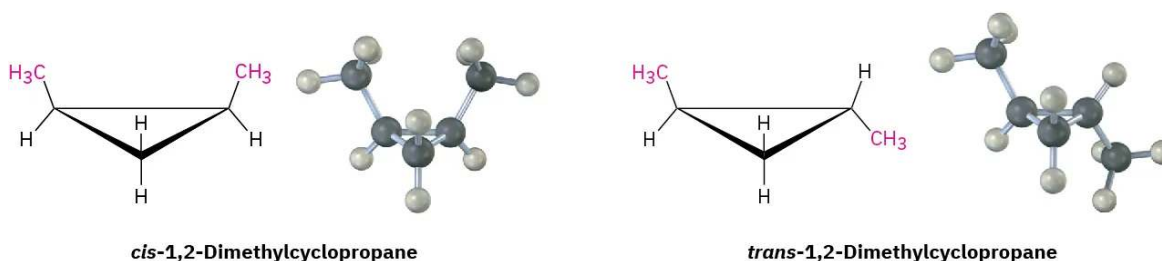


Figure 3.4.2.2: There are two different 1,2-dimethylcyclopropane isomers, one with the methyl groups on the same face of the ring (cis) and the other with the methyl groups on opposite faces of the ring (trans). The two isomers do not interconvert.

Unlike the constitutional isomers butane and isobutane, which have their atoms connected in a different order (Section 3.3), the two 1,2-dimethylcyclopropanes have the same order of connections but differ in the spatial orientation of the atoms. Such compounds, with atoms connected in the same order but differing in three-dimensional orientation, are called stereochemical isomers, or stereoisomers. As we saw in Section 3.6, the term stereochemistry is used generally to refer to the three-dimensional aspects of structure and reactivity.

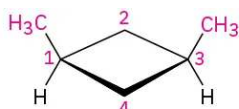
Constitutional isomers
(different connections
between atoms)



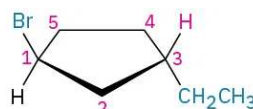
Stereoisomers
(same connections
but different three-
dimensional geometry)



The 1,2-dimethylcyclopropanes are members of a subclass of stereoisomers called cis-trans isomers. The prefixes *cis*- (Latin “on the same side”) and *trans*- (Latin “across”) are used to distinguish between them. Cis-trans isomerism is a common occurrence in substituted cycloalkanes and in many cyclic biological molecules.



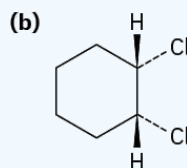
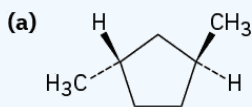
cis-1,3-Dimethylcyclobutane



trans-1-Bromo-3-ethylcyclopentane

✓ Worked Example 3.4.2.1: Naming Cycloalkanes

Name the following substances, including the *cis*- or *trans*- prefix:



Strategy

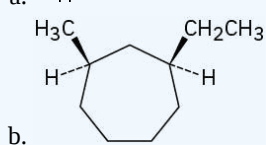
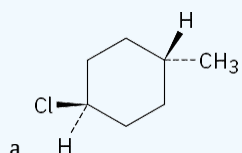
In these views, the ring is roughly in the plane of the page, a wedged bond protrudes out of the page, and a dashed bond recedes into the page. Two substituents are *cis* if they are both out of or both into the page, and they are *trans* if one is out of and one is into the page.

Solution

- trans*-1,3-Dimethylcyclopentane
- cis*-1,2-Dichlorocyclohexane

? Exercise 3.4.2.1

Name the following substances, including the *cis*- or *trans*- prefix:



Answer

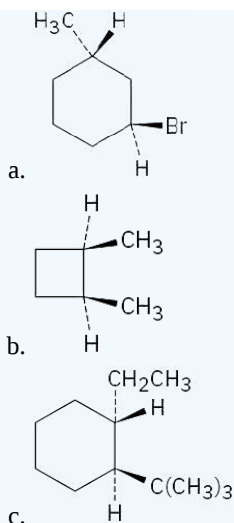
- trans*-1-Chloro-4-methylcyclohexane
- cis*-1-Ethyl-3-methylcycloheptane

? Exercise 3.4.2.2

Draw the structures of the following molecules:

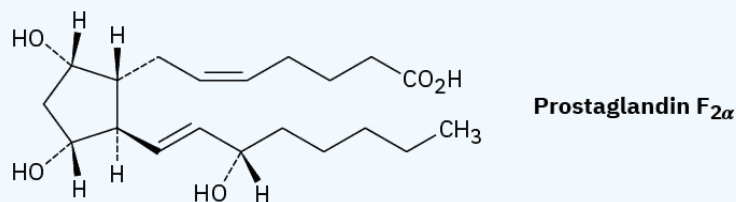
- trans*-1-Bromo-3-methylcyclohexane
- cis*-1,2-Dimethylcyclobutane
- trans*-1-*tert*-Butyl-2-ethylcyclohexane

Answer



? Exercise 3.4.2.3

Prostaglandin $F_{2\alpha}$, a hormone that causes uterine contraction during childbirth, has the following structure. Are the two hydroxyl groups ($-OH$) on the cyclopentane ring *cis* or *trans* to each other? What about the two carbon chains attached to the ring

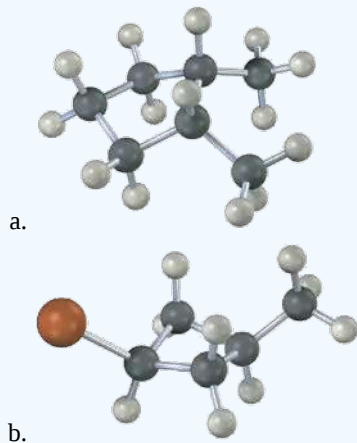


Answer

The two hydroxyl groups are *cis*. The two side chains are *trans*.

? Exercise 3.4.2.4

Name the following substances, including the *cis*- or *trans*- prefix (red-brown = Br):



Answer

a. *cis*-1,2-Dimethylcyclopentane

b. *cis*-1-Bromo-3-methylcyclobutane

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3.5: Conformations of Cycloalkanes

Cyclopropane

Cyclopropane is the most strained of all rings, primarily due to the angle strain caused by its 60° C–C–C bond angles. In addition, cyclopropane has considerable torsional strain because the C–H bonds on neighboring carbon atoms are eclipsed (Figure 3.5.1).

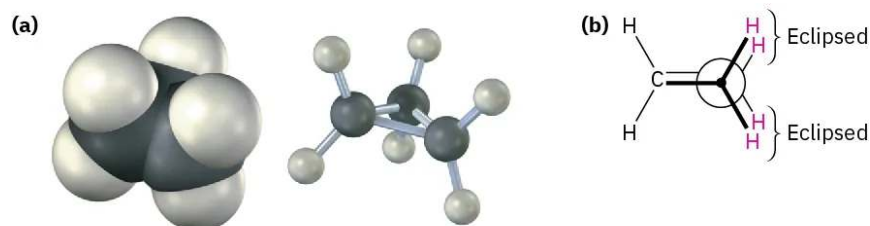
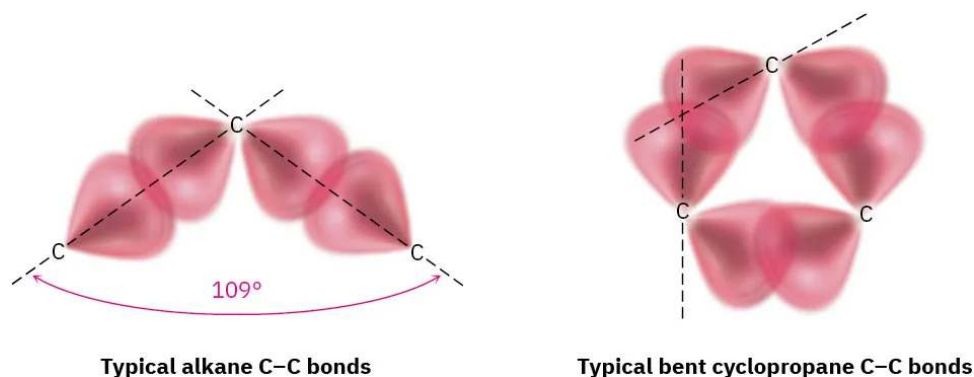


Figure 3.5.1: The structure of cyclopropane, showing the eclipsing of neighboring C–H bonds that gives rise to torsional strain. Part (b) is a Newman projection along a C–C bond.

How can the hybrid-orbital model of bonding account for the large distortion of bond angles from the normal 109° tetrahedral value to 60° in cyclopropane? The answer is that cyclopropane has *bent bonds*. In an unstrained alkane, maximum bonding is achieved when two atoms have their overlapping orbitals pointing directly toward each other. In cyclopropane, though, the orbitals can't point directly toward each other; instead, they overlap at a slight angle. The result is that cyclopropane bonds are weaker and more reactive than typical alkane bonds—255 kJ/mol (61 kcal/mol) for a C–C bond in cyclopropane versus 370 kJ/mol (88 kcal/mol) for a C–C bond in open-chain propane.



Cyclobutane

Cyclobutane has less angle strain than cyclopropane but has more torsional strain because of its larger number of ring hydrogens. As a result, the total strain for the two compounds is nearly the same—110 kJ/mol (26.4 kcal/mol) for cyclobutane versus 115 kJ/mol (27.5 kcal/mol) for cyclopropane. Cyclobutane is not quite flat but is slightly bent so that one carbon atom lies about 25° above the plane of the other three (Figure 3.5.2). The effect of this slight bend is to increase angle strain but to decrease torsional strain, until a minimum-energy balance between the two opposing effects is achieved.

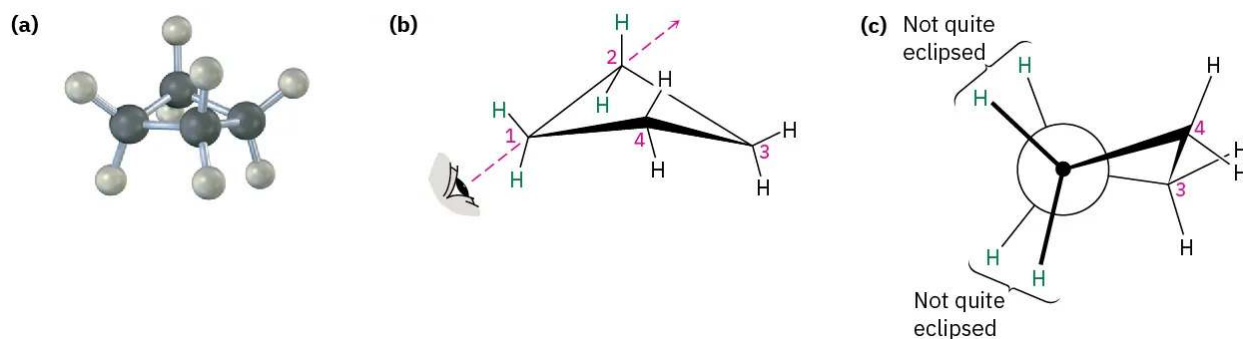


Figure 3.5.2: The conformation of cyclobutane. Part (c) is a Newman projection along a C-C bond, showing that neighboring C-H bonds are not quite eclipsed.

Cyclopentane

Cyclopentane was predicted by Baeyer to be nearly strain-free, but it actually has a total strain energy of 26 kJ/mol (6.2 kcal/mol). Although planar cyclopentane has practically no angle strain, it has a large torsional strain. Cyclopentane therefore twists to adopt a puckered, nonplanar conformation that strikes a balance between increased angle strain and decreased torsional strain. Four of the cyclopentane carbon atoms are in approximately the same plane, with the fifth carbon atom bent out of the plane. Most of the hydrogens are nearly staggered with respect to their neighbors (Figure 3.5.3).

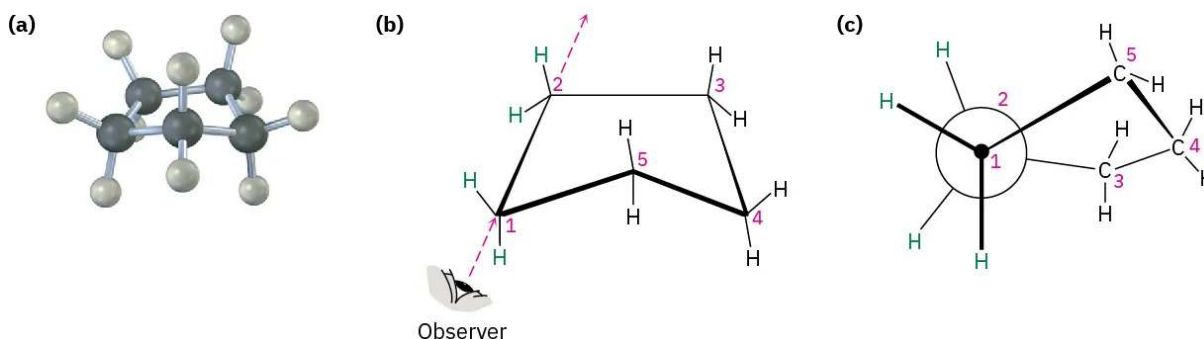


Figure 3.5.3: The conformation of cyclopentane. Carbons 1, 2, 3, and 4 are nearly coplanar, but carbon 5 is out of the plane. Part (c) is a Newman projection along the C1-C2 bond, showing that neighboring C-H bonds are nearly staggered.

? Exercise 3.5.1

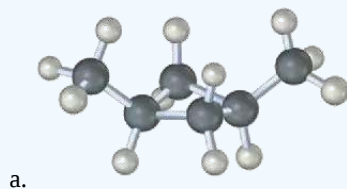
How many $\text{H} \longleftrightarrow \text{H}$ eclipsing interactions would be present if cyclopentane were planar? Assuming an energy cost of 4.0 kJ/mol for each eclipsing interaction, how much torsional strain would planar cyclopentane have? Since the measured total strain of cyclopentane is 26 kJ/mol, how much of the torsional strain is relieved by puckering?

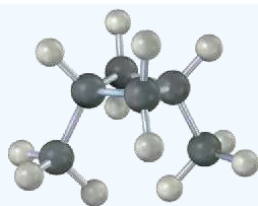
Answer

Ten eclipsing interactions; 40 kJ/mol; 35% is relieved.

? Exercise 3.5.1

Two conformations of *cis*-1,3-dimethylcyclobutane are shown. What is the difference between them, and which do you think is likely to be more stable?





b.

Answer

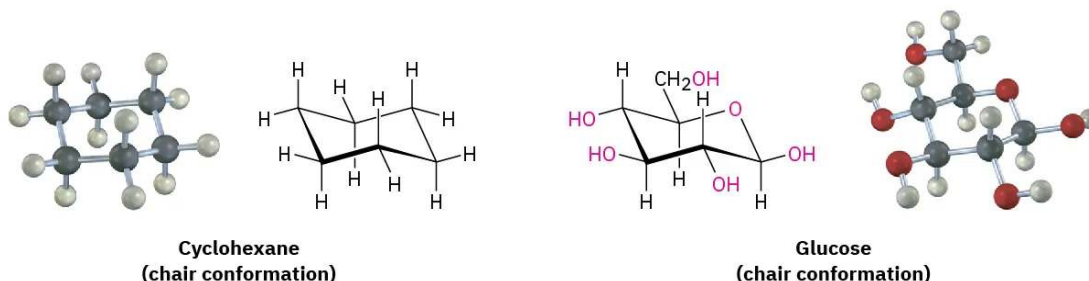
Conformation **(a)** is more stable because the methyl groups are farther apart.

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3.5.1: Axial and Equatorial Bonds in Cyclohexane

The chair conformation of cyclohexane has many consequences. We'll see in **Section 11.10**, for instance, that the chemical behavior of many substituted cyclohexanes is influenced by their conformation. In addition, we'll see in **Section 25.6** that simple carbohydrates, such as glucose, adopt a conformation based on the cyclohexane chair and that their chemistry is directly affected as a result.



Another trait of the chair conformation is that there are two kinds of positions for substituents on the cyclohexane ring: *axial* positions and *equatorial* positions (as shown in Figure 3.5.1.1). The six axial positions are parallel to the ring **axis**, while the six equatorial positions are in the rough plane of the ring, around the ring **equator**.

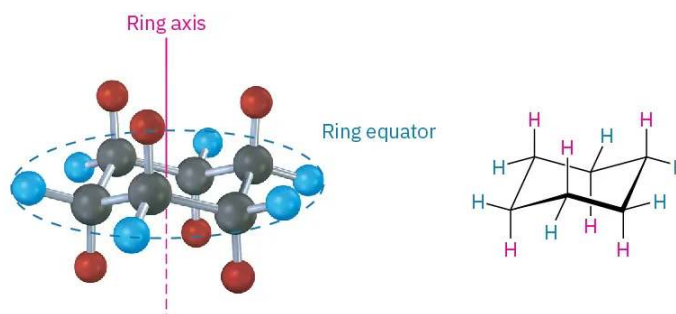


Figure 3.5.1.1: Axial and equatorial positions in chair cyclohexane. The six axial hydrogens are parallel to the ring axis, and the six equatorial hydrogens are in a band around the ring equator.

As shown in Figure 3.5.1.1, each carbon atom in chair cyclohexane has one axial and one equatorial hydrogen. Furthermore, each side of the ring has three axial and three equatorial hydrogens in an alternating arrangement. For example, if the top side of the ring has axial hydrogens on carbons 1, 3, and 5, then it has equatorial hydrogens on carbons 2, 4, and 6. The reverse is true for the bottom side: carbons 1, 3, and 5 have equatorial hydrogens, but carbons 2, 4, and 6 have axial hydrogens (Figure 3.5.1.2).

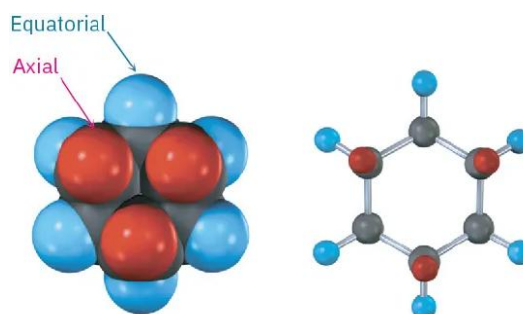


Figure 3.5.1.2: Alternating axial and equatorial positions in chair cyclohexane, looking directly down the ring axis. Each carbon atom has one axial and one equatorial position, and each face has alternating axial and equatorial positions.

Note that we haven't used the words *cis* and *trans* in this discussion of cyclohexane conformation. Two hydrogens on the same side of the ring are always *cis*, regardless of whether they're axial or equatorial and regardless of whether they're adjacent. Similarly, two hydrogens on opposite sides of the ring are always *trans*.

Axial and equatorial bonds can be drawn following the procedure shown in Figure 3.5.1.3. If possible, look at a molecular model as you practice.

Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up–down.



Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.



Completed cyclohexane

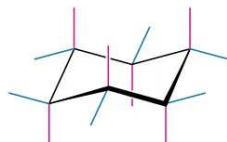


Figure 3.5.1.3: A procedure for drawing axial and equatorial bonds in chair cyclohexane.

Because chair cyclohexane has two kinds of positions—axial and equatorial—we might expect to find two isomeric forms of a monosubstituted cyclohexane. In fact, we don't. There is only one methylcyclohexane, one bromocyclohexane, one cyclohexanol (hydroxycyclohexane), and so on, because cyclohexane rings are conformationally mobile at room temperature. Different chair conformations readily interconvert, exchanging axial and equatorial positions. This interconversion, called a ring-flip, is shown in Figure 3.5.1.4.

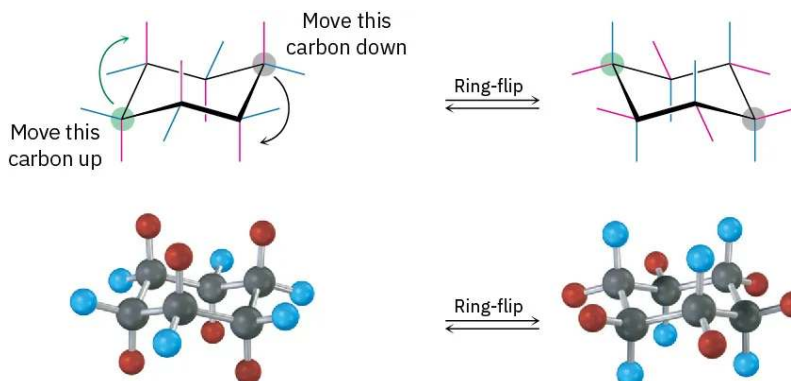
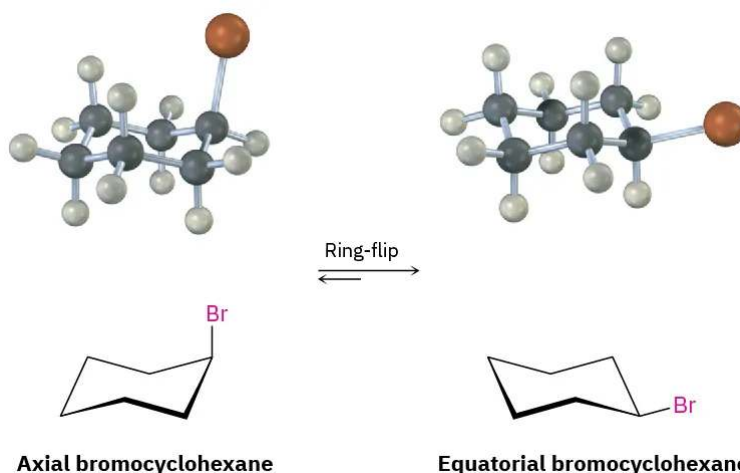


Figure 3.5.1.4: A ring-flip in chair cyclohexane interconverts axial and equatorial positions. What is **axial** in the starting structure becomes **equatorial** in the ring-flipped structure, and what is **equatorial** in the starting structure is **axial** after ring-flip.

As shown in Figure 3.5.1.4, a chair cyclohexane can be ring-flipped by keeping the middle four carbon atoms in place while folding the two end carbons in opposite directions. In so doing, an axial substituent in one chair form becomes an equatorial substituent in the ring-flipped chair form and vice versa. For example, axial bromocyclohexane becomes equatorial bromocyclohexane after a ring-flip. Since the energy barrier to chair–chair interconversion is only about 45 kJ/mol (10.8 kcal/mol), the process is rapid at room temperature and we see what appears to be a single structure rather than distinct axial and equatorial isomers.



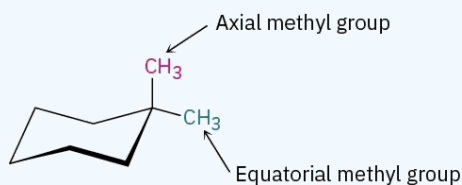
✓ Worked Example 3.5.1.1: Drawing the Chair Conformation of a Substituted Cyclohexane

Draw 1,1-dimethylcyclohexane in a chair conformation, indicating which methyl group in your drawing is axial and which is equatorial.

Strategy

Draw a chair cyclohexane ring using the procedure in Figure 3.5.1.3, and then put two methyl groups on the same carbon. The methyl group in the rough plane of the ring is equatorial, and the one directly above or below the ring is axial.

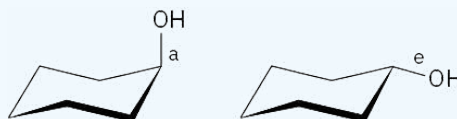
Solution



? Exercise 3.5.1.1

Draw two different chair conformations of cyclohexanol (hydroxycyclohexane), showing all hydrogen atoms. Identify each position as axial or equatorial.

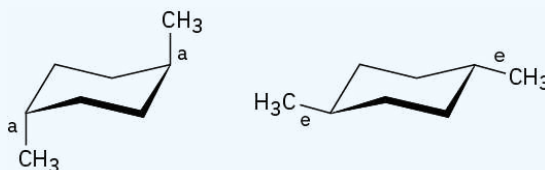
Answer



? Exercise 3.5.1.2

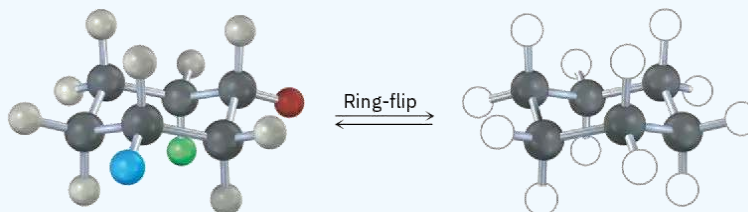
Draw two different chair conformations of *trans*-1,4-dimethylcyclohexane, and label all positions as axial or equatorial.

Answer



? Exercise 3.5.1.3

Identify each of the colored positions—red, blue, and green—as axial or equatorial. Then carry out a ring-flip, and show the new positions occupied by each color.



Answer

Before the ring-flip, red and blue are equatorial and green is axial. After the ring-flip, red and blue are axial and green is equatorial.

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3.5.2: Conformations of Monosubstituted Cyclohexanes

Even though cyclohexane rings flip rapidly between chair conformations at room temperature, the two conformations of a monosubstituted cyclohexane aren't equally stable. In methylcyclohexane, for instance, the equatorial conformation is more stable than the axial conformation by 7.6 kJ/mol (1.8 kcal/mol). The same is true of other monosubstituted cyclohexanes: a substituent is almost always more stable in an equatorial position than in an axial position.

You might recall from your general chemistry course that it's possible to calculate the percentages of two isomers at equilibrium using the equation $\Delta E = -RT \ln K$, where ΔE is the energy difference between isomers, R is the gas constant [8.315 J/(K·mol)], T is the Kelvin temperature, and K is the equilibrium constant between isomers. For example, an energy difference of 7.6 kJ/mol means that about 95% of methylcyclohexane molecules have an equatorial methyl group at any given instant while only 5% have an axial methyl group. Figure 3.5.2.1 plots the relationship between energy and isomer percentages.

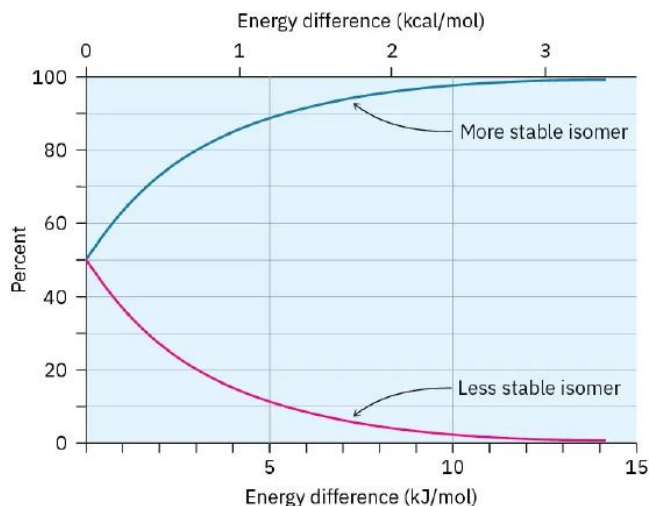


Figure 3.5.2.1: A plot of the percentages of two isomers at equilibrium versus the energy difference between them. The curves are calculated using the equation $\Delta E = -RT \ln K$.

The energy difference between axial and equatorial conformations is due to steric strain caused by 1,3-diaxial interactions. The axial methyl group on C1 is too close to the axial hydrogens three carbons away on C3 and C5, resulting in 7.6 kJ/mol of steric strain (Figure 3.5.2.2).

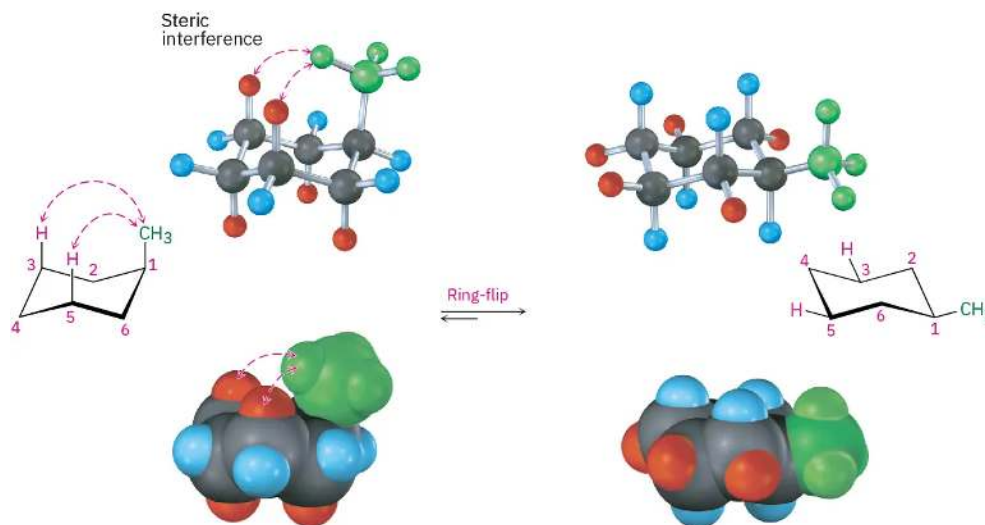


Figure 3.5.2.2: Interconversion of axial and equatorial methylcyclohexane, represented in several formats. The equatorial conformation is more stable than the axial conformation by 7.6 kJ/mol.

The 1,3-diaxial steric strain in substituted methylcyclohexane is already familiar—we saw it previously as the steric strain between methyl groups in gauche in Section 3.8). Gauche butane is less stable than anti butane by 3.8 kJ/mol (0.9 kcal/mol) because of steric interference between hydrogen atoms on the two methyl groups. Comparing a four-carbon fragment of axial methylcyclohexane with gauche butane shows that the steric interaction is the same in both (Figure 3.5.2.3). Because axial methylcyclohexane has two such interactions, it has $2 \times 3.8 = 7.6$ kJ/mol of steric strain. Equatorial methylcyclohexane has no such interactions and is therefore more stable.

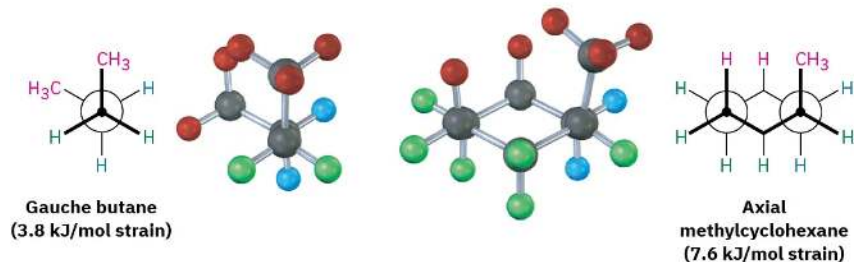
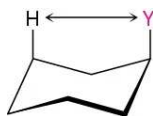


Figure 3.5.2.3: The origin of 1,3-diaxial interactions in methylcyclohexane. The steric strain between **an axial methyl group** and **an axial hydrogen atom** three carbons away is identical to the steric strain in gauche butane. (To display clearly the diaxial interactions in methylcyclohexane, two of the equatorial hydrogens are not shown.)

The exact amount of 1,3-diaxial steric strain in a given substituted cyclohexane depends on the nature and size of the substituent, as indicated in Table 3.5.2.1. Not surprisingly, the amount of steric strain increases through the series $\text{H}_3\text{C}^- < \text{CH}_3\text{CH}_2^- < (\text{CH}_3)_2\text{CH}^- \ll (\text{CH}_3)_3\text{C}^-$, paralleling the increasing size of the alkyl groups.



Note that the values given in Table 3.5.2.4 refer to 1,3-diaxial interactions of the substituent with a single hydrogen atom. These values must be doubled to arrive at the amount of strain in a monosubstituted cyclohexane.

Table 3.5.2.1: Steric Strain in Monosubstituted Cyclohexanes

Substitution (Y)	1,3-Diaxial strain (kJ/mol)	1,3-Diaxial strain (kcal/mol)
F	0.5	0.12
Cl, Br	1.0	0.25
OH	2.1	0.5
CH ₃	3.8	0.9
CH ₂ CH ₃	4.0	0.95
CH(CH ₃) ₂	4.6	1.1
C(CH ₃) ₃	11.4	2.7
C ₆ H ₅	6.3	1.5
CO ₂ H	2.9	0.7
CN	0.4	0.1

? Exercise 3.5.2.1

What is the energy difference between the axial and equatorial conformations of cyclohexanol (hydroxycyclohexane)?

Answer

4.2 kJ/mol

? Exercise 3.5.2.2

Why do you suppose an axial cyano ($-\text{CN}$) substituent causes practically no 1,3-diaxial steric strain (0.4 kJ/mol)?

Answer

Cyano group points straight up.

? Exercise 3.5.2.3

Look back at Figure 3.5.2.1 and estimate the percentages of axial and equatorial conformations present at equilibrium in bromocyclohexane.

Answer

Equatorial = 70%; axial = 30%

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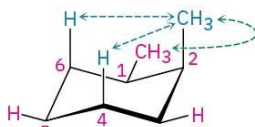
3.5.3: Conformations of Disubstituted Cyclohexanes

Monosubstituted cyclohexanes are always more stable with their substituent in an equatorial position, but the situation with disubstituted cyclohexanes is more complex because the steric effects of both substituents must be taken into account. All steric interactions for both possible chair conformations must be analyzed before deciding which conformation is favored.

Let's look at 1,2-dimethylcyclohexane as an example. There are two isomers, *cis*-1,2-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane, which must be considered separately. In the *cis* isomer, both methyl groups are on the same face of the ring and the compound can exist in either of the two chair conformations shown in Figure 3.5.3.1. (It may be easier for you to see whether a compound is *cis*- or *trans*-disubstituted by first drawing the ring as a flat representation and then converting it to a chair conformation.)

cis-1,2-Dimethylcyclohexane

One gauche
interaction (3.8 kJ/mol)
Two CH₃ ↔ H diaxial
interactions (7.6 kJ/mol)
Total strain: 3.8 + 7.6 = 11.4 kJ/mol



Ring-flip

One gauche
interaction (3.8 kJ/mol)
Two CH₃ ↔ H diaxial
interactions (7.6 kJ/mol)
Total strain: 3.8 + 7.6 = 11.4 kJ/mol

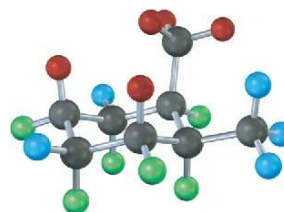
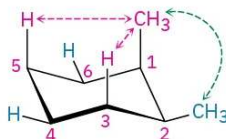


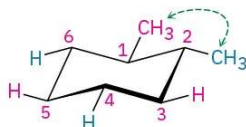
Figure 3.5.3.1: Conformations of *cis*-1,2-dimethylcyclohexane. The two chair conformations are equal in energy because each has one axial methyl group and one equatorial methyl group.

Both chair conformations of *cis*-1,2-dimethylcyclohexane have one axial methyl group and one equatorial methyl group. The top conformation in Figure 3.5.3.1 has an axial methyl group at C2, which has 1,3-diaxial interactions with hydrogens on C4 and C6. The ring-flipped conformation has an axial methyl group at C1, which has 1,3-diaxial interactions with hydrogens on C3 and C5. In addition, both conformations have gauche butane interactions between the two methyl groups. The two conformations are equal in energy, with a total steric strain of $3 \times 3.8 \text{ kJ/mol} = 11.4 \text{ kJ/mol}$ (2.7 kcal/mol).

In *trans*-1,2-dimethylcyclohexane, the two methyl groups are on opposite sides of the ring and the compound can exist in either of the two chair conformations shown in Figure 3.5.3.2. The situation here is quite different from that of the *cis* isomer. The top conformation in Figure 3.5.3.2 has both methyl groups equatorial with only a gauche butane interaction between them (3.8 kJ/mol) but no 1,3-diaxial interactions. The ring-flipped conformation, however, has both methyl groups axial. The axial methyl group at C1 interacts with axial hydrogens at C3 and C5, and the axial methyl group at C2 interacts with axial hydrogens at C4 and C6. These four 1,3-diaxial interactions produce a steric strain of $4 \times 3.8 \text{ kJ/mol} = 15.2 \text{ kJ/mol}$ and make the diaxial conformation $15.2 - 3.8 = 11.4 \text{ kJ/mol}$ less favorable than the diequatorial conformation. We therefore predict that *trans*-1,2-dimethylcyclohexane will exist almost exclusively in the diequatorial conformation.

***trans*-1,2-Dimethylcyclohexane**

One gauche
interaction (3.8 kJ/mol)



Ring-flip

Four CH₃ ↔ H diaxial
interactions (15.2 kJ/mol)

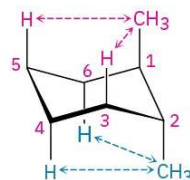
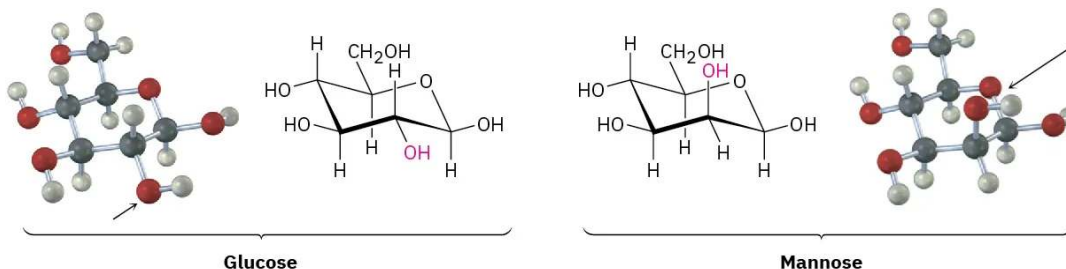


Figure 3.5.3.2: Conformations of *trans*-1,2-dimethylcyclohexane. The conformation with both methyl groups equatorial (top) is favored by 11.4 kJ/mol (2.7 kcal/mol) over the conformation with both methyl groups axial (bottom).

The same kind of conformational analysis just carried out for *cis*- and *trans*-1,2-dimethylcyclohexane can be done for any substituted cyclohexane, such as *cis*-1-*tert*-butyl-4-chlorocyclohexane (see Worked Example 4.3). As you might imagine, though, the situation becomes more complex as the number of substituents increases. For instance, compare glucose with mannose, a carbohydrate present in seaweed. Which do you think is more strained? In glucose, all substituents on the six-membered ring are equatorial, while in mannose, one of the –OH groups is axial, making it more strained.



A summary of the various axial and equatorial relationships among substituent groups in the different possible *cis* and *trans* substitution patterns for disubstituted cyclohexanes is given in Table 3.5.3.1.

Table 3.5.3.1: Axial and Equatorial Relationships in *Cis*- and *Trans*-Disubstituted Cyclohexanes

Cis/trans substitution pattern	Axial/equatorial relationships		
1,2-Cis disubstituted	a,e	or	e,a
1,2-Trans disubstituted	a,a	or	e,e
1,3-Cis disubstituted	a,a	or	e,e
1,3-Trans disubstituted	a,e	or	e,a
1,4-Cis disubstituted	a,e	or	e,a
1,4-Trans disubstituted	a,a	or	e,e

✓ **Worked Example 3.5.3.1: Drawing the Most Stable Conformation of a Substituted Cyclohexane**

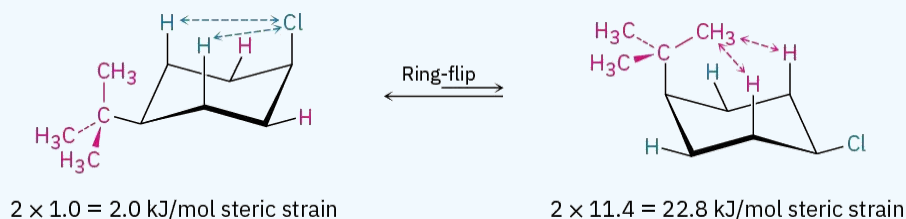
Draw the more stable chair conformation of *cis*-1-*tert*-butyl-4-chlorocyclohexane. By how much is it favored?

Strategy

Draw the two possible chair conformations, and calculate the strain energy in each. Remember that equatorial substituents cause less strain than axial substituents.

Solution

First draw the two chair conformations of the molecule:



In the conformation on the left, the *tert*-butyl group is equatorial and the chlorine is axial. In the conformation on the right, the *tert*-butyl group is axial and the chlorine is equatorial. These conformations aren't of equal energy because an axial *tert*-butyl substituent and an axial chloro substituent produce different amounts of steric strain. Table 4.1 shows that the 1,3-diaxial interaction between a hydrogen and a *tert*-butyl group costs 11.4 kJ/mol (2.7 kcal/mol), whereas the interaction between a hydrogen and a chlorine costs only 1.0 kJ/mol (0.25 kcal/mol). An axial *tert*-butyl group therefore produces $(2 \times 11.4 \text{ kJ/mol}) - (2 \times 1.0 \text{ kJ/mol}) = 20.8 \text{ kJ/mol}$ (4.9 kcal/mol) more steric strain than an axial chlorine, and the compound preferentially adopts the conformation with the chlorine axial and the *tert*-butyl equatorial.

? Exercise 3.5.3.1

Draw the more stable chair conformation of the following molecules, and estimate the amount of strain in each:

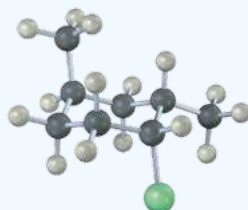
- trans*-1-Chloro-3-methylcyclohexane
- cis*-1-Ethyl-2-methylcyclohexane
- cis*-1-Bromo-4-ethylcyclohexane
- cis*-1-*tert*-Butyl-4-ethylcyclohexane

Answer

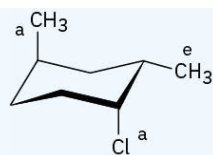
- 2.0 kJ/mol (axial Cl)
- 11.4 kJ/mol (axial CH₃)
- 2.0 kJ/mol (axial Br)
- 8.0 kJ/mol (axial CH₂CH₃)

? Exercise 3.5.3.2

Identify each substituent in the following compound as axial or equatorial, and tell whether the conformation shown is the more stable or less stable chair form (green = Cl):



Answer



1-Chloro-2,4-dimethyl-
cyclohexane
(less stable chair form)

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3.5.4: Why This Chapter?

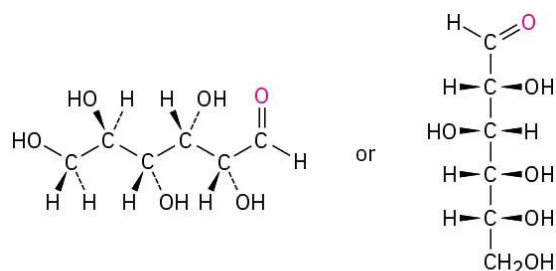
We've now seen all the common functional groups and reaction types that occur in organic and biological chemistry. In this and the next four chapters, we'll focus on the major classes of biological molecules, beginning with a look at the structures and primary biological functions of carbohydrates. Then, in Chapter 29, we'll return to the subject to see how carbohydrates are both synthesized and degraded in organisms.



Figure 3.5.4.1: Produced by honeybees from the nectar of flowers, honey is primarily a mixture of the two simple sugars fructose and glucose. (credit: modification of work "Apis mellifera" by Thomas Bresson/Flickr, CC BY 2.0)

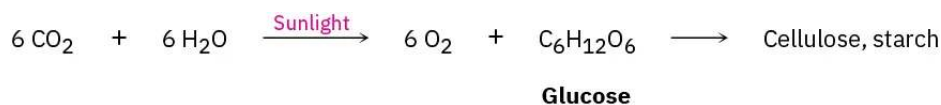
Carbohydrates occur in every living organism. The sugar and starch in food, and the cellulose in wood, paper, and cotton are nearly pure carbohydrates. Modified carbohydrates form part of the coating around living cells, other carbohydrates are part of the nucleic acids that carry our genetic information, and still others are used as medicines.

The word carbohydrate derives historically from the fact that glucose, the first simple carbohydrate to be obtained in pure form, has the molecular formula $C_6H_{12}O_6$ and was originally thought to be a "hydrate of carbon, $C_6(H_2O)_6$." This view was soon abandoned, but the name persisted. Today, the term *carbohydrate* is used to refer loosely to the broad class of polyhydroxylated aldehydes and ketones commonly called sugars. Glucose, also known as dextrose in medical work, is the most familiar example.



**Glucose (dextrose),
a pentahydroxyhexanal**

Carbohydrates are synthesized by green plants during photosynthesis, a complex process in which sunlight provides the energy to convert CO_2 and H_2O into glucose plus oxygen. Many molecules of glucose are then chemically linked for storage by the plant in the form of either cellulose or starch. It has been estimated that more than 50% of the dry weight of the earth's biomass—all plants and animals—consists of glucose polymers. When eaten and metabolized, carbohydrates then provide animals with a source of readily available energy. Thus, carbohydrates act as the chemical intermediaries by which solar energy is stored and used to support life.



Because humans and most other mammals lack the enzymes needed for digestion of cellulose, they require starch as their dietary source of carbohydrates. Grazing animals such as cows, however, have microorganisms in their first stomach that are able to digest

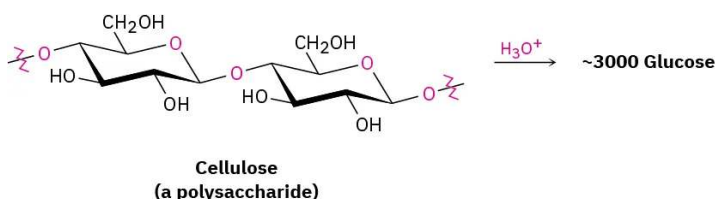
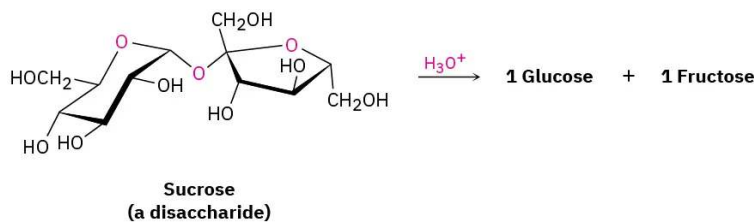
cellulose. The energy stored in cellulose is thus moved up the biological food chain when these ruminant animals eat grass and are themselves used for food.

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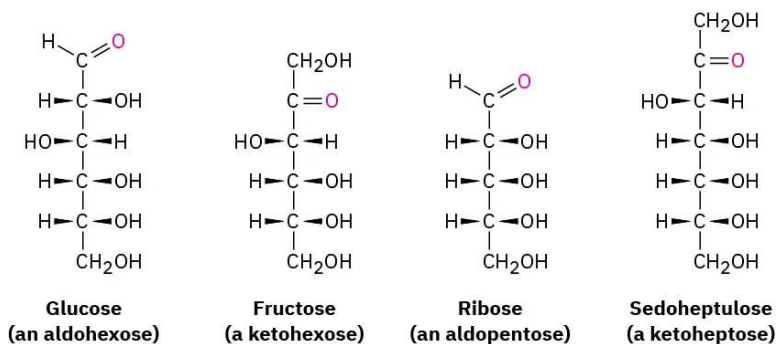
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3.5.4.1: Classification of Carbohydrates

Carbohydrates are generally classified as either simple or complex. Simple sugars, or monosaccharides, are carbohydrates like glucose and fructose that can't be converted into smaller sugars by hydrolysis. Complex carbohydrates are made of two or more simple sugars linked together by acetal bonds (Section 19.10). Sucrose (table sugar), for instance, consists of one glucose linked to one fructose. Similarly, cellulose is made up of several thousand glucose units linked together. Enzyme-catalyzed hydrolysis of a complex carbohydrate breaks it down into its constituent monosaccharides.

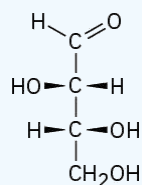


Monosaccharides are further classified as either aldoses or ketoses. The *-ose* suffix designates a carbohydrate, and the prefixes *aldo-* and *keto-* identify the kind of carbonyl group in the molecule, whether aldehyde or ketone. The number of carbon atoms in the monosaccharide is indicated by the appropriate numerical prefix *tri-*, *tetr-*, *pent-*, *hex-*, and so forth, in the name. Putting it all together, glucose is an aldohexose, a six-carbon aldehyde sugar; fructose is a ketohexose, a six-carbon keto sugar; ribose is an aldopentose, a five-carbon aldehyde sugar; and sedoheptulose is a ketoheptose, a seven-carbon keto sugar. Most of the common simple sugars are either pentoses or hexoses.

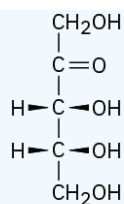


? Exercise 3.5.4.1.1

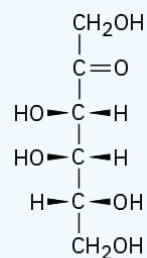
Classify each of the following monosaccharides:



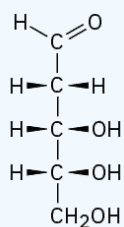
a. **Threose**



b. **Ribulose**



c. **Tagatose**



d. **2-Deoxyribose**

Answer

- a. Aldotetrose
- b. Ketopentose
- c. Ketohexose
- d. Aldopentose

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3.5.4.2: Representing Carbohydrate Stereochemistry- Fischer Projections

Because most carbohydrates have numerous chirality centers, it was recognized long ago that a quick method for representing their stereochemistry was needed. In 1891, the German chemist Emil Fischer suggested a method based on the projection of a tetrahedral carbon atom onto a flat surface. These Fischer projections were soon adopted and are still a common means of representing stereochemistry at chirality centers in carbohydrate chemistry.

A tetrahedral carbon atom is represented in a Fischer projection by two crossed lines. The horizontal lines represent bonds coming out of the page, and the vertical lines represent bonds going into the page.

For example, (*R*)-glyceraldehyde, the simplest monosaccharide, can be drawn as in Figure 3.5.4.2.1.

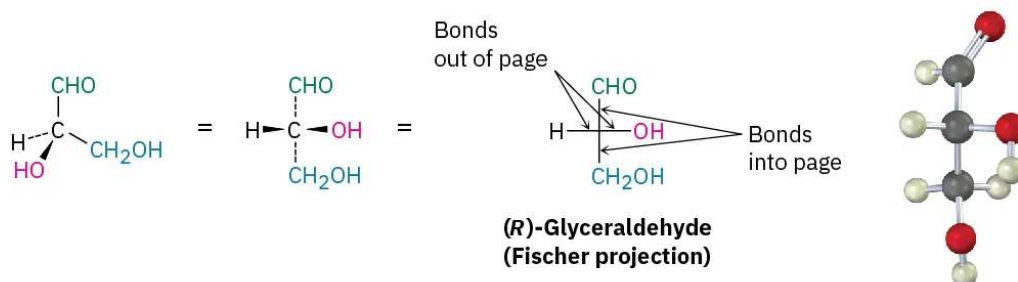
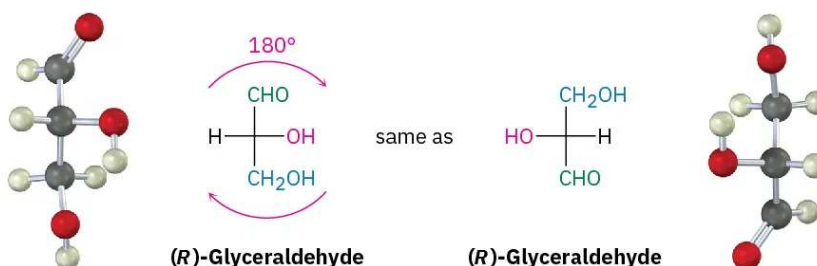


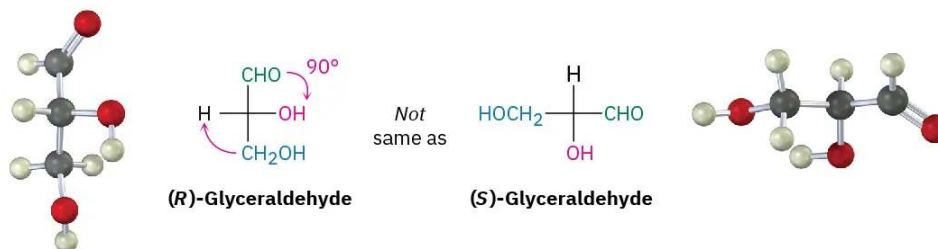
Figure 3.5.4.2.1: A Fischer projection of (*R*)-glyceraldehyde.

Because a given chiral molecule can be drawn in many ways, it's sometimes necessary to compare two projections to see if they represent the same or different enantiomers. To test for identity, Fischer projections can be moved around on the paper, but only two kinds of motions are allowed; moving a Fischer projection in any other way inverts its meaning.

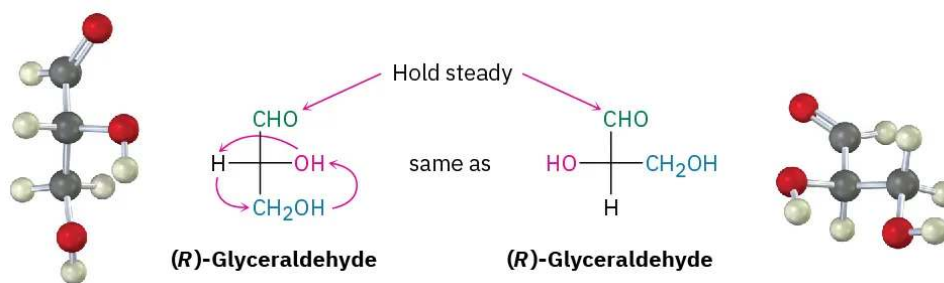
- A Fischer projection can be rotated on the page by 180°, but not by 90° or 270°. Only a 180° rotation maintains the Fischer convention by keeping the same substituent groups going into and coming out of the plane. In the following Fischer projection of (*R*)-glyceraldehyde, for instance, the –H and –OH groups come out of the plane both before and after a 180° rotation.



A 90° rotation breaks the Fischer convention by exchanging the groups that go into the plane with those that come out. In the following Fischer projections of (*R*)-glyceraldehyde, the –H and –OH groups originally come out of the plane but go into the plane after a 90° rotation. As a result, the rotated projection represents (*S*)-glyceraldehyde.



- A Fischer projection can also have one group held steady while the other three rotate in either a clockwise or a counterclockwise direction. The effect is simply to rotate around a single bond, which does not change the stereochemistry.



R,S stereochemical designations (Section 5.5) can be assigned to the chirality center in a Fischer projection by following three steps, as shown in Worked Example 3.5.4.2.1.

✚ R,S Stereochemical Designations

STEP 1

Rank the four substituents in the usual way (Section 5.5).

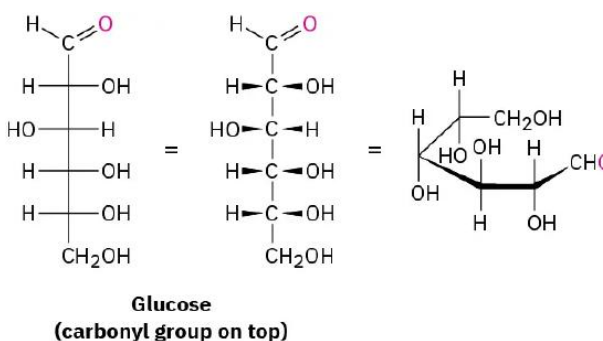
STEP 2

Place the group of lowest ranking, usually H, at the top of the Fischer projection by using one of the allowed motions. This means that the lowest-ranked group is oriented back, away from the viewer, as required for assigning configuration.

STEP 3

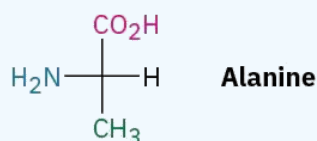
Determine the direction of rotation 1 → 2 → 3 of the remaining three groups, and assign *R* or *S* configuration.

Carbohydrates with more than one chirality center are shown in Fischer projections by stacking the centers on top of one another, with the carbonyl carbon at or near the top. Glucose, for example, has four chirality centers stacked on top of one another in a Fischer projection. Such representations don't, however, give an accurate picture of the molecule's true three-dimensional conformation, which is curled around on itself like a bracelet.



✓ Worked Example 3.5.4.2.1: Assigning R or S Configuration to a Fischer Projection

Assign *R* or *S* configuration to the following Fischer projection of alanine:



Strategy

Follow the steps in the text. (1) Rank the four substituents on the chiral carbon. (2) Manipulate the Fischer projection to place the group of lowest ranking at the top by carrying out one of the allowed motions. (3) Determine the direction 1 → 2 → 3 of the remaining three groups.

Solution

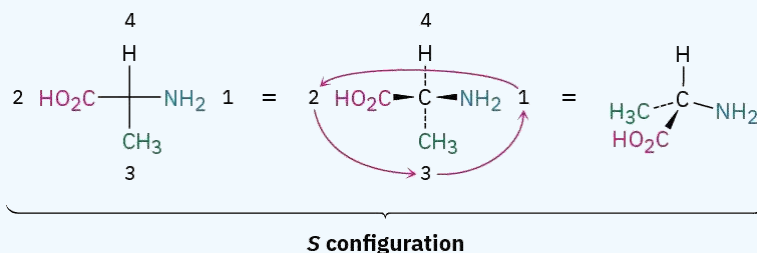
The rankings of the groups are (1) -NH_2 , (2) $\text{-CO}_2\text{H}$, (3) -CH_3 , and (4) -H . To bring the group of lowest ranking (-H) to the top, we might want to hold the -CH_3 group steady while rotating the other three groups counterclockwise.

Rotate 3 groups
counterclockwise



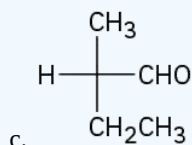
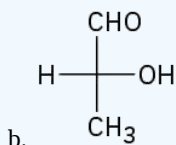
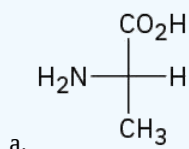
Hold CH_3
steady

Going from first- to second- to third-highest ranking requires a counterclockwise turn, corresponding to *S* stereochemistry.



? Exercise 3.5.4.2.1

Convert each of the following Fischer projections into a tetrahedral representation, and assign *R* or *S* stereochemistry:

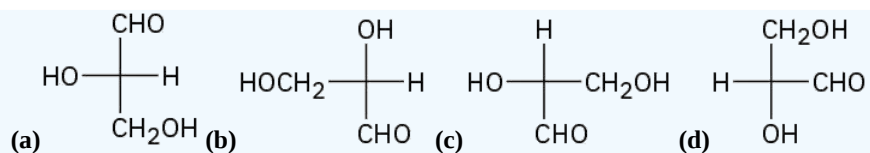


Answer

1. *S*
2. *R*
3. *S*

? Exercise 3.5.4.2.2

Which of the following Fischer projections of glyceraldehyde represent the same enantiomer?

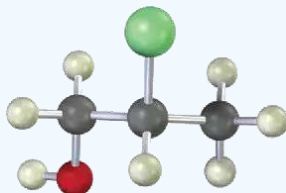


Answer

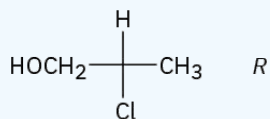
A, B, and C are the same.

? Exercise 3.5.4.2.3

Redraw the following molecule as a Fischer projection, and assign *R* or *S* configuration to the chirality center (green = Cl):

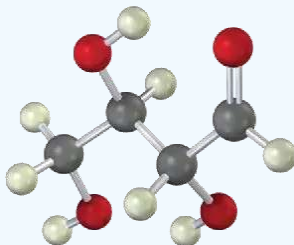


Answer

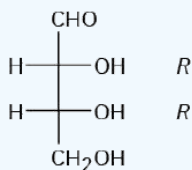


? Exercise 3.5.4.2.4

Redraw the following aldotetrose as a Fischer projection, and assign *R* or *S* configuration to each chirality center:



Answer



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3.6: A Review of Isomerism

As noted on several previous occasions, isomers are compounds with the same chemical formula but different structures. We've seen several kinds of isomers in the past few chapters, and it's a good idea at this point to see how they relate to one another (Figure 3.6.1).

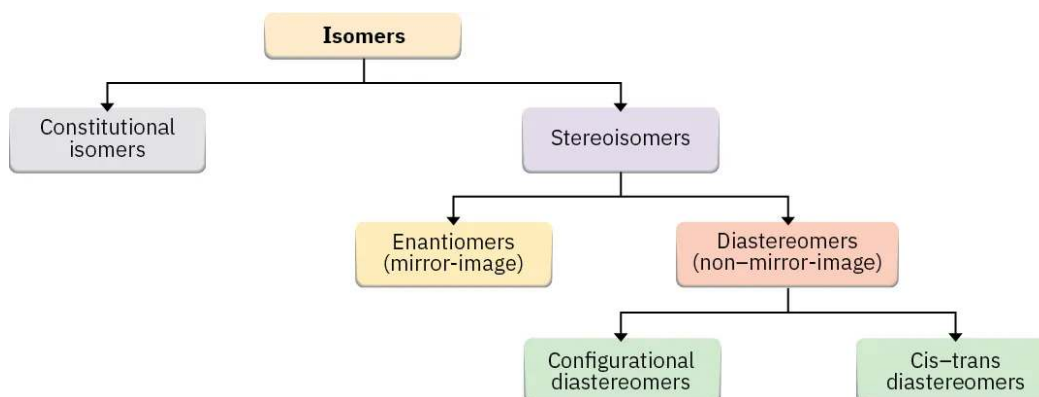


Figure 3.6.1: A summary of the different kinds of isomers.

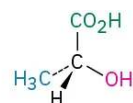
There are two fundamental types of isomers, both of which we've now encountered: constitutional isomers and stereoisomers.

Constitutional isomers (Section 3.3) are compounds whose atoms are connected differently. Among the kinds of constitutional isomers we've seen are skeletal, functional, and positional isomers.

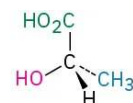
Different carbon skeletons	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_3 \end{array}$ 2-Methylpropane	and	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ Butane
Different functional groups	$\text{CH}_3\text{CH}_2\text{OH}$ Ethyl alcohol	and	CH_3OCH_3 Dimethyl ether
Different position of functional groups	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3\text{CHCH}_3 \end{array}$ Isopropylamine	and	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ Propylamine

Stereoisomers (Section 4.3) are compounds whose atoms are connected in the same order but with a different spatial arrangement. Among the kinds of stereoisomers we've seen are enantiomers, diastereomers, and cis-trans isomers of cycloalkanes. Actually, cis-trans isomers are just a subclass of diastereomers because they are non-mirror-image stereoisomers:

Enantiomers
(nonsuperimposable
mirror-image
stereoisomers)



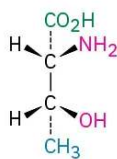
(R)-Lactic acid



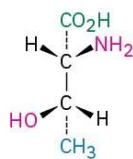
(S)-Lactic acid

Diastereomers
(nonsuperimposable
non-mirror-image
stereoisomers)

Configurational
diastereomers



(2R,3R)-2-Amino-3-hydroxybutanoic acid



(2R,3S)-2-Amino-3-hydroxybutanoic acid

Cis-trans diastereomers
(substituents on same
side or opposite side of
double bond or ring)



trans-1,3-Dimethylcyclopentane

and



cis-1,3-Dimethylcyclopentane

? Exercise 3.6.1

What kinds of isomers are the following pairs?

- (S)-5-Chloro-2-hexene and chlorocyclohexane
- (2R,3R)-Dibromopentane and (2S,3R)-dibromopentane

Answer

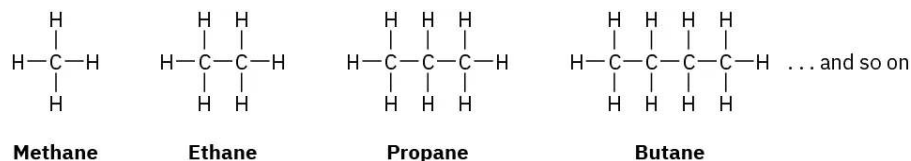
- Constitutional isomers
- Diastereomers

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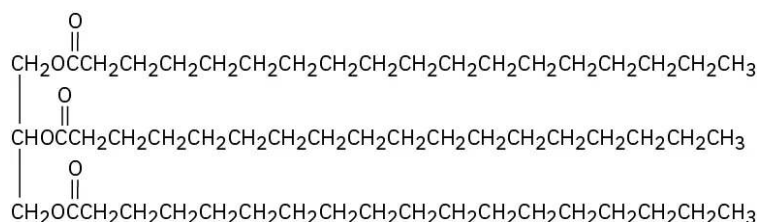
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3.6.1: Alkanes and Alkane Isomers

Before beginning a systematic study of the different functional groups, let's look first at the simplest family of molecules to develop some general ideas that apply to all families. We saw in Section 1.8 that the carbon-carbon single bond in ethane results from σ (head-on) overlap of carbon sp^3 hybrid orbitals. If we imagine joining three, four, five, or even more carbon atoms by C-C single bonds, we can generate the large family of molecules called alkanes.

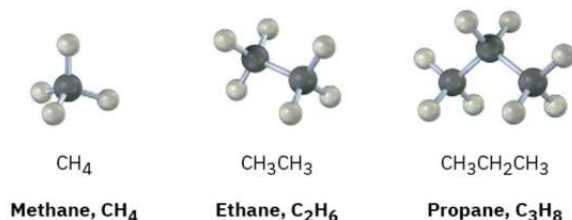


Alkanes are often described as *saturated hydrocarbons*: hydrocarbons because they contain only carbon and hydrogen; saturated because they have only C-C and C-H single bonds and thus contain the maximum possible number of hydrogens per carbon. They have the general formula C_nH_{2n+2} , where n is an integer. Alkanes are also occasionally called aliphatic compounds, a name derived from the Greek *aleiphas*, meaning "fat." We'll see in **Section 27.2** that many animal fats contain long carbon chains similar to alkanes.

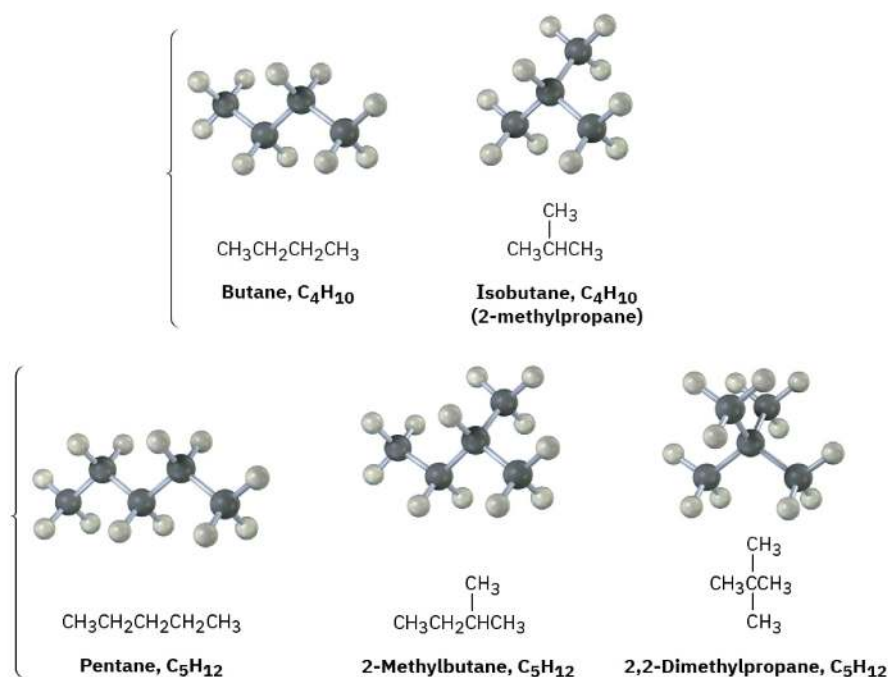


A typical animal fat

Think about the ways that carbon and hydrogen might combine to make alkanes. With one carbon and four hydrogens, only one structure is possible: methane, CH_4 . Similarly, there is only one combination of two carbons with six hydrogens (ethane, CH_3CH_3) and only one combination of three carbons with eight hydrogens (propane, $\text{CH}_3\text{CH}_2\text{CH}_3$). When larger numbers of carbons and hydrogens combine, however, more than one structure is possible. For example, there are two substances with the formula C_4H_{10} : the four carbons can all be in a row (butane), or they can branch (isobutane). Similarly, there are three C_5H_{12} molecules, and so on for larger alkanes.



Compounds like butane and pentane, whose carbons are all connected in a row, are called straight-chain alkanes, or *normal alkanes*. Compounds like 2-methylpropane (isobutane), 2-methylbutane, and 2,2-dimethylpropane, whose carbon chains branch, are called branched-chain alkanes.

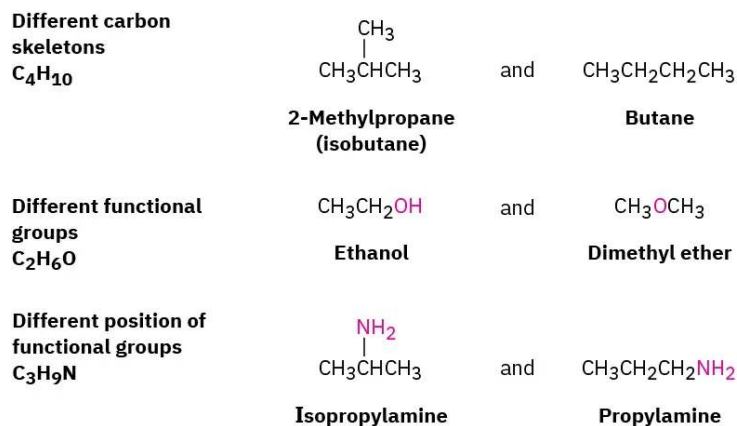


Compounds like the two C_4H_{10} molecules and the three C_5H_{12} molecules, which have the same formula but different structures, are called Isomers, from the Greek *isos* + *meros*, meaning “made of the same parts.” Isomers have the same numbers and kinds of atoms but differ in the way the atoms are arranged. Compounds like butane and isobutane, whose atoms are connected differently, are called constitutional isomers. We’ll see shortly that other kinds of isomers are also possible, even among compounds whose atoms are connected in the same order. As Table 3.6.1.1 shows, the number of possible alkane isomers increases dramatically with the number of carbon atoms.

Table 3.6.1.1: Number of Alkane Isomers

Formula	Number of isomers	Formula	Number of isomers
C_6H_{14}	5	$C_{10}H_{22}$	75
C_7H_{16}	9	$C_{15}H_{32}$	4347
C_8H_{18}	18	$C_{20}H_{42}$	366,319
C_9H_{20}	35	$C_{30}H_{62}$	4,111,846,763

Constitutional isomerism is not limited to alkanes—it occurs widely throughout organic chemistry. Constitutional isomers may have different carbon skeletons (as in isobutane and butane), different functional groups (as in ethanol and dimethyl ether), or different locations of a functional group along the chain (as in isopropylamine and propylamine). Regardless of the reason for the isomerism, constitutional isomers are always different compounds with different properties but with the same formula.



A given alkane can be drawn in many ways. For example, the straight-chain, four-carbon alkane called butane can be represented by any of the structures shown in Figure 3.3. These structures don't imply any particular three-dimensional geometry for butane; they indicate only the connections among atoms. In practice, as noted in Section 1.12, chemists rarely draw all the bonds in a molecule and usually refer to butane by the condensed structure, $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$. Still more simply, butane can be represented as $n\text{-}C_4H_{10}$, where n denotes *normal* (straight-chain) butane.

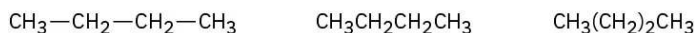
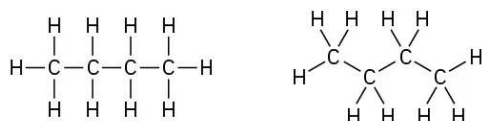


Figure 3.3: Some representations of butane, C_4H_{10} . The molecule is the same regardless of how it's drawn. These structures imply only that butane has a continuous chain of four carbon atoms; they do not imply any specific geometry.

Straight-chain alkanes are named according to the number of carbon atoms they contain, as shown in Table 3.6.1.2. With the exception of the first four compounds—methane, ethane, propane, and butane—whose names have historical roots, the alkanes are named based on Greek numbers. The suffix *-ane* is added to the end of each name to indicate that the molecule identified is an alkane. Thus, *pentane* is the five-carbon alkane, *hexane* is the six-carbon alkane, and so on. We'll soon see that these alkane names form the basis for naming all other organic compounds, so at least the first ten should be memorized.

Table 3.6.1.2 Names of Straight-Chain Alkanes

Number of carbons (n)	Name	Formula (C_nH_{2n+2})	Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4	9	Nonane	C_9H_{20}
2	Ethane	C_2H_6	10	Decane	$C_{10}H_{22}$
3	Propane	C_3H_8	11	Undecane	$C_{11}H_{24}$
4	Butane	C_4H_{10}	12	Dodecane	$C_{12}H_{26}$
5	Pentane	C_5H_{12}	13	Tridecane	$C_{13}H_{28}$
6	Hexane	C_6H_{14}	20	Icosane	$C_{20}H_{42}$
7	Heptane	C_7H_{16}	30	Triacontane	$C_{30}H_{62}$
8	Octane	C_8H_{18}			

✓ Worked Example 3.6.1.1: Drawing the Structures of Isomers

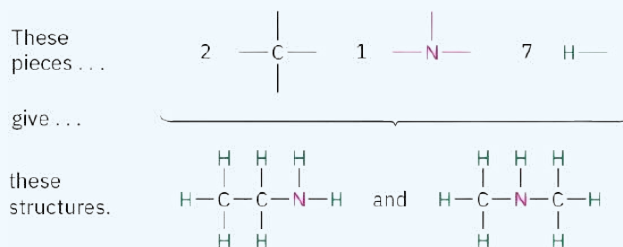
Propose structures for two isomers with the formula C_2H_7N .

Strategy

We know that carbon forms four bonds, nitrogen forms three, and hydrogen forms one. Write down the carbon atoms first, and then use trial and error plus intuition to put the pieces together.

Solution

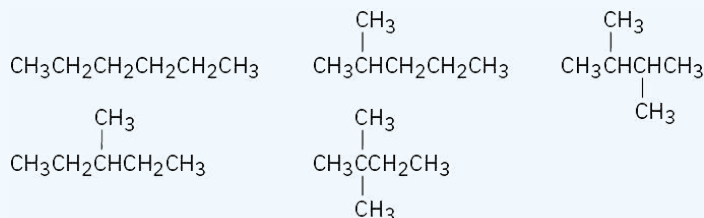
There are two isomeric structures. One has the connection $C-C-N$, and the other has the connection $C-N-C$.



? Exercise 3.6.1.1

Draw structures of the five isomers of C_6H_{14} .

Answer

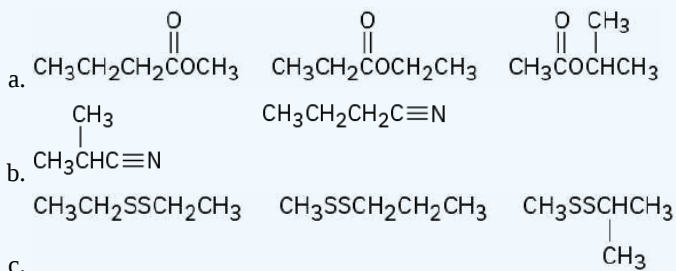


? Exercise 3.6.1.2

Propose structures that meet the following descriptions:

- Two isomeric esters with the formula $C_5H_{10}O_2$.
- Two isomeric nitriles with the formula C_4H_7N
- Two isomeric disulfides with the formula $C_4H_{10}S_2$

Answer



? Exercise 3.6.1.3

How many isomers are there with the following descriptions?

- a. Alcohols with the formula C_3H_8O
- b. Bromoalkanes with the formula C_4H_9Br
- c. Thioesters with the formula C_4H_8OS

Answer

- a. Two
- b. Four
- c. Four

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3.6.2: Enantiomers and the Tetrahedral Carbon

What causes molecular handedness? Look at generalized molecules of the type CH_3X , CH_2XY , and CHXYZ shown in Figure 3.6.2.1. On the left are three molecules, and on the right are their images reflected in a mirror. The CH_3X and CH_2XY molecules are identical to their mirror images and thus are not handed. If you make a molecular model of each molecule and its mirror image, you find that you can superimpose one on the other so that all atoms coincide. The CHXYZ molecule, by contrast, is not identical to its mirror image. You can't superimpose a model of this molecule on a model of its mirror image for the same reason that you can't superimpose a left hand on a right hand: they simply aren't the same.

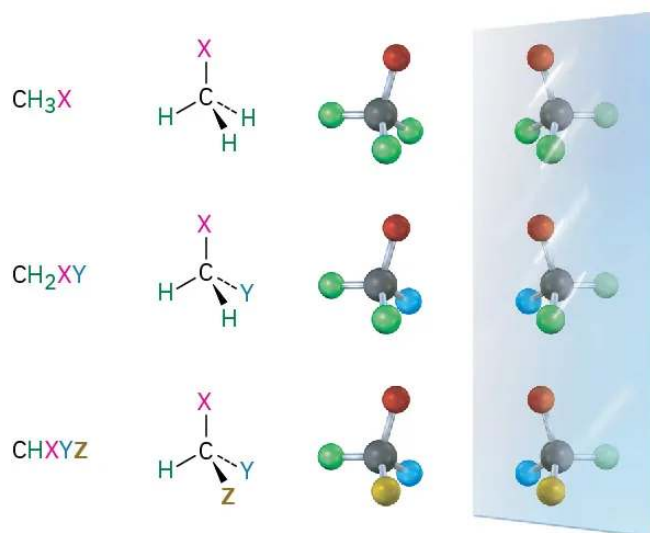
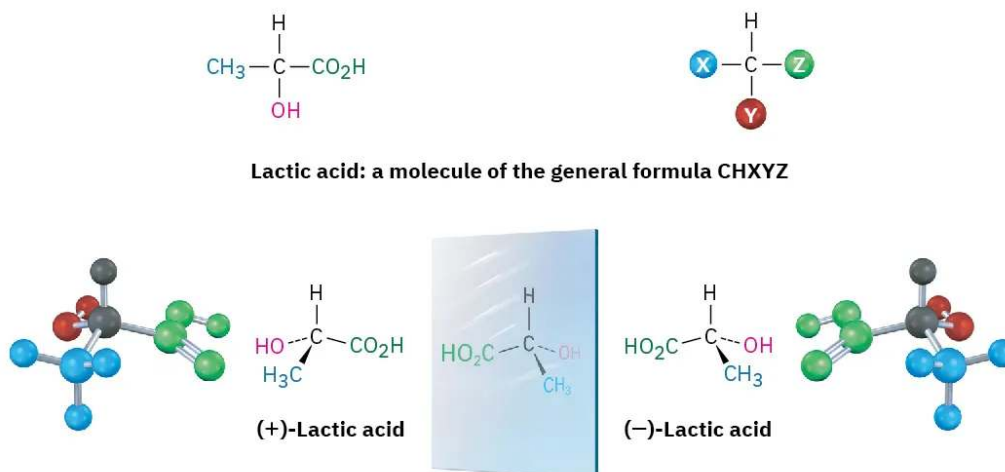


Figure 3.6.2.1: Tetrahedral carbon atoms and their mirror images. Molecules of the type CH_3X and CH_2XY are identical to their mirror images, but a molecule of the type CHXYZ is not. A CHXYZ molecule is related to its mirror image in the same way a right hand is related to a left hand.

A molecule that is not identical to its mirror image is a kind of stereoisomer (Section 4.3) called an enantiomer (e-**nan**-tee-oh-mer, from the Greek *enantio*, meaning “opposite”). Enantiomers are related to each other as a right hand is related to a left hand and result whenever a tetrahedral carbon is bonded to four different substituents (one need not be H). For example, lactic acid (2-hydroxypropanoic acid) exists as a pair of enantiomers because there are four different groups ($-\text{H}$, $-\text{OH}$, $-\text{CH}_3$, $-\text{CO}_2\text{H}$) bonded to the central carbon atom. The enantiomers are called (+)-lactic acid and (–)-lactic acid. Both are found in sour milk, but only the (+) enantiomer occurs in muscle tissue.



No matter how hard you try, you can't superimpose a molecule of (+)-lactic acid on a molecule of (–)-lactic acid. If any two groups match up, say $-\text{H}$ and $-\text{CO}_2\text{H}$, the remaining two groups don't match (Figure 3.6.2.2).

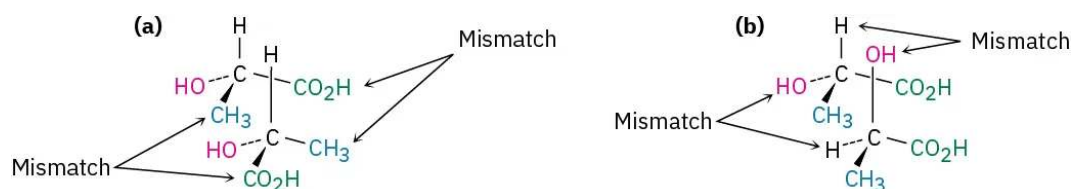


Figure 3.6.2.2: Attempts at superimposing the mirror-image forms of lactic acid. **(a)** When the -H and -OH substituents match up, the $\text{-CO}_2\text{H}$ and -CH_3 substituents don't; **(b)** when $\text{-CO}_2\text{H}$ and -CH_3 match up, -H and -OH don't. Regardless of how the molecules are oriented, they aren't identical.

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3.6.2.1: The Reason for Handedness in Molecules - Chirality

A molecule that is not identical to its mirror image is said to be chiral (**ky**-ral, from the Greek *cheir*, meaning “hand”). You can’t take a chiral molecule and its enantiomer and place one on the other so that all atoms coincide.

How can you predict whether a given molecule is or is not chiral? A molecule is not chiral if it has a plane of symmetry. A plane of symmetry is a plane that cuts through the middle of a molecule (or any object) in such a way that one half of the molecule or object is a mirror image of the other half. A coffee mug, for example, has a plane of symmetry. If you were to cut the coffee mug in half from top to bottom, one half would be a mirror image of the other half. A hand, however, does not have a plane of symmetry. One “half” of a hand is not a mirror image of the other half (Figure 3.6.2.1.1).

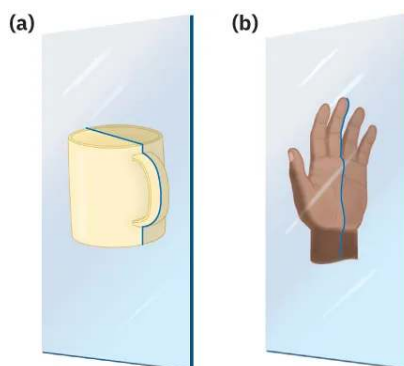


Figure 3.6.2.1.1: The meaning of symmetry plane. **(a)** An object like the coffee mug has a symmetry plane cutting through it so that right and left halves are mirror images. **(b)** An object like a hand has no symmetry plane; the right “half” of a hand is not a mirror image of the left half.

A molecule that has a plane of symmetry in any conformation must be identical to its mirror image and must be nonchiral, or achiral. Thus, propanoic acid, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$, has a plane of symmetry when lined up as shown in Figure 3.6.2.1.2 and is achiral, while lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$, has no plane of symmetry in any conformation and is chiral.

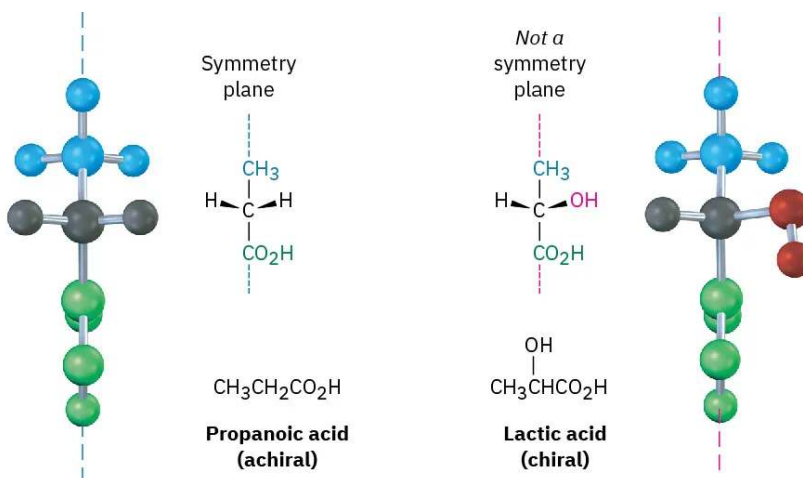
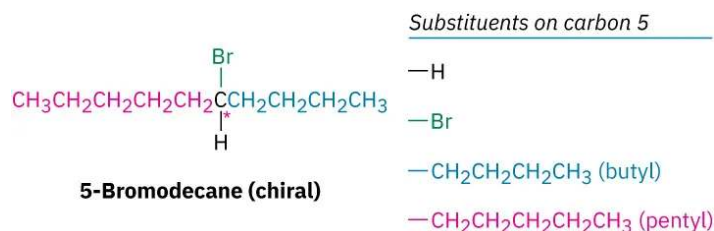


Figure 3.6.2.1.2: The achiral propanoic acid molecule versus the chiral lactic acid molecule. Propanoic acid has a plane of symmetry that makes one side of the molecule a mirror image of the other. Lactic acid has no such symmetry plane.

The most common, although not the only, cause of chirality in organic molecules is the presence of a tetrahedral carbon atom bonded to four different groups—for example, the central carbon atom in lactic acid. Such carbons are referred to as chirality centers, although other terms such as stereocenter, asymmetric center, and stereogenic center have also been used. Note that *chirality* is a property of the entire molecule, whereas a *chirality center* is the *cause* of chirality.

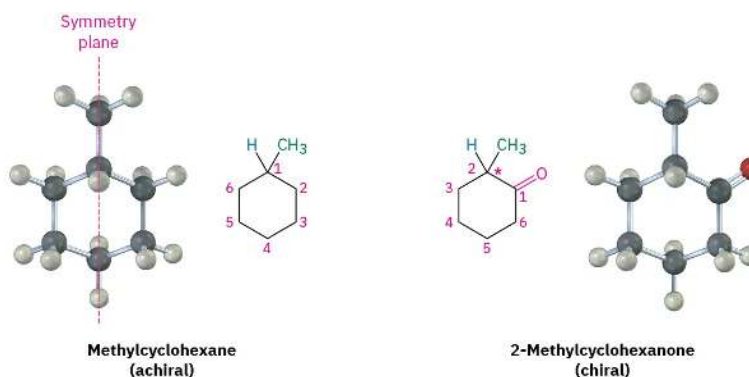
Detecting a chirality center in a complex molecule takes practice because it’s not always immediately apparent whether four different groups are bonded to a given carbon. The differences don’t necessarily appear right next to the chirality center. For example, 5-bromodecane is a chiral molecule because four different groups are bonded to C5, the chirality center (marked with an

asterisk). A butyl substituent is similar to a pentyl substituent, but it isn't identical. The difference isn't apparent until looking four carbon atoms away from the chirality center, but there's still a difference.

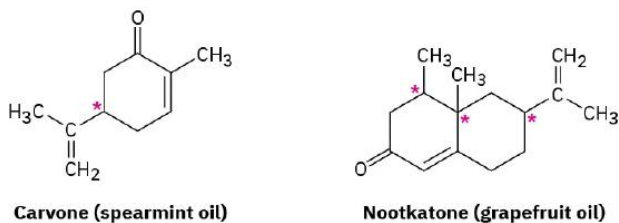


As other possible examples, look at methylcyclohexane and 2-methylcyclohexanone. Methylcyclohexane is achiral because no carbon atom in the molecule is bonded to four different groups. You can immediately eliminate all $-\text{CH}_2-$ carbons and the $-\text{CH}_3$ carbon from consideration, but what about C1 on the ring? The C1 carbon atom is bonded to a $-\text{CH}_3$ group, to an $-\text{H}$ atom, and to C2 and C6 of the ring. Carbons 2 and 6 are equivalent, however, as are carbons 3 and 5. Thus, the C6–C5–C4 “substituent” is equivalent to the C2–C3–C4 substituent, and methylcyclohexane is achiral. Another way of reaching the same conclusion is to realize that methylcyclohexane has a symmetry plane, which passes through the methyl group and through C1 and C4 of the ring.

The situation is different for 2-methylcyclohexanone. 2-Methylcyclohexanone has no symmetry plane and is chiral because its C2 is bonded to four different groups: a $-\text{CH}_3$ group, an $-\text{H}$ atom, a $-\text{COCH}_2-$ ring bond (C1), and a $-\text{CH}_2\text{CH}_2-$ ring bond (C3).



Several more examples of chiral molecules are shown below. Check for yourself that the labeled carbons are chirality centers. You might note that carbons in $-\text{CH}_2-$, $-\text{CH}_3$, $\text{C}-\text{O}$, $\text{C}=\text{C}$, and $\text{C}\equiv\text{C}$ groups can't be chirality centers. (Why not?)



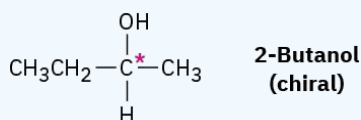
✓ Worked Example 3.6.2.1.1: Drawing the Three-Dimensional Structure of a Chiral Molecule

Draw the structure of a chiral alcohol.

Strategy

An alcohol is a compound that contains the $-\text{OH}$ functional group. To make an alcohol chiral, we need to have four different groups bonded to a single carbon atom, say $-\text{H}$, $-\text{OH}$, $-\text{CH}_3$, and $-\text{CH}_2\text{CH}_3$.

Solution



? Exercise 3.6.2.1.1

Which of the following objects are chiral?

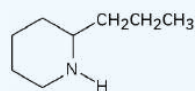
- Soda can
- Screwdriver
- Screw
- Shoe

Answer

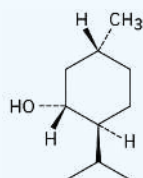
Chiral: screw, shoe

? Exercise 3.6.2.1.2

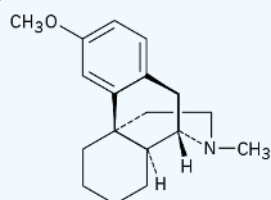
Which of the following molecules are chiral? Identify the chirality center(s) in each.



- a. **Coniine**
(poison hemlock)

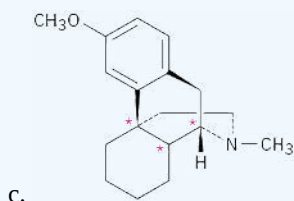
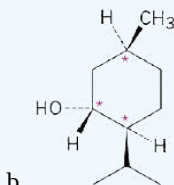
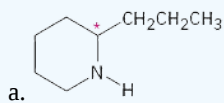


- b. **Menthol**
(flavoring agent)



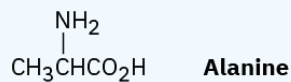
- c. **Dextromethorphan**
(cough suppressant)

Answer

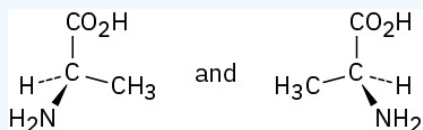


? Exercise 3.6.2.1.3

Alanine, an amino acid found in proteins, is chiral. Draw the two enantiomers of alanine using the standard convention of solid, wedged, and dashed lines.

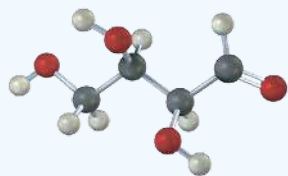


Answer



? Exercise 3.6.2.1.4

Identify the chirality centers in the following molecules (gray = H, black = C, red = O, green = Cl, yellow-green = F):

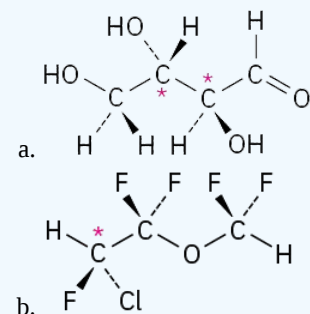


a.



b.

Answer



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3.6.3: Diastereomers

Molecules like lactic acid, alanine, and glyceraldehyde are relatively simple because each has only one chirality center and thus only two stereoisomers. The situation becomes more complex, however, with molecules that have more than one chirality center. As a general rule, a molecule with n chirality centers can have up to 2^n stereoisomers (although it may have fewer, as we'll see below). Take the amino acid threonine (2-amino-3-hydroxybutanoic acid), for example. Since threonine has two chirality centers (C2 and C3), there are four possible stereoisomers, as shown in Figure 3.6.3.1. Check for yourself that the R,S configurations of all stereoisomers are correct.

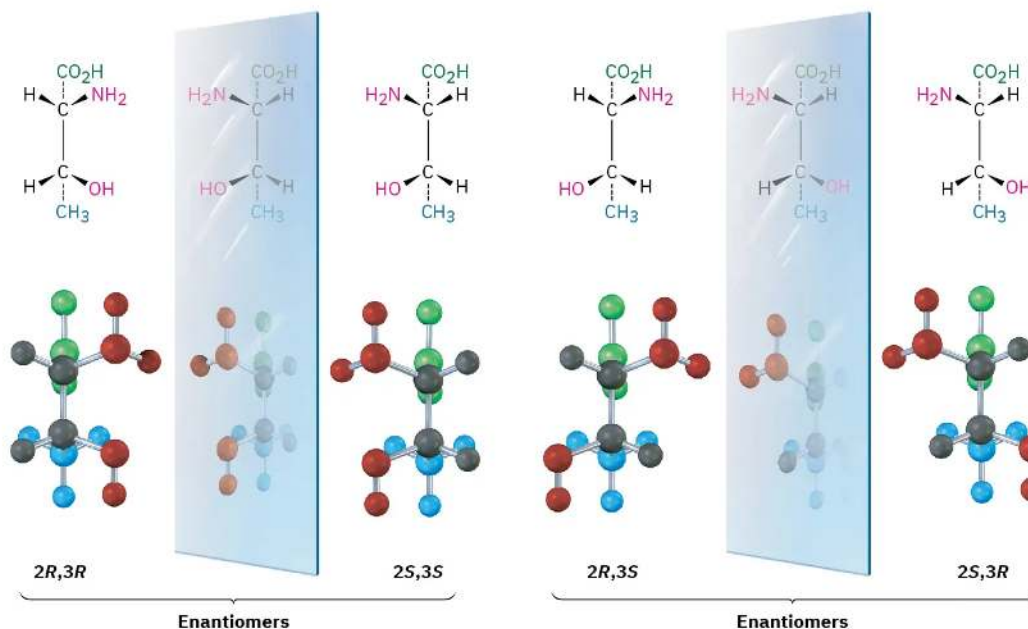


Figure 3.6.3.1: The four stereoisomers of 2-amino-3-hydroxybutanoic acid.

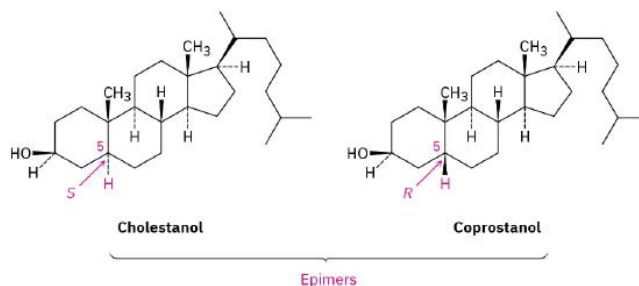
The four stereoisomers of 2-amino-3-hydroxybutanoic acid can be grouped into two pairs of enantiomers. The $2R,3R$ stereoisomer is the mirror image of $2S,3S$, and the $2R,3S$ stereoisomer is the mirror image of $2S,3R$. But what is the relationship between any two molecules that are not mirror images? What, for instance, is the relationship between the $2R,3R$ isomer and the $2R,3S$ isomer? They are stereoisomers, yet they aren't enantiomers. To describe such a relationship, we need a new term: *diastereomer*.

Diastereomers are stereoisomers that are not mirror images. Since we used the right-hand/left-hand analogy to describe the relationship between two enantiomers, we might extend the analogy by saying that the relationship between diastereomers is like that of hands from different people. Your hand and your friend's hand look similar, but they aren't identical and they aren't mirror images. The same is true of diastereomers: they're similar, but they aren't identical, and they aren't mirror images.

Note carefully the difference between enantiomers and diastereomers: enantiomers have opposite configurations at *all* chirality centers, whereas diastereomers have opposite configurations at *some* (one or more) chirality centers but the same configuration at others. A full description of the four stereoisomers of threonine is given in Table 3.6.3.1. Of the four, only the $2S,3R$ isomer, $[\alpha]_D = -28.3$, occurs naturally in plants and animals and is an essential nutrient for humans. This result is typical: most biological molecules are chiral, and usually only one stereoisomer is found in nature.

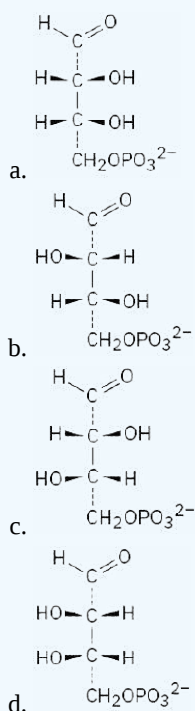
Table 3.6.3.1 Relationships among the Four Stereoisomers of Threonine

Stereoisomer	Enantiomer	Diastereomer
$2R,3R$	$2S,3S$	$2R,3S$ and $2S,3R$
$2S,3S$	$2R,3R$	$2R,3S$ and $2S,3R$
$2R,3S$	$2S,3R$	$2R,3R$ and $2S,3S$
$2S,3R$	$2R,3S$	$2R,3R$ and $2S,3S$



? Exercise 3.6.3.1

One of the following molecules (**a**)–(**d**) is D-erythrose 4-phosphate, an intermediate in the Calvin photosynthetic cycle by which plants incorporate CO₂ into carbohydrates. If D-erythrose 4-phosphate has *R* stereochemistry at both chirality centers, which of the structures is it? Which of the remaining three structures is the enantiomer of D-erythrose 4-phosphate, and which are diastereomers?

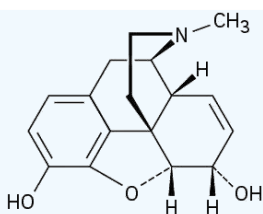


Answer

Compound **(a)** is D-erythrose 4-phosphate, **(d)** is its enantiomer, and **(b)** and **(c)** are diastereomers.

? Exercise 3.6.3.2

How many chirality centers does morphine have? How many stereoisomers of morphine are possible in principle?



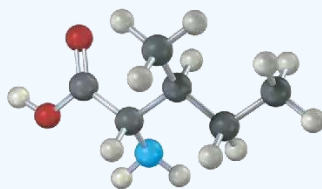
Morphine

Answer

Five chirality centers and $2^5 = 32$ stereoisomers

? Exercise 3.6.3.3

Assign *R* or *S* configuration to each chirality center in the following molecular model of the amino acid isoleucine (blue = N):



Answer

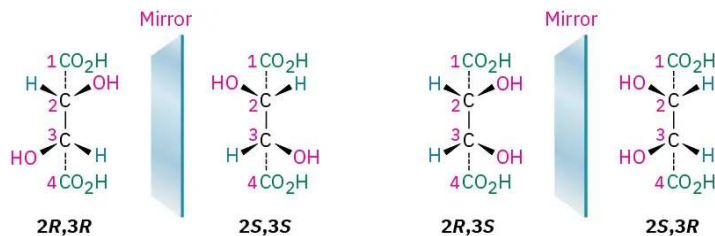
S,S

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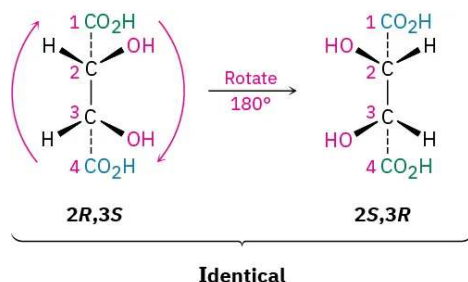
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3.6.4: Meso Compounds

Let's look at another example (Section 5.5) of a compound with more than one chirality center: the tartaric acid used by Pasteur. The four stereoisomers can be drawn as follows:



The $2R,3R$ and $2S,3S$ structures are nonsuperimposable mirror images and therefore represent a pair of enantiomers. A close look at the $2R,3S$ and $2S,3R$ structures, however, shows that they *are* superimposable, and thus identical, as can be seen by rotating one structure 180° .



The $2R,3S$ and $2S,3R$ structures are identical because the molecule has a plane of symmetry and is therefore achiral. The symmetry plane cuts through the C2–C3 bond, making one half of the molecule a mirror image of the other half (Figure 3.6.4.1). Because of the plane of symmetry, the molecule is achiral, despite the fact that it has two chirality centers. Such compounds, which are achiral, yet contain chirality centers, are called **meso compounds (me-zo)**. Thus, tartaric acid exists in three stereoisomeric forms: two enantiomers and one meso form.

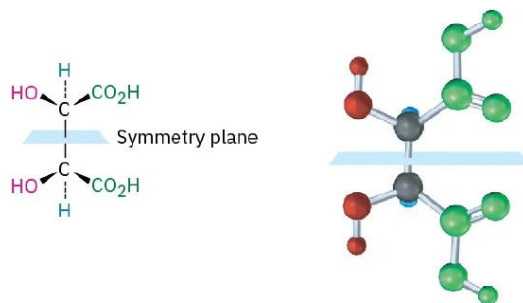


Figure 3.6.4.1: A symmetry plane through the C2–C3 bond of *meso*-tartaric acid makes the molecule achiral.

Some physical properties of the three stereoisomers are listed in Table 3.6.4.1. The (+)- and (–)-tartaric acids have identical melting points, solubilities, and densities, but they differ in the sign of their rotation of plane-polarized light. The meso isomer, by contrast, is diastereomeric with the (+) and (–) forms. It has no mirror-image relationship to (+)- and (–)-tartaric acids, is a different compound altogether, and thus has different physical properties.

Table 3.6.4.1 Some Properties of the Stereoisomers of Tartaric Acid

Stereoisomer	Melting point ($^\circ\text{C}$)	$[\alpha]_D$	Density (g/cm^3)	Solubility at 20°C ($\text{g}/100\text{ mL H}_2\text{O}$)
(+)	168–170	+12	1.7598	139.0
(–)	168–170	–12	1.7598	139.0
Meso	146–148	0	1.6660	125.0

✓ Worked Example 3.6.4.1: Distinguishing Chiral Compounds from Meso Compounds

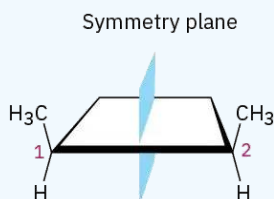
Does *cis*-1,2-dimethylcyclobutane have any chirality centers? Is it chiral?

Strategy

To see whether a chirality center is present, look for a carbon atom bonded to four different groups. To see whether the molecule is chiral, look for the presence or absence of a symmetry plane. Not all molecules with chirality centers are chiral overall—meso compounds are an exception.

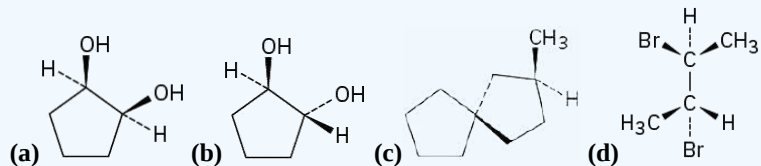
Solution

A look at the structure of *cis*-1,2-dimethylcyclobutane shows that both methyl-bearing ring carbons (C1 and C2) are chirality centers. Overall, though, the compound is achiral because there is a symmetry plane bisecting the ring between C1 and C2. Thus, the molecule is a meso compound.



? Exercise 3.6.4.1

Which of the following structures represent meso compounds?



Answer

Compounds (a) and (d) are meso.

? Exercise 3.6.4.2

Which of the following have a meso form? (Recall that the *-ol* suffix refers to an alcohol, ROH.)

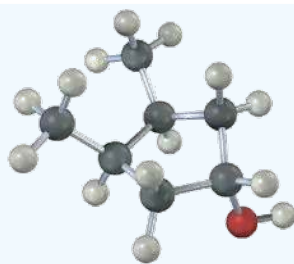
- 2,3-Butanediol
- 2,3-Pentanediol
- 2,4-Pentanediol

Answer

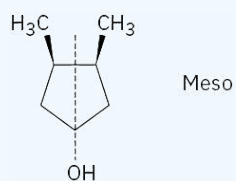
Compounds (a) and (c) have meso forms.

? Exercise 3.6.4.3

Does the following structure represent a meso compound? If so, indicate the symmetry plane.



Answer



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CHAPTER OVERVIEW

4: Functional Groups

- 4.1: Polar Covalent Bonds - Electronegativity
- 4.2: Naming Alkanes
 - 4.2.1: Alkyl Groups
- 4.3: Sequence Rules for Specifying Configuration
- 4.4: Naming Alkenes
 - 4.4.1: Cis-Trans Isomerism in Alkenes
 - 4.4.2: Alkene Stereochemistry and the E,Z Designation
- 4.5: Names and Properties of Alkyl Halides
- 4.6: Naming Aromatic Compounds
- 4.7: Naming Alcohols and Phenols
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4.1: Polar Covalent Bonds - Electronegativity

Up to this point, we've treated chemical bonds as either ionic or covalent. The bond in sodium chloride, for instance, is ionic. Sodium transfers an electron to chlorine to produce Na^+ and Cl^- ions, which are held together in the solid by electrostatic attractions between unlike charges. The C–C bond in ethane, however, is covalent. The two bonding electrons are shared equally by the two equivalent carbon atoms, resulting in a symmetrical electron distribution in the bond. Most bonds, however, are neither fully ionic nor fully covalent but are somewhere between the two extremes. Such bonds are called polar covalent bonds, meaning that the bonding electrons are attracted more strongly by one atom than the other so that the electron distribution between atoms is not symmetrical (Figure 4.1.1).

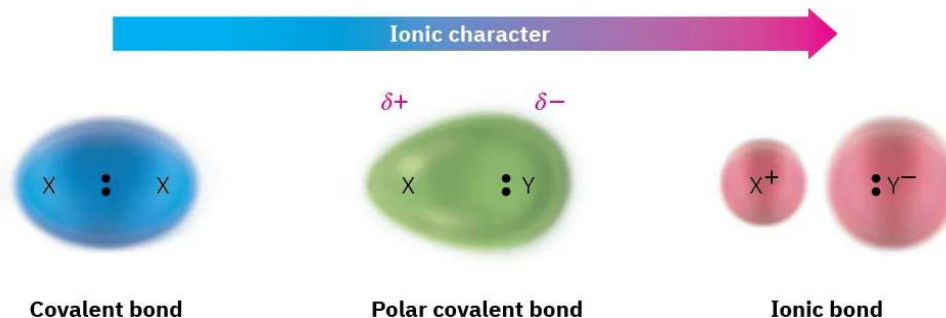


Figure 4.1.1: The continuum in bonding from covalent to ionic is a result of an unequal distribution of bonding electrons between atoms.

The symbol δ (lowercase Greek letter delta) means *partial* charge, either partial positive (δ^+) for the electron-poor atom or partial negative (δ^-) for the electron-rich atom.

Bond polarity is due to differences in electronegativity (EN), the intrinsic ability of an atom to attract the shared electrons in a covalent bond. As shown in Figure 4.1.2, electronegativities are based on an arbitrary scale, with fluorine the most electronegative (EN = 4.0) and cesium the least (EN = 0.7). Metals on the left side of the periodic table attract electrons weakly and have lower electronegativities, while oxygen, nitrogen, and halogens on the right side of the periodic table attract electrons strongly and have higher electronegativities. Carbon, the most important element in organic compounds, has an intermediate electronegativity value of 2.5.

H 2.1																		He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0		Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0		Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8		Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5		Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1		Rn

Figure 4.1.2 Electronegativity values and trends. Electronegativity generally increases from left to right across the periodic table and decreases from top to bottom. The values are on an arbitrary scale, with F = 4.0 and Cs = 0.7. Elements in **red** are the most electronegative, those in **yellow** are medium, and those in **green** are the least electronegative.

As a rough guide, bonds between atoms whose electronegativities differ by less than 0.5 are nonpolar covalent, bonds between atoms whose electronegativities differ by 0.5 to 2 are polar covalent, and bonds between atoms whose electronegativities differ by more than 2 are largely ionic. Carbon–hydrogen bonds, for example, are relatively nonpolar because carbon (EN = 2.5) and hydrogen (EN = 2.1) have similar electronegativities. Bonds between carbon and more electronegative elements such as oxygen (EN = 3.5) and nitrogen (EN = 3.0), by contrast, are polarized so that the bonding electrons are drawn away from carbon toward the electronegative atom. This leaves carbon with a partial positive charge, δ^+ , and the electronegative atom with a partial negative charge, δ^- . An example is the C–O bond in methanol, CH_3OH (Figure 4.1.3a). Bonds between carbon and less electronegative elements are polarized so that carbon bears a partial negative charge and the other atom bears a partial positive charge. An example is the C–Li bond in methyllithium, CH_3Li (Figure 4.1.3b).

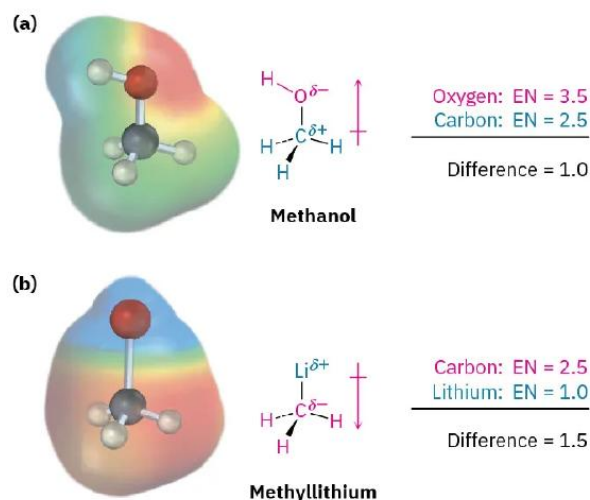


Figure 4.1.3: Polar covalent bonds. (a) Methanol, CH_3OH , has a polar covalent C–O bond, and (b) methyllithium, CH_3Li , has a polar covalent C–Li bond. The computer-generated representations, called electrostatic potential maps, use color to show calculated charge distributions, ranging from **red (electron-rich; δ^-)** to **blue (electron-poor; δ^+)**.

Note in the representations of methanol and methyllithium in Figure 4.1.3 that a crossed arrow $\text{+} \rightarrow$ is used to indicate the direction of bond polarity. By convention, electrons are displaced in the direction of the arrow. The tail of the arrow (which looks like a plus sign) is electron-poor (δ^+), and the head of the arrow is electron-rich (δ^-).

Note also in Figure 4.1.3 that calculated charge distributions in molecules can be displayed visually with what are called electrostatic potential maps, which use color to indicate electron-rich (red; δ^-) and electron-poor (blue; δ^+) regions. In methanol, oxygen carries a partial negative charge and is colored red, while the carbon and hydrogen atoms carry partial positive charges and are colored blue-green. In methyllithium, lithium carries a partial positive charge (blue), while carbon and the hydrogen atoms carry partial negative charges (red). Electrostatic potential maps are useful because they show at a glance the electron-rich and electron-poor atoms in molecules. We'll make frequent use of these maps throughout the text and will see many examples of how electronic structure correlates with chemical reactivity.

When speaking of an atom's ability to polarize a bond, we often use the term *inductive effect*. An inductive effect is simply the shifting of electrons in a σ bond in response to the electronegativity of nearby atoms. Metals, such as lithium and magnesium, inductively donate electrons, whereas reactive nonmetals, such as oxygen and nitrogen, inductively withdraw electrons. Inductive effects play a major role in understanding chemical reactivity, and we'll use them many times throughout this text to explain a variety of chemical observations.

? Exercise 4.1.1

Which element in each of the following pairs is more electronegative?

- Li or H
- B or Br
- Cl or I
- C or H

Answer

- H
- Br
- Cl
- C

? Exercise 4.1.2

Use the δ^+/δ^- convention to indicate the direction of expected polarity for each of the bonds indicated.

- $\text{H}_3\text{C}-\text{Cl}$
- $\text{H}_3\text{C}-\text{NH}_2$
- $\text{H}_2\text{N}-\text{H}$
- $\text{H}_3\text{C}-\text{SH}$
- $\text{H}_3\text{C}-\text{MgBr}$
- $\text{H}_3\text{C}-\text{F}$

Answer

- $\text{H}_3\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{Cl}}$
- $\text{H}_3\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{N}}\text{H}_2$
- $\text{H}_2\overset{\delta-}{\text{N}}-\overset{\delta+}{\text{H}}$
- $\text{H}_3\text{C}-\text{SH}$ Carbon and sulfur have identical electronegativities.
- $\text{H}_3\overset{\delta}{\text{C}}-\overset{\delta+}{\text{Mg}}\text{Br}$
- $\text{H}_3\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{F}}$

? Exercise 4.1.3

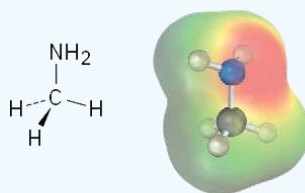
Use the electronegativity values shown in Figure 4.1.2 to rank the following bonds from least polar to most polar: $\text{H}_3\text{C}-\text{Li}$, $\text{H}_3\text{C}-\text{K}$, $\text{H}_3\text{C}-\text{F}$, $\text{H}_3\text{C}-\text{MgBr}$, $\text{H}_3\text{C}-\text{OH}$

Answer

$\text{H}_3\text{C}-\text{OH} < \text{H}_3\text{C}-\text{MgBr} < \text{H}_3\text{C}-\text{Li} = \text{H}_3\text{C}-\text{F} < \text{H}_3\text{C}-\text{K}$

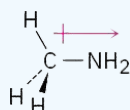
? Exercise 4.1.4

Look at the following electrostatic potential map of methylamine, a substance responsible for the odor of rotting fish, and tell the direction of polarization of the C-N bond:



Answer

The nitrogen is electron-rich, and the carbon is electron-poor.



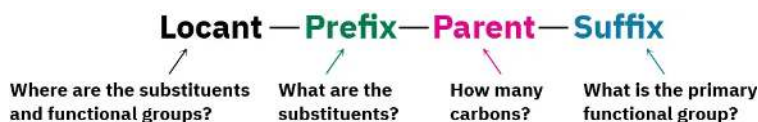
- **2.1: Polar Covalent Bonds - Electronegativity** by OpenStax is licensed CC BY-NC-SA 4.0. Original source: <https://openstax.org/details/books/organic-chemistry>.

4.2: Naming Alkanes

In earlier times, when relatively few pure organic chemicals were known, new compounds were named at the whim of their discoverer. Thus, urea ($\text{CH}_4\text{N}_2\text{O}$) is a crystalline substance isolated from urine; morphine ($\text{C}_{17}\text{H}_{19}\text{NO}_3$) is an analgesic (painkiller) named after Morpheus, the Greek god of dreams; and acetic acid, the primary organic constituent of vinegar, is named from the Latin word for vinegar, *acetum*.

As the science of organic chemistry slowly grew in the 19th century, so too did the number of known compounds and the need for a systematic method of naming them. The system of naming (nomenclature) we'll use in this book is that devised by the International Union of Pure and Applied Chemistry (IUPAC, usually spoken as **eye-you-pac**).

A chemical name typically has four parts in the IUPAC system: parent, prefix, locant, and suffix. The **parent** name identifies the main part of the molecule and tells how many carbon atoms are in that part. **Prefixes** identify the various substituent groups attached to the parent. **Locants** give the positions of the attached substituents. And the **suffix** identifies the primary functional group attached to the parent.

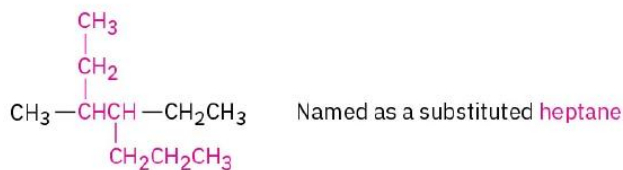


As we cover new functional groups in later chapters, the applicable IUPAC rules of nomenclature will be given. In addition, Appendix A at the back of this book gives an overall view of organic nomenclature and shows how compounds that contain more than one functional group are named. (If preferred, you can study that appendix now.) For the present, let's see how to name branched-chain alkanes and learn some general rules that are applicable to all compounds.

All but the most complex branched-chain alkanes can be named by following four steps. For a very few compounds, a fifth step is needed.

STEP 1: Identify the parent hydrocarbon

(a) Find the longest continuous chain of carbon atoms in the molecule, and use the name of that chain as the parent name. The longest chain may not always be apparent from the manner of writing; you may have to “turn corners.”

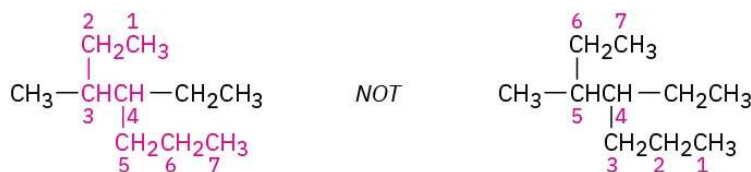


(b) If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.



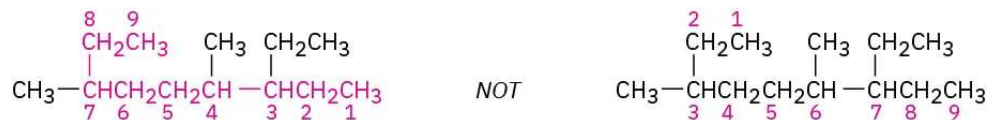
STEP 2: Number the atoms in the longest chain

(a) Beginning at the end nearer the first branch point, number each carbon atom in the parent chain.



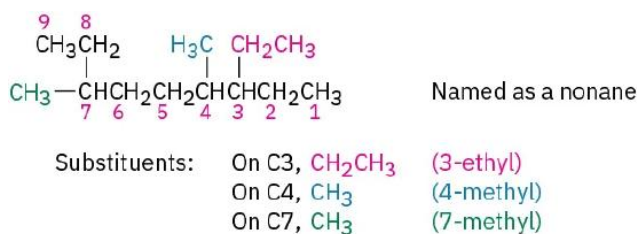
The first branch occurs at C3 in the proper system of numbering, not at C4.

(b) If there is branching an equal distance away from both ends of the parent chain, begin numbering at the end nearer the second branch point.

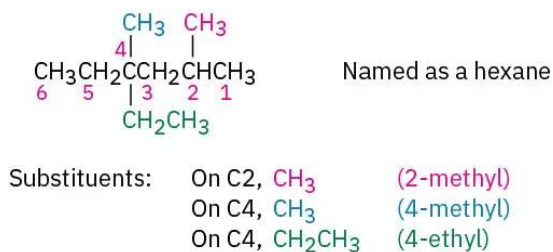


STEP 3: Identify and number the substituents

(a) Assign a number to each substituent to locate its point of attachment to the parent chain.

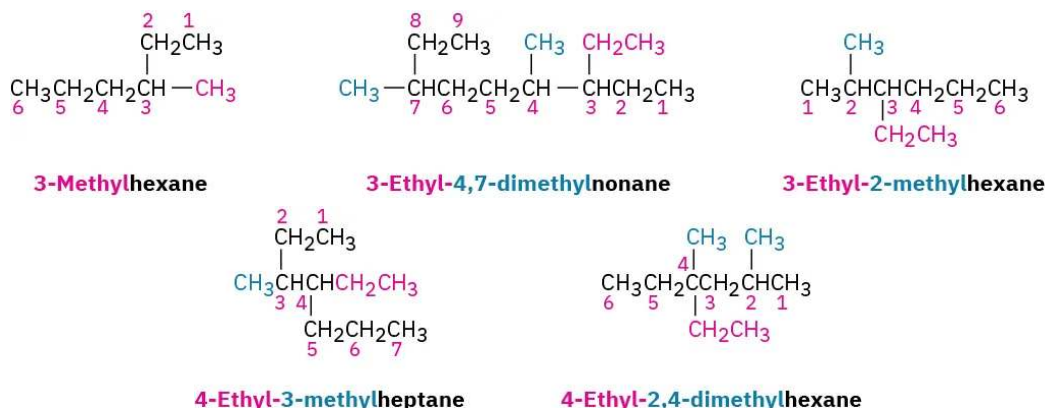


(b) If there are two substituents on the same carbon, give both the same number. There must be as many numbers in the name as there are substituents.



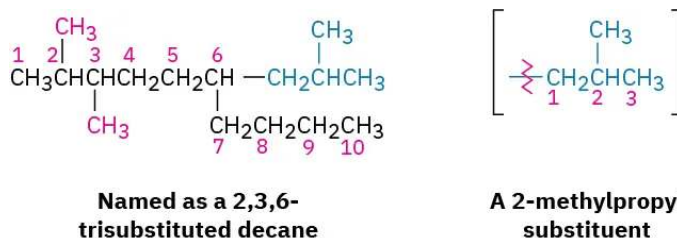
STEP 4: Write the name as a single word

Use hyphens to separate the different prefixes, and use commas to separate numbers. If two or more different substituents are present, cite them in alphabetical order. If two or more identical substituents are present on the parent chain, use one of the multiplier prefixes *di-*, *tri-*, *tetra-*, and so forth, but don't use these prefixes for alphabetizing. Full names for some of the examples we have been using are as follows:

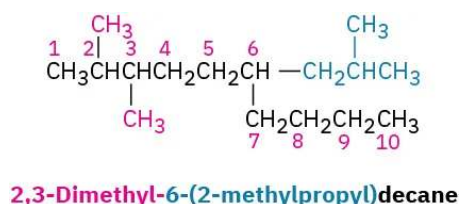


STEP 5: Name a branched substituent as though it were itself a compound

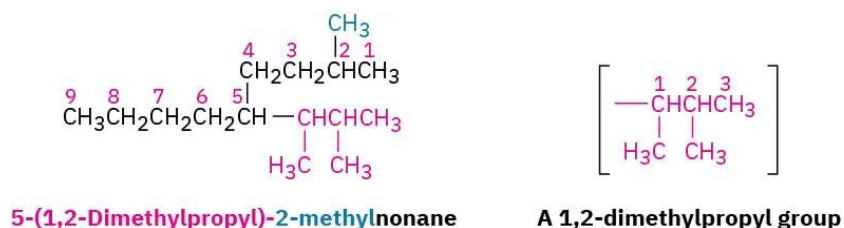
In some particularly complex cases, a fifth step is necessary. It occasionally happens that a substituent on the main chain is itself branched. In the following case, for instance, the substituent at C6 is a three-carbon chain with a methyl group. To name the compound fully, the branched substituent must first be named.



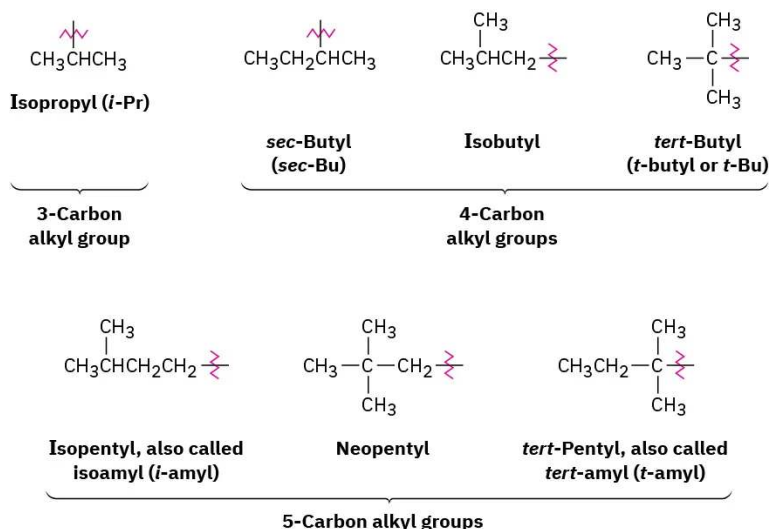
Number the branched substituent beginning at the point of its attachment to the main chain, and identify it—in this case, a 2-methylpropyl group. The substituent is treated as a whole and is alphabetized according to the first letter of its complete name, including any numerical prefix. It is set off in parentheses when naming the entire molecule.



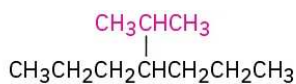
As a further example:



For historical reasons, some of the simpler branched-chain alkyl groups also have nonsystematic, common names, as noted earlier.



The common names of these simple alkyl groups are so well entrenched in the chemical literature that IUPAC rules make allowance for them. Thus, the following compound is properly named either 4-(1-methylethyl)heptane or 4-isopropylheptane. There's no choice but to memorize these common names; fortunately, there are only a few of them.

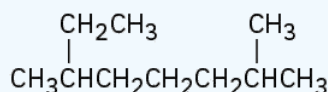


4-(1-Methylethyl)heptane or 4-Isopropylheptane

When writing an alkane name, the nonhyphenated prefix *iso-* is considered part of the alkyl-group name for alphabetizing purposes, but the hyphenated and italicized prefixes *sec-* and *tert-* are not. Thus, isopropyl and isobutyl are listed alphabetically under *i*, but *sec*-butyl and *tert*-butyl are listed under *b*.

✓ **Worked Example 4.2.1: Naming Alkanes**

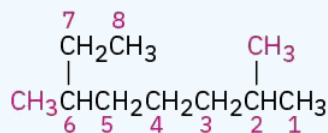
What is the IUPAC name for the following alkane?



Strategy

Find the longest continuous carbon chain in the molecule, and use that as the parent name. This molecule has a chain of eight carbons—octane—with two methyl substituents. (You have to turn corners to see it.) Numbering from the end nearer the first methyl substituent indicates that the methyls are at C2 and C6.

Solution



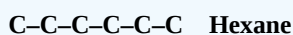
2,6-Dimethyloctane

✓ **Worked Example 4.2.2: Converting a Chemical Name into a Structure**

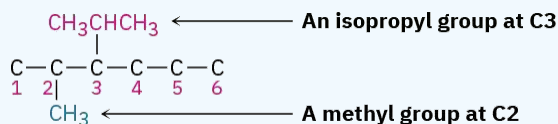
Draw the structure of 3-isopropyl-2-methylhexane.

Strategy

This is the reverse of Worked Example 3.2 and uses a reverse strategy. Look at the parent name (hexane), and draw its carbon structure.

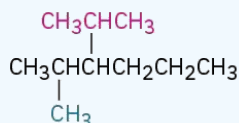


Next, find the substituents (3-isopropyl and 2-methyl), and place them on the proper carbons.



Finally, add hydrogens to complete the structure.

Solution

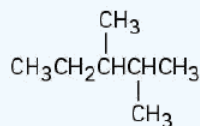


3-Isopropyl-2-methylhexane

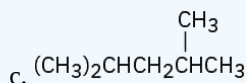
? Exercise 4.2.1

Give IUPAC names for the following compounds:

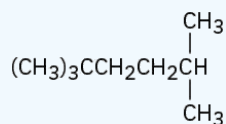
- a. The three isomers of C_5H_{12}



b.



c.



d.

Answer

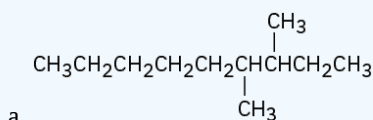
- Pentane, 2-methylbutane, 2,2-dimethylpropane
- 2,3-Dimethylpentane
- 2,4-Dimethylpentane
- 2,2,5-Trimethylhexane

? Exercise 4.2.2

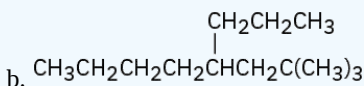
Draw structures corresponding to the following IUPAC names:

- 3,4-Dimethylnonane
- 3-Ethyl-4,4-dimethylheptane
- 2,2-Dimethyl-4-propyloctane
- 2,2,4-Trimethylpentane

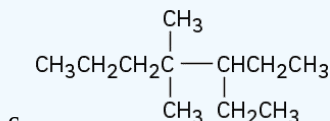
Answer



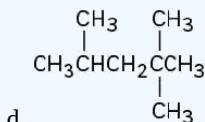
a.



b.



c.



d.

? Exercise 4.2.3

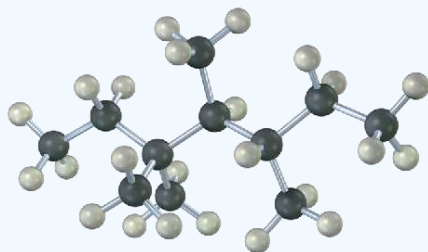
Name the eight 5-carbon alkyl groups you drew in Exercise 3.4.1.

Answer

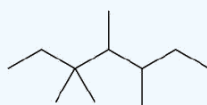
Pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl

? Exercise 4.2.4

Give the IUPAC name for the following hydrocarbon, and convert the drawing into a skeletal structure.



Answer



3,3,4,5-Tetramethylheptane

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4.2.1: Alkyl Groups

If you imagine removing a hydrogen atom from an alkane, the partial structure that remains is called an alkyl group. Alkyl groups are not stable compounds themselves, they are simply parts of larger compounds and are named by replacing the *-ane* ending of the parent alkane with an *-yl* ending. For example, removal of a hydrogen from methane, CH_4 , generates a methyl group, $-\text{CH}_3$, and removal of a hydrogen from ethane, CH_3CH_3 , generates an ethyl group, $-\text{CH}_2\text{CH}_3$. Similarly, removal of a hydrogen atom from the end carbon of any straight-chain alkane gives the series of straight-chain alkyl groups shown in Table 4.2.1.1. Combining an alkyl group with any of the functional groups listed earlier makes it possible to generate and name many thousands of compounds. For example:

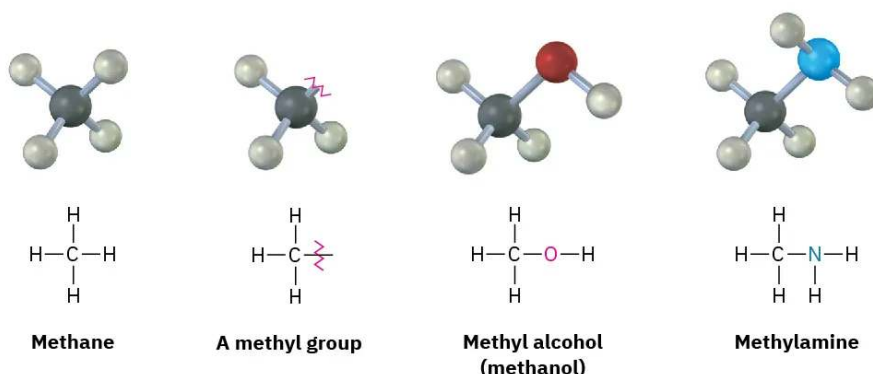
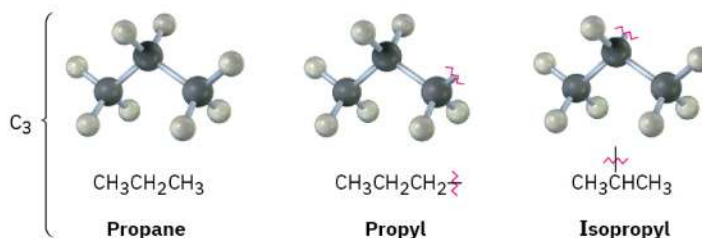


Table 4.2.1.1 Some Straight-Chain Alkyl Groups

Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	$-\text{CH}_3$	Methyl (Me)
CH_3CH_3	Ethane	$-\text{CH}_2\text{CH}_3$	Ethyl (Et)
$\text{CH}_3\text{CH}_2\text{CH}_3$	Propane	$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl (Pr)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	Butane	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl (Bu)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Pentane	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Pentyl, or amyl

Just as straight-chain alkyl groups are generated by removing a hydrogen from an end carbon, branched alkyl groups are generated by removing a hydrogen atom from an internal carbon. Two 3-carbon alkyl groups and four 4-carbon alkyl groups are possible (Figure 4.2.1.1).



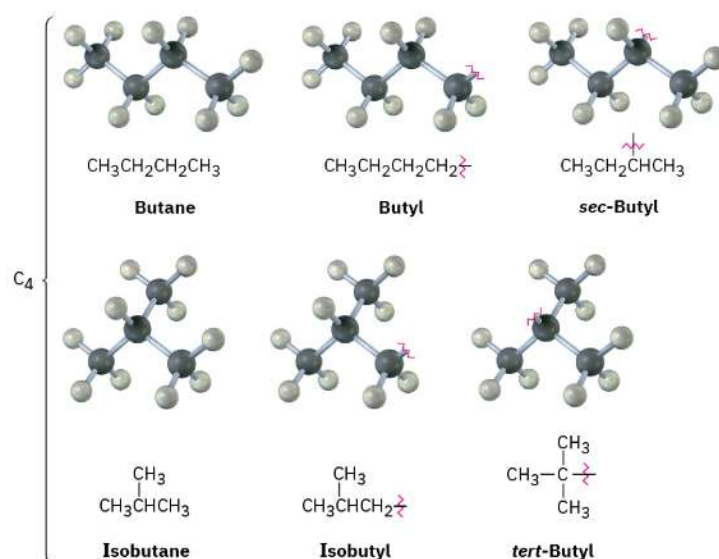
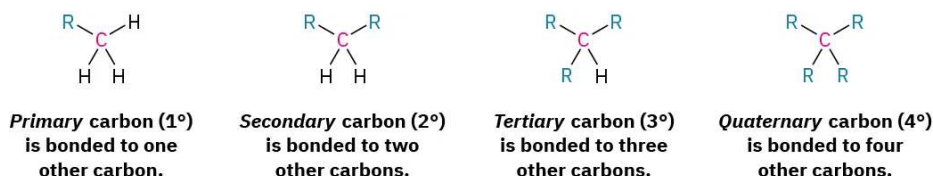


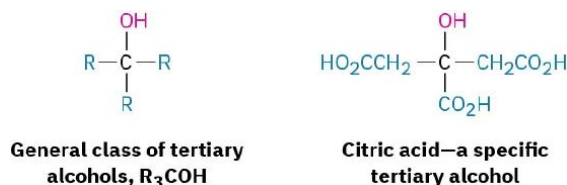
Figure 4.2.1.1: Alkyl groups generated from straight-chain alkanes.

One further comment about naming alkyl groups: the prefixes *sec-* (for secondary) and *tert-* (for tertiary) used for the C_4 alkyl groups in Figure 4.2.1.1 refer to the number of other carbon atoms attached to the branching carbon atom. There are four possibilities: primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).

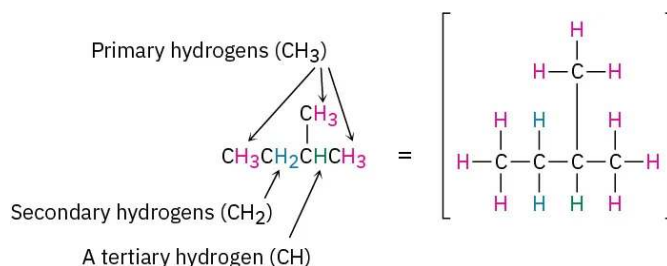


The symbol R is used here and throughout organic chemistry to represent a generalized organic group. The R group can be methyl, ethyl, propyl, or any of a multitude of others. You might think of **R** as representing the **R**est of the molecule, which isn't specified.

The terms *primary*, *secondary*, *tertiary*, and *quaternary* are routinely used in organic chemistry, and their meanings need to become second nature. For example, if we were to say, "Citric acid is a tertiary alcohol," we would mean that it has an alcohol functional group ($-OH$) bonded to a carbon atom that is itself bonded to three other carbons.



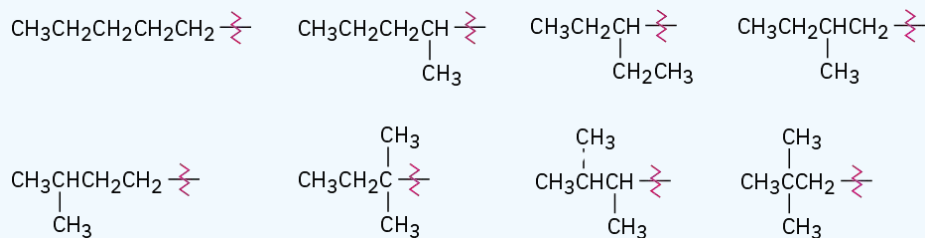
In addition to speaking of carbon atoms as being primary, secondary, or tertiary, we speak of hydrogens in the same way. Primary hydrogen atoms are attached to primary carbons (RCH_3), secondary hydrogens are attached to secondary carbons (R_2CH_2), and tertiary hydrogens are attached to tertiary carbons (R_3CH). There is, however, no such thing as a quaternary hydrogen. (Why not?)



? Exercise 4.2.1.1

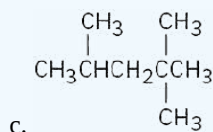
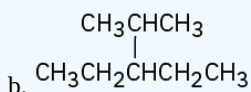
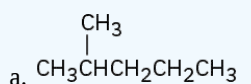
Draw the eight 5-carbon alkyl groups (pentyl isomers).

Answer

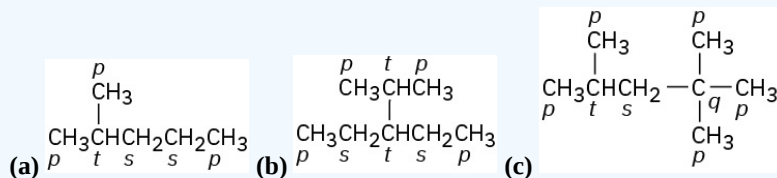


? Exercise 4.2.1.2

Identify the carbon atoms in the following molecules as primary, secondary, tertiary, or quaternary:



Answer



? Exercise 4.2.1.3

Identify the hydrogen atoms on the compounds shown in Problem 4.2.1.2 as primary, secondary, or tertiary.

Answer

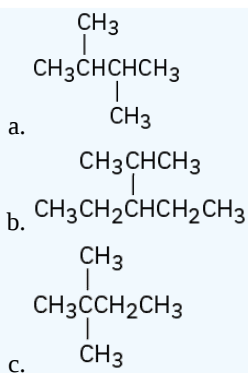
Primary carbons have primary hydrogens, secondary carbons have secondary hydrogens, and tertiary carbons have tertiary hydrogens.

? Exercise 4.2.1.4

Draw structures of alkanes that meet the following descriptions:

- An alkane with two tertiary carbons
- An alkane that contains an isopropyl group
- An alkane that has one quaternary and one secondary carbon

Answer



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4.3: Sequence Rules for Specifying Configuration

Structural drawings provide a visual representation of stereochemistry, but a written method for indicating the three-dimensional arrangement, or configuration, of substituents at a chirality center is also needed. The method used a set of **sequence rules** to rank the four groups attached to the chirality center and then looks at the handedness with which those groups are attached. Called the **Cahn-Ingold-Prelog rules** after the chemists who proposed them, the sequence rules are as follows:

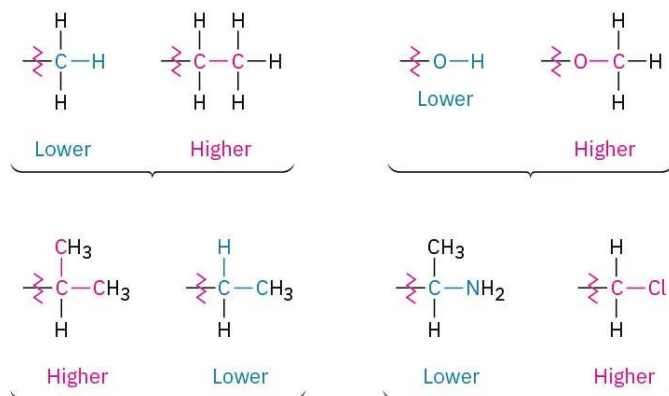
RULE 1

Look at the four atoms directly attached to the chirality center, and rank them according to atomic number. The atom with the highest atomic number has the highest ranking (first), and the atom with the lowest atomic number (usually hydrogen) has the lowest ranking (fourth). When different isotopes of the same element are compared, such as deuterium (^2H) and protium (^1H), the heavier isotope ranks higher than the lighter isotope. Thus, atoms commonly found in organic compounds have the following order.

Atomic number	35	17	16	15	8	7	6	(2)	(1)									
Higher rank	Br	>	Cl	>	S	>	P	>	O	>	N	>	C	>	² H	>	¹ H	Lower rank

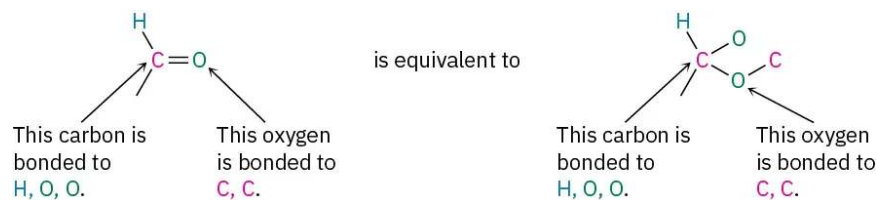
RULE 2

If a decision can't be reached by ranking the first atoms in the substituent, look at the second, third, or fourth atoms away from the chirality center until the first difference is found. A $-\text{CH}_2\text{CH}_3$ substituent and a $-\text{CH}_3$ substituent are equivalent by rule 1 because both have carbon as the first atom. By rule 2, however, ethyl ranks higher than methyl because ethyl has a carbon as its highest second atom, while methyl has only hydrogen as its second atom. Look at the following pairs of examples to see how the rule works:

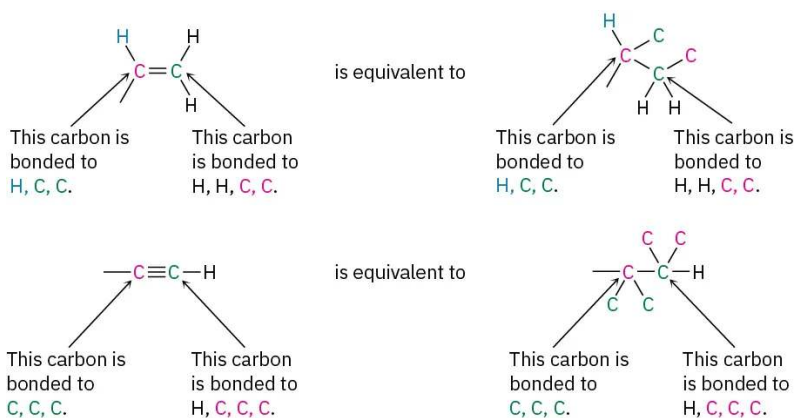


RULE 3

Multiple-bonded atoms are equivalent to the same number of single-bonded atoms. For example, an aldehyde substituent ($-\text{CH}=\text{O}$), which has a carbon atom *doubly* bonded to *one* oxygen, is equivalent to a substituent having a carbon atom *singly* bonded to *two* oxygens:



As further examples, the following pairs are equivalent:



Having ranked the four groups attached to a chiral carbon, we describe the stereochemical configuration around the carbon by orienting the molecule so that the group with the lowest ranking (4) points directly away from us. We then look at the three remaining substituents, which now appear to radiate toward us like the spokes on a steering wheel (Figure 4.3.1). If a curved arrow drawn from the highest to second-highest to third-highest ranked substituent ($1 \rightarrow 2 \rightarrow 3$) is clockwise, we say that the chirality center has the *R* configuration (*S* for the Latin *rectus*, meaning “right”). If an arrow from $1 \rightarrow 2 \rightarrow 3$ is counterclockwise, the chirality center has the *S* configuration (Latin *sinister*, meaning “left”). To remember these assignments, think of a car’s steering wheel when making a Right (clockwise) turn.

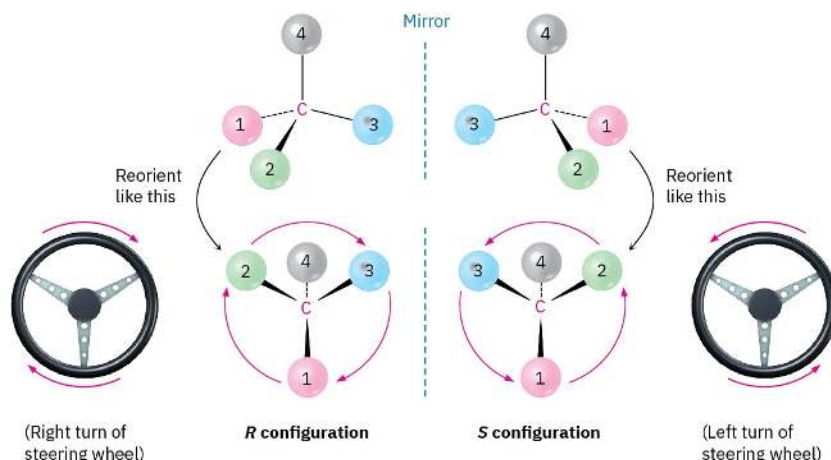


Figure 4.3.1: Assigning *R* and *S* configurations to chirality centers. When the molecule is oriented so that the lowest-ranked group (4) is toward the rear, the remaining three groups radiate toward the viewer like the spokes of a steering wheel. If the direction of travel $1 \rightarrow 2 \rightarrow 3$ is clockwise (right turn), the center has the *R* configuration. If the direction of travel $1 \rightarrow 2 \rightarrow 3$ is counterclockwise (left turn), the center is *S*.

Look at (–)-lactic acid in Figure 4.3.2 for an example of how to assign configuration. Sequence rule 1 says that –OH is ranked 1 and –H is ranked 4, but it doesn’t allow us to distinguish between –CH₃ and –CO₂H because both groups have carbon as their first atom. Sequence rule 2, however, says that –CO₂H ranks higher than –CH₃ because O (the highest second atom in –CO₂H) outranks H (the highest second atom in –CH₃). Now, turn the molecule so that the fourth-ranked group (–H) is oriented toward the rear, away from the observer. Since a curved arrow from 1 (–OH) to 2 (–CO₂H) to 3 (–CH₃) is clockwise (right turn of the steering wheel), (–)-lactic acid has the *R* configuration. Applying the same procedure to (+)-lactic acid leads to the opposite assignment.

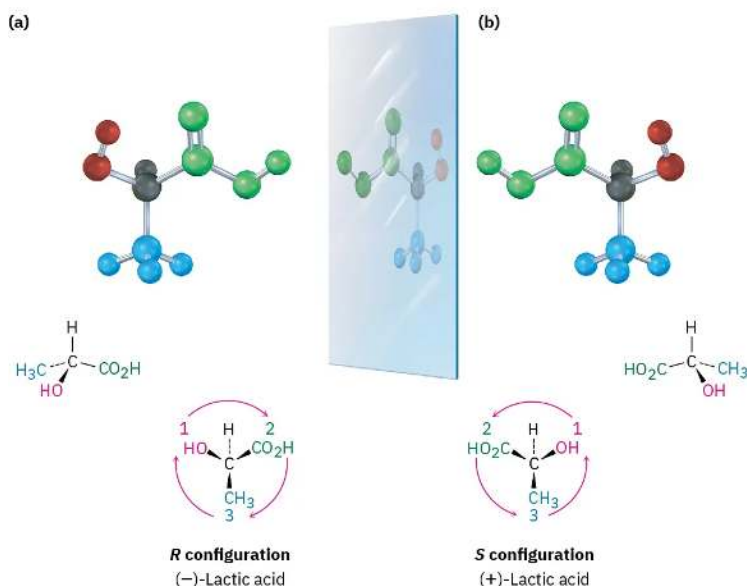


Figure 4.3.2: Assigning configuration to (a) (R)-(-)-lactic acid and (b) (S)-(+)-lactic acid.

Further examples are provided by naturally occurring (-)-glyceraldehyde and (+)-alanine, which both have the *S* configuration as shown in Figure 4.3.3. Note that the sign of optical rotation, (+) or (-), is not related to the *R,S* designation. (*S*)-Glyceraldehyde happens to be levorotatory (-), and (*S*)-alanine happens to be dextrorotatory (+). There is no simple correlation between *R,S* configuration and direction or magnitude of optical rotation.

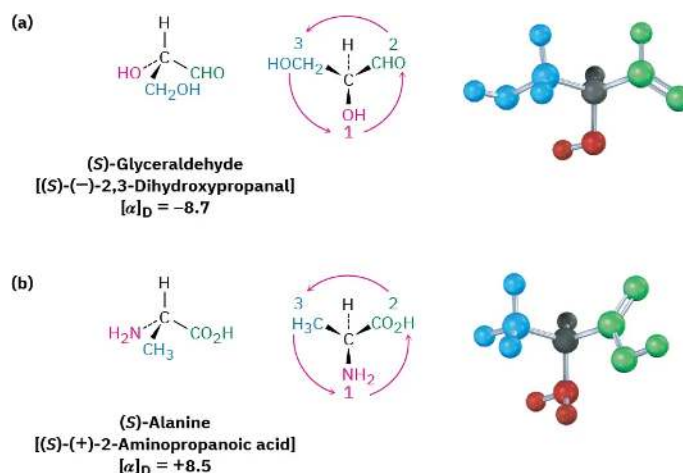
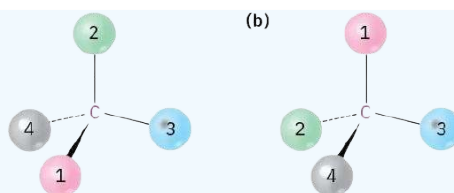


Figure 4.3.3: Assigning configuration to (a) (-)-glyceraldehyde. (b) (+)-alanine. Both happen to have the *S* configuration, although one is levorotatory and the other is dextrorotatory.

One additional point needs to be mentioned—the matter of absolute configuration. How do we know that the assignments of *R* and *S* configuration are correct in an absolute sense, rather than a relative, sense? Since there is no correlation between the *R,S* configuration and the direction or magnitude of optical rotation, how do we know that the *R* configuration belongs to the levorotatory enantiomer of lactic acid? This difficult question was finally solved in 1951, when an X-ray diffraction method was found for determining the absolute spatial arrangement of atoms in a molecule. Based on those results, we can say with certainty that the *R,S* conventions are correct.

✓ Worked Example 4.3.1: Assigning Configuration to Chirality Centers

Orient each of the following drawings so that the lowest-ranked group is toward the rear, and then assign *R* or *S* configuration to each:

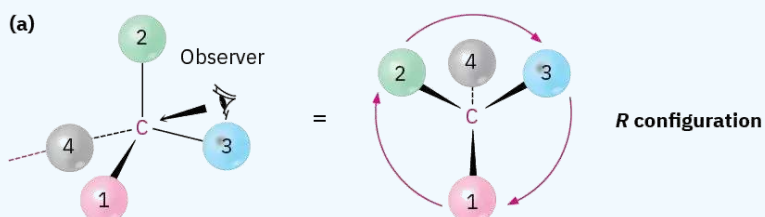


Strategy

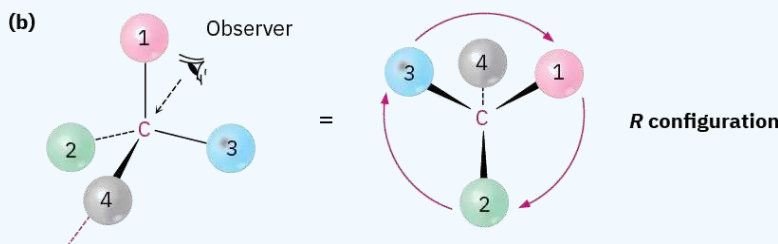
It takes practice to be able to visualize and orient a chirality center in three dimensions. You might start by indicating where the observer must be located— 180° opposite the lowest-ranked group. Then imagine yourself in the position of the observer, and redraw what you would see.

Solution

In (a), you would be located in front of the page toward the top right of the molecule, and you would see group 2 to your left, group 3 to your right, and group 1 below you. This corresponds to an *R* configuration.



In (b), you would be located behind the page toward the top left of the molecule from your point of view, and you would see group 3 to your left, group 1 to your right, and group 2 below you. This also corresponds to an *R* configuration.



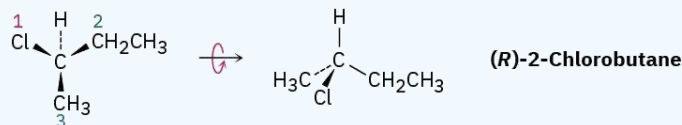
✓ Worked Example 4.3.2: Drawing the Three-Dimensional Structure of a Specific Enantiomer

Draw a tetrahedral representation of (*R*)-2-chlorobutane.

Strategy

Begin by ranking the four substituents bonded to the chirality center: (1) -Cl , (2) $\text{-CH}_2\text{CH}_3$, (3) -CH_3 , (4) -H . To draw a tetrahedral representation of the molecule, orient the lowest-ranked group (-H) away from you and imagine that the other three groups are coming out of the page toward you. Then, place the remaining three substituents such that the direction of travel $1 \rightarrow 2 \rightarrow 3$ is clockwise (right turn), and tilt the molecule toward you to bring the rear hydrogen into view. Using molecular models is a real help in working problems of this sort.

Solution



? Exercise 4.3.1

Which member in each of the following sets ranks higher?

- -H or -Br
- -Cl or -Br

- c. $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_3$
- d. $-\text{NH}_2$ or $-\text{OH}$
- e. $-\text{CH}_2\text{OH}$ or $-\text{CH}_3$
- f. $-\text{CH}_2\text{OH}$ or $-\text{CH}=\text{O}$

Answer

- a. $-\text{Br}$
- b. $-\text{Br}$
- c. $-\text{CH}_2\text{CH}_3$
- d. $-\text{OH}$
- e. $-\text{CH}_2\text{OH}$
- f. $-\text{CH}=\text{O}$

? Exercise 4.3.2

Rank each of the following sets of substituents:

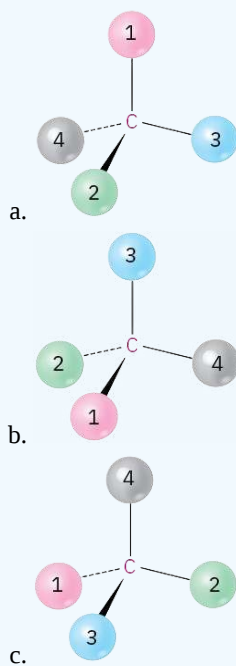
- a. $-\text{H}$, $-\text{OH}$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{OH}$
- b. $-\text{CO}_2\text{H}$, $-\text{CO}_2\text{CH}_3$, $-\text{CH}_2\text{OH}$, $-\text{OH}$
- c. $-\text{CN}$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{NHCH}_3$, $-\text{NH}_2$
- d. $-\text{SH}$, $-\text{CH}_2\text{SCH}_3$, $-\text{CH}_3$, $-\text{SSCH}_3$

Answer

- a. $-\text{OH}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_3$, $-\text{H}$
- b. $-\text{OH}$, $-\text{CO}_2\text{CH}_3$, $-\text{CO}_2\text{H}$, $-\text{CH}_2\text{OH}$
- c. $-\text{NH}_2$, $-\text{CN}$, $-\text{CH}_2\text{NHCH}_3$, $-\text{CH}_2\text{NH}_2$
- d. $-\text{SSCH}_3$, $-\text{SH}$, $-\text{CH}_2\text{SCH}_3$, $-\text{CH}_3$

? Exercise 4.3.1

Orient each of the following drawings so that the lowest-ranked group is toward the rear, and then assign *R* or *S* configuration:

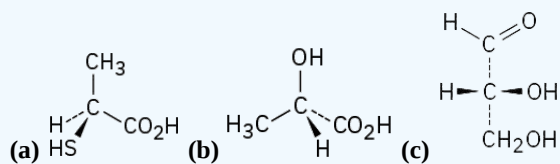


Answer

- a. *S*
- b. *R*
- c. *S*

? Exercise 4.3.4

Assign *R* or *S* configuration to the chirality center in each of the following molecules:

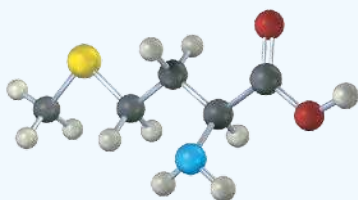


Answer

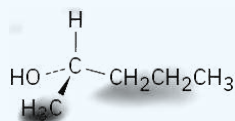
(a) *S* (b) *S* (c) *R*

? Exercise 4.3.5

Assign *R* or *S* configuration to the chirality center in the following molecular model of the amino acid methionine (blue = N, yellow = S):



Answer



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4.4: Naming Alkenes

Alkenes are named using a series of rules similar to those for alkanes (Section 3.4), with the suffix *-ene* used instead of *-ane* to identify the functional group. There are three steps to this process.

STEP 1: Name the parent hydrocarbon

Find the longest carbon chain containing the double bond, and name the compound accordingly, using the suffix *-ene*:



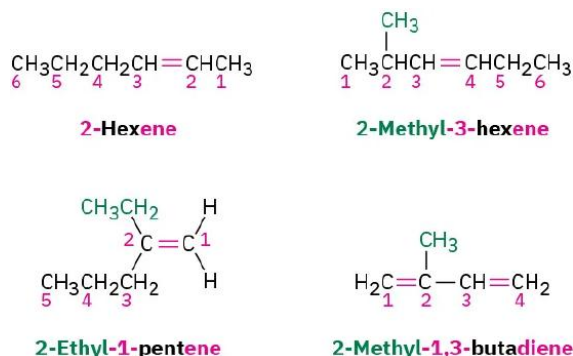
STEP 2: Number the carbon atoms in the chain

Begin at the end nearer the double bond or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point. This rule ensures that the double-bond carbons receive the lowest possible numbers.

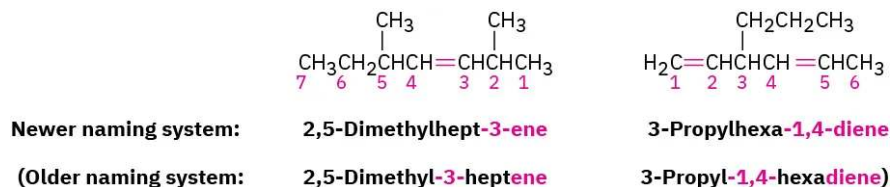


STEP 3: Write the full name

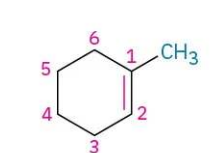
Number the substituents according to their positions in the chain, and list them alphabetically. Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number directly before the parent name. If more than one double bond is present, indicate the position of each and use one of the suffixes *-diene*, *-triene*, and so on.



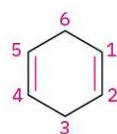
We should also note that IUPAC changed their naming recommendations in 1993 to place the locant indicating the position of the double bond immediately before the *-ene* suffix rather than before the parent name: but-2-ene rather than 2-butene, for instance. This change has not been widely accepted by the chemical community in the United States, however, so we'll stay with the older but more commonly used names. Be aware, though, that you may occasionally encounter the newer system.



Cycloalkenes are named similarly, but because there is no chain end to begin from, we number the cycloalkene so that the double bond is between C1 and C2, and the first substituent has as low a number as possible. It's not necessary to indicate the position of the double bond in the name because it's always between C1 and C2. As with open-chain alkenes, the newer but not yet widely accepted naming rules place the locant immediately before the suffix in a cyclic alkene.

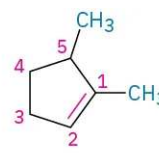


1-Methylcyclohexene



1,4-Cyclohexadiene

(New: Cyclohexa-1,4-diene)



1,5-Dimethylcyclopentene

For historical reasons, there are a few alkenes whose names are firmly entrenched in common usage but don't conform to the rules. For example, the alkene derived from ethane should be called *ethene*, but the name *ethylene* has been used for so long that it is accepted by IUPAC. Table 4.4.1 lists several other common names that are often used and are recognized by IUPAC. Note also that a $=\text{CH}_2$ substituent is called a **methylene group**, a $\text{H}_2\text{C}-\text{CH}-$ substituent is called a **vinyl group**, and a $\text{H}_2\text{C}-\text{CHCH}_2-$ substituent is called an **allyl group**.

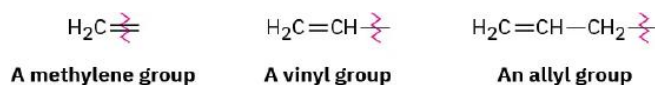


Table 4.4.1: Common Names of Some Alkenes

Compound	Systematic name	Common name
$\text{H}_2\text{C}=\text{CH}_2$	Ethene	Ethylene
$\text{CH}_3\text{CH}=\text{CH}_2$	Propene	Propylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}=\text{CH}_2 \end{array}$	2-Methylpropene	Isobutylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2 \end{array}$	2-Methyl-1,3-butadiene	Isoprene

? Exercise 4.4.1

Give IUPAC names for the following compounds:

- a.
$$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ | \quad | \\ \text{H}_2\text{C}=\text{CHCHCCH}_3 \\ | \\ \text{CH}_3 \end{array}$$
- b.
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}=\text{CCH}_2\text{CH}_3 \end{array}$$
- c.
$$\begin{array}{c} \text{CH}_3 \quad \quad \text{CH}_3 \\ | \quad \quad | \\ \text{CH}_3\text{CH}=\text{CHCHCH}=\text{CHCHCH}_3 \end{array}$$
- d.
$$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CHCHCH}_2\text{CH}_3 \end{array}$$

Answer

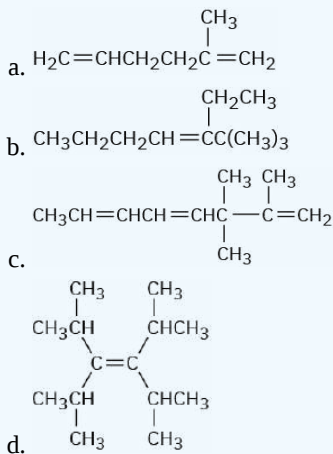
- 3,4,4-Trimethyl-1-pentene
- 3-Methyl-3-hexene
- 4,7-Dimethyl-2,5-octadiene
- 6-Ethyl-7-methyl-4-nonene

? Exercise 4.4.2

Draw structures corresponding to the following IUPAC names:

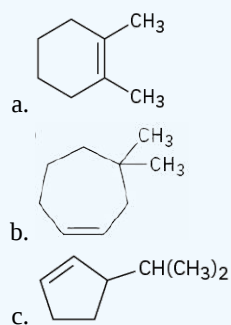
- 2-Methyl-1,5-hexadiene
- 3-Ethyl-2,2-dimethyl-3-heptene
- 2,3,3-Trimethyl-1,4,6-octatriene
- 3,4-Diisopropyl-2,5-dimethyl-3-hexene

Answer



? Exercise 4.4.3

Name the following cycloalkenes:



Answer

- 1,2-Dimethylcyclohexene
- 4,4-Dimethylcycloheptene
- 3-Isopropylcyclopentene

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4.4.1: Cis-Trans Isomerism in Alkenes

We saw in the chapter on Structure and Bonding that the carbon–carbon double bond can be described in two ways. In valence bond language (Section 1.9), the carbons are sp^2 -hybridized and have three equivalent hybrid orbitals that lie in a plane at angles of 120° to one another. The carbons form a σ bond by a head-on overlap of sp^2 orbitals and form a π bond by sideways overlap of unhybridized p orbitals oriented perpendicular to the sp^2 plane.

In molecular orbital language (Section 1.12), interaction between the p orbitals leads to one bonding and one antibonding π molecular orbital. The π bonding MO has no node between nuclei and results from a combination of p orbital lobes with the same algebraic sign. The π antibonding MO has a node between nuclei and results from a combination of lobes with different algebraic signs.

Although essentially free rotation around single bonds is possible (Section 3.7), the same is not true of double bonds. For rotation to occur around a double bond, the π bond must break and re-form (Figure 4.4.1.1). Thus, the barrier to double-bond rotation must be at least as great as the strength of the π bond itself, an estimated 350 kJ/mol (84 kcal/mol). Recall that the barrier to bond rotation in ethane is only 12 kJ/mol.

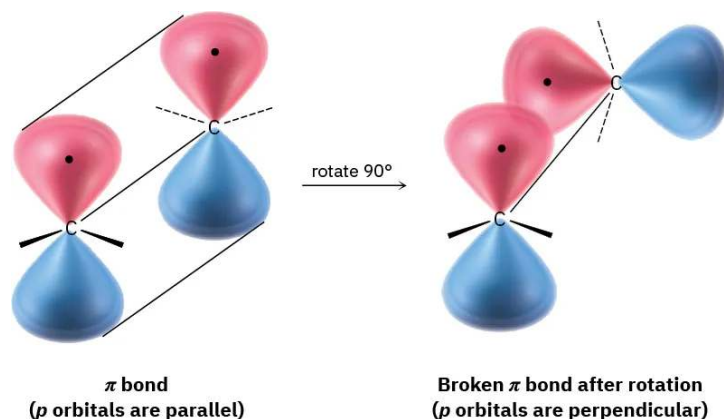


Figure 4.4.1.1: The π bond must break for rotation to take place around a carbon–carbon double bond.

The lack of rotation around carbon–carbon double bonds is of more than just theoretical interest; it also has chemical consequences. Imagine the situation for a disubstituted alkene such as 2-butene. (Disubstituted means that two substituents other than hydrogen are bonded to the double-bond carbons.) The two methyl groups in 2-butene can either be on the same side of the double bond or on opposite sides, a situation similar to that in disubstituted cycloalkanes (Section 4.3).

Since bond rotation can't occur, the two 2-butenes can't spontaneously interconvert; they are different, isolable compounds. As with disubstituted cycloalkanes, we call such compounds *cis-trans* stereoisomers. The compound with substituents on the same side of the double bond is called *cis*-2-butene, and the isomer with substituents on opposite sides is *trans*-2-butene (Figure 4.4.1.2).

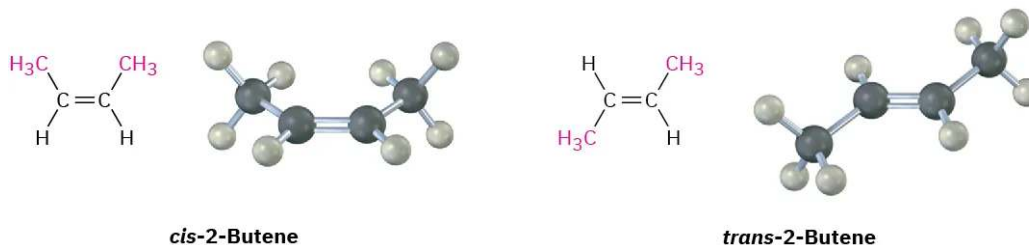
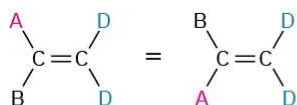
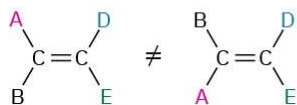


Figure 4.4.1.2: *Cis* and *trans* isomers of 2-butene. The *cis* isomer has the two methyl groups on the same side of the double bond, and the *trans* isomer has methyl groups on opposite sides.

Cis-trans isomerism is not limited to disubstituted alkenes. It can occur whenever both double-bond carbons are attached to two different groups. If one of the double-bond carbons is attached to two identical groups, however, *cis-trans* isomerism is not possible (Figure 4.4.1.3).



These two compounds are identical; they are not cis-trans isomers.



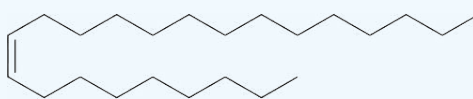
These two compounds are not identical; they are cis-trans isomers.

Figure 4.4.1.3: The requirement for cis-trans isomerism in alkenes. Compounds that have one of their carbons bonded to two identical groups can't exist as cis-trans isomers. Only when both carbons are bonded to two different groups is cis-trans isomerism possible.

? Exercise 4.4.1.1

The sex attractant of the common housefly is an alkene named *cis*-9-tricosene. Draw its structure. (Tricosane is the straight-chain alkane $\text{C}_{23}\text{H}_{48}$.)

Answer



? Exercise 4.4.1.2

Which of the following compounds can exist as pairs of cis-trans isomers? Draw each pair, and indicate the geometry of each isomer.

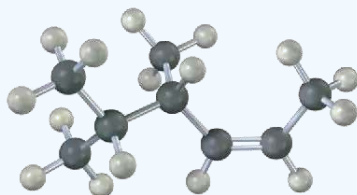
- $\text{CH}_3\text{CH}=\text{CH}_2$
- $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$
- $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$
- $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$
- $\text{ClCH}=\text{CHCl}$
- $\text{BrCH}=\text{CH}$

Answer

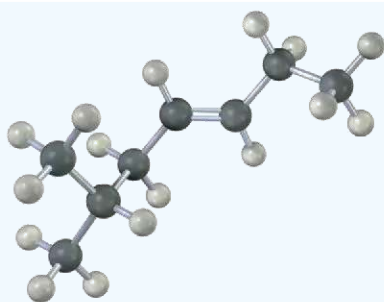
Compounds (c), (e), and (f) have cis-trans isomers.

? Exercise 4.4.1.3

Name the following alkenes, including a cis or trans designation:



a.



b.

Answer

- a. cis-4,5-Dimethyl-2-hexene
- b. trans-6-Methyl-3-heptene

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4.4.2: Alkene Stereochemistry and the E,Z Designation

The cis–trans naming system used in the previous section works only with disubstituted alkenes—compounds that have two substituents other than hydrogen on the double bond. With trisubstituted and tetrasubstituted double bonds, a more general method is needed for describing double-bond geometry. (*Trisubstituted* means three substituents other than hydrogen on the double bond; *tetrasubstituted* means four substituents other than hydrogen.)

The method used for describing alkene stereochemistry is called the **E,Z system** and employs the same Cahn–Ingold–Prelog sequence rules given in Section 5.6 for specifying the configuration of a chirality center. Let’s briefly review the sequence rules and then see how they’re used to specify double-bond geometry. For a more thorough review, reread Section 5.6.

RULE 1

Considering each of the double-bond carbons separately, look at the two substituents attached and rank them according to the atomic number of the first atom in each (8 for oxygen, 6 for carbon, 1 for hydrogen, and so forth). An atom with higher atomic number ranks higher than an atom with lower atomic number.

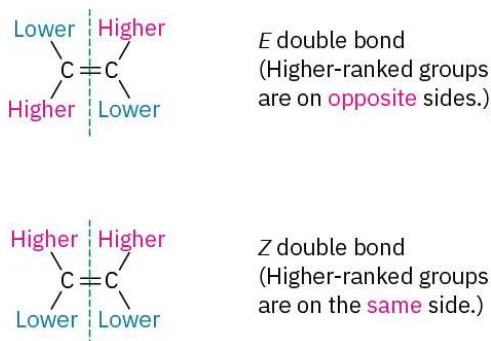
RULE 2

If a decision can’t be reached by ranking the first atoms in the two substituents, look at the second, third, or fourth atoms away from the double-bond until the first difference is found.

RULE 3

Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.

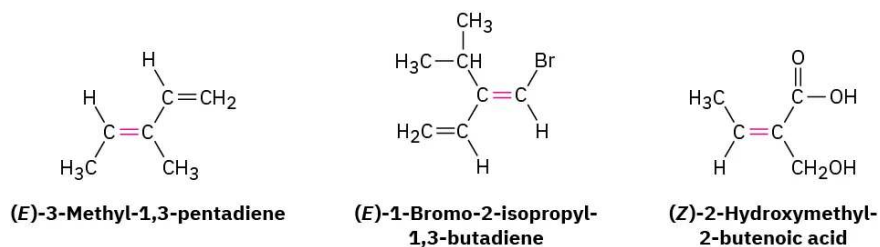
Once the two groups attached to each double-bonded carbon have been ranked as either higher or lower, look at the entire molecule. If the higher-ranked groups on each carbon are on the same side of the double bond, the alkene is said to have a *Z* configuration, for the German *zusammen*, meaning “together.” If the higher-ranked groups are on opposite sides, the alkene has an *E* configuration, for the German *entgegen*, meaning “opposite.” (For a simple way to remember which is which, note that the groups are on “ze zame zide” in the *Z* isomer.)



As an example, look at the following two isomers of 2-chloro-2-butene. Because chlorine has a higher atomic number than carbon, a –Cl substituent is ranked higher than a –CH₃ group. Methyl is ranked higher than hydrogen, so isomer **(a)** is designated *E* because the higher-ranked groups are on opposite sides of the double bond. Isomer **(b)** has a *Z* configuration because its higher-ranked groups are on the same side of the double bond.

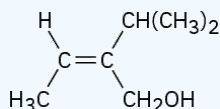


In the following examples observe the configuration, and identify the high rank groups that make the assignment correct:



✓ Worked Example 4.4.2.1: Assigning E and Z Configurations to Alkenes

Assign *E* or *Z* configuration to the double bond in the following compound:

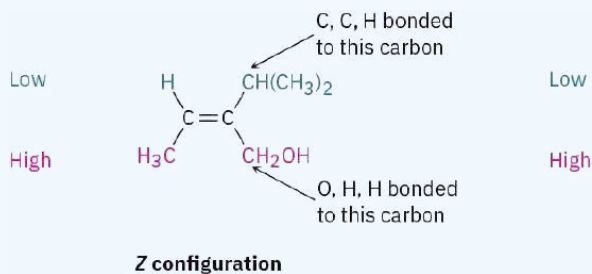


Strategy

Look at the two substituents connected to each double-bonded carbon, and determine their ranking using the Cahn–Ingold–Prelog rules. Then, check whether the two higher-ranked groups are on the same or opposite sides of the double bond.

Solution

The left-hand carbon has -H and -CH_3 substituents, of which -CH_3 ranks higher by sequence rule 1. The right-hand carbon has $\text{-CH(CH}_3)_2$ and $\text{-CH}_2\text{OH}$ substituents, which are equivalent by rule 1. By rule 2, however, $\text{-CH}_2\text{OH}$ ranks higher than $\text{-CH(CH}_3)_2$ because the substituent $\text{-CH}_2\text{OH}$ has an oxygen as its highest second atom, but $\text{-CH(CH}_3)_2$ has a carbon as its highest second atom. The two higher-ranked groups are on the same side of the double bond, so we assign a *Z* configuration.



? Exercise 4.4.2.2

Which member in each of the following sets ranks higher?

- -H or -CH_3
- -Cl or $\text{-CH}_2\text{Cl}$
- $\text{-CH}_2\text{CH}_2\text{Br}$ or -CH=CH_2
- -NHCH_3 or -OCH_3
- $\text{-CH}_2\text{OH}$ or -CH=O
- $\text{-CH}_2\text{OCH}_3$ or -CH=O

Answer

- -CH_3
- -Cl
- -CH=CH_2
- -OCH_3
- -CH=O
- -CH=O

? Exercise 4.4.2.3

Rank the substituents in each of the following sets according to the sequence rules:

- $-\text{CH}_3$, $-\text{OH}$, $-\text{H}$, $-\text{Cl}$
- $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{OH}$
- $-\text{CO}_2\text{H}$, $-\text{CH}_2\text{OH}$, $-\text{C}\equiv\text{N}$, $-\text{CH}_2\text{NH}_2$
- $-\text{CH}_2\text{CH}_3$, $-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{N}$, $-\text{CH}_2\text{OCH}_3$

Answer

- $-\text{Cl}$, $-\text{OH}$, $-\text{CH}_3$, $-\text{H}$
- $-\text{CH}_2\text{OH}$, $-\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}_3$, $-\text{CH}_3$
- $-\text{CO}_2\text{H}$, $-\text{CH}_2\text{OH}$, $-\text{C}\equiv\text{N}$, $-\text{CH}_2\text{NH}_2$
- $-\text{CH}_2\text{OCH}_3$, $-\text{C}\equiv\text{N}$, $-\text{C}\equiv\text{CH}$, $-\text{CH}_2\text{CH}_3$

? Exercise 4.4.2.4

Assign *E* or *Z* configuration to the following alkenes:

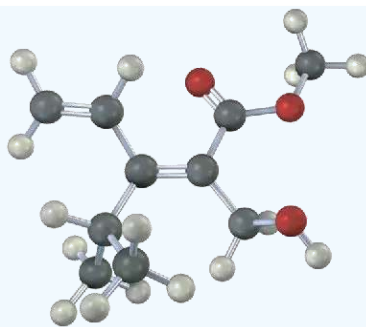
-
-
-
-

Answer

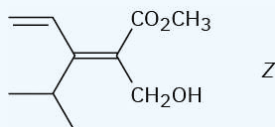
- Z*
- E*
- Z*
- E*

? Exercise 4.4.2.5

Assign stereochemistry (*E* or *Z*) to the double bond in the following compound, and convert the drawing into a skeletal structure (red = O):



Answer



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4.5: Names and Properties of Alkyl Halides

Although commonly called *alkyl halides*, halogen-substituted alkanes are named systematically as *haloalkanes* (Section 3.5), treating the halogen as a substituent on a parent alkane chain. There are three steps:

STEP 1

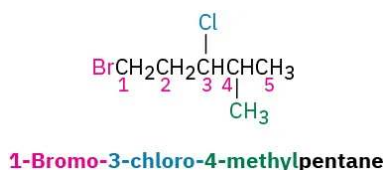
Find the longest chain, and name it as the parent. If a double or triple bond is present, the parent chain must contain it.

STEP 2

Number the carbons of the parent chain beginning at the end nearer the first substituent, whether alkyl or halo. Assign each substituent a number according to its position on the chain.

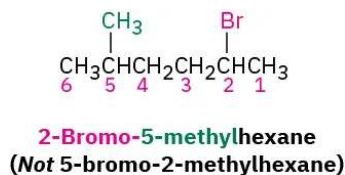


If different halogens are present, number each one and list them in alphabetical order when writing the name.



STEP 3

If the parent chain can be properly numbered from either end by step 2, begin at the end nearer the substituent that has alphabetical precedence.



In addition to their systematic names, many simple alkyl halides are also named by identifying first the alkyl group and then the halogen. For example, CH_3I can be called either iodomethane or methyl iodide. Such names are well entrenched in the chemical literature and in daily usage, but they won't be used in this book.

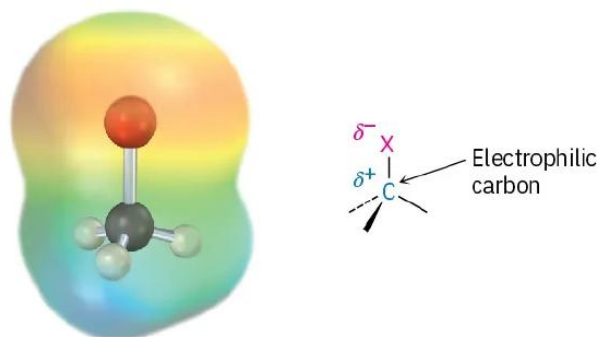


Halogens increase in size going down the periodic table, so the lengths of the corresponding carbon-halogen bonds increase accordingly (Table 4.5.1). In addition, C-X bond strengths decrease going down the periodic table. As we've been doing thus far, we'll continue using an X to represent any of the halogens F, Cl, Br, or I.

Table 4.5.1: A Comparison of the Halomethanes

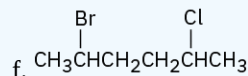
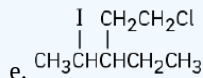
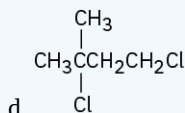
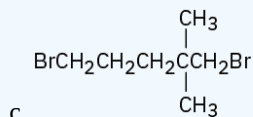
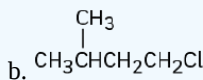
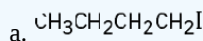
Halomethane	Bond length (pm)	Bond strength		Dipole moment (<i>D</i>)
		(kJ/mol)	(kcal/mol)	
CH ₃ F	139	460	110	1.85
CH ₃ Cl	178	350	84	1.87
CH ₃ Br	193	294	70	1.81
CH ₃ I	214	239	57	1.62

In our discussion of bond polarity in functional groups in Section 6.4, we noted that halogens are more electronegative than carbon. The C–X bond is therefore polar, with the carbon atom bearing a slight positive charge (δ^+) and the halogen a slight negative charge (δ^-). This polarity results in a dipole moment for all the halomethanes (Table 10.1) and implies that the alkyl halide C–X carbon atom should behave as an electrophile in polar reactions. We'll soon see that this is indeed the case.



? Exercise 4.5.1

Give IUPAC names for the following alkyl halides:



Answer

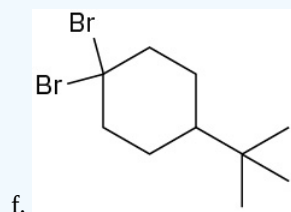
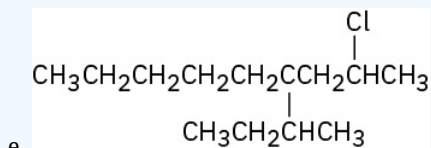
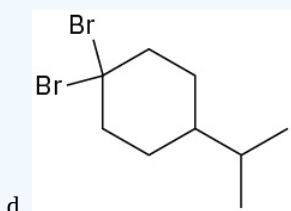
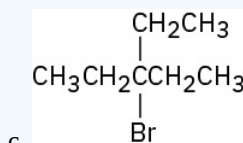
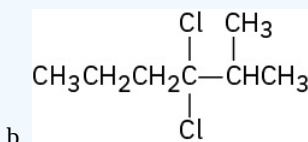
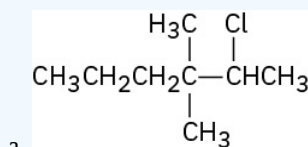
- 1-Iodobutane
- 1-Chloro-3-methylbutane
- 1,5-Dibromo-2,2-dimethylpentane
- 1,3-Dichloro-3-methylbutane
- 1-Chloro-3-ethyl-4-iodopentane

? Exercise 4.5.1

Draw structures corresponding to the following IUPAC names:

- 2-Chloro-3,3-dimethylhexane
- 3,3-Dichloro-2-methylhexane
- 3-Bromo-3-ethylpentane
- 1,1-Dibromo-4-isopropylcyclohexane
- 4-sec-Butyl-2-chlorononane
- 1,1-Dibromo-4-tert-butylcyclohexane

Answer



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4.6: Naming Aromatic Compounds

Simple aromatic hydrocarbons come from two main sources: coal and petroleum. Coal is an enormously complex mixture consisting primarily of large arrays of benzene-like rings joined together. Thermal breakdown of coal occurs when heated to 1000 °C in the absence of air, and a mixture of volatile products called *coal tar* boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and a host of other aromatic compounds (Figure 4.6.1).

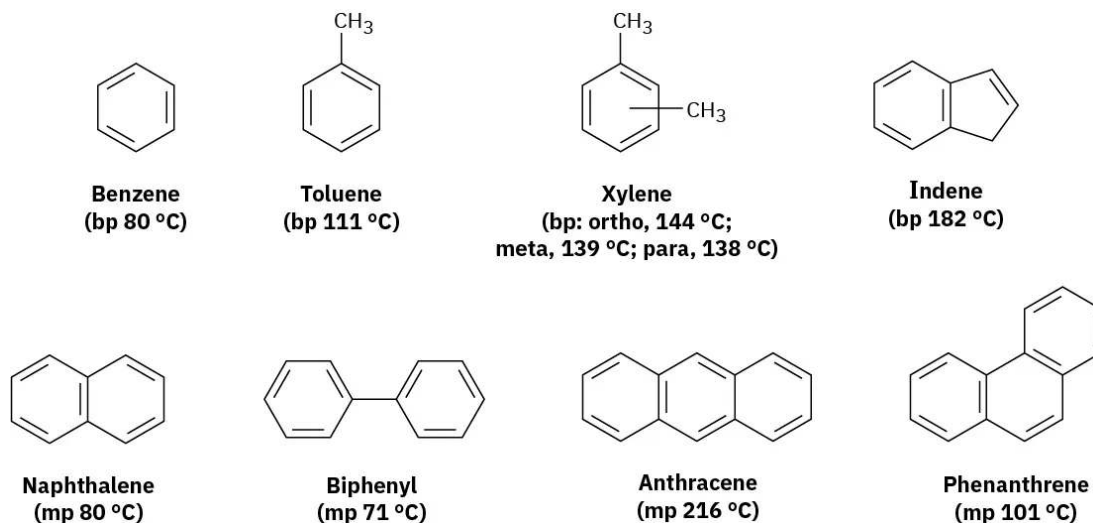
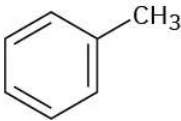
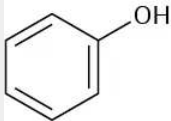
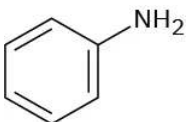
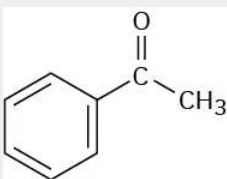
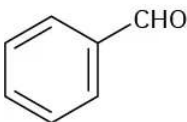
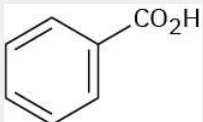
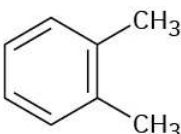
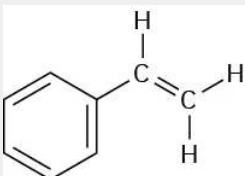


Figure 4.6.1: Some aromatic hydrocarbons found in coal tar.

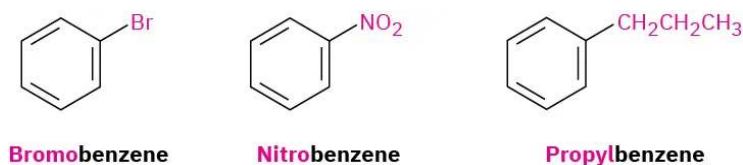
Unlike coal, petroleum contains few aromatic compounds and consists largely of alkanes (see Chapter 3 *Chemistry Matters*). During petroleum refining, however, aromatic molecules are formed when alkanes are passed over a catalyst at about 500 °C under high pressure.

Aromatic substances, more than any other class of organic compounds, have acquired a large number of nonsystematic names. IUPAC rules discourage the use of most such names but do allow some of the more widely used ones to be retained (Figure 4.6.1). Thus, methylbenzene is known commonly as *toluene*; hydroxybenzene as *phenol*; aminobenzene as *aniline*; and so on.

Figure 4.6.1 Common Names of Some Aromatic Compounds

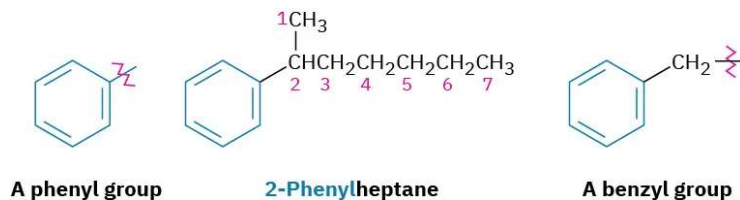
Structure	Name
	Toluene (bp 111 °C)
	Phenol (mp 43 °C)
	Aniline (bp 184 °C)
	Acetophenone (mp 21 °C)
	Benzaldehyde (bp 178 °C)
	Benzoic acid (mp 122 °C)
	<i>ortho</i> -Xylene (bp 144 °C)
	Styrene (bp 145 °C)

Monosubstituted benzenes are named systematically in the same manner as other hydrocarbons, with *-benzene* as the parent name. Thus, $\text{C}_6\text{H}_5\text{Br}$ is bromobenzene, $\text{C}_6\text{H}_5\text{NO}_2$ is nitrobenzene, and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ is propylbenzene.

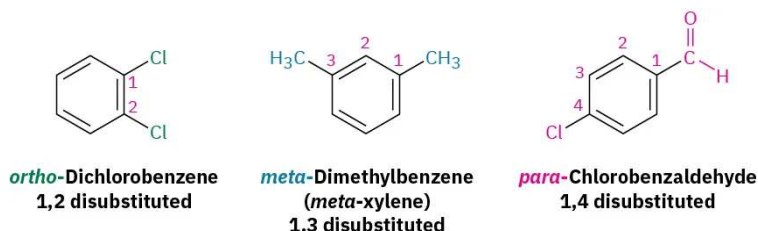


Alkyl-substituted benzenes are sometimes referred to as arenes and are named in different ways depending on the size of the alkyl group. If the alkyl substituent is smaller than the ring (six or fewer carbons), the arene is referred to as an alkyl-substituted benzene. If the alkyl substituent is larger than the ring (seven or more carbons), the compound is referred to as a phenyl-substituted alkane.

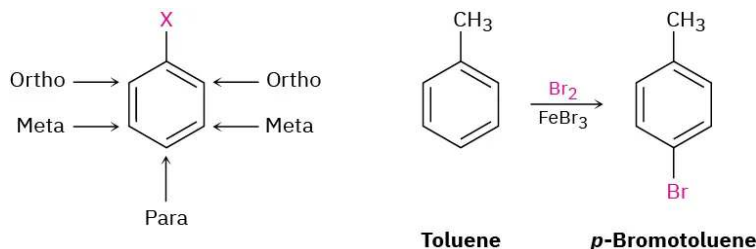
The name phenyl, pronounced **fen**-nil and sometimes abbreviated as Ph or Φ (Greek *phi*), is used for the $\text{-C}_6\text{H}_5$ unit when the benzene ring is considered a substituent. The word is derived from the Greek *pheno* ("I bear light"), commemorating the discovery of benzene by Michael Faraday in 1825 from the oily residue left by the illuminating gas used in London street lamps. In addition, the name benzyl is used for the $\text{C}_6\text{H}_5\text{CH}_2\text{-}$ group.



Disubstituted benzenes are named using the prefixes ortho (*o*), meta (*m*), or para (*p*). An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para-disubstituted benzene has its substituents in a 1,4 relationship.



The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, we might describe the reaction of bromine with toluene by saying, "Reaction occurs at the para position," meaning at the position para to the methyl group already present on the ring.



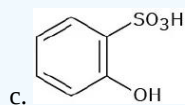
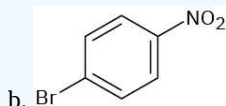
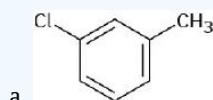
As with cycloalkanes (Section 4.1), benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found. The substituents are listed alphabetically when writing the name.



Note in the second and third examples shown that *-phenol* and *-toluene* are used as the parent names rather than *-benzene*. Any of the monosubstituted aromatic compounds shown in Figure 4.6.1 can serve as a parent name, with the principal substituent (-OH in phenol or -CH_3 in toluene) attached to C1 on the ring.

? Exercise 4.6.1

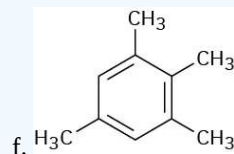
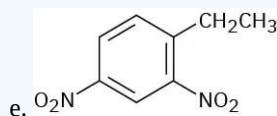
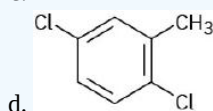
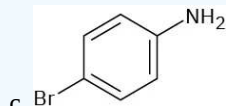
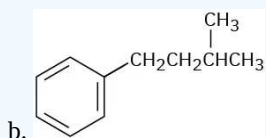
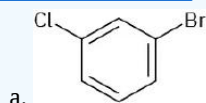
Tell whether the following compounds are ortho-, meta-, or para-disubstituted:



Answer

- a. Meta
- b. Para
- c. Ortho

? Exercise 4.6.2



Answer

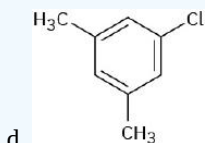
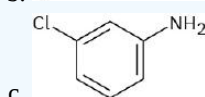
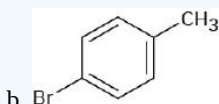
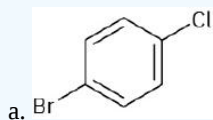
- a. m-Bromochlorobenzene
- b. (3-Methylbutyl)benzene
- c. p-Bromoaniline
- d. 2,5-Dichlorotoluene
- e. 1-Ethyl-2,4-dinitrobenzene
- f. 1,2,3,5-Tetramethylbenzene

? Exercise 4.6.3

Draw structures corresponding to the following IUPAC names:

- p-Bromochlorobenzene
- p-Bromotoluene
- m-Chloroaniline
- 1-Chloro-3,5-dimethylbenzene

Answer



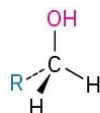
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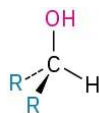
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4.7: Naming Alcohols and Phenols

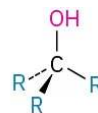
Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of organic groups bonded to the hydroxyl-bearing carbon.



A primary (1°) alcohol



A secondary (2°) alcohol



A tertiary (3°) alcohol

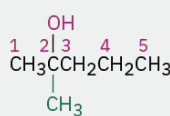
Simple alcohols are named in the IUPAC system as derivatives of the parent alkane, using the suffix *-ol*.

Alcohol Nomenclature

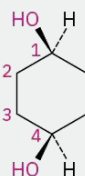
RULE 1: Select the longest carbon chain containing the hydroxyl group, and derive the parent name by replacing the *-e* ending of the corresponding alkane with *-ol*. The *-e* is deleted to prevent the occurrence of two adjacent vowels: propanol rather than propan*eo*l, for example.

RULE 2: Number the alkane chain beginning at the end nearer the hydroxyl group.

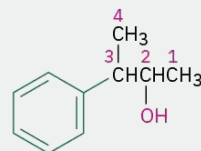
RULE 3: Number the substituents according to their position on the chain, and write the name, listing the substituents in alphabetical order and identifying the position to which the *-OH* is bonded. Note that in naming *cis*-1,4-cyclohexanediol, the final *-e* of cyclohexane is not deleted because the next letter, *d*, is not a vowel; that is, cyclohexanediol rather than cyclohexandiol. Also, as with alkenes (Section 7.3), newer IUPAC naming recommendations place the locant immediately before the suffix rather than before the parent.



2-Methyl-2-pentanol
(New: **2-Methylpentan-2-ol**)

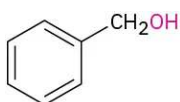


cis-1,4-Cyclohexanediol
(New: **cis-Cyclohexane-1,4-diol**)



3-Phenyl-2-butanol
(New: **3-Phenylbutan-2-ol**)

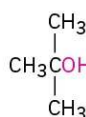
Some simple and widely occurring alcohols have common names that are accepted by IUPAC. For example:



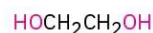
Benzyl alcohol
(phenylmethanol)



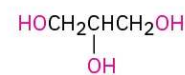
Allyl alcohol
(2-propen-1-ol)



tert-Butyl alcohol
(2-methyl-2-propanol)

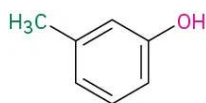


Ethylene glycol
(1,2-ethanediol)

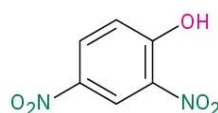


Glycerol
(1,2,3-propanetriol)

Phenols are named as described previously for aromatic compounds according to the rules discussed in Section 15.1, with *-phenol* used as the parent name rather than *-benzene*.



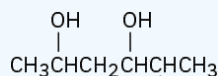
m-Methylphenol
(*m*-Cresol)

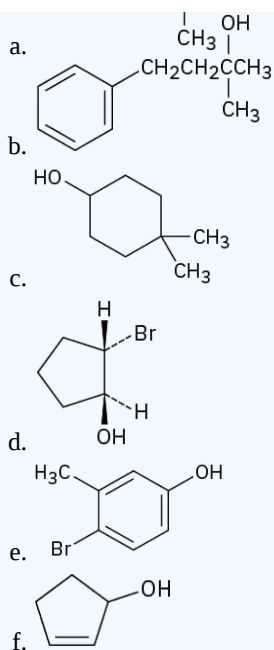


2,4-Dinitrophenol

? Exercise 4.7.1

Give IUPAC names for the following compounds:





Answer

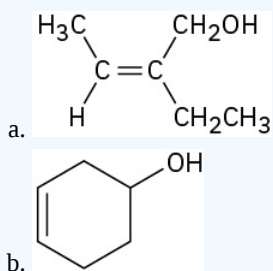
- 5-Methyl-2,4-hexanediol
- 2-Methyl-4-phenyl-2-butanol
- 4,4-Dimethylcyclohexanol
- trans*-2-Bromocyclopentanol
- 4-Bromo-3-methylphenol
- 2-Cyclopenten-1-ol

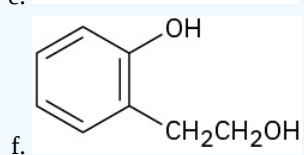
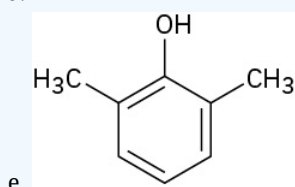
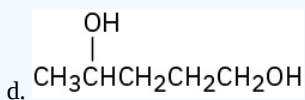
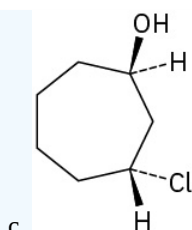
? Exercise 4.7.2

Draw structures corresponding to the following IUPAC names:

- (*Z*)-2-Ethyl-2-buten-1-ol
- 3-Cyclohexen-1-ol
- trans*-3-Chlorocycloheptanol
- 1,4-Pentanediol
- 2,6-Dimethylphenol
- o*-(2-Hydroxyethyl)phenol

Answer



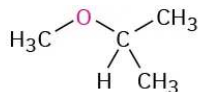


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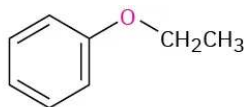
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4.8: Names and Properties of Ethers

Simple ethers with no other functional groups are named by identifying the two organic substituents and adding the word *ether*.

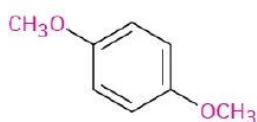


Isopropyl methyl ether

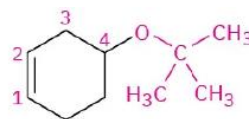


Ethyl phenyl ether

If other functional groups are present, the ether part is considered an *alkoxy* substituent. For example:

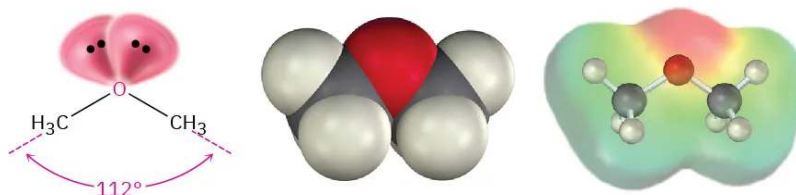


***p*-Dimethoxybenzene**



4-*tert*-Butoxy-1-cyclohexene

Like alcohols, ethers have nearly the same geometry as water. The R–O–R bonds have an approximately tetrahedral bond angle (112° in dimethyl ether), and the oxygen atom is sp^3 -hybridized.



The electronegative oxygen atom gives ethers a slight dipole moment, and the boiling points of ethers are often slightly higher than the boiling points of comparable alkanes. Table 4.8.1 compares the boiling points of some common ethers and their corresponding hydrocarbons.

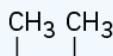
Table 4.8.1: Comparison of Boiling Points of Ethers and Hydrocarbons

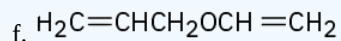
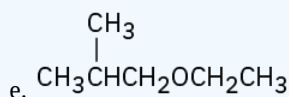
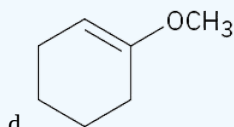
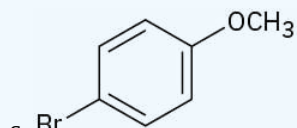
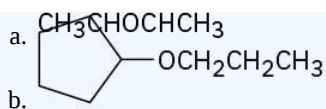
Ether	Boiling point °C	Hydrocarbon	Boiling point °C
CH_3OCH_3	–25	$\text{CH}_3\text{CH}_2\text{CH}_3$	–45
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	34.6	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	36
	65		49
	158		136

Ethers are relatively stable and unreactive in many respects, but some ethers react slowly with the oxygen in air to give *peroxides*, compounds that contain an O–O bond. The peroxides from low-molecular-weight ethers such as diisopropyl ether and tetrahydrofuran are explosive and extremely dangerous, even in small amounts. Ethers are very useful as solvents in the laboratory, but they must always be used cautiously and should not be stored for long periods of time.

? Exercise 4.8.1

Name the following ethers:





Answer

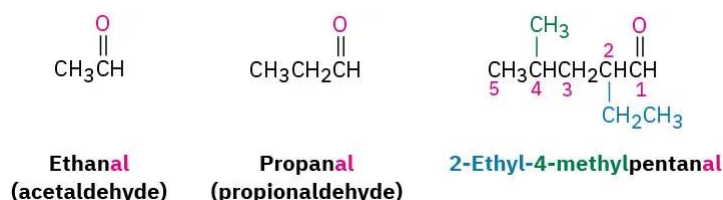
- Diisopropyl ether
- Cyclopentyl propyl ether
- p*-Bromoanisole or 4-bromo-1-methoxybenzene
- 1-Methoxycyclohexene
- Ethyl isobutyl ether
- Allyl vinyl ether

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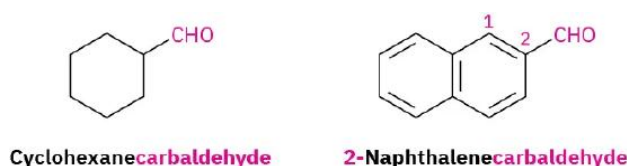
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4.9: Naming Aldehydes and Ketones

Aldehydes are named by replacing the terminal *-e* of the corresponding alkane name with *-al*. The parent chain must contain the -CHO group, and the -CHO carbon is numbered as carbon 1. Note in the following examples that the longest chain in 2-ethyl-4-methylpentanal is actually a hexane, but this chain does not include the -CHO group and thus is not the parent.

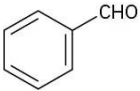


For cyclic aldehydes in which the -CHO group is directly attached to a ring, the ring name followed by *carbaldehyde* is used.

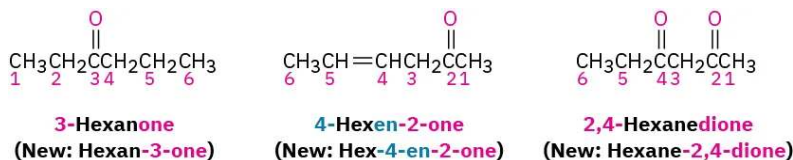


A few simple and well-known aldehydes have common names that are recognized by IUPAC. Several that you might encounter are listed in Table 4.9.1.

Table 4.9.1: Common Names of Some Simple Aldehydes

Formula	Common name	Systematic name
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
$\text{H}_2\text{C=CHCHO}$	Acrolein	Propenal
$\text{CH}_3\text{CH=CHCHO}$	Crotonaldehyde	2-Butenal
	Benzaldehyde	Benzenecarbaldehyde

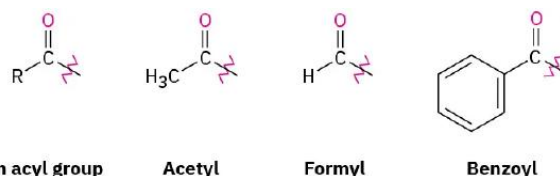
Ketones are named by replacing the terminal *-e* of the corresponding alkane name with *-one*. The parent chain is the longest one that includes the ketone group, and the numbering begins at the end nearer the carbonyl carbon. As with alkenes (Section 7.3) and alcohols (Section 17.1), the locant is placed before the parent name using older rules but before the suffix with the newer IUPAC guidelines. For example:



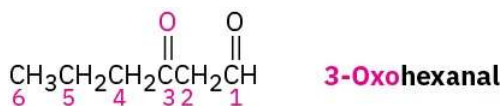
A few ketones are allowed by IUPAC to retain their common names.



When it's necessary to refer to the R-C=O group as a substituent, the name acyl (a-sil) group is used and the name ending *-yl* is attached. Thus, -COCH_3 is an *acetyl* group, -CHO is a *formyl* group, -COAr is an *aroyl* group, and $\text{-COC}_6\text{H}_5$ is a *benzoyl* group.

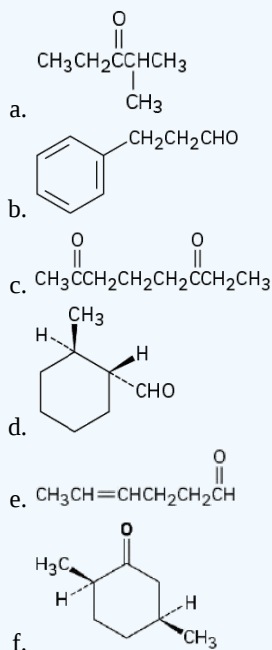


If other functional groups are present and the double-bonded oxygen is considered a substituent on a parent chain, the prefix *oxo-* is used. For example:



? Exercise 4.9.1

Name the following aldehydes and ketones:



Answer

- 2-Methyl-3-pentanone
- 3-Phenylpropanal
- 2,6-Octanedione
- trans-2-Methylcyclohexanecarbaldehyde
- 4-Hexenal
- cis-2,5-Dimethylcyclohexanone

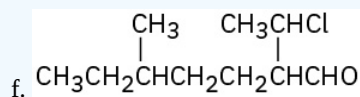
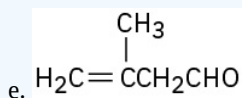
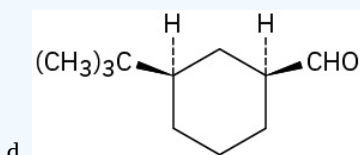
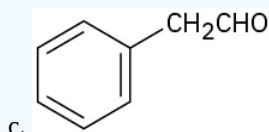
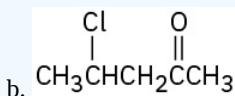
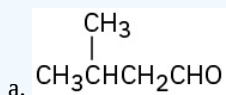
? Exercise 4.9.2

Draw structures corresponding to the following names:

- 3-Methylbutanal
- 4-Chloro-2-pentanone
- Phenylacetaldehyde
- cis-3-tert-Butylcyclohexanecarbaldehyde
- 3-Methyl-3-butenal

f. 2-(1-Chloroethyl)-5-methylheptanal

Answer



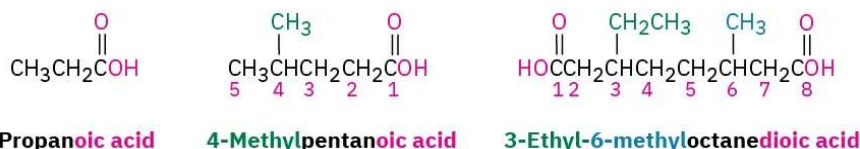
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4.10: Naming Carboxylic Acids and Nitriles

Carboxylic Acids, RCO_2H

Simple carboxylic acids derived from open-chain alkanes are systematically named by replacing the terminal $-e$ of the corresponding alkane name with $-oic\ acid$. The $-\text{CO}_2\text{H}$ carbon atom is numbered C1.



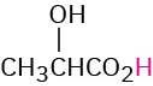
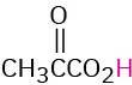
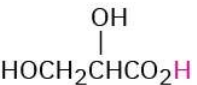
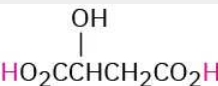
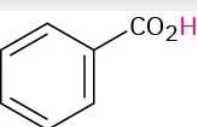
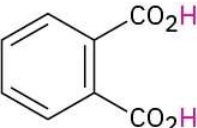
Compounds that have a $-\text{CO}_2\text{H}$ group bonded to a ring are named using the suffix $-carboxylic\ acid$. The CO_2H carbon is attached to C1 in this system and is not itself numbered. As a substituent, the CO_2H group is called a carboxyl group.



Because many carboxylic acids were among the first organic compounds to be isolated and purified, quite a few common names exist (Table 4.10.1). Biological chemists, in particular, make frequent use of these names, so you may find yourself referring back to this list on occasion. We'll use systematic names in this book, with a few exceptions such as formic (methanoic) acid and acetic (ethanoic) acid, whose names are accepted by IUPAC and are so well known that it makes little sense to refer to them any other way.

Also listed in Table 4.10.1 are the names of acyl groups $\left(\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\right)$ derived from the parent acids. Except for the eight entries at the top of Table 4.10.1, whose names have a $-yl$ ending, all other acyl groups are named using an $-oyl$ ending.

Table 4.10.1 Common Names of Some Carboxylic Acids and Acyl Groups

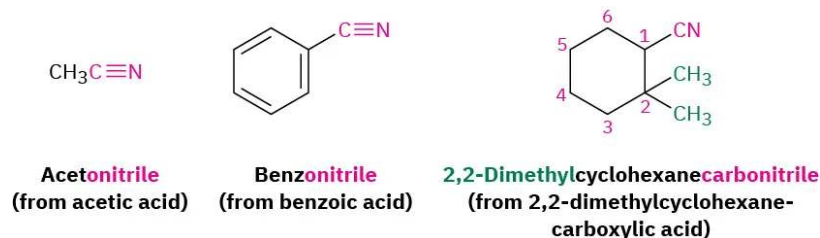
Structure	Name	Acyl group
HCO_2H	Formic	Formyl
$\text{CH}_3\text{CO}_2\text{H}$	Acetic	Acetyl
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	Propionic	Propionyl
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	Butyric	Butyryl
$\text{HO}_2\text{CCO}_2\text{H}$	Oxalic	Oxalyl
$\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$	Malonic	Malonyl
$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$	Succinic	Succinyl
$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	Glutaric	Glutaryl
$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	Adipic	Adipoyl
$\text{H}_2\text{C}=\text{CHCO}_2\text{H}$	Acrylic	Acryloyl
$\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$	Maleic (cis) Fumaric (trans)	Maleoyl Fumaroyl
$\text{HOCH}_2\text{CO}_2\text{H}$	Glycolic	Glycoloyl
	Lactic	Lactoyl
	Pyruvic	Pyruvoyl
	Glyceric	Glyceroyl
	Malic	Maloyl
	Oxaloacetic	Oxaloacetyl
	Benzoic	Benzoyl
	Phthalic	Phthaloyl

Nitriles, $\text{RC}\equiv\text{N}$

Compounds containing the $\text{-C}\equiv\text{N}$ functional group are called nitriles and can undergo some chemistry similar to that of carboxylic acids. Simple open-chain nitriles are named by adding *-nitrile* as a suffix to the alkane name, with the nitrile carbon numbered C1.



Nitriles can also be named as derivatives of carboxylic acids by replacing the *-ic acid* or *-oic acid* ending with *-onitrile*, or by replacing the *-carboxylic acid* ending with *-carbonitrile*. The nitrile carbon atom is attached to C1 but is not itself numbered.

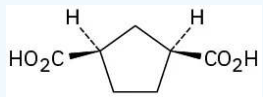


If another carboxylic acid derivative is present in the same molecule, the prefix *ciano-* is used for the $\text{C}\equiv\text{N}$ group.



? Exercise 4.10.1

Give IUPAC names for the following compounds:

- $\begin{array}{c} \text{CH}_3 \quad \text{O} \\ | \quad || \\ \text{CH}_3\text{CHCH}_2\text{COH} \end{array}$
- $\begin{array}{c} \text{Br} \quad \text{O} \\ | \quad || \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{COH} \end{array}$
- $\begin{array}{c} \text{CO}_2\text{H} \\ | \\ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \end{array}$
- $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_3\text{C} \quad \text{CH}_2\text{CH}_2\text{COH} \end{array}$
- $\begin{array}{c} \text{CH}_3 \quad \text{CN} \\ | \quad | \\ \text{CH}_3\text{CHCH}_2\text{CHCH}_3 \end{array}$
- 

Answer

- 3-Methylbutanoic acid
- 4-Bromopentanoic acid
- 2-Ethylpentanoic acid
- cis-4-Hexenoic acid
- 2,4-Dimethylpentanenitrile
- cis-1,3-Cyclopentanedicarboxylic acid

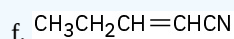
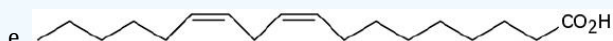
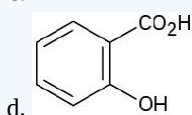
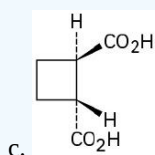
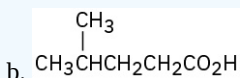
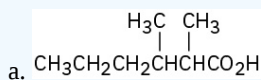
? Exercise 4.10.2

Draw structures corresponding to the following IUPAC names:

- 2,3-Dimethylhexanoic acid
- 4-Methylpentanoic acid

- c. trans-1,2-Cyclobutanedicarboxylic acid
- d. o-Hydroxybenzoic acid
- e. (9Z,12Z)-9,12-Octadecadienoic acid
- f. 2-Pentenitrile

Answer



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CHAPTER OVERVIEW

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5.1: Functional Groups and Physical Properties

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5.1.1: Polar Covalent Bonds - Electronegativity

Up to this point, we've treated chemical bonds as either ionic or covalent. The bond in sodium chloride, for instance, is ionic. Sodium transfers an electron to chlorine to produce Na^+ and Cl^- ions, which are held together in the solid by electrostatic attractions between unlike charges. The C–C bond in ethane, however, is covalent. The two bonding electrons are shared equally by the two equivalent carbon atoms, resulting in a symmetrical electron distribution in the bond. Most bonds, however, are neither fully ionic nor fully covalent but are somewhere between the two extremes. Such bonds are called polar covalent bonds, meaning that the bonding electrons are attracted more strongly by one atom than the other so that the electron distribution between atoms is not symmetrical (Figure 5.1.1.1).

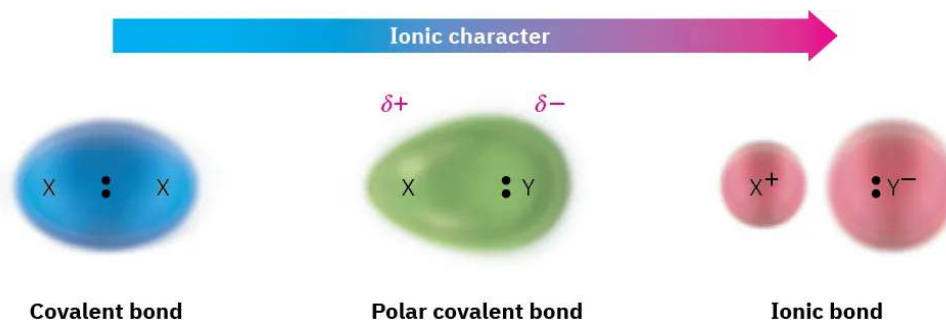


Figure 5.1.1.1: The continuum in bonding from covalent to ionic is a result of an unequal distribution of bonding electrons between atoms.

The symbol δ (lowercase Greek letter delta) means *partial* charge, either partial positive (δ^+) for the electron-poor atom or partial negative (δ^-) for the electron-rich atom.

Bond polarity is due to differences in electronegativity (EN), the intrinsic ability of an atom to attract the shared electrons in a covalent bond. As shown in Figure 5.1.1.2, electronegativities are based on an arbitrary scale, with fluorine the most electronegative (EN = 4.0) and cesium the least (EN = 0.7). Metals on the left side of the periodic table attract electrons weakly and have lower electronegativities, while oxygen, nitrogen, and halogens on the right side of the periodic table attract electrons strongly and have higher electronegativities. Carbon, the most important element in organic compounds, has an intermediate electronegativity value of 2.5.

H 2.1																	He
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1	Rn

Figure 5.1.1.2 Electronegativity values and trends. Electronegativity generally increases from left to right across the periodic table and decreases from top to bottom. The values are on an arbitrary scale, with F = 4.0 and Cs = 0.7. Elements in **red** are the most electronegative, those in **yellow** are medium, and those in **green** are the least electronegative.

As a rough guide, bonds between atoms whose electronegativities differ by less than 0.5 are nonpolar covalent, bonds between atoms whose electronegativities differ by 0.5 to 2 are polar covalent, and bonds between atoms whose electronegativities differ by more than 2 are largely ionic. Carbon–hydrogen bonds, for example, are relatively nonpolar because carbon (EN = 2.5) and hydrogen (EN = 2.1) have similar electronegativities. Bonds between carbon and more electronegative elements such as oxygen (EN = 3.5) and nitrogen (EN = 3.0), by contrast, are polarized so that the bonding electrons are drawn away from carbon toward the electronegative atom. This leaves carbon with a partial positive charge, δ^+ , and the electronegative atom with a partial negative charge, δ^- . An example is the C–O bond in methanol, CH_3OH (Figure 5.1.1.3a). Bonds between carbon and less electronegative elements are polarized so that carbon bears a partial negative charge and the other atom bears a partial positive charge. An example is the C–Li bond in methyllithium, CH_3Li (Figure 5.1.1.3b).

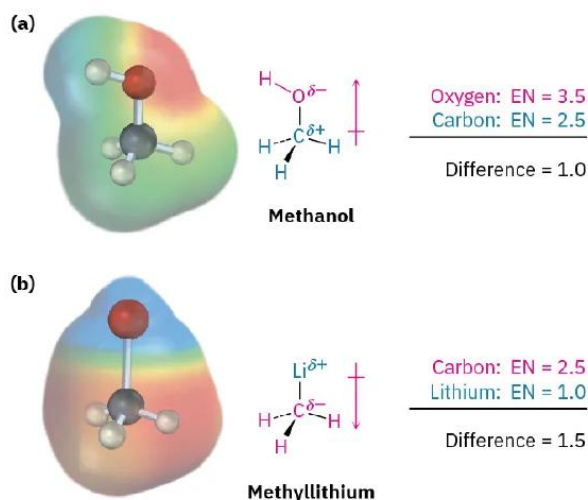


Figure 5.1.1.3: Polar covalent bonds. (a) Methanol, CH_3OH , has a polar covalent C–O bond, and (b) methyllithium, CH_3Li , has a polar covalent C–Li bond. The computer-generated representations, called electrostatic potential maps, use color to show calculated charge distributions, ranging from **red (electron-rich; δ^-)** to **blue (electron-poor; δ^+)**.

Note in the representations of methanol and methyllithium in Figure 5.1.1.3 that a crossed arrow $\longleftrightarrow$ is used to indicate the direction of bond polarity. By convention, electrons are displaced in the direction of the arrow. The tail of the arrow (which looks like a plus sign) is electron-poor (δ^+), and the head of the arrow is electron-rich (δ^-).

Note also in Figure 5.1.1.3 that calculated charge distributions in molecules can be displayed visually with what are called electrostatic potential maps, which use color to indicate electron-rich (red; δ^-) and electron-poor (blue; δ^+) regions. In methanol, oxygen carries a partial negative charge and is colored red, while the carbon and hydrogen atoms carry partial positive charges and are colored blue-green. In methyllithium, lithium carries a partial positive charge (blue), while carbon and the hydrogen atoms carry partial negative charges (red). Electrostatic potential maps are useful because they show at a glance the electron-rich and electron-poor atoms in molecules. We'll make frequent use of these maps throughout the text and will see many examples of how electronic structure correlates with chemical reactivity.

When speaking of an atom's ability to polarize a bond, we often use the term *inductive effect*. An inductive effect is simply the shifting of electrons in a σ bond in response to the electronegativity of nearby atoms. Metals, such as lithium and magnesium, inductively donate electrons, whereas reactive nonmetals, such as oxygen and nitrogen, inductively withdraw electrons. Inductive effects play a major role in understanding chemical reactivity, and we'll use them many times throughout this text to explain a variety of chemical observations.

? Exercise 5.1.1.1

Which element in each of the following pairs is more electronegative?

- Li or H
- B or Br
- Cl or I
- C or H

Answer

- H
- Br
- Cl
- C

? Exercise 5.1.1.2

Use the δ^+/δ^- convention to indicate the direction of expected polarity for each of the bonds indicated.

- $\text{H}_3\text{C}-\text{Cl}$
- $\text{H}_3\text{C}-\text{NH}_2$
- $\text{H}_2\text{N}-\text{H}$
- $\text{H}_3\text{C}-\text{SH}$
- $\text{H}_3\text{C}-\text{MgBr}$
- $\text{H}_3\text{C}-\text{F}$

Answer

- $\text{H}_3\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{Cl}}$
- $\text{H}_3\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{N}}\text{H}_2$
- $\text{H}_2\overset{\delta-}{\text{N}}-\overset{\delta+}{\text{H}}$
- $\text{H}_3\text{C}-\text{SH}$ Carbon and sulfur have identical electronegativities.
- $\text{H}_3\overset{\delta}{\text{C}}-\overset{\delta+}{\text{Mg}}\text{Br}$
- $\text{H}_3\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{F}}$

? Exercise 5.1.1.3

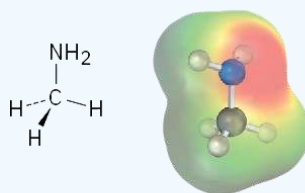
Use the electronegativity values shown in Figure 5.1.1.2 to rank the following bonds from least polar to most polar: $\text{H}_3\text{C}-\text{Li}$, $\text{H}_3\text{C}-\text{K}$, $\text{H}_3\text{C}-\text{F}$, $\text{H}_3\text{C}-\text{MgBr}$, $\text{H}_3\text{C}-\text{OH}$

Answer

$\text{H}_3\text{C}-\text{OH} < \text{H}_3\text{C}-\text{MgBr} < \text{H}_3\text{C}-\text{Li} = \text{H}_3\text{C}-\text{F} < \text{H}_3\text{C}-\text{K}$

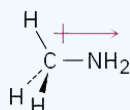
? Exercise 5.1.1.4

Look at the following electrostatic potential map of methylamine, a substance responsible for the odor of rotting fish, and tell the direction of polarization of the C-N bond:



Answer

The nitrogen is electron-rich, and the carbon is electron-poor.



- **2.1: Polar Covalent Bonds - Electronegativity** by OpenStax is licensed CC BY-NC-SA 4.0. Original source: <https://openstax.org/details/books/organic-chemistry>.

5.1.2: Polar Covalent Bonds - Dipole Moments

Just as individual bonds are often polar, molecules as a whole are often polar as well. Molecular polarity results from the vector summation of all individual bond polarities and lone-pair contributions in the molecule. As a practical matter, strongly polar substances are often soluble in polar solvents like water, whereas less polar substances are insoluble in water.

Net polarity is measured by a quantity called the *dipole moment* and can be thought of in the following way: assume that there is a center of mass of all positive charges (nuclei) in a molecule and a center of mass of all negative charges (electrons). If these two centers don't coincide, then the molecule has a net polarity.

The dipole moment, μ (lowercase Greek letter mu), is defined as the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges, $\mu = Q \times r$. Dipole moments are expressed in *debyes* (D), where $1 \text{ D} = 3.336 \times 10^{-30} \text{ coulomb meters (C} \cdot \text{m)}$ in SI units. For example, the unit charge on an electron is $1.60 \times 10^{-19} \text{ C}$. Thus, if one positive charge and one negative charge are separated by 100 pm (a bit less than the length of a typical covalent bond), the dipole moment is $1.60 \times 10^{-29} \text{ C} \cdot \text{m}$, or 4.80 D.

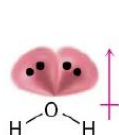
$$\mu = Q \times r$$

$$\mu = (1.60 \times 10^{-19} \text{ C}) (100 \times 10^{-12} \text{ m}) \left(\frac{1 \text{ D}}{3.336 \times 10^{-36} \text{ C} \cdot \text{m}} \right) = 4.80 \text{ D} \quad (5.1.2.1)$$

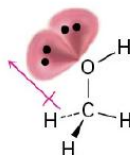
Dipole moments for some common substances are given in Table 5.1.2.1. Of the compounds shown in the table, sodium chloride has the largest dipole moment (9.00 D) because it is ionic. Even small molecules like water ($\mu = 1.85 \text{ D}$), methanol (CH_3OH ; $\mu = 1.70 \text{ D}$), and ammonia ($\mu = 1.47 \text{ D}$), have substantial dipole moments, however, both because they contain strongly electronegative atoms (oxygen and nitrogen) and because all three molecules have lone-pair electrons. The lone-pair electrons on oxygen and nitrogen stick out into space away from the positively charged nuclei, giving rise to a considerable charge separation and making a large contribution to the dipole moment.

Table 5.1.2.1: Dipole Moments of Some Compounds

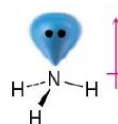
Compound	Dipole moment (D)	Compound	Dipole moment (D)
NaCl	9.00	NH ₃	1.47
CH ₂ O	2.33	CH ₃ NH ₂	1.31
CH ₃ Cl	1.87	CO ₂	0
H ₂ O	1.85	CH ₄	0
CH ₃ OH	1.70	CH ₃ CH ₃	0
CH ₃ CO ₂ H	1.70	 Benzene	0
CH ₃ SH	1.52		



Water
($\mu = 1.85 \text{ D}$)



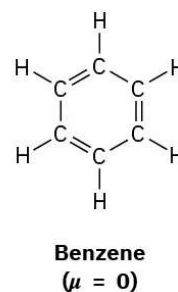
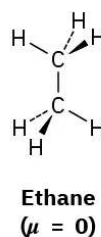
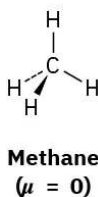
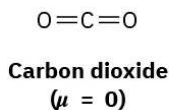
Methanol
($\mu = 1.70 \text{ D}$)



Ammonia
($\mu = 1.47 \text{ D}$)

In contrast with water, methanol, and ammonia, molecules such as carbon dioxide, methane, ethane, and benzene have zero dipole moments. Because of the symmetrical structures of these molecules, the individual bond polarities and lone-pair contributions

exactly cancel.



✓ Worked Example 5.1.2.1: Predicting the Direction of a Dipole Moment

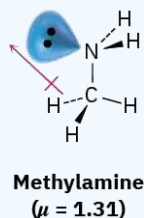
Make a three-dimensional drawing of methylamine, CH_3NH_2 , and show the direction of its dipole moment ($\mu = 1.31$).

Strategy

Look for any lone-pair electrons, and identify any atom with an electronegativity substantially different from that of carbon. (Usually, this means O, N, F, Cl, or Br.) Electron density will be displaced in the general direction of the electronegative atoms and the lone pairs.

Solution

Methylamine contains an electronegative nitrogen atom with a lone pair of electrons. The dipole moment thus points generally from $-\text{CH}_3$ toward the lone pair.

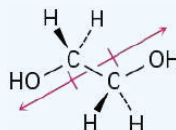


? Exercise 5.1.2.1

Ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, may look nonpolar when drawn, but an internal hydrogen bond between the two $-\text{OH}$ groups results in a dipole moment. Explain.

Answer

The two $\text{C}-\text{O}$ dipoles cancel because of the symmetry of the molecule:

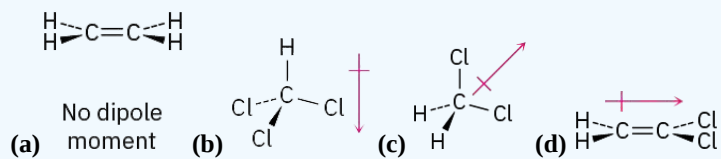


? Exercise 5.1.2.2

Make three-dimensional drawings of the following molecules, and predict whether each has a dipole moment. If you expect a dipole moment, show its direction.

- $\text{H}_2\text{C}=\text{CH}_2$
- CHCl_3
- CH_2Cl_2
- $\text{H}_2\text{C}=\text{CCl}_2$

Answer



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5.1.3: Functional Groups

The structural features that make it possible to classify compounds into families are called *functional groups*. A functional group is a group of atoms within a molecule that has a characteristic chemical behavior. Chemically, a given functional group behaves in nearly the same way in every molecule it's a part of. For example, compare ethylene, a plant hormone that causes fruit to ripen, with menthene, a much more complicated molecule found in peppermint oil. Both substances contain a carbon–carbon double-bond functional group, and both therefore react with Br_2 in the same way to give a product in which a Br atom has added to each of the double-bond carbons (Figure 5.1.3.1). This example is typical: *the chemistry of every organic molecule, regardless of size and complexity, is determined by the functional groups it contains.*

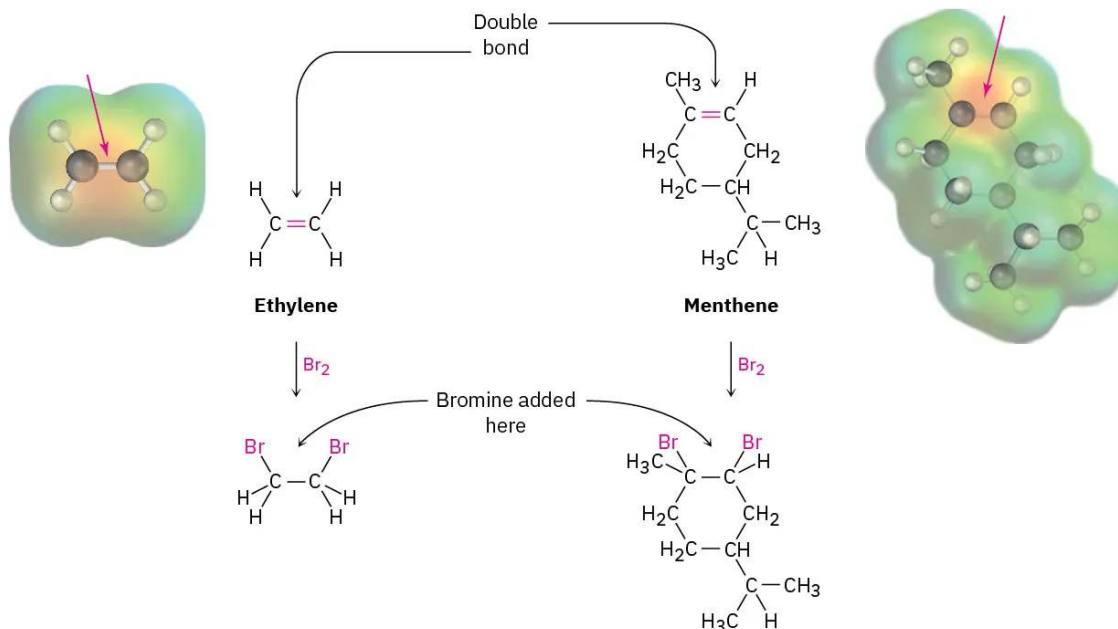


Figure 5.1.3.1: The reactions of ethylene and menthene with bromine. In both molecules, the carbon–carbon double-bond functional group has a similar polarity pattern, so both molecules react with Br_2 in the same way. The size and complexity of the molecules are not important.

Look at Table 5.1.3.1, which lists many of the common functional groups and gives simple examples of their occurrence. Some functional groups have only carbon–carbon double or triple bonds; others have halogen atoms; and still others contain oxygen, nitrogen, or sulfur. Much of the chemistry you'll be studying is the chemistry of these functional groups.

Functional Groups with Carbon–Carbon Multiple Bonds

Alkenes, alkynes, and arenes (aromatic compounds) all contain carbon–carbon multiple bonds. *Alkenes* have a double bond, *alkynes* have a triple bond, and *arenes* have alternating double and single bonds in a six-membered ring of carbon atoms. They look different, but because of their structural similarities, they also have chemical similarities.

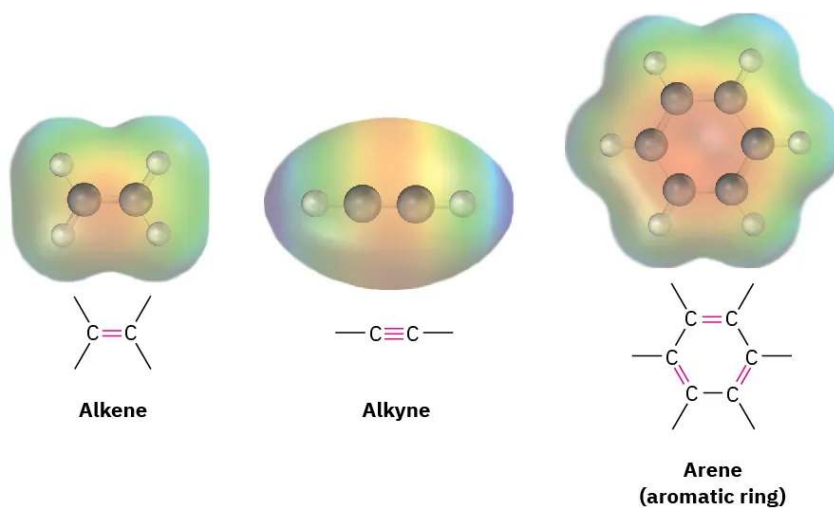
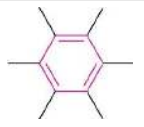
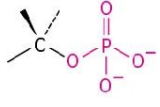
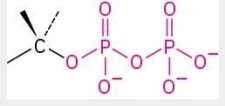
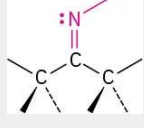
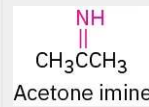
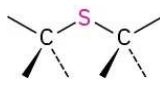
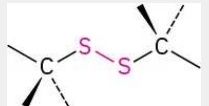
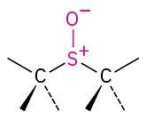
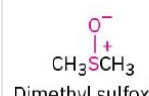
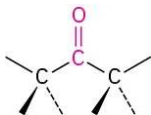
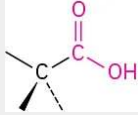
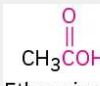
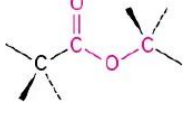
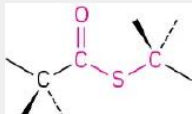
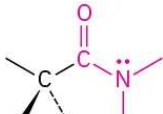
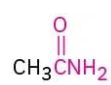
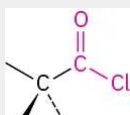
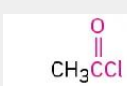
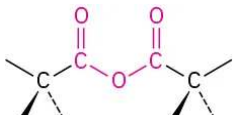


Table 5.1.3.1 Structures of Some Common Functional Groups

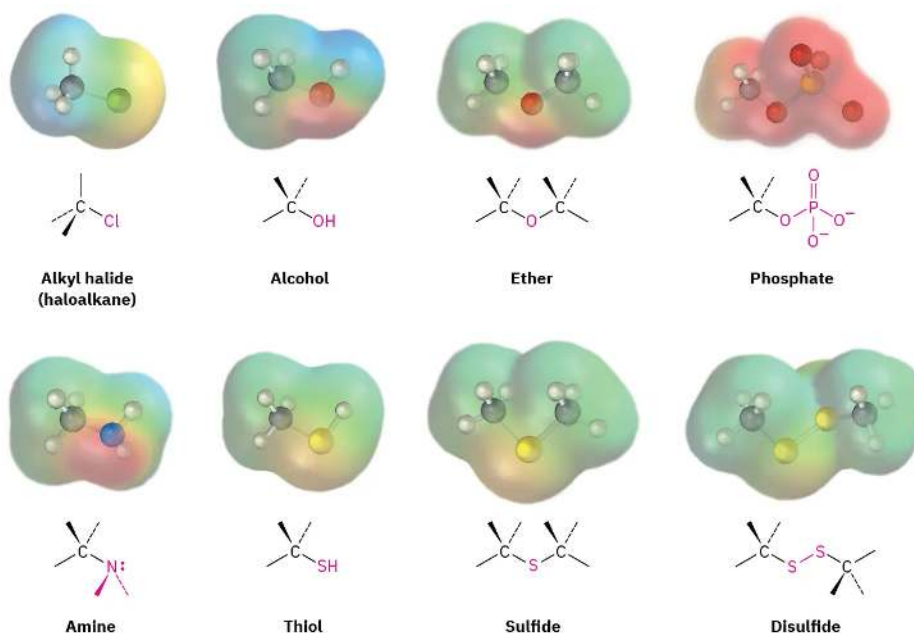
Name	Structure*	Name ending	Example
Alkene (double bond)		-ene	$\text{H}_2\text{C}=\text{CH}_2$ Ethene
Alkyne (triple bond)		-yne	$\text{HC}\equiv\text{CH}$ Ethyne
Arene (aromatic ring)		None	 Benzene
Halide	 (X=F, Cl, Br, I)	None	CH_3Cl Chloromethane
Alcohol		-ol	CH_3OH Methanol
Ether		ether	CH_3OCH_3 Dimethyl ether
Monophosphate		phosphate	$\text{CH}_3\text{OPO}_3^{2-}$ Methyl phosphate
Diphosphate		diphosphate	$\text{CH}_3\text{OP}_2\text{O}_6^{3-}$ Methyl diphosphate
Amine		-amine	CH_3NH_2 Methylamine
Imine (Schiff base)		None	 Acetone imine
Nitrile		-nitrile	$\text{CH}_3\text{C}\equiv\text{N}$ Ethanenitrile
Thiol		-thiol	CH_3SH Methanethiol
Sulfide		sulfide	CH_3SCH_3 Dimethyl sulfide
Disulfide		disulfide	CH_3SSCH_3 Dimethyl disulfide
Sulfoxide		sulfoxide	 Dimethyl sulfoxide

Name	Structure*	Name ending	Example
Aldehyde		-al	 Ethanal
Ketone		-one	 Propanone
Carboxylic acid		-oic acid	 Ethanoic acid
Ester		-oate	 Methyl ethanoate
Thioester		-thioate	 Methyl ethanethioate
Amide		-amide	 Ethanamide
Acid chloride		-oyl chloride	 Ethanoyl chloride
Carboxylic acid anhydride		-oic anhydride	 Ethanoic anhydride

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

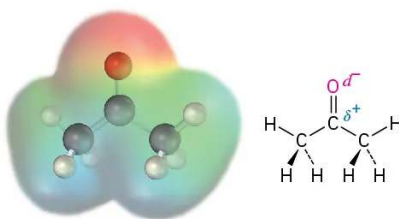
Functional Groups with Carbon Singly Bonded to an Electronegative Atom

Alkyl halides (haloalkanes), alcohols, ethers, alkyl phosphates, amines, thiols, sulfides, and disulfides all have a carbon atom singly bonded to an electronegative atom—halogen, oxygen, nitrogen, or sulfur. Alkyl halides have a carbon atom bonded to halogen ($-X$), alcohols have a carbon atom bonded to the oxygen of a hydroxyl group ($-OH$), ethers have two carbon atoms bonded to the same oxygen, organophosphates have a carbon atom bonded to the oxygen of a phosphate group ($-OPO_3^{2-}$), amines have a carbon atom bonded to a nitrogen, thiols have a carbon atom bonded to the sulfur of an $-SH$ group, sulfides have two carbon atoms bonded to the same sulfur, and disulfides have carbon atoms bonded to two sulfurs that are joined together. In all cases, the bonds are polar, with the carbon atom bearing a partial positive charge (δ^+) and the electronegative atom bearing a partial negative charge (δ^-).

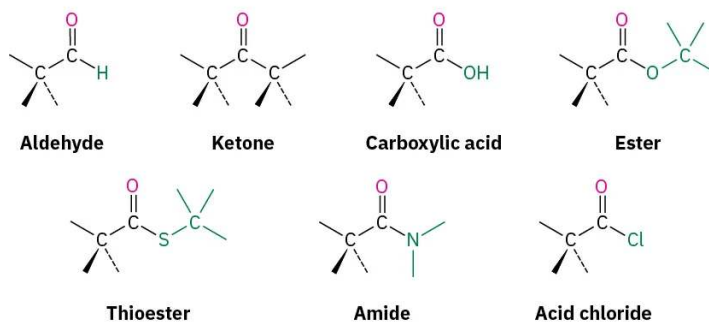


Functional Groups with a Carbon–Oxygen Double Bond (Carbonyl Groups)

The carbonyl group $\text{C}=\text{O}$ appears in several functional groups. Aldehydes have at least one H atom bonded to the $\text{C}=\text{O}$, ketones have two carbon atoms bonded to the $\text{C}=\text{O}$, carboxylic acids have an $-\text{OH}$ group bonded to the $\text{C}=\text{O}$, thioesters have a sulfide-like sulfur bonded to the $\text{C}=\text{O}$, amides have an amine-like nitrogen bonded to the $\text{C}=\text{O}$, acid chlorides have a chlorine bonded to the $\text{C}=\text{O}$, and so on. In all of these functional groups, the carbonyl carbon atom bears a partial positive charge (δ^+), and the oxygen atom bears a partial negative charge (δ^-).



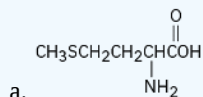
Acetone—a typical carbonyl compound



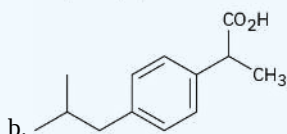
? Exercise 5.1.3.1

Use Table 5.1.3.1 to identify the functional groups in each of the following molecules:

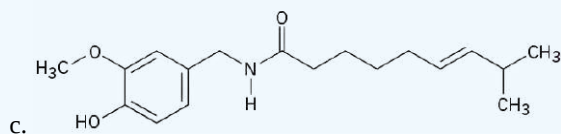
Methionine, an amino acid:



Ibuprofen, a pain reliever:



Capsaicin, the pungent substance in chili peppers:



Answer

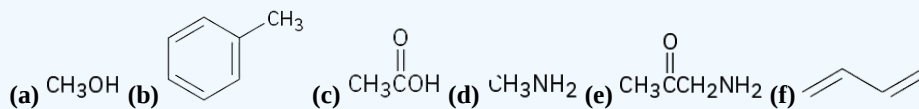
- Sulfide, carboxylic acid, amine
- Aromatic ring, carboxylic acid
- Ether, alcohol, aromatic ring, amide, C=C bond

? Exercise 5.1.3.2

Propose structures for simple molecules that contain the following functional groups:

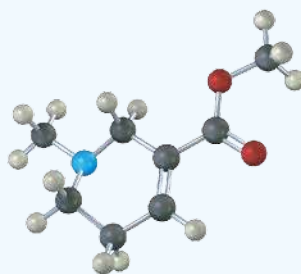
- Alcohol
- Aromatic ring
- Carboxylic acid
- Amine
- Both ketone and amine
- Two double bonds

Answer

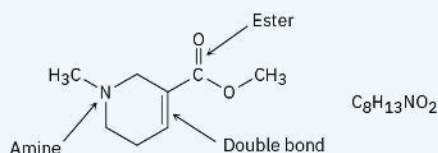


? Exercise 5.1.3.3

Identify the functional groups in the following model of arecoline, a veterinary drug used to control worms in animals. Convert the drawing into a line-bond structure and a molecular formula (red = O, blue = N, black = C, gray = H).



Answer



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5.1.4: Noncovalent Interactions Between Molecules

When thinking about chemical reactivity, chemists usually focus their attention on bonds, the covalent interactions between atoms within molecules. Also important, however, particularly in large biomolecules like proteins and nucleic acids, are a variety of interactions *between* molecules that strongly affect molecular properties. Collectively called either intermolecular forces, van der Waals forces, or noncovalent interactions, they are of several different types: dipole–dipole forces, dispersion forces, and hydrogen bonds.

Dipole–dipole forces occur between polar molecules as a result of electrostatic interactions among dipoles. The forces can be either attractive or repulsive depending on the orientation of the molecules—attractive when unlike charges are together and repulsive when like charges are together. The attractive geometry is lower in energy and therefore predominates (Figure 5.1.4.1).

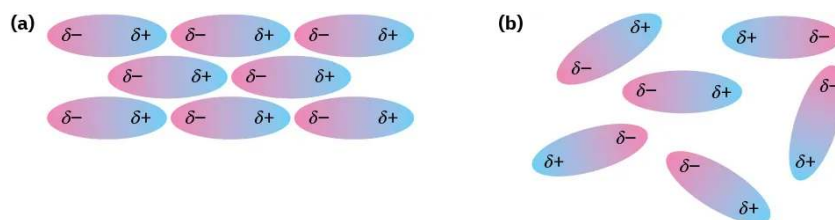


Figure 5.1.4.1: Dipole–dipole forces cause polar molecules (a) to attract one another when they orient with unlike charges together, but (b) to repel one another when they orient with like charges together.

Dispersion forces occur between all neighboring molecules and arise because the electron distribution within molecules is constantly changing. Although uniform on a time-averaged basis, the electron distribution even in nonpolar molecules is likely to be nonuniform at any given instant. One side of a molecule may, by chance, have a slight excess of electrons relative to the opposite side, giving the molecule a temporary dipole. This temporary dipole in one molecule causes a nearby molecule to adopt a temporarily opposite dipole, resulting in a tiny attraction between the two (Figure 5.1.4.2). Temporary molecular dipoles have only a fleeting existence and are constantly changing, but their cumulative effect is often strong enough to hold molecules close together so that a substance is a liquid or solid rather than a gas.

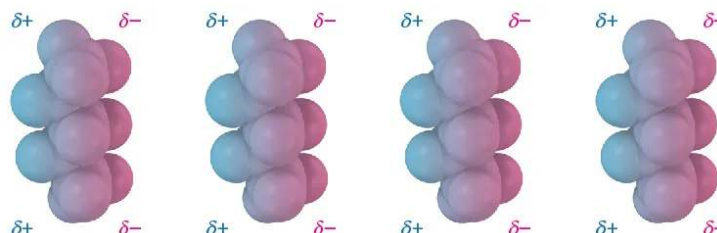
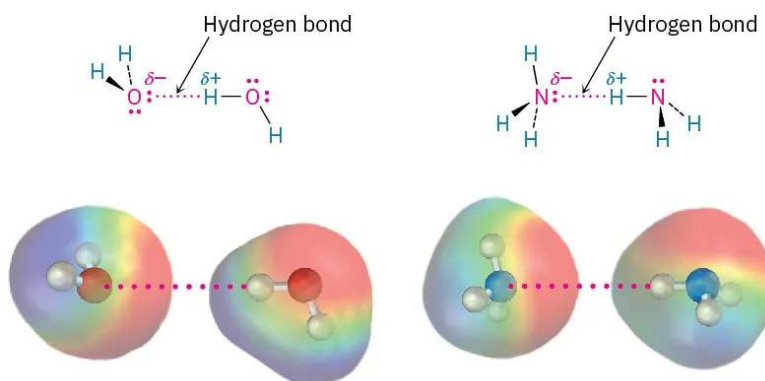
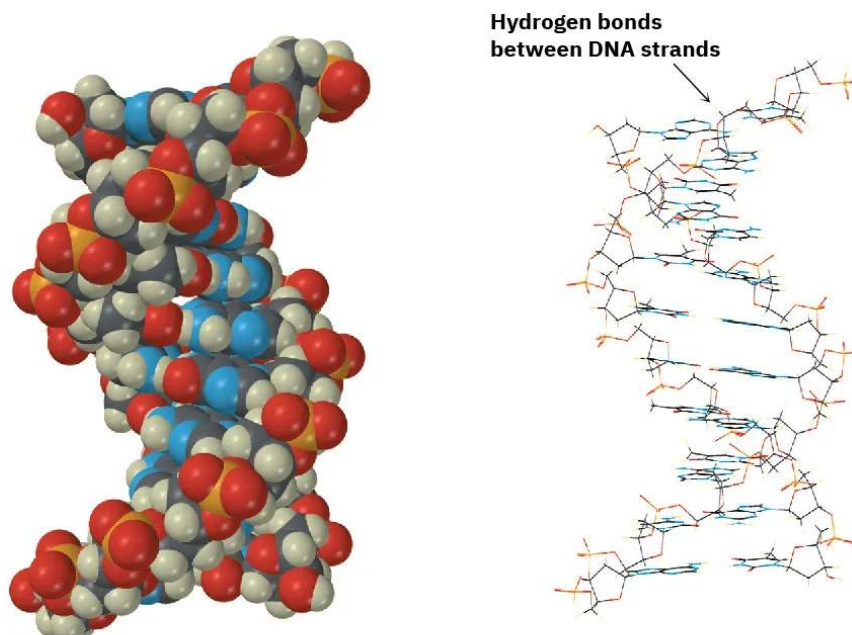


Figure 5.1.4.2: Attractive dispersion forces in nonpolar molecules are caused by temporary dipoles, as shown in these models of pentane, C_5H_{12} .

Perhaps the most important noncovalent interaction in biological molecules is the hydrogen bond, an attractive interaction between a hydrogen atom bonded to an electronegative O or N atom and an unshared electron pair on another O or N atom. In essence, a hydrogen bond is a very strong dipole–dipole interaction involving polarized O–H or N–H bonds. Electrostatic potential maps of water and ammonia clearly show the positively polarized hydrogens (blue) and the negatively polarized oxygens and nitrogens (red).

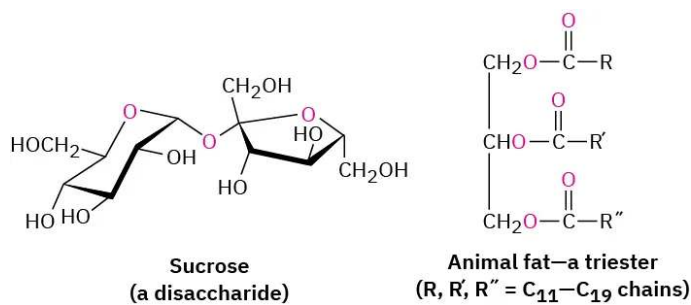


Hydrogen bonding has enormous consequences for living organisms. Hydrogen bonds cause water to be a liquid rather than a gas at ordinary temperatures, they hold enzymes in the shapes necessary for catalyzing biological reactions, and they cause strands of deoxyribonucleic acid (DNA) to pair up and coil into the double helix that stores genetic information.



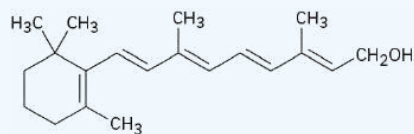
A deoxyribonucleic acid segment

One further point before leaving the subject of noncovalent interactions: biochemists frequently use the term hydrophilic, meaning “water-loving,” to describe a substance that is attracted to water and the term hydrophobic, meaning “water-fearing,” to describe a substance that is not strongly attracted to water. Hydrophilic substances, such as table sugar, often have a number of -OH groups in their structure so they can form hydrogen bonds and dissolve in water, whereas hydrophobic substances, such as vegetable oil, do not have groups that form hydrogen bonds and do not dissolve in water.

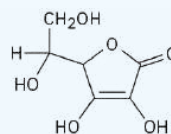


? Exercise 5.1.4.1

Of the two vitamins A and C, one is hydrophilic and water-soluble while the other is hydrophobic and fat-soluble. Which is which?



Vitamin A
(retinol)



Vitamin C
(ascorbic acid)

Answer

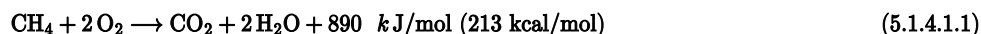
Vitamin C is water-soluble (hydrophilic); vitamin A is fat-soluble (hydrophobic).

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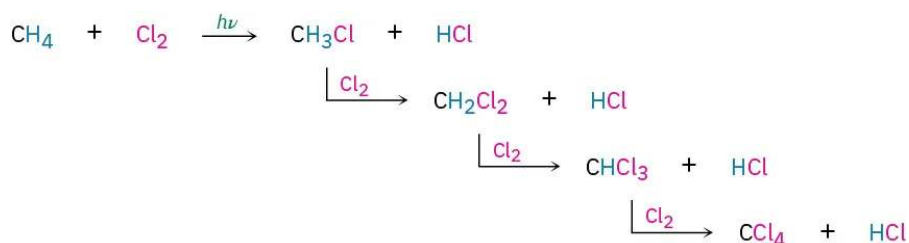
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5.1.4.1: Properties of Alkanes

Alkanes are sometimes referred to as *paraffins*, a word derived from the Latin *parum affinis*, meaning “little affinity.” This term aptly describes their behavior, for alkanes show little chemical affinity for other substances and are chemically inert to most laboratory reagents. They are also relatively inert biologically and are not often involved in the chemistry of living organisms. Alkanes do, however, react with oxygen, halogens, and a few other substances under appropriate conditions. Reaction with oxygen occurs during combustion in an engine or furnace when an alkane is used as a fuel. Carbon dioxide and water are formed as products, and a large amount of heat is released. For example, methane (natural gas) reacts with oxygen according to the equation



The reaction of an alkane with Cl_2 occurs when a mixture of the two is irradiated with ultraviolet light (denoted $h\nu$, where ν is the Greek letter *nu*). Depending on the time allowed and the relative amounts of the two reactants, a sequential substitution of the alkane hydrogen atoms by chlorine occurs, leading to a mixture of chlorinated products. Methane, for instance, reacts with Cl_2 to yield a mixture of CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 . We'll look at this reaction in more detail in **Section 6.7**.



Alkanes show regular increases in both boiling point and melting point as molecular weight increases (Figure 5.1.4.1.1), an effect due to the presence of weak dispersion forces between molecules (Section 2.13). Only when sufficient energy is applied to overcome these forces does the solid melt or liquid boil. As you might expect, dispersion forces increase as molecular size increases, accounting for the higher melting and boiling points of larger alkanes.

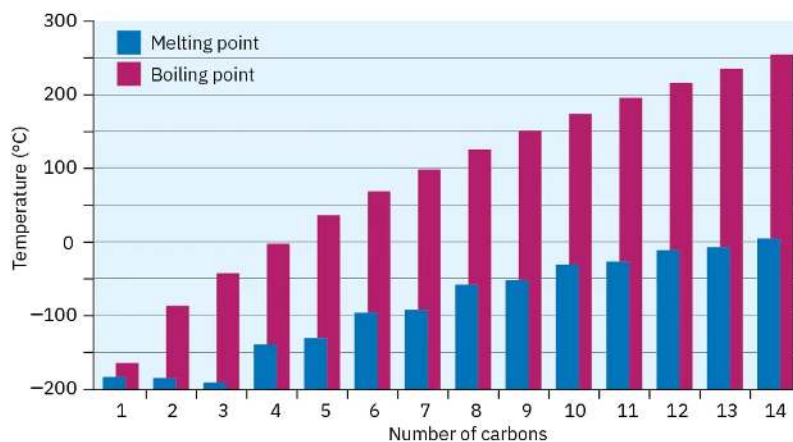


Figure 5.1.4.1.1: A plot of melting and boiling points versus number of carbon atoms for the C1–C14 straight-chain alkanes. There is a regular increase with molecular size.

Another effect seen in alkanes is that increased branching lowers an alkane's boiling point. Thus, pentane has no branches and boils at 36.1 °C, isopentane (2-methylbutane) has one branch and boils at 27.85 °C, and neopentane (2,2-dimethylpropane) has two branches and boils at 9.5 °C. Similarly, octane boils at 125.7 °C, whereas isooctane (2,2,4-trimethylpentane) boils at 99.3 °C. Branched-chain alkanes are lower-boiling because they are more nearly spherical than straight-chain alkanes, have smaller surface areas, and consequently have smaller dispersion forces.

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5.1.4.2: Why This Chapter?

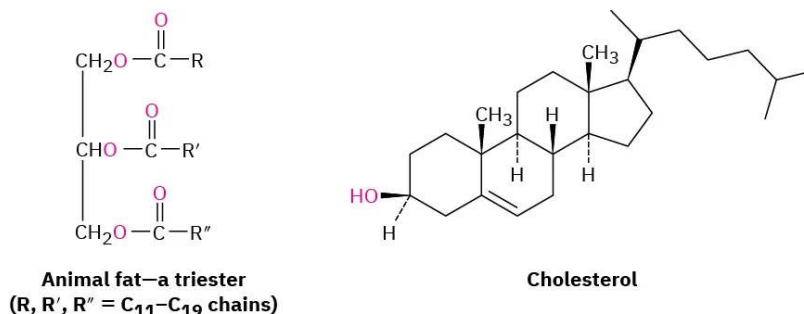
We've now covered two of the four major classes of biomolecules—proteins and carbohydrates—and have two remaining. In this chapter, we'll cover lipids, the largest and most diverse class of biomolecules, looking both at their structure and function and at their metabolism.



Figure 5.1.4.2.1: Soap bubbles, so common yet so beautiful, are made from animal fat, a lipid. (credit: "Reflections in soap bubbles" by Image Picture Photography/Flickr, CC BY 2.0)

Lipids are naturally occurring organic molecules that have limited solubility in water and can be isolated from organisms by extraction with nonpolar organic solvents. Fats, oils, waxes, many vitamins and hormones, and most nonprotein cell-membrane components are some examples. Note that this definition differs from the sort used for carbohydrates and proteins in that lipids are defined by a physical property (solubility) rather than by structure. Of the many kinds of lipids, we'll be concerned in this chapter with only a few: triacylglycerols, eicosanoids, terpenoids, and steroids.

Lipids are classified into two broad types: those like fats and waxes, which contain ester linkages and can be hydrolyzed, and those like cholesterol and other steroids, which don't have ester linkages and can't be hydrolyzed.

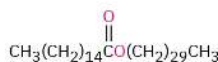


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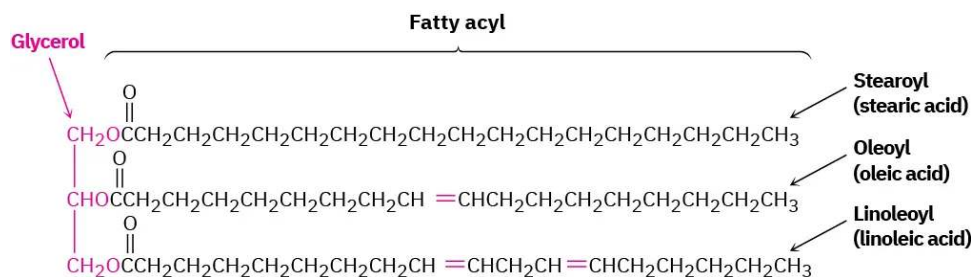
5.1.4.3: Waxes, Fats, and Oils

Waxes are mixtures of esters of long-chain carboxylic acids with long-chain alcohols. The carboxylic acid usually has an even number of carbons from 16 to 36, while the alcohol has an even number of carbons from 24 to 36. One of the major components of beeswax, for instance, is triacontyl hexadecanoate, the ester of the C_{30} alcohol (1-triacontanol) and the C_{16} acid (hexadecanoic acid). The waxy protective coatings on most fruits, berries, leaves, and animal furs have similar structures.



Triacontyl hexadecanoate (from beeswax)

Animal fats and vegetable oils are the most widely occurring lipids. Although they appear different—animal fats like butter and lard are solids, whereas vegetable oils like corn and peanut oil are liquid—their structures are closely related. Chemically, fats and oils are *triglycerides*, or triacylglycerols—triesters of glycerol with three long-chain carboxylic acids called fatty acids. Animals use fats for long-term energy storage because they are far less highly oxidized than carbohydrates and provide about six times as much energy as an equal weight of stored, hydrated glycogen.



A triacylglycerol

Hydrolysis of a fat or oil with aqueous NaOH yields glycerol and three fatty acids. The fatty acids are generally unbranched and contain an even number of carbon atoms between 12 and 20. If double bonds are present, they have mostly, although not entirely, Z, or cis, geometry. The three fatty acids of a specific triacylglycerol molecule need not be the same, and the fat or oil from a given source is likely to be a complex mixture of many different triacylglycerols. Table 5.1.4.3.1 lists some of the commonly occurring fatty acids, and Table 5.1.4.3.2 lists the approximate composition of fats and oils from different sources.

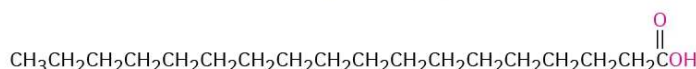
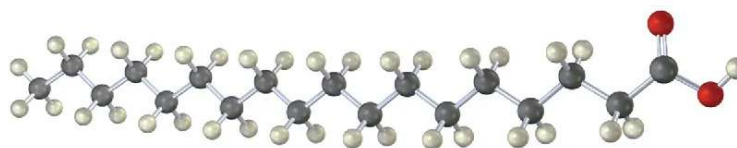
Table 5.1.4.3.1: Structures of Some Common Fatty Acids

Name	No. of carbons	Melting point (°C)	Structure
Saturated			
Lauric	12	43.2	$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$
Myristic	14	53.9	$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$
Palmitic	16	63.1	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$
Stearic	18	68.8	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$
Arachidic	20	76.5	$\text{CH}_3(\text{CH}_2)_{18}\text{CO}_2\text{H}$
Unsaturated			
Palmitoleic	16	−0.1	$(Z)\text{—CH}_3(\text{CH}_2)_5\text{CH=CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Oleic	18	13.4	$(Z)\text{—CH}_3(\text{CH}_2)_7\text{CH=CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
Linoleic	18	−12	$(Z, Z)\text{—CH}_3(\text{CH}_2)_4(\text{CH=CHCH}_2)_2(\text{CH}_2)_6\text{CO}_2\text{H}$
Linolenic	18	−11	$(\text{all } Z)\text{—CH}_3\text{CH}_2(\text{CH=CHCH}_2)_3(\text{CH}_2)_6\text{CO}_2\text{H}$
Arachidonic	20	−49.5	$(\text{all } Z)\text{—CH}_3(\text{CH}_2)_4(\text{CH=CHCH}_2)_4\text{CH}_2\text{CO}_2\text{H}$

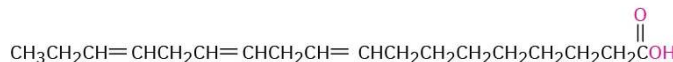
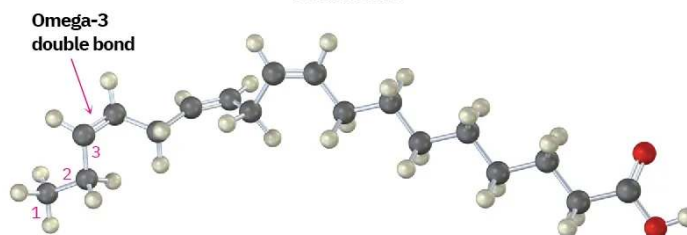
Table 5.1.4.3.2 Composition of Some Fats and Oils

Source	Saturated fatty acids (%)				Unsaturated fatty acids (%)	
	C ₁₂ lauric	C ₁₄ myristic	C ₁₆ palmitic	C ₁₈ stearic	C ₁₈ oleic	C ₁₈ linoleic
Animal fat						
Lard	—	1	25	15	50	6
Butter	2	10	25	10	25	5
Human fat	1	3	25	8	46	10
Whale blubber	—	8	12	3	35	10
Vegetable oil						
Coconut	50	18	8	2	6	1
Corn	—	1	10	4	35	45
Olive	—	1	5	5	80	7
Peanut	—	—	7	5	60	20

More than 100 different fatty acids are known and about 40 occur widely. Palmitic acid (C₁₆) and stearic acid (C₁₈) are the most abundant saturated fatty acids; oleic and linoleic acids (both C₁₈) are the most abundant unsaturated ones. Oleic acid is monounsaturated because it has only one double bond, whereas linoleic, linolenic, and arachidonic acids are polyunsaturated fatty acids because they have more than one double bond. Linoleic and linolenic acids occur in cream and are essential in the human diet; infants grow poorly and develop skin lesions if fed a diet of nonfat milk for prolonged periods. Linolenic acid, in particular, is an example of an omega-3 fatty acid, which has been found to lower blood triglyceride levels and reduce the risk of heart attack. The name omega-3 means that there is a double bond three carbons in from the noncarboxyl end of the chain.



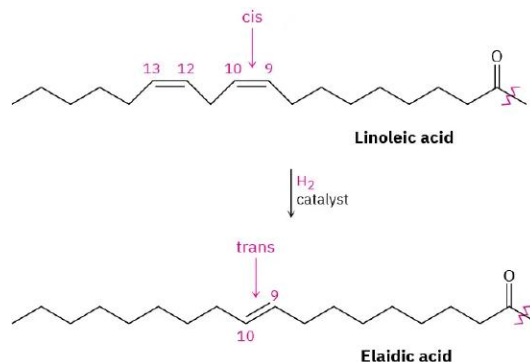
Stearic acid



Linolenic acid, an omega-3 polyunsaturated fatty acid

The data in Table 5.1.4.3.1 show that unsaturated fatty acids generally have lower melting points than their saturated counterparts, a trend that is also true for triacylglycerols. Since vegetable oils generally have a higher proportion of unsaturated to saturated fatty acids than animal fats (Table 5.1.4.3.2), they have lower melting points. The difference is a consequence of structure. Saturated fats have a uniform shape that allows them to pack together efficiently in a crystal lattice. In unsaturated vegetable oils, however, the C=C bonds introduce bends and kinks into the hydrocarbon chains, making crystal formation more difficult. The more double bonds there are, the harder it is for the molecules to crystallize, and the lower the melting point of the oil.

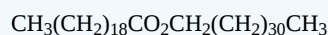
The C—C bonds in vegetable oils can be reduced by catalytic hydrogenation, typically carried out at high temperature using a nickel catalyst, to produce saturated solid or semisolid fats. Prior to 2015, industrially produced margarine and shortening were produced by hydrogenating soybean, peanut, or cottonseed oil until the proper consistency is obtained. As of 2015, trans fats are no longer considered safe by the FDA and have since been phased out of industrially produced foods. Unfortunately, the hydrogenation reaction is accompanied by some cis–trans isomerization of the remaining double bonds, producing fats with about 10% to 15% trans unsaturated fatty acids. Dietary intake of trans fatty acids increases cholesterol levels in the blood, thereby increasing the risk of heart problems. The conversion of linoleic acid into elaidic acid is an example.



? Exercise 5.1.4.3.1

Carnauba wax, used in floor and furniture polishes, contains an ester of a C_{32} straight-chain alcohol with a C_{20} straight-chain carboxylic acid. Draw its structure.

Answer



? Exercise 5.1.4.3.2

Draw structures of glyceryl tripalmitate and glyceryl trioleate. Which would you expect to have a higher melting point?

Answer

Glyceryl tripalmitate is higher melting.

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5.1.4.4: Soap

Soap has been in use for nearly 5000 years. As early as 2800 BC, the Babylonians boiled fats with ashes to create a soap-like substance. Ancient Egyptian medical papyri dating from 1550 BC reveals that Egyptians bathed regularly with soap made from a mixture of animal fats, vegetable oils, and alkaline salts. Chemically, soap is a mixture of the sodium or potassium salts of the long-chain fatty acids produced by hydrolysis (saponification) of animal fat with alkali. Wood ash was used as a source of alkali until the early 1800s, when the LeBlanc process for making Na_2CO_3 by heating sodium sulfate with limestone became available.



Crude soap curds contain glycerol and excess alkali as well as soap but can be purified by boiling with water and adding NaCl or KCl to precipitate the pure carboxylate salts. The smooth soap that precipitates is dried, perfumed, and pressed into bars for household use. Dyes are added to make colored soaps, antiseptics are added for medicated soaps, pumice is added for scouring soaps, and air is blown in for soaps that float. Regardless of these extra treatments and regardless of price, though, all soaps are basically the same.

Soaps act as cleansers because the two ends of a soap molecule are so different. The carboxylate end of the long-chain molecule is ionic and therefore hydrophilic (Section 2.12), or attracted to water. The long hydrocarbon portion of the molecule, however, is nonpolar and hydrophobic, avoiding water and therefore more soluble in oils. The net effect of these two opposing tendencies is that soaps are attracted to both oils and water and are therefore useful as cleansers.

When soaps are dispersed in water, the long hydrocarbon tails cluster together on the inside of a tangled, hydrophobic ball, while the ionic heads on the surface of the cluster protrude into the water layer. These spherical clusters, called micelles, are shown schematically in Figure 5.1.4.4.1. Grease and oil droplets are solubilized in water when they are coated by the nonpolar, hydrophobic tails of soap molecules in the center of micelles. Once solubilized, the grease and dirt can be rinsed away.

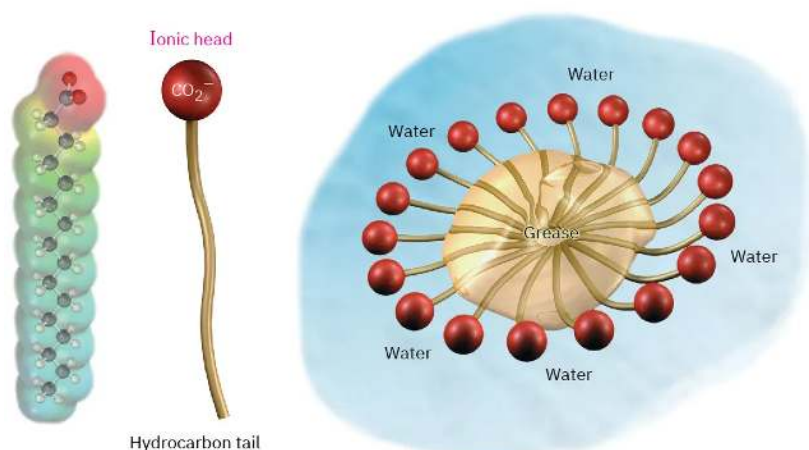
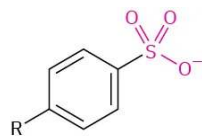


Figure 5.1.4.4.1: A soap micelle solubilizing a grease particle in water. An electrostatic potential map of a fatty acid carboxylate shows how the negative charge is located in the head group.

As useful as they are, soaps also have drawbacks. In hard water, which contains metal ions, soluble sodium carboxylates are converted into insoluble magnesium and calcium salts, leaving the familiar ring of scum around bathtubs and a gray tinge on white clothes. Chemists have circumvented this problem by synthesizing a class of synthetic detergents based on salts of long-chain

alkylbenzenesulfonic acids. The mechanism of synthetic detergents is the same as that of soaps: the alkylbenzene end of the molecule is attracted to grease, while the anionic sulfonate end is attracted to water. Unlike soaps, though, sulfonate detergents don't form insoluble metal salts in hard water and don't leave an unpleasant scum.

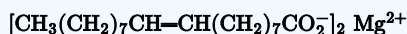


A synthetic detergent
(R = various C₁₂ chains)

? Exercise 5.1.4.4.1

Draw the structure of magnesium oleate, a component of bathtub scum.

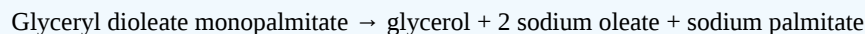
Answer



? Exercise 5.1.4.4.2

Write the saponification reaction of glyceryl dioleate monopalmitate with aqueous NaOH.

Answer



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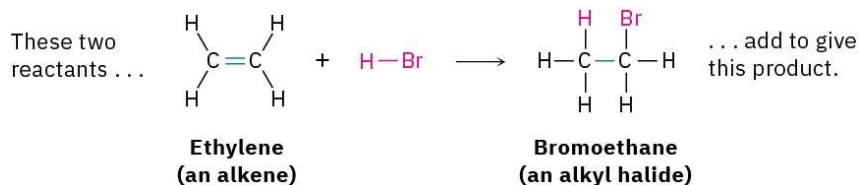
5.2: Reactions overview

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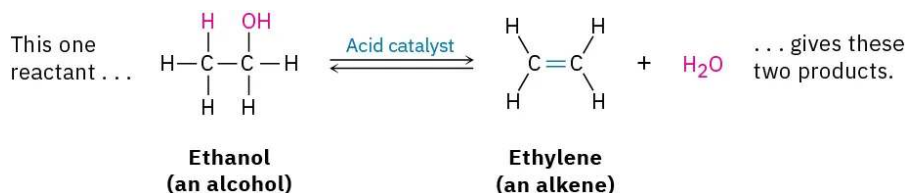
5.2.1: Kinds of Organic Reactions

Organic chemical reactions can be organized broadly in two ways—by what kinds of reactions occur and by how those reactions occur. Let's look first at the kinds of reactions that take place. There are four general types of organic reactions: *additions*, *eliminations*, *substitutions*, and *rearrangements*.

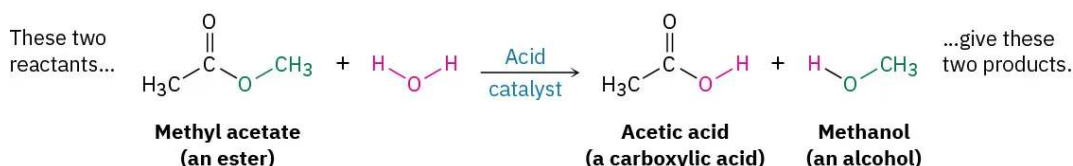
- Addition reactions occur when two reactants add together to form a single product with no atoms “left over.” An example that we'll be studying soon is the reaction of an alkene, such as ethylene, with HBr to yield an alkyl bromide.



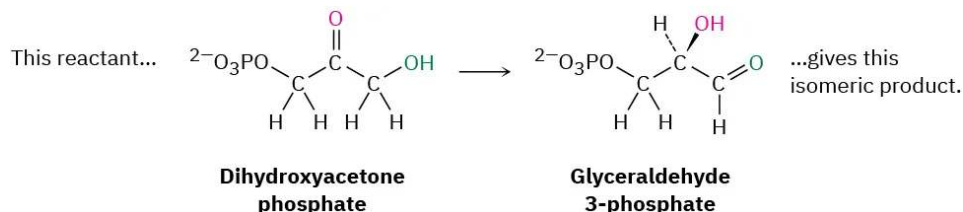
- Elimination reactions are, in a sense, the opposite of addition reactions. They occur when a single reactant splits into two products, often with the formation of a small molecule such as water or HBr. An example is the acid-catalyzed reaction of an alcohol to yield water and an alkene.



- Substitution reactions occur when two reactants exchange parts to give two new products. An example is the reaction of an ester such as methyl acetate with water to yield a carboxylic acid plus an alcohol. Similar reactions occur in many biological pathways, including the metabolism of dietary fats.



- Rearrangement reactions occur when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product. An example is the conversion of dihydroxyacetone phosphate into its constitutional isomer glyceraldehyde 3-phosphate, a step in the glycolysis pathway by which carbohydrates are metabolized.



? Exercise 5.2.1.1

Classify each of the following reactions as an addition, elimination, substitution, or rearrangement:

- $\text{CH}_3\text{Br} + \text{KOH} \longrightarrow \text{CH}_3\text{OH} + \text{KBr}$
- $\text{CH}_3\text{CH}_2\text{Br} \longrightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{HBr}$
- $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_3\text{CH}_3$

Answer

- Substitution
- Elimination

c. Addition

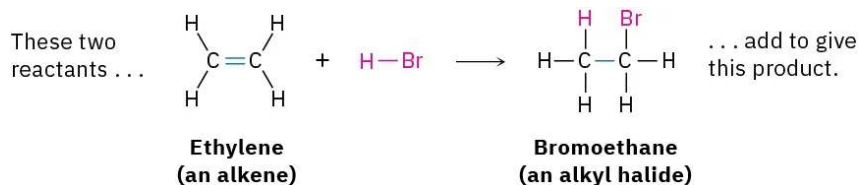
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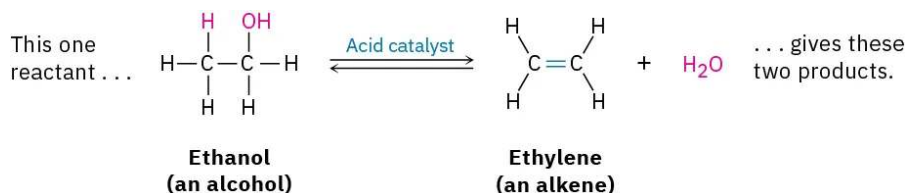
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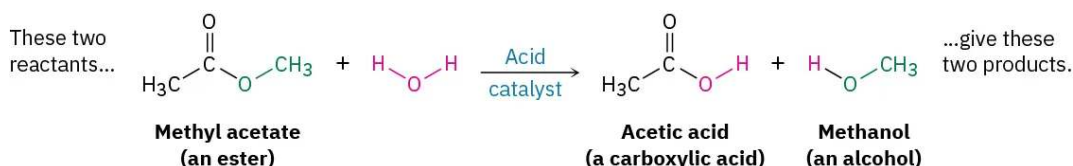
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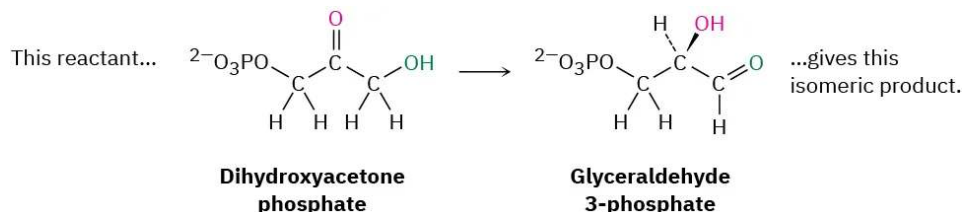
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- Substitution reactions occur when two reactants exchange parts to give two new products. An example is the reaction of an ester such as methyl acetate with water to yield a carboxylic acid plus an alcohol. Similar reactions occur in many biological pathways, including the metabolism of dietary fats.



- Rearrangement reactions occur when a single reactant undergoes a reorganization of bonds and atoms to yield an isomeric product. An example is the conversion of dihydroxyacetone phosphate into its constitutional isomer glyceraldehyde 3-phosphate, a step in the glycolysis pathway by which carbohydrates are metabolized.



? Exercise 5.2.2.1

Classify each of the following reactions as an addition, elimination, substitution, or rearrangement:

- $\text{CH}_3\text{Br} + \text{KOH} \longrightarrow \text{CH}_3\text{OH} + \text{KBr}$
- $\text{CH}_3\text{CH}_2\text{Br} \longrightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{HBr}$
- $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2 \longrightarrow \text{CH}_3\text{CH}_3$

Answer

- Substitution
- Elimination

c. Addition

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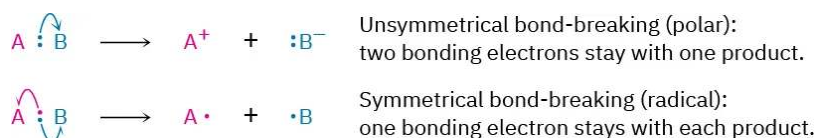
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5.2.3: How Organic Reactions Occur - Mechanisms

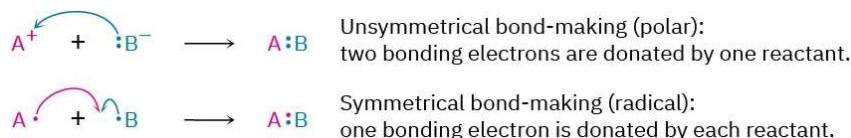
Having looked at the kinds of reactions that take place, let's now see how they occur. An overall description of how a reaction occurs is called a reaction mechanism. A mechanism describes in detail exactly what takes place at each stage of a chemical transformation—which bonds are broken and in what order, which bonds are formed and in what order, and what the relative rates are for each step. A complete mechanism must also account for all reactants used and all products formed.

All chemical reactions involve bond-breaking and bond-making. When two molecules come together, react, and yield products, specific bonds in the reactant molecules are broken and specific bonds in the product molecules are formed. Fundamentally, there are two ways in which a covalent two-electron bond can break. A bond can break in an electronically unsymmetrical way so that both bonding electrons remain with one product fragment, leaving the other with a vacant orbital, or a bond can break in an electronically symmetrical way so that one electron remains with each product fragment. The unsymmetrical cleavage is said to be *heterolytic*, and the symmetrical cleavage is said to be *homolytic*.

We'll develop this point in more detail later, but note for now that the movement of *two* electrons in the unsymmetrical process is indicated using a full-headed curved arrow ($\curvearrowright$), whereas the movement of *one* electron in the symmetrical process is indicated using a half-headed, or "fishhook," arrow ($\frown$).



Just as there are two ways in which a bond can break, there are two ways in which a covalent two-electron bond can form. A bond can form in an electronically unsymmetrical way if both bonding electrons are donated to the new bond by one reactant, or in a symmetrical way if one electron is donated by each reactant.



Processes that involve unsymmetrical bond-breaking and bond-making are called polar reactions. Polar reactions involve species that have an even number of electrons and thus have only electron pairs in their orbitals. Polar processes are by far the more common reaction type in both organic and biological chemistry, and a large part of this book is devoted to their description.

Processes that involve symmetrical bond-breaking and bond-making are called radical reactions. A radical, often called a **free radical**, is a neutral chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals.

In addition to polar and radical reactions, there is a third, less commonly encountered process called a *pericyclic reaction*. Rather than explain pericyclic reactions now, though, we'll look at them more carefully in Chapter 30.

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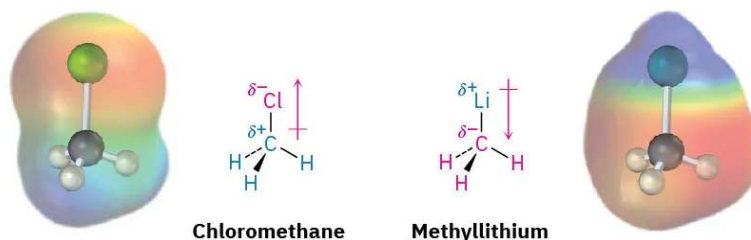
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5.2.4: Polar Reactions

Polar reactions occur because of the electrical attraction between positively polarized and negatively polarized centers on functional groups in molecules. To see how these reactions take place, let's first recall the discussion of polar covalent bonds in Section 2.2 and then look more deeply into the effects of bond polarity on organic molecules.

Most organic compounds are electrically neutral; they have no net charge, either positive or negative. We saw in Section 2.2, however, that certain bonds within a molecule, particularly the bonds in functional groups, are polar. Bond polarity is a consequence of an unsymmetrical electron distribution in a bond and is due to the difference in electronegativity of the bonded atoms.

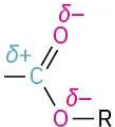
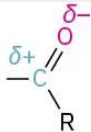
Elements such as oxygen, nitrogen, fluorine, and chlorine are more electronegative than carbon, so a carbon atom bonded to one of these atoms has a partial positive charge (δ^+). Metals are less electronegative than carbon, so a carbon atom bonded to a metal has a partial negative charge (δ^-). Electrostatic potential maps of chloromethane and methyllithium illustrate these charge distributions, showing that the carbon atom in chloromethane is electron-poor (blue) while the carbon in methyllithium is electron-rich (red).



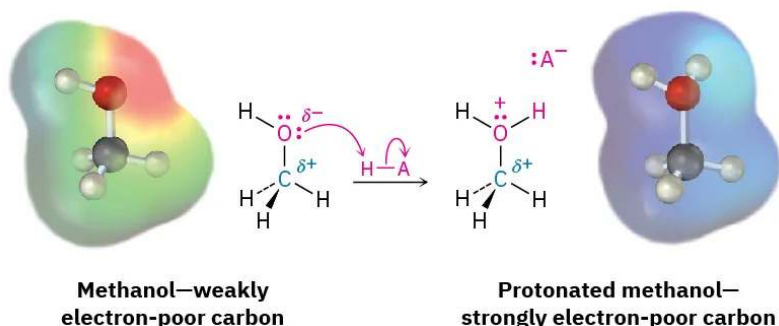
The polarity patterns of some common functional groups are shown in Table 65.2.4.1. Note that carbon is always positively polarized except when bonded to a metal.

Table 5.2.4.1: Polarity Patterns in Some Common Functional Groups

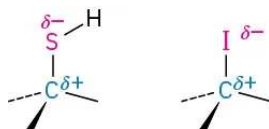
Compound type	Functional group structure
Alcohol	
Alkene	 Symmetrical, nonpolar
Alkyl halide	
Amine	
Ether	
Thiol	
Nitrile	
Grignard reagent	
Alkyl lithium	
Carbonyl	
Carboxylic acid	
Carboxylic acid chloride	
Thioester	
Aldehyde	

Compound type	Functional group structure
Ester	
Ketone	

This discussion of bond polarity is oversimplified in that we've considered only bonds that are inherently polar due to differences in electronegativity. Polar bonds can also result from the interaction of functional groups with acids or bases. Take an alcohol such as methanol, for example. In neutral methanol, the carbon atom is somewhat electron-poor because the electronegative oxygen attracts the electrons in the C–O bond. On protonation of the methanol oxygen by an acid, however, a full positive charge on oxygen attracts the electrons in the C–O bond much more strongly and makes the carbon much more electron-poor. We'll see numerous examples throughout this book of reactions that are catalyzed by acids because of the resultant increase in bond polarity upon protonation.

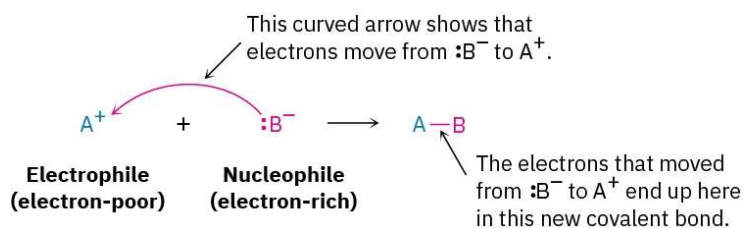


Yet a further consideration is the polarizability (as opposed to polarity) of atoms in a molecule. As the electric field around a given atom changes because of changing interactions with solvent or other polar molecules nearby, the electron distribution around that atom also changes. The measure of this response to an external electrical influence is called the polarizability of the atom. Larger atoms with more loosely held electrons are more polarizable, and smaller atoms with fewer, tightly held electrons are less polarizable. Thus, sulfur is more polarizable than oxygen, and iodine is more polarizable than chlorine. The effect of this higher polarizability of sulfur and iodine is that carbon–sulfur and carbon–iodine bonds, although nonpolar according to electronegativity values (Figure 2.3), nevertheless usually react as if they were polar.



What does functional-group polarity mean with respect to chemical reactivity? Because unlike charges attract, the fundamental characteristic of all polar organic reactions is that electron-rich sites react with electron-poor sites. Bonds are made when an electron-rich atom donates a pair of electrons to an electron-poor atom, and bonds are broken when one atom leaves with both electrons from the former bond.

As we saw in Section 2.12, the movement of an electron pair during a polar reaction is indicated using a curved, full-headed arrow to show where electrons move when reactant bonds are broken and product bonds are formed during the reaction.



In referring to the electron-rich and electron-poor species involved in polar reactions, chemists use the words *nucleophile* and *electrophile*. A nucleophile is a substance that is “nucleus-loving.” (Remember that a nucleus is positively charged.) A nucleophile has a negatively polarized, electron-rich atom and can form a bond by donating a pair of electrons to a positively polarized, electron-poor atom. Nucleophiles can be either neutral or negatively charged; ammonia, water, hydroxide ion, and chloride ion are examples. An electrophile, by contrast, is “electron-loving.” An electrophile has a positively polarized, electron-poor atom and can form a bond by accepting a pair of electrons from a nucleophile. Electrophiles can be either neutral or positively charged. Acids (H^+ donors), alkyl halides, and carbonyl compounds are examples (Figure 6.2).

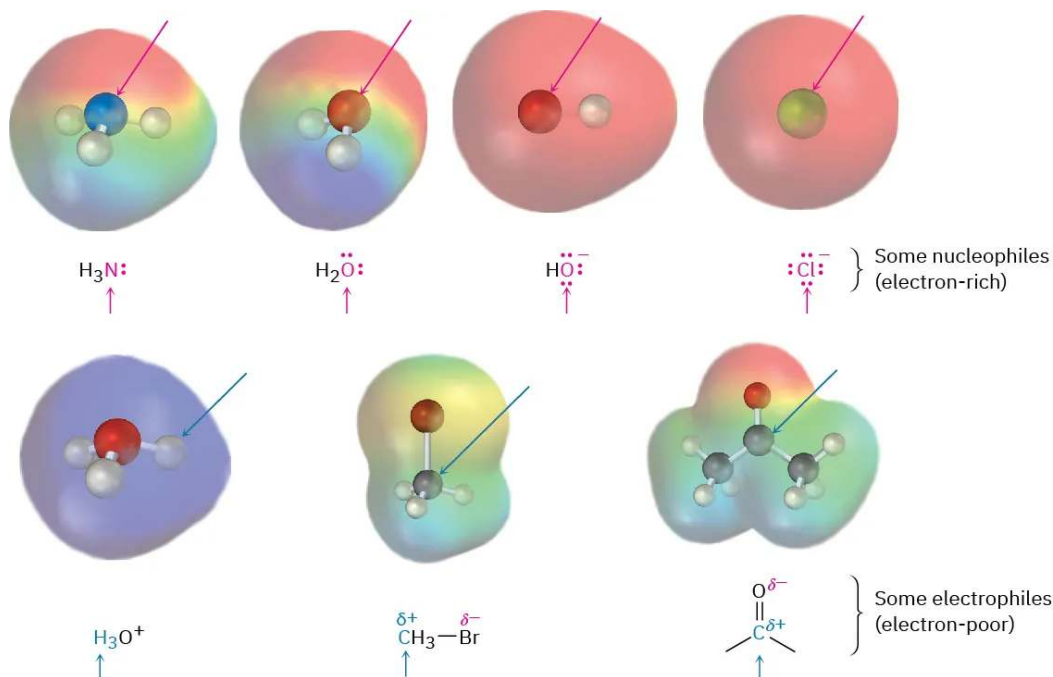


Figure 6.2: Some nucleophiles and electrophiles. Electrostatic potential maps identify the nucleophilic (**negative**) and electrophilic (**positive**) atoms.

Note that neutral compounds can often react either as nucleophiles or as electrophiles, depending on the circumstances. After all, if a compound is neutral yet has an electron-rich nucleophilic site, it must also have a corresponding electron-poor electrophilic site. Water, for instance, acts as an electrophile when it donates H^+ but acts as a nucleophile when it donates a nonbonding pair of electrons. Similarly, a carbonyl compound acts as an electrophile when it reacts at its positively polarized carbon atom, yet acts as a nucleophile when it reacts at its negatively polarized oxygen atom.

If the definitions of nucleophiles and electrophiles sound similar to those given in Section 2.12 for Lewis acids and Lewis bases, that's because there is indeed a correlation. Lewis bases are electron donors and behave as nucleophiles, whereas Lewis acids are electron acceptors and behave as electrophiles. Thus, much of organic chemistry is explainable in terms of acid-base reactions. The main difference is that the words *acid* and *base* are used broadly in all fields of chemistry, while the words *nucleophile* and *electrophile* are used primarily in organic chemistry when carbon bonding is involved.

✓ Worked Example 5.2.4.1: Identifying Electrophiles and Nucleophiles

Which of the following species is likely to behave as a nucleophile and which as an electrophile?

a. NO_2^+

- b. CN^-
- c. CH_3NH_2
- d. $(\text{CH}_3)_3\text{S}^+$

Strategy

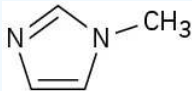
A nucleophile has an electron-rich site, either because it is negatively charged or because it has a functional group containing an atom that has a lone pair of electrons. An electrophile has an electron-poor site, either because it is positively charged or because it has a functional group containing an atom that is positively polarized.

Solution

- a. NO_2^+ (nitronium ion) is likely to be an electrophile because it is positively charged.
- b. $:\text{C}\equiv\text{N}^-$ (cyanide ion) is likely to be a nucleophile because it is negatively charged.
- c. CH_3NH_2 (methylamine) might be either a nucleophile or an electrophile, depending on the circumstances. The lone pair of electrons on the nitrogen atom makes methylamine a potential nucleophile, while positively polarized N–H hydrogens make methylamine a potential acid (electrophile).
- d. $(\text{CH}_3)_3\text{S}^+$ (trimethylsulfonium ion) is likely to be an electrophile because it is positively charged.

? Exercise 5.2.4.1

Which of the following species are likely to be nucleophiles and which electrophiles? Which might be both?

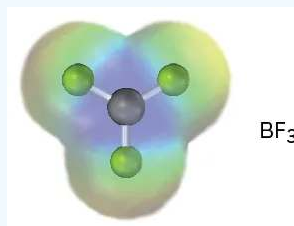
- a. CH_3Cl
- b. CH_3S^-
- c. 
- d. 

Answer

- a. Carbon is electrophilic.
- b. Sulfur is nucleophilic.
- c. Nitrogens are nucleophilic (for reasons that will be explained in Chapter 15).
- d. Oxygen is nucleophilic; carbon is electrophilic.

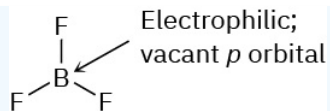
? Exercise 5.2.4.2

An electrostatic potential map of boron trifluoride is shown. Is BF_3 likely to be a nucleophile or an electrophile? Draw a Lewis structure for BF_3 , and explain your answer.



Answer

Electrophile; Boron has a vacant p orbital.

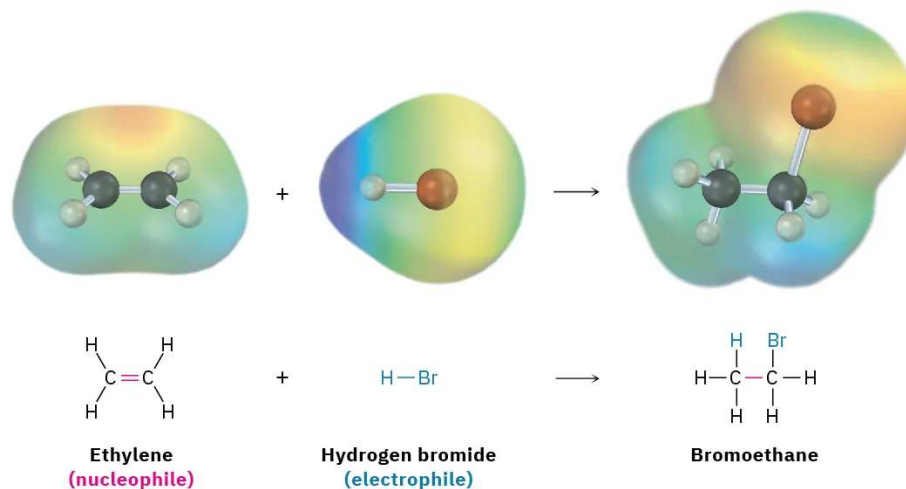


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5.2.5: An Example of a Polar Reaction - Addition of HBr to Ethylene

Let's look at a typical polar process—the addition reaction of an alkene, such as ethylene, with hydrogen bromide. When ethylene is treated with HBr at room temperature, bromoethane is produced. Overall, the reaction can be formulated as



The reaction is an example of a polar reaction type known as an *electrophilic addition reaction* and can be understood using the general ideas discussed in the previous section. Let's begin by looking at the two reactants.

What do we know about ethylene? We know from Section 1.9 that a carbon–carbon double bond results from the orbital overlap of two sp^2 -hybridized carbon atoms. The σ part of the double bond results from sp^2 – sp^2 overlap, and the π part results from p – p overlap.

What kind of chemical reactivity might we expect from a $\text{C}=\text{C}$ bond? We know that alkanes, such as ethane, are relatively inert because all valence electrons are tied up in strong, nonpolar, C–C and C–H bonds. Furthermore, the bonding electrons in alkanes are relatively inaccessible to approaching reactants because they are sheltered in σ bonds between nuclei. The electronic situation in alkenes is quite different, however. For one thing, double bonds have a greater electron density than single bonds—four electrons in a double bond versus only two in a single bond. In addition, the electrons in the π bond are accessible to approaching reactants because they are located above and below the plane of the double bond rather than being sheltered between the nuclei (Figure 5.2.5.1). As a result, the double bond is nucleophilic and the chemistry of alkenes is dominated by reactions with electrophiles.

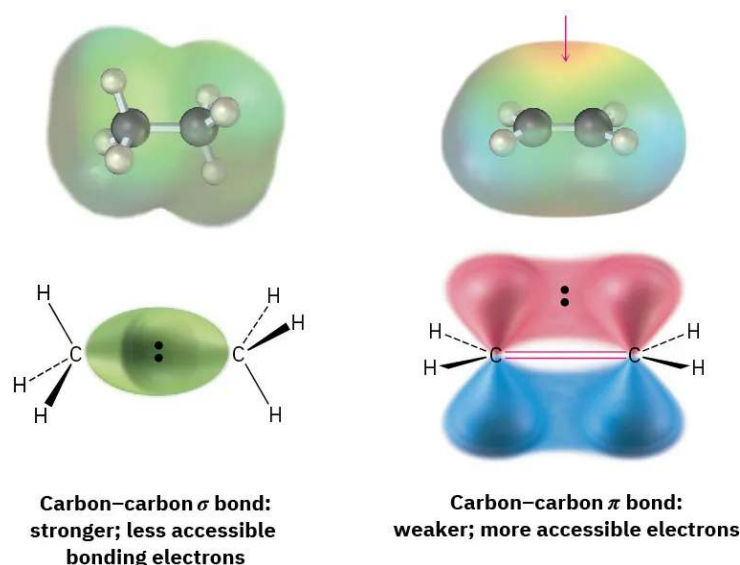


Figure 5.2.5.1: A comparison of carbon–carbon single and double bonds. A double bond is both more accessible to approaching reactants than a single bond and more electron-rich (more nucleophilic). An electrostatic potential map of ethylene indicates that the double bond is the region of **highest negative charge**.

What about the second reactant, HBr? As a strong acid, HBr is a powerful proton (H^+) donor and electrophile. Thus, the reaction between HBr and ethylene is a typical electrophile–nucleophile combination, characteristic of all polar reactions.

We'll see more details about alkene electrophilic addition reactions shortly, but for the present we can imagine the reaction as taking place by the pathway shown in Figure 5.2.5.2. The reaction begins when the alkene nucleophile donates a pair of electrons from its $\text{C}=\text{C}$ bond to **HBr** to form a new $\text{C}-\text{H}$ bond plus Br^- , as indicated by the path of the curved arrows in the first step of Figure 5.2.5.2. One curved arrow begins at the middle of the double bond (the source of the electron pair) and points to the hydrogen atom in HBr (the atom to which a bond will form). This arrow indicates that a new $\text{C}-\text{H}$ bond forms using electrons from the former $\text{C}=\text{C}$ bond. Simultaneously, a second curved arrow begins in the middle of the $\text{H}-\text{Br}$ bond and points to the Br, indicating that the $\text{H}-\text{Br}$ bond breaks and the electrons remain with the Br atom, giving Br^- .

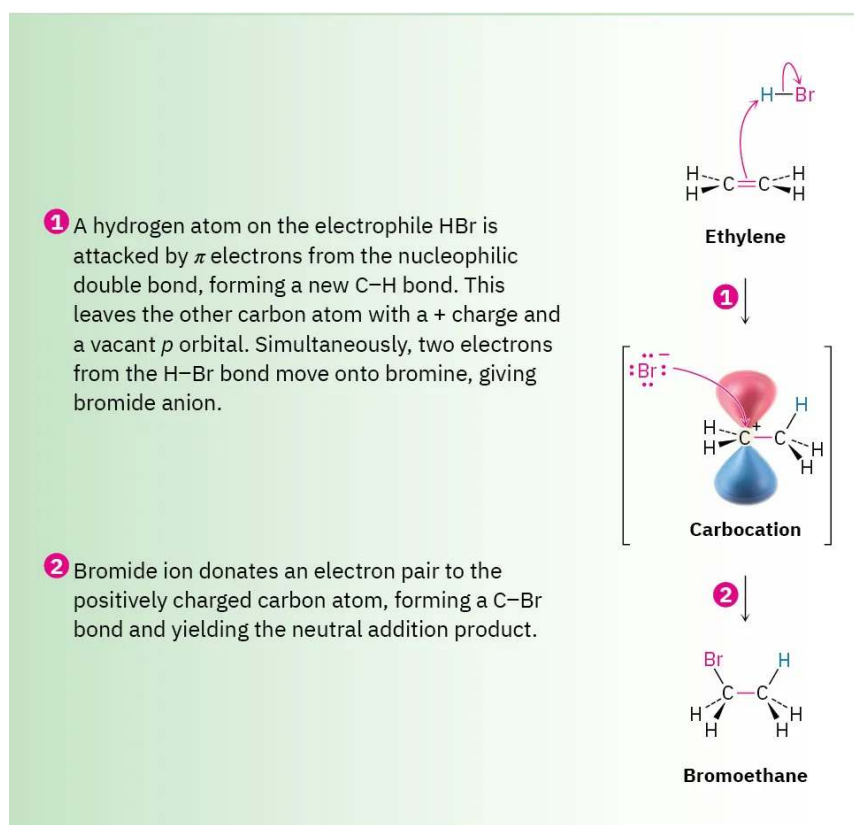


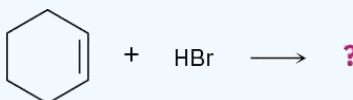
Figure 5.2.5.2: The electrophilic addition reaction of ethylene and **HBr**. The reaction takes place in two steps, both of which involve electrophile–nucleophile interactions.

When one of the alkene carbon atoms bonds to the incoming hydrogen, the other carbon atom, having lost its share of the double-bond electrons, now has only six valence electrons and is left with a positive charge. This positively charged species—a carbonation, or carbocation—is itself an electrophile that can accept an electron pair from nucleophilic Br^- anion in a second step, forming a $\text{C}-\text{Br}$ bond and yielding the observed addition product. Once again, a curved arrow in Figure 5.2.5.2 shows the electron-pair movement from Br^- to the positively charged carbon.

The electrophilic addition of HBr to ethylene is only one example of a polar process; there are many others that we'll study in depth in later chapters. But regardless of the details of individual reactions, all polar reactions take place between an electron-poor site and an electron-rich site and involve the donation of an electron pair from a nucleophile to an electrophile.

? Exercise 5.2.5.1

What product would you expect from the reaction of cyclohexene with **HBr**? With **HCl**?

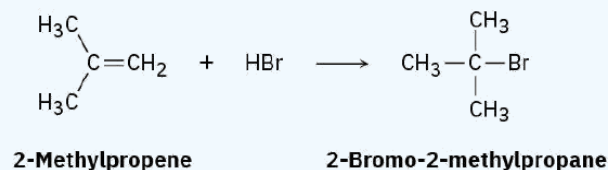


Answer

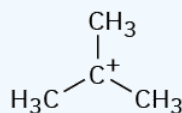
Bromocyclohexane; chlorocyclohexane.

? Exercise 5.2.5.2

Reaction of HBr with 2-methylpropene yields 2-bromo-2-methylpropane. What is the structure of the carbocation formed during the reaction? Show the mechanism of the reaction.



Answer



The mechanism is shown in Figure 5.2.5.2.

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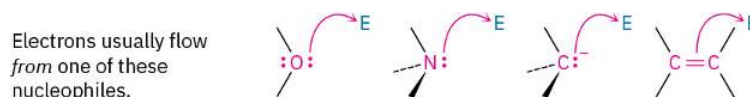
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5.2.6: Using Curved Arrows in Polar Reaction Mechanisms

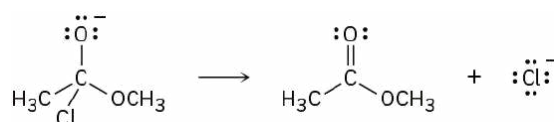
It takes practice to use curved arrows properly in reaction mechanisms, but there are a few rules and a few common patterns you should look for that will help you become more proficient:

RULE 1

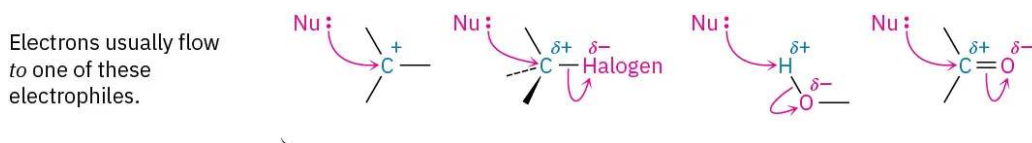
Electrons move from a nucleophilic source (Nu: or Nu⁻) to an electrophilic sink (E or E⁺). The nucleophilic source must have an electron pair available, usually either as a lone pair or in a multiple bond.



For example:

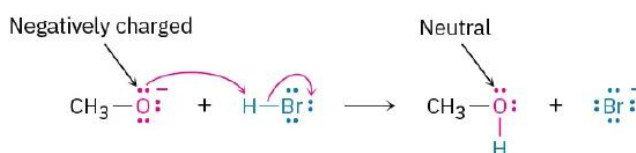


The electrophilic sink must be able to accept an electron pair, usually because it has either a positively charged atom or a positively polarized atom in a functional group. For example:

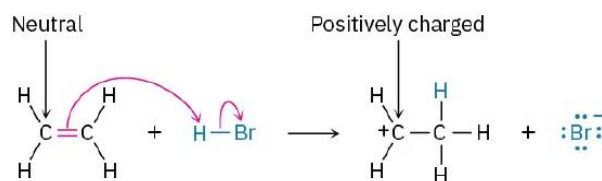


RULE 2

The nucleophile can be either negatively charged or neutral. If the nucleophile is negatively charged, the atom that donates an electron pair becomes neutral. For example:

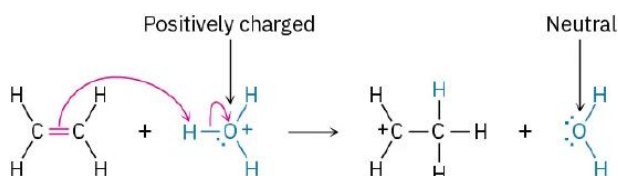


If the nucleophile is neutral, the atom that donates the electron pair acquires a positive charge. For example:



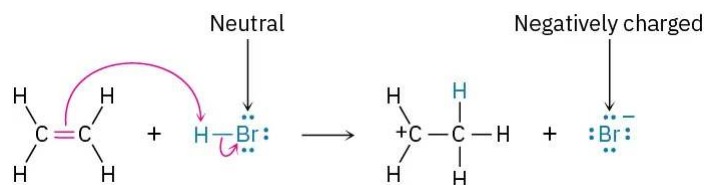
RULE 3

The electrophile can be either positively charged or neutral. If the electrophile is positively charged, the atom bearing that charge becomes neutral after accepting an electron pair. For example:



If the electrophile is neutral, the atom that ultimately accepts the electron pair acquires a negative charge. For this to happen, however, the negative charge must be stabilized by being on an electronegative atom such as oxygen, nitrogen, or a halogen.

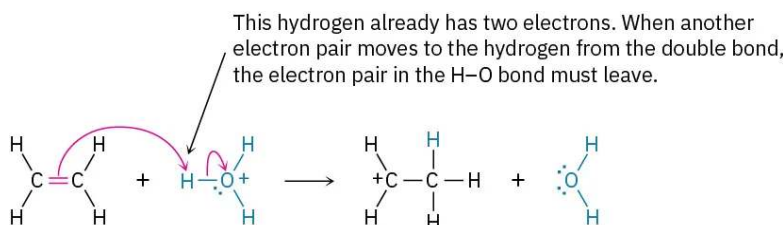
Carbon and hydrogen do not typically stabilize a negative charge. For example:



The result of Rules 2 and 3 together is that charge is conserved during the reaction. A negative charge in one of the reactants gives a negative charge in one of the products, and a positive charge in one of the reactants gives a positive charge in one of the products.

RULE 4

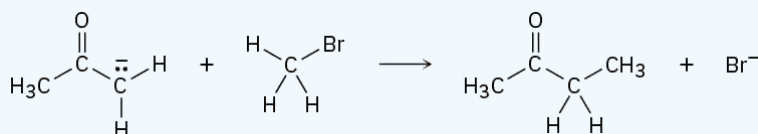
The octet rule must be followed. That is, no second-row atom can be left with ten electrons (or four for hydrogen). If an electron pair moves *to* an atom that already has an octet (or two electrons for hydrogen), another electron pair must simultaneously move from that atom to maintain the octet. When two electrons move from the $\text{C}=\text{C}$ bond of ethylene to the hydrogen atom of H_3O^+ , for instance, two electrons must leave that hydrogen. This means that the $\text{H}-\text{O}$ bond must break and the electrons must stay with the oxygen, giving neutral water.



Worked Example 6.2 gives another example of drawing curved arrows.

✓ Worked Example 5.2.6.1: Using Curved Arrows in Reaction Mechanisms

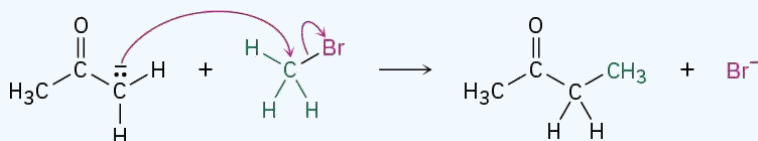
Add curved arrows to the following polar reaction to show the flow of electrons:



Strategy

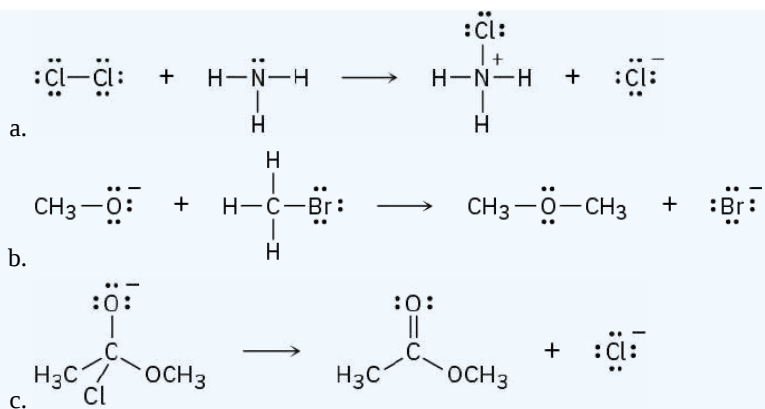
Look at the reaction, and identify the bonding changes that have occurred. In this case, a $\text{C}-\text{Br}$ bond has broken and a $\text{C}-\text{C}$ bond has formed. The formation of the $\text{C}-\text{C}$ bond involves the donation of an electron pair from the nucleophilic carbon atom of the reactant on the left to the electrophilic carbon atom of CH_3Br , so we draw a curved arrow originating from the lone pair on the negatively charged C atom and pointing to the C atom of CH_3Br . At the same time that the $\text{C}-\text{C}$ bond forms, the $\text{C}-\text{Br}$ bond must break so that the octet rule is not violated. We therefore draw a second curved arrow from the $\text{C}-\text{Br}$ bond to Br . The bromine is now a stable Br^- ion.

Solution

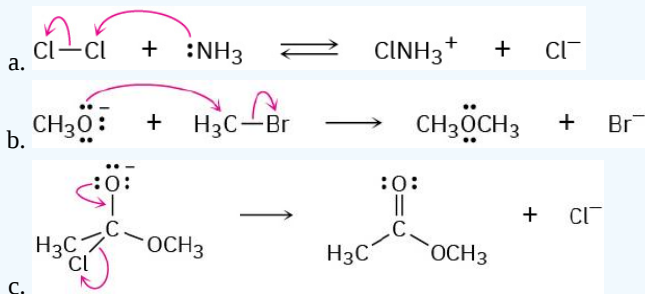


? Exercise 5.2.6.1

Add curved arrows to the following polar reactions to indicate the flow of electrons in each:

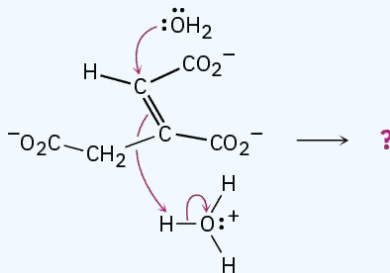


Answer

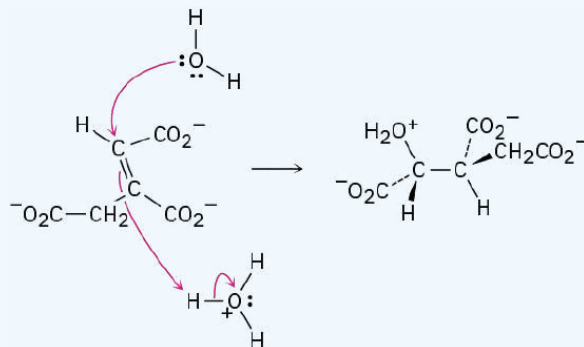


? Exercise 5.2.6.2

Predict the products of the following polar reaction, a step in the citric acid cycle for food metabolism, by interpreting the flow of electrons indicated by the curved arrows:



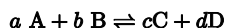
Answer



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5.2.7: Describing a Reaction - Equilibria, Rates, and Energy Changes

Every chemical reaction can go in either a forward or reverse direction. Reactants can go forward to products, and products can revert to reactants. As you may remember from your general chemistry course, the position of the resulting chemical equilibrium is expressed by an equation in which K_{eq} , the equilibrium constant, is equal to the product concentrations multiplied together, divided by the reactant concentrations multiplied together, with each concentration raised to the power of its coefficient in the balanced equation. For the generalized reaction



we have

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The value of the equilibrium constant tells which side of the reaction arrow is energetically favored. If K_{eq} is much larger than 1, then the product concentration term $[C]^c [D]^d$ is much larger than the reactant concentration term $[A]^a [B]^b$, and the reaction proceeds as written from left to right. If K_{eq} is near 1, appreciable amounts of both reactant and product are present at equilibrium. And if K_{eq} is much smaller than 1, the reaction does not take place as written but instead goes in the reverse direction, from right to left.

For example, consider the reaction of ethylene with **HBr**:



We can write the following equilibrium expression and determine experimentally that the equilibrium constant at room temperature is approximately 7.1×10^7 :

$$K_{eq} = \frac{[CH_3CH_2Br]}{[H_2C=CH_2][HBr]} = 7.1 \times 10^7 \quad (5.2.7.1)$$

Because K_{eq} is relatively large, the reaction proceeds as written and more than 99.99999% of the ethylene is converted into bromoethane. For practical purposes, an equilibrium constant greater than about 10^3 means that the amount of reactant left over will be barely detectable (less than 0.1%).

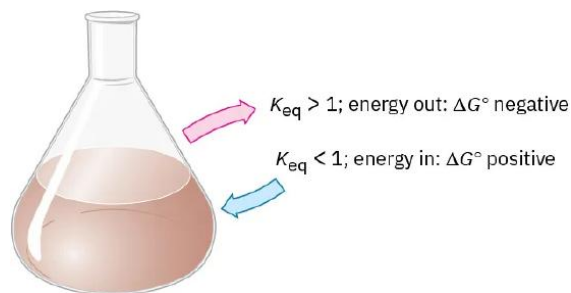
What determines the magnitude of the equilibrium constant? For a reaction to have a favorable equilibrium constant and proceed as written, the energy of the products must be lower than the energy of the reactants. In other words, energy must be released. This situation is analogous to that of a rock poised precariously in a high-energy position near the top of a hill. When it rolls downhill, the rock releases energy until it reaches a more stable, low-energy position at the bottom.

The energy change that occurs during a chemical reaction is called the **Gibbs free-energy change** (ΔG), which is equal to the free energy of the products minus the free energy of the reactants:

$$\Delta G = G_{products} - G_{reactants} \quad (5.2.7.2)$$

For a favorable reaction, ΔG has a negative value, meaning that energy is lost by the chemical system and released to the surroundings, usually as heat. Such reactions are said to be exergonic. For an unfavorable reaction, ΔG has a positive value, meaning that energy is absorbed by the chemical system from the surroundings. Such reactions are said to be endergonic.

You might also recall from general chemistry that the *standard* free-energy change for a reaction is denoted as ΔG° , where the superscript $^\circ$ means that the reaction is carried out under standard conditions, with pure substances in their most stable form at 1 atm pressure and a specified temperature, usually 298 K. For biological reactions, the standard free-energy change is denoted as $\Delta G'^\circ$ and refers to a reaction carried out at pH = 7.0 with solute concentrations of 1.0 M.



Because the equilibrium constant, K_{eq} , and the standard free-energy change, ΔG° , both measure whether a reaction is favorable, they are mathematically related by the equation

$$\Delta G^\circ = -RT \ln K_{eq} \quad (5.2.7.3)$$

or

$$K_{eq} = e^{-\Delta G^\circ/RT} \quad (5.2.7.4)$$

where

$$\begin{aligned} R &= 8.314 \text{ J/(K} \cdot \text{mol)} = 1.987 \text{ cal/(K} \cdot \text{mol)} \\ T &= \text{Kelvin temperature} \\ e &= 2.718 \\ \ln K_{eq} &= \text{natural logarithm of } K_{eq} \end{aligned} \quad (5.2.7.5)$$

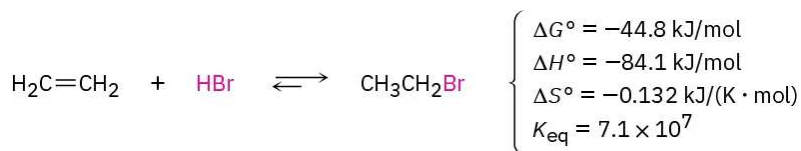
For example, the reaction of ethylene with **HBr** (Equation 5.2.7.2) has $K_{eq} = 7.1 \times 10^7$, so $\Delta G^\circ = -44.8 \text{ kJ/mol}$ (-10.7 kcal/mol) at 298 K:

$$\begin{aligned} K_{eq} &= 7.1 \times 10^7 \text{ and } \ln K_{eq} = 18.08 \\ \Delta G^\circ &= -RT \ln K_{eq} = -[8.314 \text{ J/(K} \cdot \text{mol)}](298 \text{ K})(18.08) \\ &= -44,800 \text{ J/mol} = -44.8 \text{ kJ/mol} \end{aligned} \quad (5.2.7.6)$$

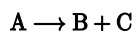
The free-energy change ΔG is made up of two terms, an *enthalpy* term, ΔH , and a temperature-dependent *entropy* term, $T\Delta S$. Of the two terms, the enthalpy term is often larger and more dominant.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5.2.7.7)$$

For the reaction of ethylene with HBr at room temperature (298 K), the approximate values are

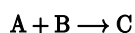


The enthalpy change (ΔH), also called the **heat of reaction**, is a measure of the change in total bonding energy during a reaction. If ΔH is negative, as in the reaction of HBr with ethylene, the products have less energy than the reactants. Thus, the products are more stable and have stronger bonds than the reactants, heat is released, and the reaction is said to be exothermic. If ΔH is positive, the products are less stable and have weaker bonds than the reactants, heat is absorbed, and the reaction is said to be endothermic. For example, if a reaction breaks reactant bonds with a total strength of 380 kJ/mol and forms product bonds with a total strength of 400 kJ/mol, then ΔH for the reaction is 400 kJ/mol – 380 kJ/mol = –20 kJ/mol and the reaction is exothermic. The entropy change (ΔS) is a measure of the change in the amount of molecular randomness, or freedom of motion, that accompanies a reaction. For example, in an elimination reaction of the type



there is more freedom of movement and molecular randomness in the products than in the reactant because one molecule has split into two. Thus, there is a net increase in entropy during the reaction and ΔS has a positive value.

On the other hand, for an addition reaction of the type



the opposite is true. Because such reactions restrict the freedom of movement of two molecules by joining them together, the product has less randomness than the reactants and ΔS has a negative value. The reaction of ethylene and HBr to yield bromoethane, which has $\Delta S^\circ = -0.132 \text{ kJ}/(\text{K} \cdot \text{mol})$, is an example. Table 5.2.7.1 describes the thermodynamic terms more fully.

Table 5.2.7.1: Explanation of Thermodynamic Quantities: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Term	Name	Explanation
ΔG°	Gibbs free-energy change	The energy difference between reactants and products. When ΔG° is negative, the reaction is exergonic , has a favorable equilibrium constant, and can occur spontaneously. When ΔG° is positive, the reaction is endergonic , has an unfavorable equilibrium constant, and cannot occur spontaneously.
ΔH°	Enthalpy change	The heat of reaction, or difference in strength between the bonds broken in a reaction and the bonds formed. When ΔH° is negative, the reaction releases heat and is exothermic . When ΔH° is positive, the reaction absorbs heat and is endothermic .
ΔS°	Entropy change	The change in molecular randomness during a reaction. When ΔS° is negative, randomness decreases. When ΔS° is positive, randomness increases.

Knowing the value of K_{eq} for a reaction is useful, but it's important to realize its limitations. An equilibrium constant tells only the position of the equilibrium, or how much product is theoretically possible. It doesn't tell the rate of reaction, or how fast the equilibrium is established. Some reactions are extremely slow even though they have favorable equilibrium constants. Gasoline is stable at room temperature, for instance, because the rate of its reaction with oxygen is slow at 298 K. Only at higher temperatures, such as contact with a lighted match, does gasoline react rapidly with oxygen and undergo complete conversion to the equilibrium products water and carbon dioxide. Rates (how fast a reaction occurs) and equilibria (how much a reaction occurs) are entirely different.

- **Rate** → Is the reaction fast or slow?
- **Equilibrium** → In what direction does the reaction proceed?

? Exercise 5.2.7.1

Which reaction is more energetically favored, one with $\Delta G^\circ = -44 \text{ kJ/mol}$ or one with $\Delta G^\circ = +44 \text{ kJ/mol}$?

Answer

Negative ΔG° is favored.

? Exercise 5.2.7.2

Which reaction is more exergonic, one with $K_{\text{eq}}=1000$ or one with $K_{\text{eq}}=0.001$?

Answer

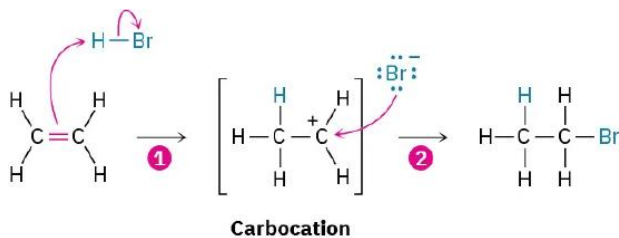
Larger K_{eq} is more exergonic.

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5.2.8: Describing a Reaction - Energy Diagrams and Transition States

For a reaction to take place, reactant molecules must collide and reorganization of atoms and bonds must occur. Let's again look at the addition reaction of HBr and ethylene.



As the reaction proceeds, ethylene and HBr approach each other, the ethylene π bond and the H-Br bond break, a new C-H bond forms in step 1 and a new C-Br bond forms in step 2.

To depict graphically the energy changes that occur during a reaction, chemists use energy diagrams, such as that in Figure 5.2.8.1. The vertical axis of the diagram represents the total energy of all reactants, and the horizontal axis, called the reaction coordinate, represents the progress of the reaction from beginning to end. Let's see how the addition of HBr to ethylene can be described in an energy diagram.

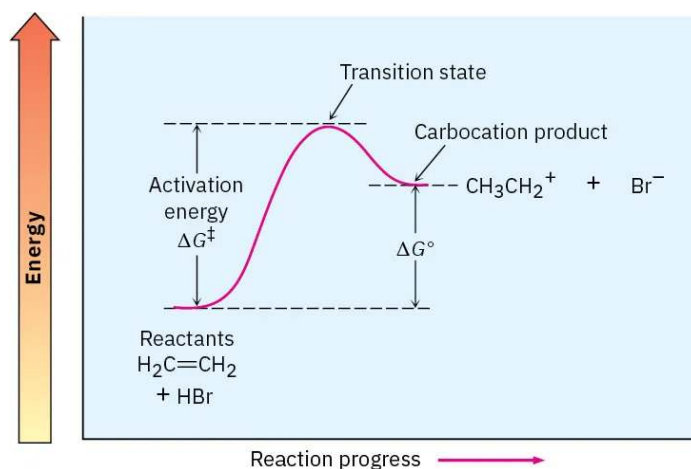


Figure 5.2.8.1: An energy diagram for the first step in the reaction of ethylene with HBr. The energy difference between reactants and the transition state, $\Delta G^\ddagger$, defines the reaction rate. The energy difference between reactants and carbocation product, ΔG° , defines the position of the equilibrium.

At the beginning of the reaction, ethylene and HBr have the total amount of energy indicated by the reactant level on the left side of the diagram in Figure 5.2.8.1. As the two reactants collide and reaction commences, their electron clouds repel each other, causing the energy level to rise. If the collision has occurred with enough force and proper orientation, however, the reactants continue to approach each other despite the rising repulsion until the new C-H bond starts to form. At some point, a structure of maximum energy is reached, a structure called the transition state.

The transition state represents the highest-energy structure involved in this step of the reaction. It is unstable and can't be isolated, but we can imagine it to be an activated complex of the two reactants in which both the $\text{C}=\text{C}$ π bond and H-Br bond are partially broken and the new C-H bond is partially formed (Figure 5.2.8.2).

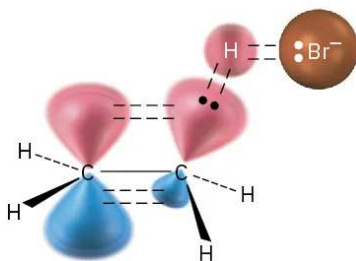


Figure 5.2.8.2: A hypothetical transition-state structure for the first step of the reaction of ethylene with HBr. The $\text{C}=\text{C}$ π bond and $\text{H}-\text{Br}$ bond are just beginning to break, and the $\text{C}-\text{H}$ bond is just beginning to form.

The energy difference between reactants and the transition state is called the activation energy, $\Delta G^\ddagger$, and determines how rapidly the reaction occurs at a given temperature. (The double-dagger superscript, ‡ , always refers to the transition state.) A high activation energy results in a slow reaction because few collisions occur with enough energy for the reactants to reach the transition state. A low activation energy results in a rapid reaction because almost all collisions occur with enough energy for the reactants to reach the transition state.

As an analogy, you might think of reactants that need enough energy to climb the activation barrier to the transition state as hikers who need enough energy to climb to the top of a mountain pass. If the pass is a high one, the hikers need a lot of energy and surmount the barrier with difficulty. If the pass is low, the hikers need less energy and reach the top easily.

As a rough generalization, many organic reactions have activation energies in the range 40 to 150 kJ/mol (10–35 kcal/mol). The reaction of ethylene with HBr, for example, has an activation energy of approximately 140 kJ/mol (34 kcal/mol). Reactions with activation energies less than 80 kJ/mol take place at or below room temperature, while reactions with higher activation energies normally require a higher temperature to give the reactants enough energy to climb the activation barrier.

Once the transition state is reached, the reaction can either continue on to give the carbocation product or revert back to reactants. When reversion to reactants occurs, the transition-state structure comes apart and an amount of free energy corresponding to $-\Delta G^\ddagger$ is released. When the reaction continues on to give the carbocation, the new $\text{C}-\text{H}$ bond forms fully and an amount of energy is released corresponding to the difference between the transition state and carbocation product. The net energy change for the step, ΔG° , is represented in the diagram as the difference in level between reactant and product. Since the carbocation is higher in energy than the starting alkene, the step is endergonic, has a positive value of ΔG° , and absorbs energy.

Not all energy diagrams are like that shown for the reaction of ethylene and HBr. Each reaction has its own energy profile. Some reactions are fast (small $\Delta G^\ddagger$) and some are slow (large $\Delta G^\ddagger$); some have a negative ΔG° , and some have a positive ΔG° . Figure 5.2.8.3 illustrates some different possibilities.

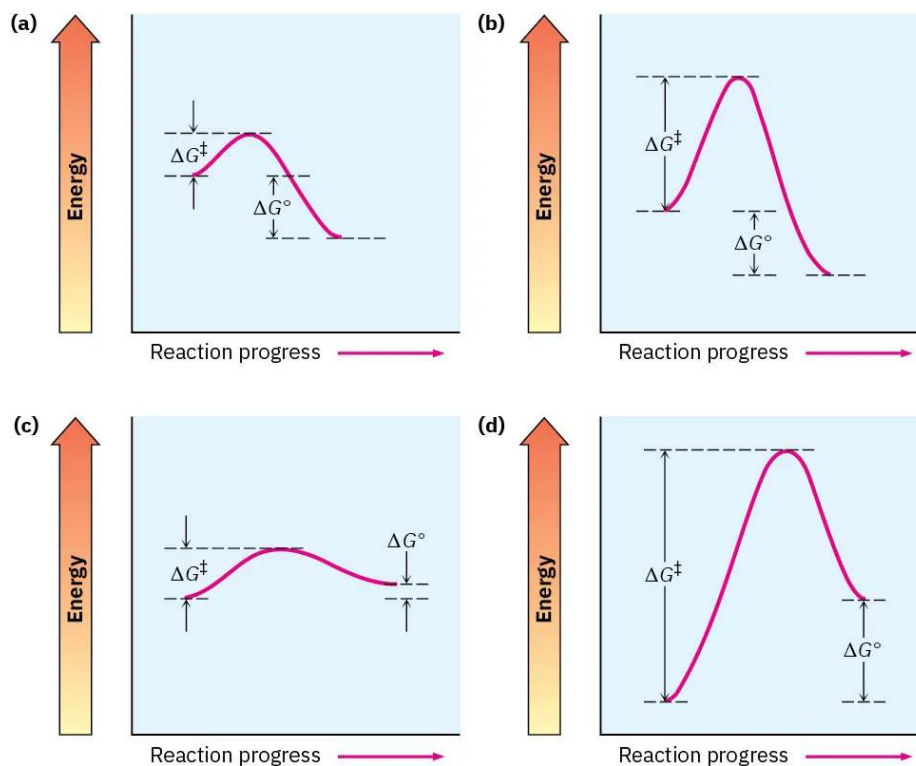


Figure 5.2.8.3: Some hypothetical energy diagrams: **(a)** a fast exergonic reaction (low $\Delta G^\ddagger$, negative ΔG°); **(b)** a slow exergonic reaction (high $\Delta G^\ddagger$, negative ΔG°); **(c)** a fast endergonic reaction (small $\Delta G^\ddagger$, small positive ΔG°); **(d)** a slow endergonic reaction (high $\Delta G^\ddagger$, positive ΔG°).

? Exercise 5.2.8.1

Which reaction is faster, one with $\Delta G^\ddagger = +45 \text{ kJ/mol}$ or one with $\Delta G^\ddagger = +70 \text{ kJ/mol}$?

Answer

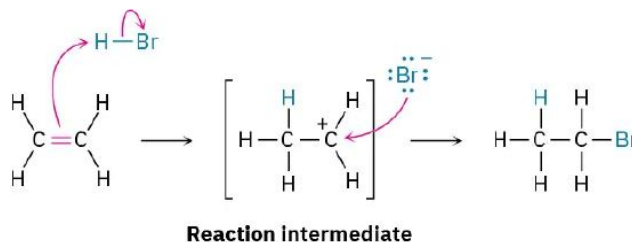
Lower $\Delta G^\ddagger$ is faster.

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5.2.9: Describing a Reaction- Intermediates

How can we describe the carbocation formed in the first step of the reaction of ethylene with HBr? The carbocation is clearly different from the reactants, yet it isn't a transition state and it isn't a final product.



We call the carbocation, which exists only transiently during the course of the multistep reaction, a reaction intermediate. As soon as the intermediate is formed in the first step by reaction of ethylene with H^+ , it reacts further with Br^- in a second step to give the final product, bromoethane. This second step has its own activation energy ($\Delta G^\ddagger$), its own transition state, and its own energy change (ΔG°). We can picture the second transition state as an activated complex between the electrophilic carbocation intermediate and the nucleophilic bromide anion, in which Br^- donates a pair of electrons to the positively charged carbon atom as the new C-Br bond just starts to form.

A complete energy diagram for the overall reaction of ethylene with HBr is shown in Figure 5.2.9.1. In essence, we draw a diagram for each of the individual steps and then join them so that the carbocation product of step 1 is the reactant for step 2. As indicated in Figure 5.2.9.1, the reaction intermediate lies at an energy minimum between steps. Because the energy level of the intermediate is higher than the level of either the reactant that formed it or the product it yields, the intermediate can't normally be isolated. It is, however, more stable than its two neighboring transition states.

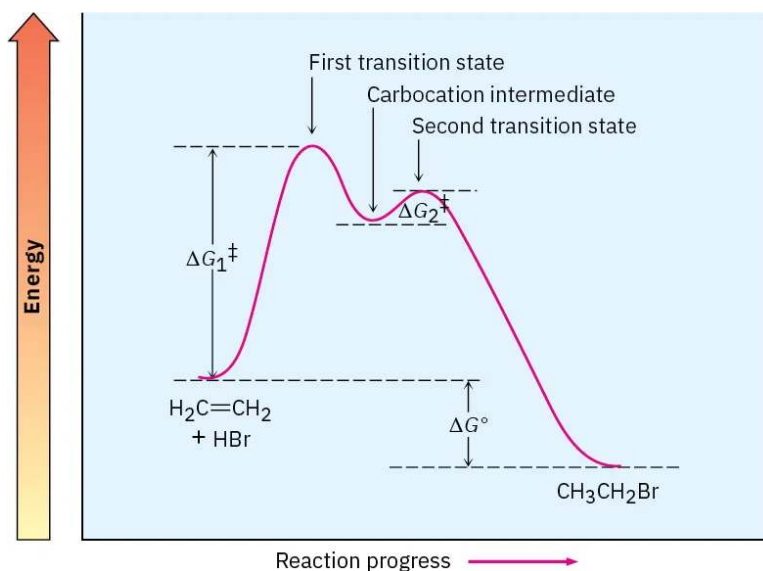


Figure 5.2.9.1: An energy diagram for the reaction of ethylene with HBr. Two separate steps are involved, each with its own activation energy ($\Delta G^\ddagger$) and free-energy change (ΔG°). The overall $\Delta G^\ddagger$ for the complete reaction is the energy difference between reactants and the highest transition state (which corresponds to $\Delta G_1^\ddagger$ in this case), and the overall ΔG° for the reaction is the energy difference between reactants and final products.

Each step in a multistep process can always be considered separately. Each step has its own $\Delta G^\ddagger$ and its own ΔG° . The overall activation energy that controls the rate of the reaction, however, is the energy difference between initial reactants and the highest transition state, regardless of which step it occurs in. The overall ΔG° of the reaction is the energy difference between reactants and final products.

The biological reactions that take place in living organisms have the same energy requirements as reactions that take place in the laboratory and can be described in similar ways. They are, however, constrained by the fact that they must have low enough activation energies to occur at moderate temperatures, and they must release energy in relatively small amounts to avoid

overheating the organism. These constraints can be met through the use of large, structurally complex, enzyme catalysts that alter the mechanism of a reaction to a pathway that can proceed through a series of small steps rather than one or two large steps. Thus, an energy diagram for a biological reaction might look like that in Figure 5.2.9.2.

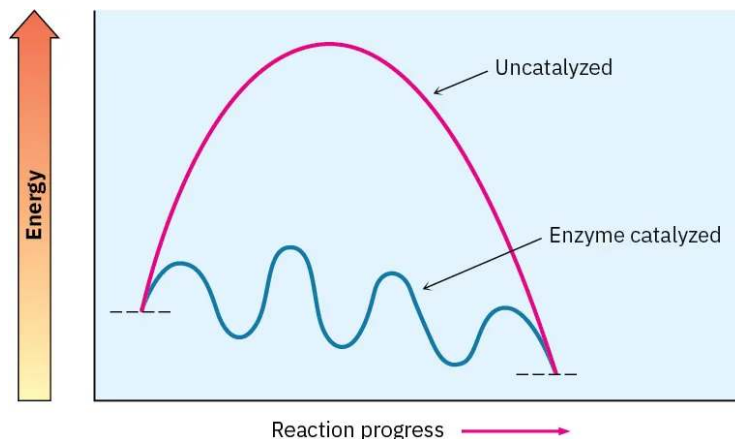


Figure 5.2.9.2: Energy diagrams for a typical, enzyme-catalyzed biological reaction and an **uncatalyzed laboratory reaction**. The biological reaction involves many steps, each of which has a relatively small activation energy and small energy change. The end result is the same, however.

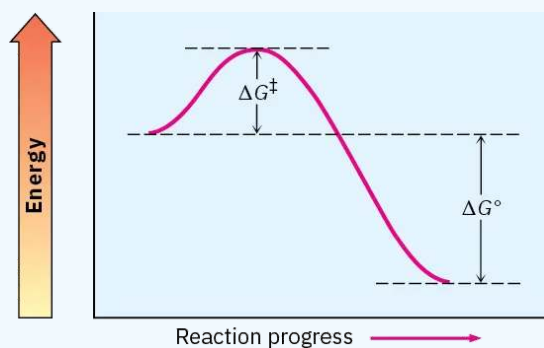
✓ Worked Example 5.2.9.1: Drawing a Reaction Energy Diagram

Sketch an energy diagram for a one-step reaction that is fast and highly exergonic.

Strategy

A fast reaction has a small $\Delta G^\ddagger$, and a highly exergonic reaction has a large negative ΔG° .

Solution



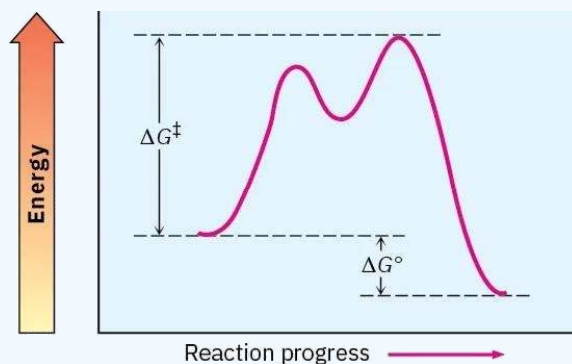
✓ Worked Example 5.2.9.2: Drawing a Reaction Energy Diagram

Sketch an energy diagram for a two-step exergonic reaction whose second step has a higher-energy transition state than its first step. Show $\Delta G^\ddagger$ and ΔG° for the overall reaction.

Strategy

A two-step reaction has two transition states and an intermediate between them. The $\Delta G^\ddagger$ for the overall reaction is the energy change between reactants and the highest-energy transition state—the second one in this case. An exergonic reaction has a negative overall ΔG° .

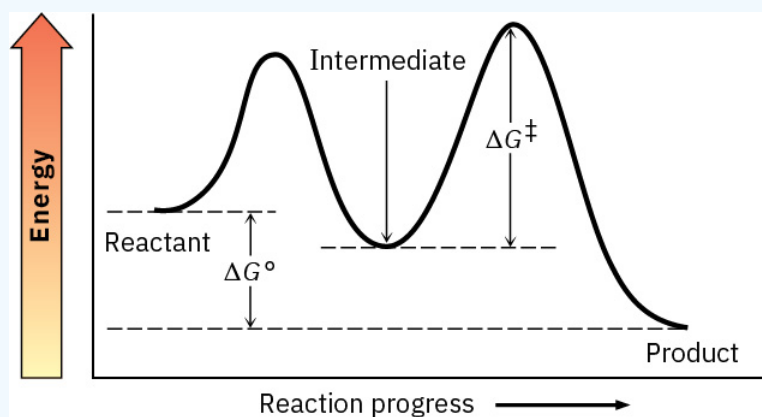
Solution



? Exercise 5.2.9.1

Sketch an energy diagram for a two-step reaction in which both steps are exergonic and in which the second step has a higher-energy transition state than the first. Label the parts of the diagram corresponding to reactant, product, intermediate, overall $\Delta G^\ddagger$, and overall ΔG° .

Answer



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5.2.10: Additional Problems

Visualizing Chemistry

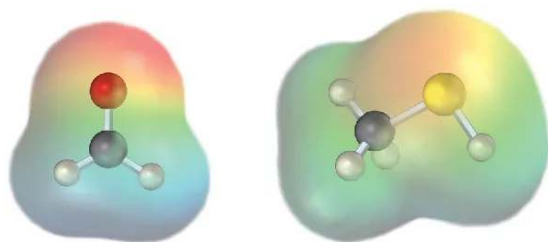
PROBLEM 6-14 The following alkyl halide can be prepared by the addition of HBr to two different alkenes. Draw the structures of both (reddish-brown = Br).



PROBLEM 6-15 The following structure represents the carbocation intermediate formed in the addition reaction of HBr to two different alkenes. Draw the structures of both.

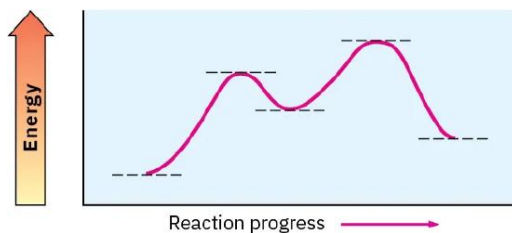


PROBLEM 6-16 Electrostatic potential maps of (a) formaldehyde (CH_2O) and (b) methanethiol (CH_3SH) are shown. Is the formaldehyde carbon atom likely to be electrophilic or nucleophilic? What about the methanethiol sulfur atom? Explain.



(a) Formaldehyde (b) Methanethiol

PROBLEM 6-17 Look at the following energy diagram:



- Is ΔG° for the reaction positive or negative? Label it on the diagram.
- How many steps are involved in the reaction?
- How many transition states are there? Label them on the diagram.

PROBLEM 6-18 Look at the following energy diagram for an enzyme-catalyzed reaction:



- How many steps are involved?
- Which step is most exergonic?
- Which step is the slowest?

Energy Diagrams and Reaction Mechanisms

PROBLEM 6-19 What is the difference between a transition state and an intermediate?

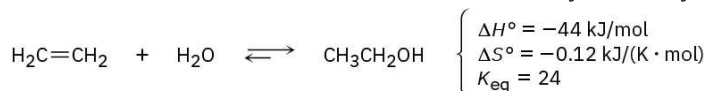
PROBLEM 6-20 Draw an energy diagram for a one-step reaction with $K_{eq} < 1$. Label the parts of the diagram corresponding to reactants, products, transition state, ΔG° , and $\Delta G^\ddagger$. Is ΔG° positive or negative?

PROBLEM 6-21 Draw an energy diagram for a two-step reaction with $K_{eq} > 1$. Label the overall ΔG° , transition states, and intermediate. Is ΔG° positive or negative?

PROBLEM 6-22 Draw an energy diagram for a two-step exergonic reaction whose second step is faster than its first step.

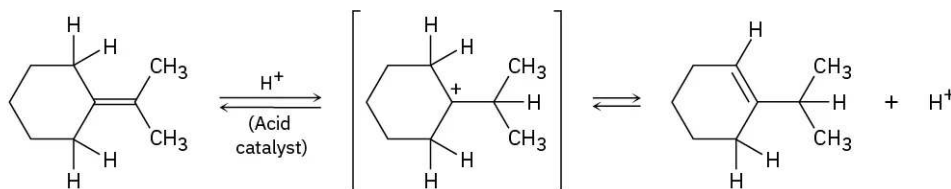
PROBLEM 6-23 Draw an energy diagram for a reaction with $K_{eq} = 1$. What is the value of ΔG° in this reaction?

PROBLEM 6-24 The addition of water to ethylene to yield ethanol has the following thermodynamic parameters:



- (a) Is the reaction exothermic or endothermic?
- (b) Is the reaction favorable (spontaneous) or unfavorable (nonspontaneous) at room temperature (298 K)?

PROBLEM 6-25 When isopropylidenecyclohexane is treated with strong acid at room temperature, isomerization occurs by the mechanism shown below to yield 1-isopropylcyclohexene:



Isopropylidenecyclohexane

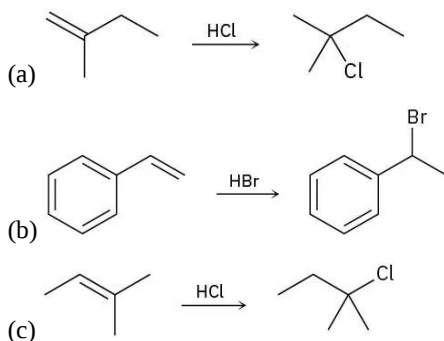
1-Isopropylcyclohexene

At equilibrium, the product mixture contains about 30% isopropylidenecyclohexane and about 70% 1-isopropylcyclohexene.

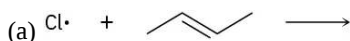
- (a) What is an approximate value of K_{eq} for the reaction?
- (b) Since the reaction occurs slowly at room temperature, what is its approximate $\Delta G^\ddagger$?
- (c) Draw an energy diagram for the reaction.

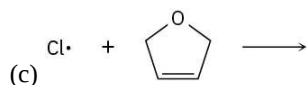
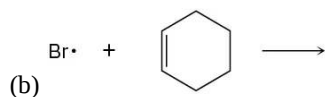
PROBLEM 6-26 Add curved arrows to the mechanism shown in Problem 6-25 to indicate the electron movement in each step.

PROBLEM 6-27 Draw the complete mechanism for each of the following polar reactions.



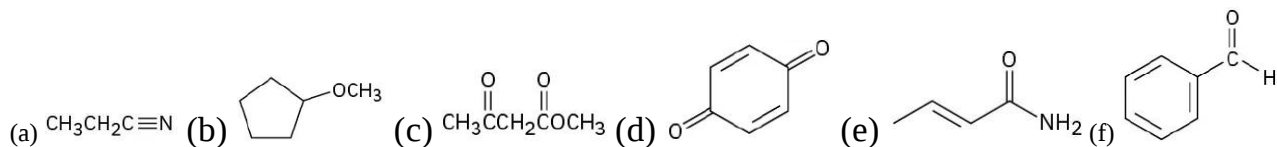
PROBLEM 6-28 Use curved arrows to show the flow of electrons, and draw the carbon radical that is formed when the halogen radicals below add to the corresponding alkenes.



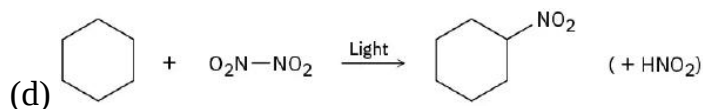
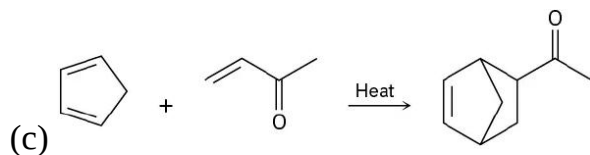
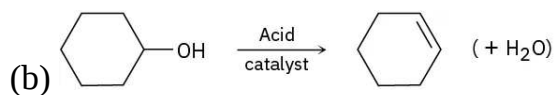


Polar Reactions

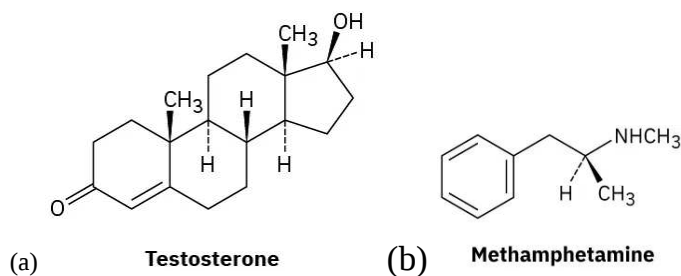
PROBLEM 6-29 Identify the functional groups in the following molecules, and show the polarity of each:



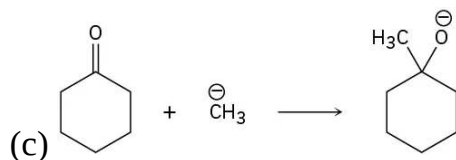
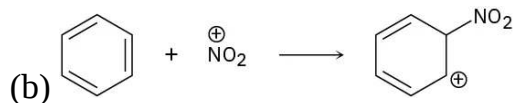
PROBLEM 6-30 Identify the following reactions as additions, eliminations, substitutions, or rearrangements:



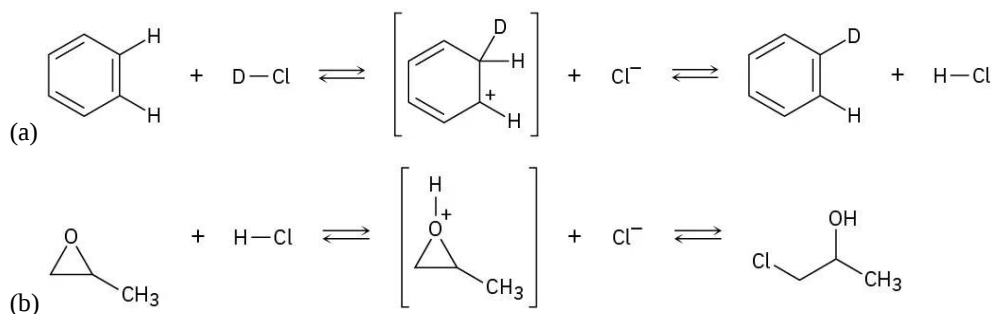
PROBLEM 6-31 Identify the likely electrophilic and nucleophilic sites in each of the following molecules:



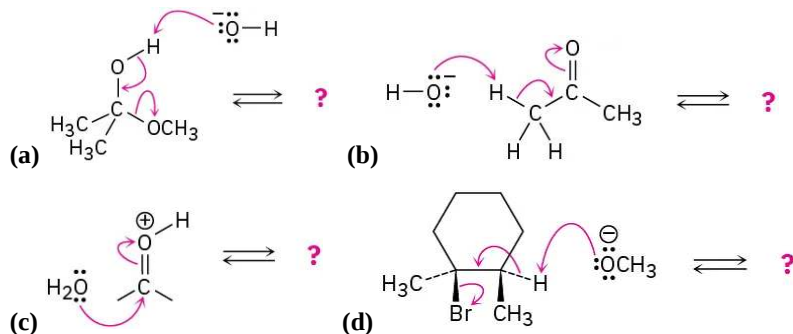
PROBLEM 6-32 Identify the electrophile and the nucleophile.



PROBLEM 6-33 Add curved arrows to the following polar reactions to indicate the flow of electrons in each:



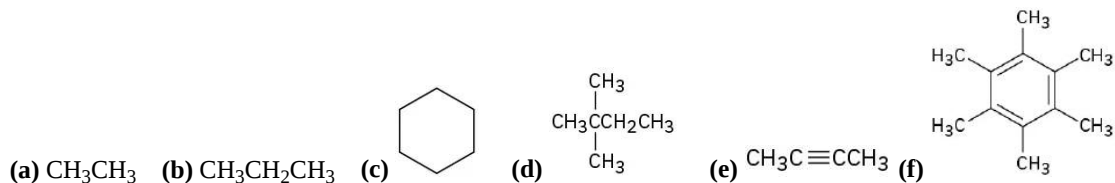
PROBLEM 6-34 Follow the flow of electrons indicated by the curved arrows in each of the following polar reactions, and predict the products that result:



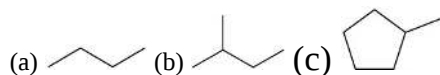
Radical Reactions

PROBLEM 6-35 Radical chlorination of pentane is a poor way to prepare 1-chloropentane, but radical chlorination of neopentane, $(\text{CH}_3)_4\text{C}$, is a good way to prepare neopentyl chloride, $(\text{CH}_3)_3\text{CCH}_2\text{Cl}$. Explain.

PROBLEM 6-36 Despite the limitations of radical chlorination of alkanes, the reaction is still useful for synthesizing certain halogenated compounds. For which of the following compounds does radical chlorination give a single monochloro product?

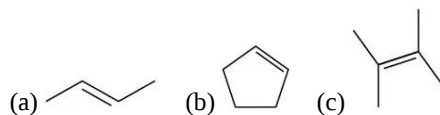


PROBLEM 6-37 Draw the different monochlorinated constitutional isomers you would obtain by the radical chlorination of the following compounds.



PROBLEM 6-38 Answer question 37 taking all stereoisomers into account.

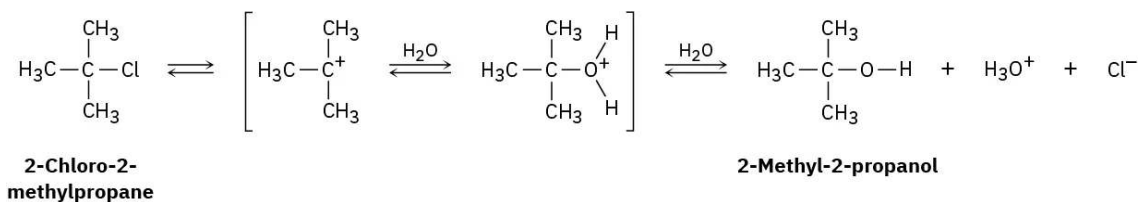
PROBLEM 6-39 Show the structure of the carbocation that would result when each of the following alkenes reacts with an acid, H^+ .



General Problems

PROBLEM 6-40 2-Chloro-2-methylpropane reacts with water in three steps to yield 2-methyl-2-propanol. The first step is slower than the second, which in turn is much slower than the third. The reaction takes place slowly at room temperature, and the

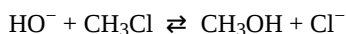
equilibrium constant is approximately 1.



- (a) Give approximate values for $\Delta G^\ddagger$ and ΔG° that are consistent with the above information.
- (b) Draw an energy diagram for the reaction, labeling all points of interest and placing relative energy levels on the diagram consistent with the information given.

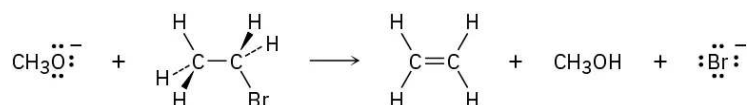
PROBLEM 6-41 Add curved arrows to the mechanism shown in Problem 6-40 to indicate the electron movement in each step.

PROBLEM 6-42 The reaction of hydroxide ion with chloromethane to yield methanol and chloride ion is an example of a general reaction type called a nucleophilic substitution reaction:



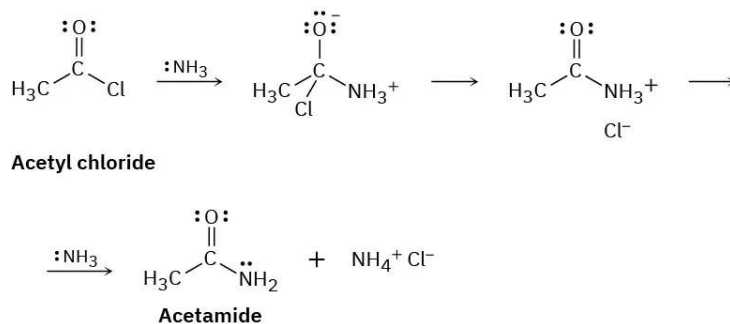
The value of ΔH° for the reaction is -75 kJ/mol , and the value of ΔS° is $+54 \text{ J/(K}\cdot\text{mol)}$. What is the value of ΔG° (in kJ/mol) at 298 K ? Is the reaction exothermic or endothermic? Is it exergonic or endergonic?

PROBLEM 6-43 Methoxide ion (CH_3O^-) reacts with bromoethane in a single step according to the following equation:

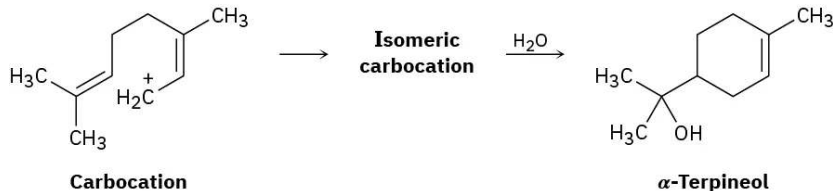


Identify the bonds broken and formed, and draw curved arrows to represent the flow of electrons during the reaction.

PROBLEM 6-44 Ammonia reacts with acetyl chloride (CH_3COCl) to give acetamide (CH_3CONH_2). Identify the bonds broken and formed in each step of the reaction, and draw curved arrows to represent the flow of electrons in each step.

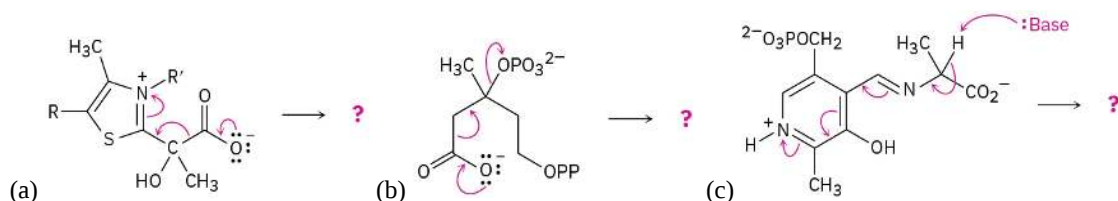


PROBLEM 6-45 The naturally occurring molecule α -terpineol is biosynthesized by a route that includes the following step:



- (a) Propose a likely structure for the isomeric carbocation intermediate.
- (b) Show the mechanism of each step in the biosynthetic pathway, using curved arrows to indicate electron flow.

PROBLEM 6-46 Predict the product(s) of each of the following biological reactions by interpreting the flow of electrons as indicated by the curved arrows:



PROBLEM 6-47 Reaction of 2-methylpropene with HBr might, in principle, lead to a mixture of two alkyl bromide addition products. Name them, and draw their structures.

PROBLEM 6-48 Draw the structures of the two carbocation intermediates that might form during the reaction of 2-methylpropene with HBr (Problem 47). We'll see in the next chapter that the stability of carbocations depends on the number of alkyl substituents attached to the positively charged carbon—the more alkyl substituents there are, the more stable the cation. Which of the two carbocation intermediates you drew is more stable?

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5.3: Elementary Mechanistic Steps

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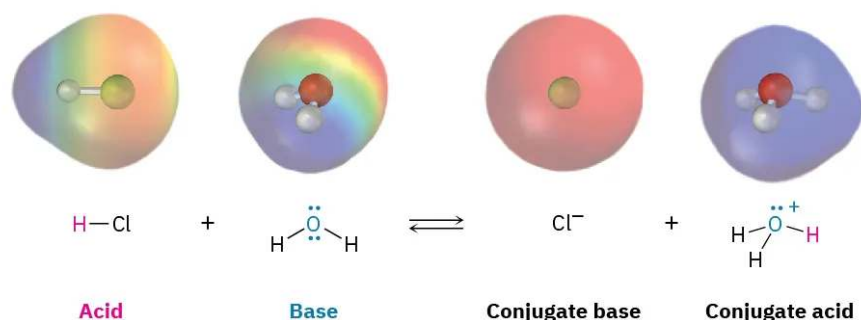
5.4: Apply to Acids and Bases

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5.4.1: Acids and Bases - The Brønsted-Lowry Definition

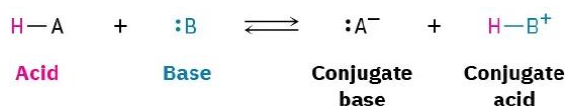
Perhaps the most important of all concepts related to electronegativity and polarity is that of *acidity* and *basicity*. We'll soon see, in fact, that the acid–base behavior of organic molecules explains much of their chemistry. You may recall from a course in general chemistry that two definitions of acidity are frequently used: the *Brønsted–Lowry definition* and the *Lewis definition*. We'll look at the Brønsted–Lowry definition in this and the following three sections and then discuss the Lewis definition in **Section 2.12**.

A Brønsted–Lowry acid is a substance that donates a hydrogen ion, H^+ , and a Brønsted–Lowry base is a substance that accepts a hydrogen ion. (The name *proton* is often used as a synonym for H^+ because loss of the valence electron from a neutral hydrogen atom leaves only the hydrogen nucleus—a proton.) When gaseous hydrogen chloride dissolves in water, for example, a polar HCl molecule acts as an acid and donates a proton, while a water molecule acts as a base and accepts the proton, yielding chloride anion (Cl^-) and hydronium cation (H_3O^+). This and other acid–base reactions are reversible, so we'll write them with double, forward-and-backward arrows.

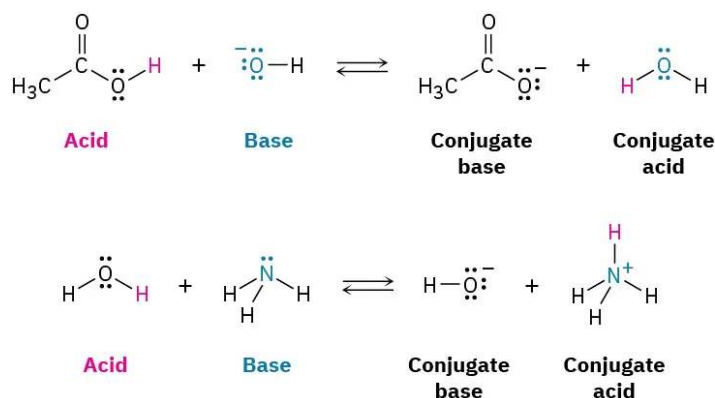


Chloride ion, the product that results when the acid HCl loses a proton, is called the conjugate base of the acid, and hydronium ion, the product that results when the base H_2O gains a proton, is called the conjugate acid of the base. Other common mineral acids such as H_2SO_4 and HNO_3 behave similarly, as do organic acids such as acetic acid, $\text{CH}_3\text{CO}_2\text{H}$.

In a general sense,



For example:

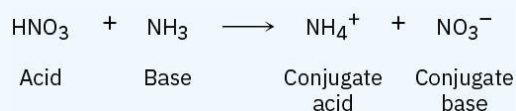


Notice that water can act either as an acid or as a base, depending on the circumstances. In its reaction with HCl, water is a base that accepts a proton to give the hydronium ion, H_3O^+ . In its reaction with ammonia (NH_3), however, water is an acid that donates a proton to give ammonium ion (NH_4^+) and hydroxide ion, OH^- .

? Exercise 5.4.1.1

Nitric acid (HNO_3) reacts with ammonia (NH_3) to yield ammonium nitrate. Write the reaction, and identify the acid, the base, the conjugate acid product, and the conjugate base product.

Answer

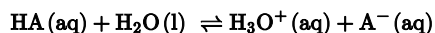


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5.4.2: Acid and Base Strength

Different acids differ in their ability to donate H^+ . Stronger acids, such as HCl , react almost completely with water, whereas weaker acids, such as acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), react only slightly. The exact strength of a given acid HA in water solution is described using the **acidity constant** (K_a) for the acid-dissociation equilibrium.



the acid ionization constant is written

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Recall from general chemistry that the solvent concentration does not appear in the equilibrium expression, and that brackets [] around a substance refer to the concentration of the enclosed species in moles per liter (molarity).

Note

Equilibrium constant expressions are actually ratios of **activities**, and the value of K is determined at the limit of infinite dilution of the solutes. In these very dilute solutions, the activity of the solvent has a value of unity (1) and the activity of each solute can be approximated by its molar concentration.

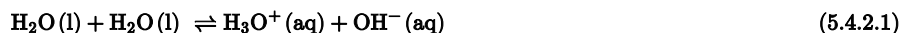
Stronger acids have their equilibria toward the right and thus have larger acidity constants, whereas weaker acids have their equilibria toward the left and have smaller acidity constants. The range of K_a values for different acids is enormous, running from about 10^{15} for the strongest acids to about 10^{-60} for the weakest. Common inorganic acids such as H_2SO_4 , HNO_3 , and HCl have K_a 's in the range of 10^1 to 10^9 , while organic acids generally have K_a 's in the range of 10^{-5} to 10^{-15} . As you gain experience, you'll develop a rough feeling for which acids are "strong" and which are "weak" (always remembering that the terms are relative, not absolute).

Acid strengths are normally expressed using $\text{p}K_a$ values rather than K_a values, where the $\text{p}K_a$ is the negative common logarithm of the K_a :

$$\text{p}K_a = -\log K_a$$

A stronger acid (larger K_a) has a smaller $\text{p}K_a$, and a weaker acid (smaller K_a) has a larger $\text{p}K_a$. Table 5.4.2.1 lists the $\text{p}K_a$'s of some common acids in order of their strength, and a more comprehensive table is given in Appendix B.

Notice that the $\text{p}K_a$ value shown in Table 5.4.2.1 for water is 14.00, which results from the following calculation.



with

$$K_w = K_a = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (5.4.2.2)$$

As explained above, because the water is the solvent and has an activity of unity (1), water is not shown explicitly in the equilibrium constant expression for K_w .

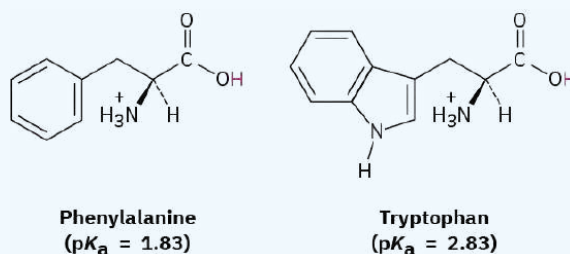
Notice also in Table 5.4.2.1 that there is an inverse relationship between the acid strength of an acid and the base strength of its conjugate base. A strong acid has a weak conjugate base, and a weak acid has a strong conjugate base. To understand this inverse relationship, think about what is happening to the acidic hydrogen in an acid–base reaction. A strong acid is one that loses H^+ easily, meaning that its conjugate base holds the H^+ weakly and is therefore a weak base. A weak acid is one that loses H^+ with difficulty, meaning that its conjugate base holds the proton tightly and is therefore a strong base. The fact that HCl is a strong acid, for example, means that Cl^- does not hold H^+ tightly and is thus a weak base. Water, on the other hand, is a weak acid, meaning that OH^- holds H^+ tightly and is a strong base.

Table 5.4.2.1: Relative Strengths of Some Common Acids and Their Conjugate Bases

	Acid	Name	pK_a	Conjugate base	Name	
Weaker acid Stronger acid	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	16.00	$\text{CH}_3\text{CH}_2\text{O}^-$	Ethoxide ion	Stronger base Weaker base
	H_2O	Water	14.00	HO^-	Hydroxide ion	
	HCN	Hydrocyanic acid	9.31	CN^-	Cyanide ion	
	H_2PO_4^-	Dihydrogen phosphate ion	7.21	HPO_4^{2-}	Hydrogen phosphate ion	
	$\text{CH}_3\text{CO}_2\text{H}$	Acetic acid	4.76	CH_3CO_2^-	Acetate ion	
	H_3PO_4	Phosphoric acid	2.16	H_2PO_4^-	Dihydrogen phosphate ion	
	H_3O^+	Hydronium ion	0.0	H_2O	Water	
	HNO_3	Nitric acid	-1.3	NO_3^-	Nitrate ion	
	HCl	Hydrochloric acid	-7.0	Cl^-	Chloride ion	

? Exercise 5.4.2.1

The amino acid phenylalanine has $pK_a = 1.83$, and tryptophan has $pK_a = 2.83$. Which is the stronger acid?



Answer

Phenylalanine is stronger.

? Exercise 5.4.2.2

Amide ion, H_2N^- , is a much stronger base than hydroxide ion, HO^- . Which is the stronger acid, NH_3 or H_2O ? Explain.

Answer

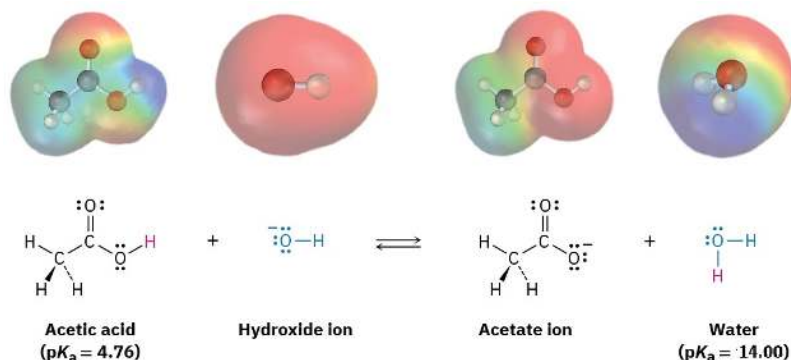
Water is a stronger acid.

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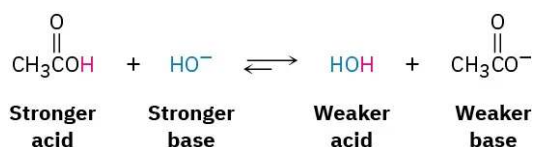
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5.4.3: Predicting Acid-Base Reactions from pK_a Values

Compilations of pK_a values like those in Table 2.3 and Appendix B are useful for predicting whether a given acid–base reaction will take place, because H⁺ will always go *from* the stronger acid *to* the stronger base. That is, an acid will donate a proton to the conjugate base of a weaker acid, and the conjugate base of a weaker acid will remove a proton from a stronger acid. Since water (pK_a = 14.00) is a weaker acid than acetic acid (pK_a = 4.76), for example, hydroxide ion holds a proton more tightly than acetate ion does. Hydroxide ion will therefore react to a large extent with acetic acid, CH₃CO₂H, to yield acetate ion and H₂O.

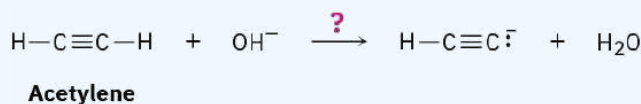


Another way to predict acid–base reactivity is to remember that the product conjugate acid in an acid–base reaction must be weaker and less reactive than the starting acid and the product conjugate base must be weaker and less reactive than the starting base. In the reaction of acetic acid with hydroxide ion, for example, the product conjugate acid (H₂O) is weaker than the starting acid (CH₃CO₂H), and the product conjugate base (CH₃CO₂[−]) is weaker than the starting base (OH[−]).



✓ Worked Example 5.4.3.1: Predicting Acid Strengths from pK_a Values

Water has pK_a = 14.00, and acetylene has pK_a = 25. Which is the stronger acid? Does hydroxide ion react to a significant extent with acetylene?



Strategy

When comparing two acids, the one with the lower pK_a is stronger. Thus, water is a stronger acid than acetylene and gives up H⁺ more easily.

Solution

Because water is a stronger acid and gives up H⁺ more easily than acetylene, the HO[−] ion must have less affinity for H⁺ than the HC≡C:⁻ ion. In other words, the anion of acetylene is a stronger base than hydroxide ion, and the reaction will not proceed significantly as written.

✓ Worked Example 5.4.3.2: Calculating K_a from pK_a

According to the data in Table 2.3, acetic acid has pK_a = 4.76. What is its K_a?

Strategy

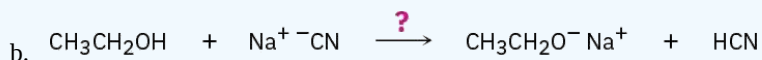
Since pK_a is the negative logarithm of K_a, it's necessary to use a calculator with an ANTILOG or INV LOG function. Enter the value of the pK_a (4.76), change the sign (−4.76), and then find the antilog (1.74 × 10^{−5}).

Solution

$$K_a = 1.74 \times 10^{-5}.$$

? Exercise 5.4.3.1

Will either of the following reactions take place to a significant extent as written, according to the data in Table 2.3?

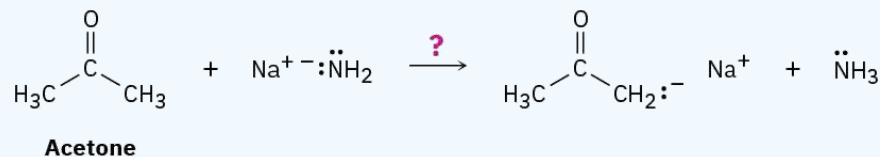


Answer

Neither reaction will take place.

? Exercise 5.4.3.2

Ammonia, NH_3 , has $\text{p}K_a \approx 36$, and acetone has $\text{p}K_a \approx 19$. Will the following reaction take place to a significant extent?



Answer

The reaction will take place.

? Exercise 5.4.3.3

What is the K_a of HCN if its $\text{p}K_a = 9.31$?

Answer

$$K_a = 4.9 \times 10^{-10}$$

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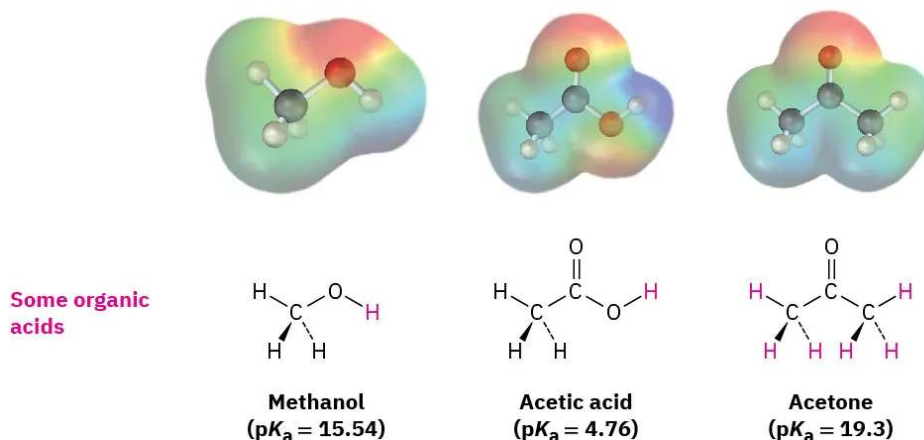
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5.4.4: Organic Acids and Organic Bases

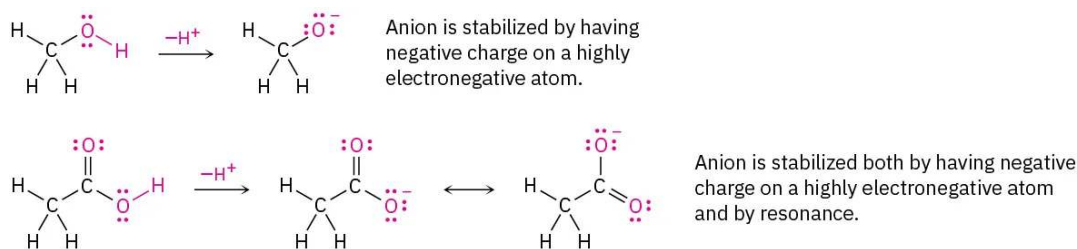
Many of the reactions we'll be seeing in future chapters, including practically all biological reactions, involve organic acids and organic bases. Although it's too early to go into the details of these processes now, you might keep the following generalities in mind:

Organic Acids

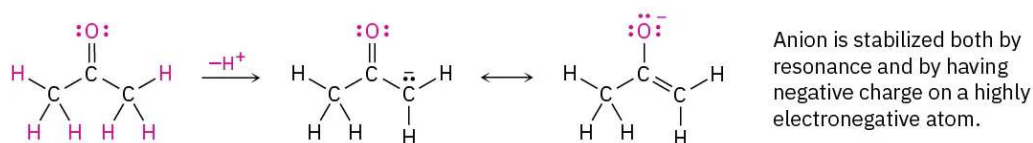
Organic acids are characterized by the presence of a positively polarized hydrogen atom (blue in electrostatic potential maps) and are of two main kinds: acids such as methanol and acetic acid that contain a hydrogen atom bonded to an electronegative oxygen atom (O–H) and those such as acetone (Section 2.6) that contain a hydrogen atom bonded to a carbon atom next to a C=O bond (O=C–C–H).



Methanol contains an O–H bond and is a weak acid, while acetic acid also contains an O–H bond and is a somewhat stronger acid. In both cases, acidity is due to the fact that the conjugate base resulting from loss of H^+ is stabilized by having its negative charge on a strongly electronegative oxygen atom. In addition, the conjugate base of acetic acid is stabilized by resonance (Section 2.5 and Section 2.6).



The acidity of acetone and other compounds with C=O bonds is due to the fact that the conjugate base resulting from the loss of H^+ is stabilized by resonance. In addition, one of the resonance forms stabilizes the negative charge by placing it on an electronegative oxygen atom.



Electrostatic potential maps of the conjugate bases from methanol, acetic acid, and acetone are shown in Figure 2.5. As you might expect, all three show a substantial amount of negative charge (red) on oxygen.

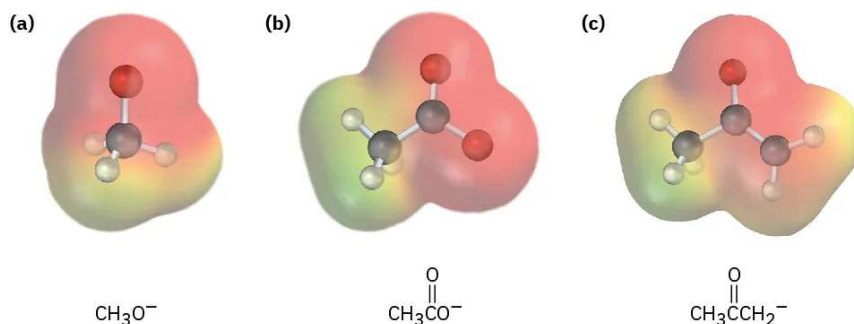
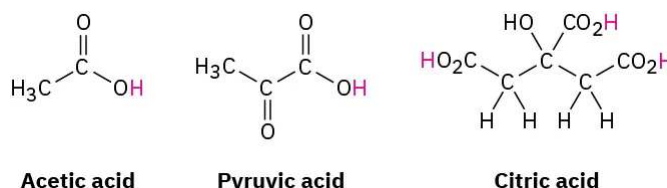


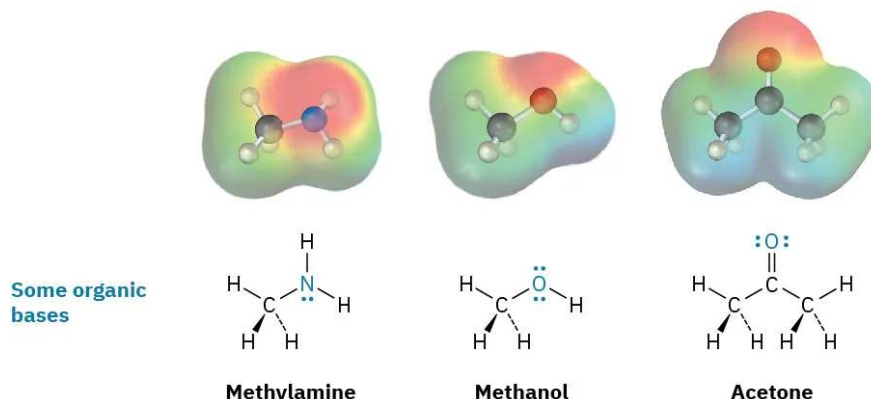
Figure 2.5 Electrostatic potential maps of the conjugate bases of (a) methanol, (b) acetic acid, and (c) acetone. The electronegative oxygen atoms stabilize the negative charge in all three.

Compounds called *carboxylic acids*, which contain the $-\text{CO}_2\text{H}$ grouping, occur abundantly in all living organisms and are involved in almost all metabolic pathways. Acetic acid, pyruvic acid, and citric acid are examples. You might note that at the typical pH of 7.3 found within cells, carboxylic acids are usually dissociated and exist as their carboxylate anions, $-\text{CO}_2^-$.

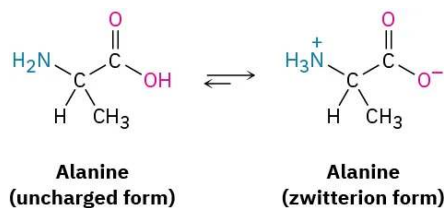


Organic Bases

Organic bases are characterized by the presence of an atom (reddish in electrostatic potential maps) with a lone pair of electrons that can bond to H^+ . Nitrogen-containing compounds such as methylamine are the most common organic bases and are involved in almost all metabolic pathways, but oxygen-containing compounds can also act as bases when reacting with a sufficiently strong acid. Note that some oxygen-containing compounds can act both as acids and as bases depending on the circumstances, just as water can. Methanol and acetone, for instance, act as acids when they donate a proton but as bases when their oxygen atom accepts a proton.



Substances called amino acids, so-named because they are both amines ($-\text{NH}_2$) and carboxylic acids ($-\text{CO}_2\text{H}$), are the building blocks from which the proteins in all living organisms are made. Twenty different amino acids go into making up proteins—alanine is an example. Interestingly, alanine and other amino acids exist primarily in a doubly charged form called a *zwitterion* rather than in the uncharged form. The zwitterion form arises because amino acids have both acidic and basic sites within the same molecule and therefore undergo an internal acid–base reaction.

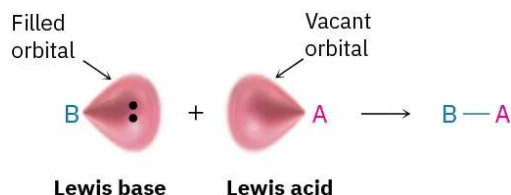


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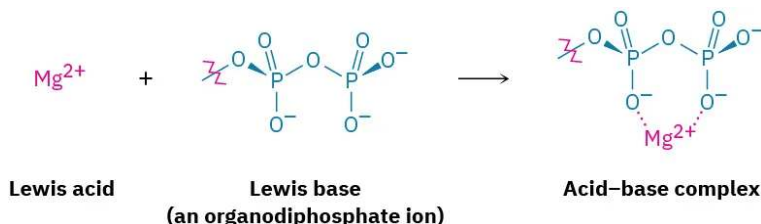
5.4.5: Acids and Bases - The Lewis Definition

The Lewis definition of acids and bases is more encompassing than the Brønsted–Lowry definition because it's not limited to substances that donate or accept just protons. A Lewis acid is a substance that accepts an electron pair, and a Lewis base is a substance that donates an electron pair. The donated electron pair is shared between the acid and the base in a covalent bond.



Lewis Acids and the Curved Arrow Formalism

The fact that a Lewis acid is able to accept an electron pair means that it must have either a vacant, low-energy orbital or a polar bond to hydrogen so that it can donate H^+ (which has an empty $1s$ orbital). Thus, the Lewis definition of acidity includes many species in addition to H^+ . For example, various metal cations, such as Mg^{2+} , are Lewis acids because they accept a pair of electrons when they form a bond to a base. We'll also see in later chapters that certain metabolic reactions begin with an acid–base reaction between Mg^{2+} as a Lewis acid and an organic diphosphate or triphosphate ion as the Lewis base.



In the same way, compounds of group 3A elements, such as BF_3 and $AlCl_3$, are Lewis acids because they have unfilled valence orbitals and can accept electron pairs from Lewis bases, as shown in Figure 5.4.5.1. Similarly, many transition-metal compounds, such as $TiCl_4$, $FeCl_3$, $ZnCl_2$, and $SnCl_4$, are Lewis acids.

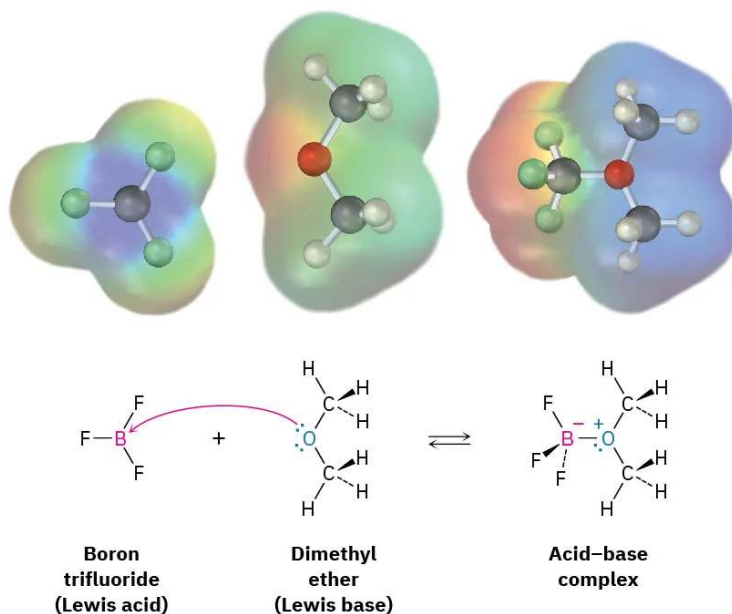
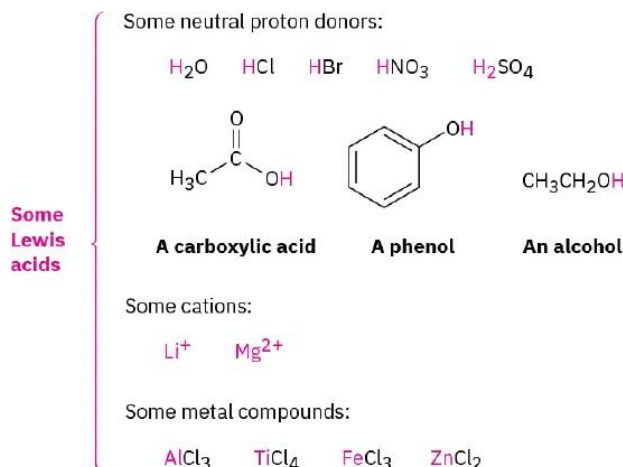


Figure 5.4.5.1: The reaction of boron trifluoride, a Lewis acid, with dimethyl ether, a Lewis base. The Lewis acid accepts a pair of electrons, and the Lewis base donates a pair of nonbonding electrons. Note how the movement of electrons from the Lewis base to the Lewis acid is indicated by a curved arrow. Note also how, in electrostatic potential maps, **the boron becomes more negative (red)** after reaction because it has gained electrons and **the oxygen atom becomes more positive (blue)** because it has donated electrons.

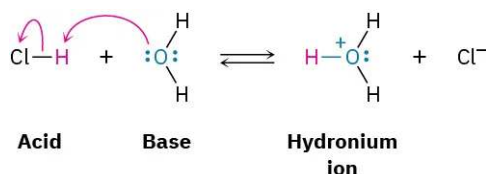
Look closely at the acid–base reaction in Figure 5.4.5.1, and notice how it's shown. Dimethyl ether, the Lewis base, donates an electron pair to a vacant valence orbital of the boron atom in BF_3 , a Lewis acid. The direction of electron-pair flow from base to acid is shown using a curved arrow, just as the direction of electron flow from one resonance structure to another was shown using curved arrows in Section 2.6. We'll use this curved-arrow notation throughout the remainder of this text to indicate electron flow during reactions, so get used to seeing it.

Some further examples of Lewis acids follow:

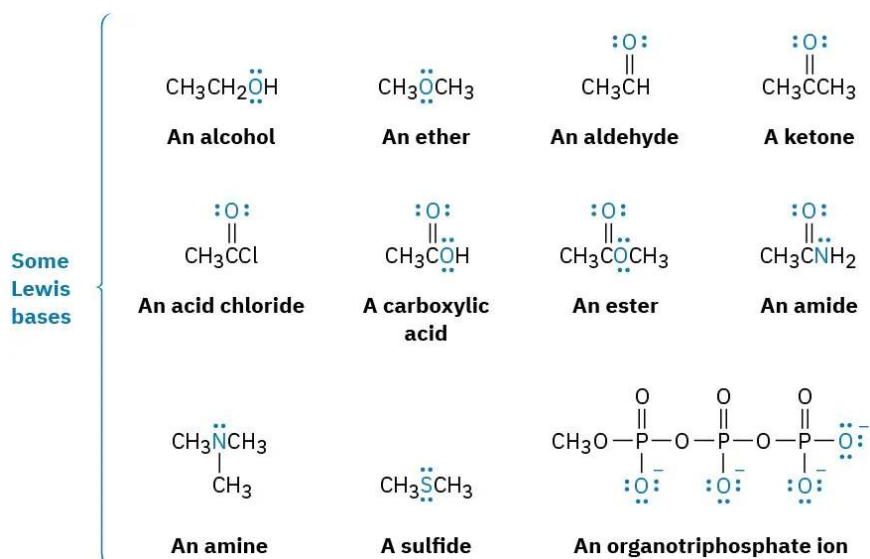


Lewis Bases

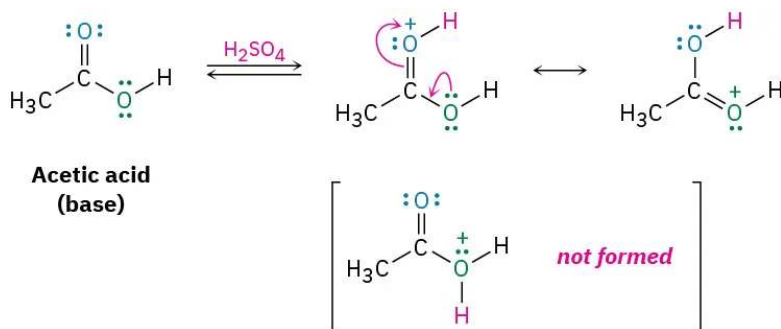
The Lewis definition of a base—a compound with a pair of nonbonding electrons that it can use to bond to a Lewis acid—is similar to the Brønsted–Lowry definition. Thus, H_2O , with its two pairs of nonbonding electrons on oxygen, acts as a Lewis base by donating an electron pair to an H^+ in forming the hydronium ion, H_3O^+ .



In a more general sense, most oxygen- and nitrogen-containing organic compounds can act as Lewis bases because they have lone pairs of electrons. A divalent oxygen compound has two lone pairs of electrons, and a trivalent nitrogen compound has one lone pair. Note in the following examples that some compounds can act as both acids and bases, just as water can. Alcohols and carboxylic acids, for instance, act as acids when they donate an H^+ but as bases when their oxygen atom accepts an H^+ .



Note also that some Lewis bases, such as carboxylic acids, esters, and amides, have more than one atom with a lone pair of electrons and can therefore react at more than one site. Acetic acid, for example, can be protonated either on the doubly bonded oxygen atom or on the singly bonded oxygen atom. The reaction normally occurs only once in such instances, and the more stable of the two possible protonation products are formed. For acetic acid, protonation by reaction with sulfuric acid occurs on the doubly bonded oxygen because that product is stabilized by two resonance forms.



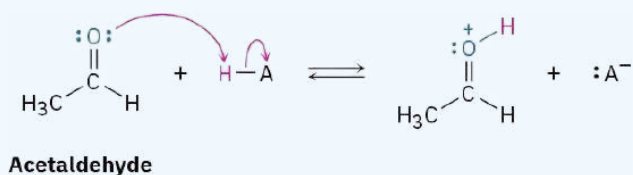
✓ Worked Example 5.4.5.1: Using Curved Arrows to Show Electron Flow

Using curved arrows, show how acetaldehyde, CH_3CHO , can act as a Lewis base.

Strategy

A Lewis base donates an electron pair to a Lewis acid. We therefore need to locate the electron lone pairs on acetaldehyde and use a curved arrow to show the movement of a pair toward the H atom of the acid.

Solution

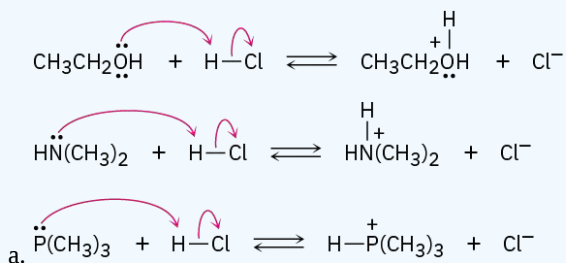


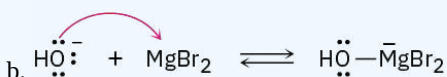
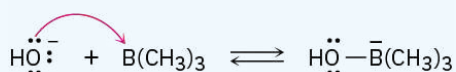
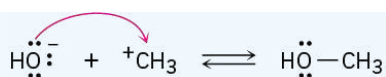
? Exercise 5.4.5.1

Using curved arrows, show how the species in part (a) can act as Lewis bases in their reactions with HCl , and show how the species in part (b) can act as Lewis acids in their reaction with OH^- .

- $\text{CH}_3\text{CH}_2\text{OH}$, $\text{HN}(\text{CH}_3)_2$, $\text{P}(\text{CH}_3)_3$
- H_3C^+ , $\text{B}(\text{CH}_3)_3$, MgBr_2

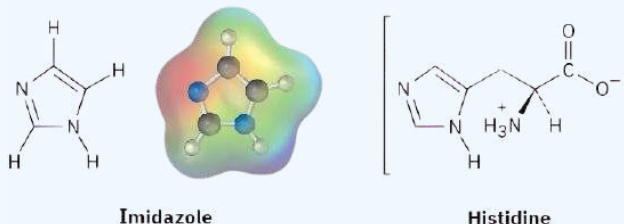
Answer





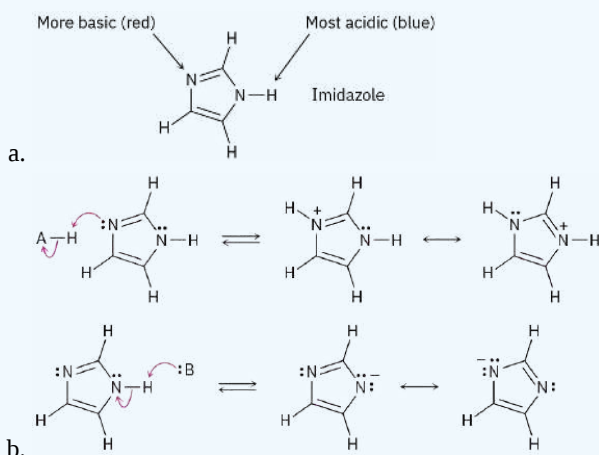
? Exercise 5.4.5.2

Imidazole, which forms part of amino acid histidine, can act as both an acid and a base.



- Look at the electrostatic potential map of imidazole, and identify the most acidic hydrogen atom and the most basic nitrogen atom.
- Draw structures for the resonance forms of the products that result when imidazole is protonated by an acid and deprotonated by a base.

Answer



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