

ORGANIC CHEMISTRY I



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SHU Organic Chemistry I

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TABLE OF CONTENTS

Licensing

1: Chapter 1 Structure Determines Properties

- 1.1: Development of Chemical Bonding Theory
- 1.2: The Nature of Chemical Bonds - Valence Bond Theory
- 1.3: Polar Covalent Bonds - Electronegativity
- 1.4: Polar Covalent Bonds - Dipole Moments
- 1.5: Formal Charges
- 1.6: Resonance
- 1.7: Rules for Resonance Forms
- 1.8: Drawing Resonance Forms
- 1.9: Acids and Bases - The Brønsted-Lowry Definition
- 1.10: Acid and Base Strength
- 1.11: Predicting Acid-Base Reactions from pKa Values
- 1.12: Organic Acids and Organic Bases
- 1.13: Acids and Bases - The Lewis Definition
- 1.14: Noncovalent Interactions Between Molecules
- 1.15: Molecular Models
- 1.1 Atoms, Electrons, and Orbitals

2: Chapter 2 Alkanes

- 2.1: Functional Groups
- 2.2: Alkanes and Alkane Isomers
- 2.3: Alkyl Groups
- 2.4: Naming Alkanes
- 2.5: Naming Cycloalkanes
- 2.6: The Nature of Chemical Bonds: Molecular Orbital Theory
- 2.7: sp^3 Hybrid Orbitals and the Structure of Methane
- 2.8: sp^3 Hybrid Orbitals and the Structure of Ethane
- 2.9: sp^2 Hybrid Orbitals and the Structure of Ethylene
- 2.10: sp Hybrid Orbitals and the Structure of Acetylene
- 2.11: Drawing Chemical Structures

3: Chapter 3 Conformations and Cycloalkanes

- 3.1: Conformations of Ethane
- 3.2: Conformations of Other Alkanes
- 3.3: Cis-Trans Isomerism in Cycloalkanes
- 3.4: Stability of Cycloalkanes - Ring Strain
- 3.5: Conformations of Cycloalkanes
- 3.6: Conformations of Cyclohexane

- 3.7: Axial and Equatorial Bonds in Cyclohexane
- 3.8: Conformations of Monosubstituted Cyclohexanes
- 3.9: Conformations of Disubstituted Cyclohexanes
- 3.10: Conformations of Polycyclic Molecules

4: Chapter 4 Alcohols and Alkyl Halides

5: Chapter 5 Alkenes and Elimination Reactions

Index

Glossary

Detailed Licensing

Licensing

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

1: CHAPTER 1 STRUCTURE DETERMINES PROPERTIES

- 1.1: Development of Chemical Bonding Theory
- 1.2: The Nature of Chemical Bonds - Valence Bond Theory
- 1.3: Polar Covalent Bonds - Electronegativity
- 1.4: Polar Covalent Bonds - Dipole Moments
- 1.5: Formal Charges
- 1.6: Resonance
- 1.7: Rules for Resonance Forms
- 1.8: Drawing Resonance Forms
- 1.9: Acids and Bases - The Brønsted-Lowry Definition
- 1.10: Acid and Base Strength
- 1.11: Predicting Acid-Base Reactions from pKa Values
- 1.12: Organic Acids and Organic Bases
- 1.13: Acids and Bases - The Lewis Definition
- 1.14: Noncovalent Interactions Between Molecules
- 1.15: Molecular Models
- 1.1 Atoms, Electrons, and Orbitals

1.1: Development of Chemical Bonding Theory

Objectives

After completing this section, you should be able to

1. draw Lewis Dot Symbols for main group elements and ions.
2. describe the three-dimensional nature of molecules.
3. sketch a tetrahedral molecule, CX_4 , using the “wedge-and-broken-line” method of representation.
4. make a ball-and-stick model of a simple tetrahedral molecule such as methane, CH_4 .
5. draw Lewis Dot Structures for 2 electron group molecules.
6. draw Lewis Dot Structures for 3 electron group molecules.
7. draw Lewis Dot Structures for 4 electron group molecules.

Study Notes

When drawing any organic structure, you must remember that a neutral carbon atom will almost always have four bonds. Similarly, hydrogen always has one bond; neutral oxygen atoms have two bonds; and neutral nitrogen atoms have three bonds. By committing these simple rules to memory, you can avoid making unnecessary mistakes later in the course.

The “wedge-and-broken-line” type of representation, which helps to convey the three-dimensional nature of organic compounds, will be used throughout the course.

Bonding Overview [Edit section](#)

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond and the general properties found in typical substances in which the bond type occurs will be discussed.

1. Ionic bonds results from **electrostatic forces that exist between ions of opposite charge**. These bonds typically involve a metal with a nonmetal
2. Covalent bonds **result from the sharing of electrons between two atoms**. The bonds typically involve one nonmetallic element with another
3. Metallic bonds are found in solid metals (copper, iron, aluminum) with each metal atom bonded to several neighboring metal atoms and the bonding electrons are free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

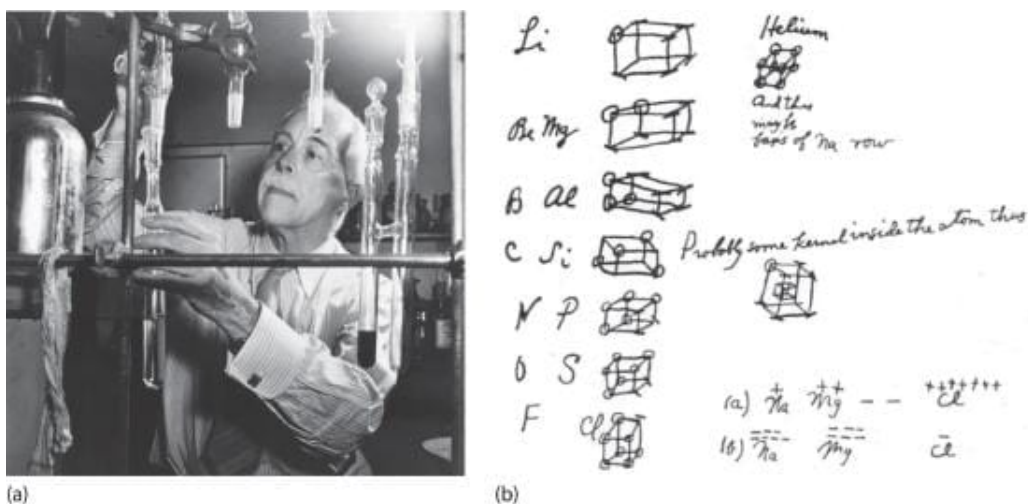


Figure 1.4.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

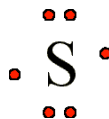
Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

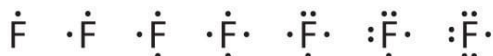
Lewis Dot symbols:

- provide a convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is $[\text{Ne}]3s^23p^4$, thus there are **six** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration $[\text{He}]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 1.4.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol

for nitrogen in Figure 1.4.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	[He]2s ¹	Li •
Be	[He]2s ²	•Be•
B	[He]2s ² 2p ¹	•B•
C	[He]2s ² 2p ²	•C•
N	[He]2s ² 2p ³	•N•
O	[He]2s ² 2p ⁴	•O•
F	[He]2s ² 2p ⁵	•F•
Ne	[He]2s ² 2p ⁶	•Ne•

Figure 1.4.2: Lewis Dot Symbols for the Elements in Period 2

The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called [octet rule](#) explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom. Common exceptions to the octet rule are helium, whose 1s² electron configuration gives it a full *n* = 1 shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs⁺ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs⁺ ion, which has the valence electron configuration of Xe, and the F[−] ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

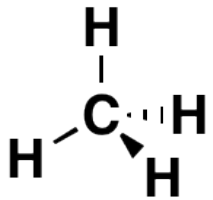
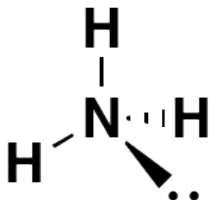
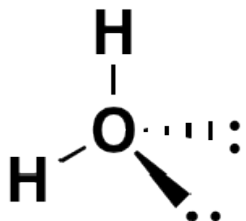
Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

Molecular Shape

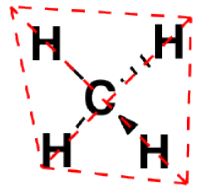
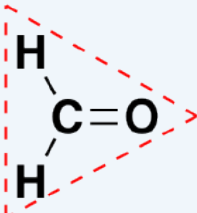
A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)



The following examples make use of this notation, and also illustrate the importance of including non-bonding valence shell electron pairs when viewing such configurations.

		
Methane	Ammonia	Water

Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as **VSEPR** in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories.

Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5°	
Trigonal Planar	3	120°	

Configuration	Bonding Partners	Bond Angles	Example
Linear	2	180°	

Figure 1.4.3 In the three examples shown above, the central atom (carbon) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. However, for molecules of water and ammonia, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds (H_2O 104.5° & NH_3 107.3°) show that they are closer to being tetrahedral than trigonal planar or linear. Of course, it is the configuration of atoms (not electrons) that defines the the shape of a molecule, and in this sense ammonia is said to be pyramidal (not tetrahedral). The compound boron trifluoride, BF_3 , does not have non-bonding valence electrons and the configuration of its atoms is trigonal. Nice treatments of VSEPR theory have been provided by Oxford and Purdue. The best way to study the three-dimensional shapes of molecules is by using molecular models. Many kinds of model kits are available to students and professional chemists.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, .

AX₂: BeH₂

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is



Figure 1.4.4: Lewis Structure for BeH₂

2. There are two electron groups around the central atom. We see from Figure 1.4.3 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH₂ is designated as AX₂.

4. From Figure 1.4.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH₂ is *linear*.

AX₂: CO₂

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH₂, the arrangement that minimizes repulsions places the groups 180° apart.

3. Once again, both groups around the central atom are bonding pairs (BP), so CO₂ is designated as AX₂.

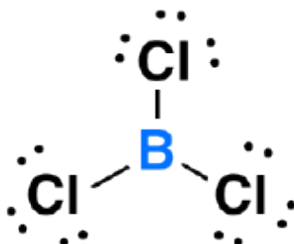
4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular

geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 1.4.3).

Three Electron Groups

AX_3 : BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



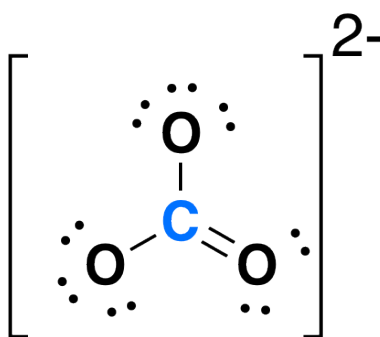
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3 .

4. From Figure 1.4.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*.

AX_3 : CO_3^{2-}

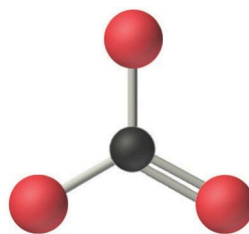
1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $4/3$. We minimize repulsions by placing the three groups 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3 .

4. We see from Figure 1.4.3 that the molecular geometry of CO_3^{2-} is trigonal planar.

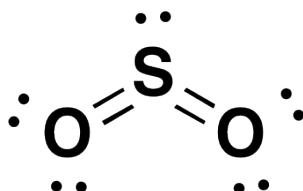


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX₂E: SO₂

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 1.4.3).

3. There are two bonding pairs and one lone pair, so the structure is designated as AX₂E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 1.4.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP-BP < LP-BP < LP-LP. In SO₂, we have one BP-BP interaction and two LP-BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 1.4.2.1 and 1.4.3).

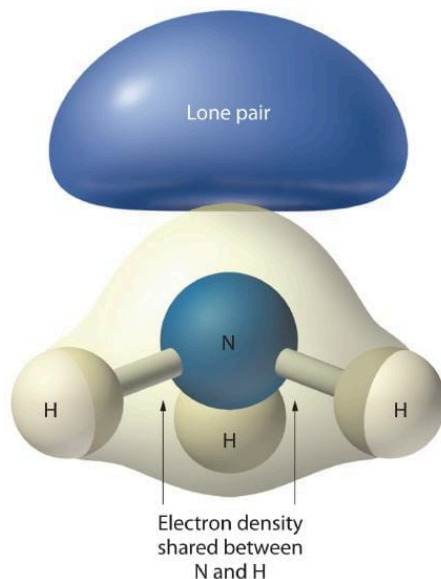
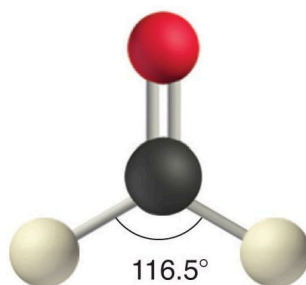


Figure 1.4.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

As with SO_2 , this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an $\text{H}-\text{C}-\text{H}$ bond angle of 116.5° rather than 120°).

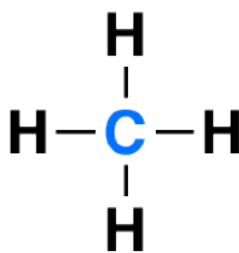


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX₄: CH₄

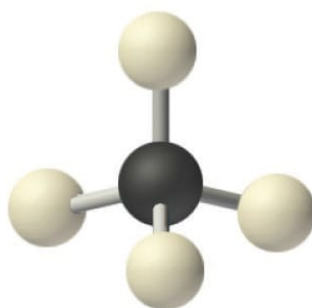
1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



2. There are four electron groups around the central atom. As shown in Figure 1.4.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5° .

3. All electron groups are bonding pairs, so the structure is designated as AX_4 .

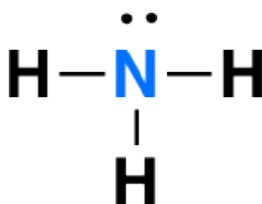
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 1.4.3).



Molecular geometry
(tetrahedral)

AX₃E: NH₃

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



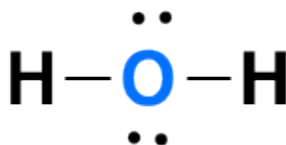
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX₃E. This designation has a total of four electron pairs, three X and one E. We expect the LP-BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 1.4.3). However, the H-N-H bond angles are less than the ideal angle of 109.5° because of LP-BP repulsions.

AX₂E₂: H₂O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

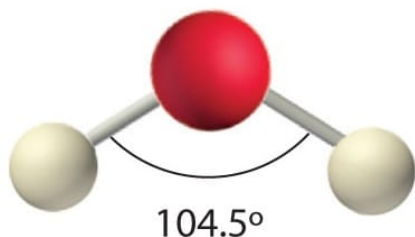


2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 1.4.3.

3. With two bonding pairs and two lone pairs, the structure is designated as AX₂E₂ with a total of four electron pairs. Due to LP-LP, LP-BP, and BP-BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two

nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3 , as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.



Exercises

Questions

Q1.4.1

List the bond angles for each of the following compounds: BH_3 , CF_4 , H_2O .

Q1.4.2

Why is sulfur dioxide a bent molecule (bond angle less than 180°)?

Solutions

S1.4.1

$\text{HBH} = 120^\circ$

$\text{FCF} = 109.5^\circ$

$\text{OHO} = 104^\circ$

S1.4.2

This deviation is due to the lone pairs on the sulfur. These force the molecule to exhibit a “bent” geometry and therefore a deviation from the 180° .

1.2: The Nature of Chemical Bonds - Valence Bond Theory

Objectives

After completing this section, you should be able to

1. explain how covalent bonds are formed as a result of the ability of atoms to share electrons.
2. draw Lewis structures (also known as Lewis formulas or electron-dot formulas) of simple species, such as CH_4 , H_2O , H_3O^+ , CH_3OH , and NH_3 , without the aid of a periodic table.
3. draw structural formulas (i.e., Kekulé structures or line-bond structures) of simple species without the aid of a periodic table.
4. describe the formation of covalent bonds in terms of the overlapping of atomic orbitals.

Key Terms

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

- bond strength
- covalent bond
- ionic bond
- Lewis structure
- lone-pair electron
- non-bonding electron
- sigma (σ) bond
- pi (π) bond
- valence bond theory

Study Notes

To draw Lewis structures successfully, you need to know the number of valence electrons present in each of the atoms involved. Memorize the number of valence electrons possessed by each of the elements commonly encountered in organic chemistry: C, H, O, N, S, P and the halogens.

Ionic bonding

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged.

Ionic bonding is the attraction between positively- and negatively-charged **ions**. These oppositely charged ions attract each other to form ionic networks (or lattices). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes more stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

Example 1.5.1: Sodium Chloride

For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, the ions of sodium and chloride attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is **NaCl**.

For full video of making NaCl from sodium metal and chlorine gas, see <https://www.youtube.com/watch?v=WVonUBjCrNo>. These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):

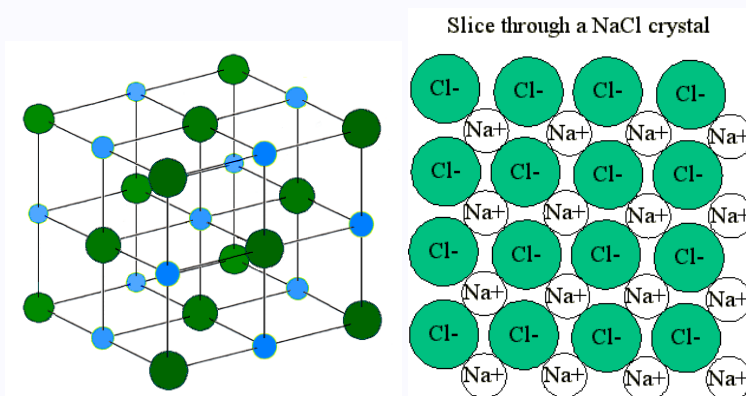


Figure: NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattices. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization potential. Thus the chlorine gains an electron from the sodium atom. This can be represented using **electron-dot symbols** (here we will consider one chlorine atom, rather than Cl_2):



The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its **valence** shell:

- Na^+ : $2s^2 2p^6$
- Cl^- : $3s^2 3p^6$

The importance of noble gas structures

A lot of importance is attached to the electronic structures of noble gases like neon or argon which have eight electrons in their outer energy levels (or two in the case of helium). These noble gas structures are thought of as being in some way a "desirable" thing for an atom to have. You may well have been left with the strong impression that when other atoms react, they try to achieve noble gas structures. As well as achieving noble gas structures by transferring electrons from one atom to another as in ionic bonding, it is also possible for atoms to reach these stable structures by sharing electrons to give covalent bonds.

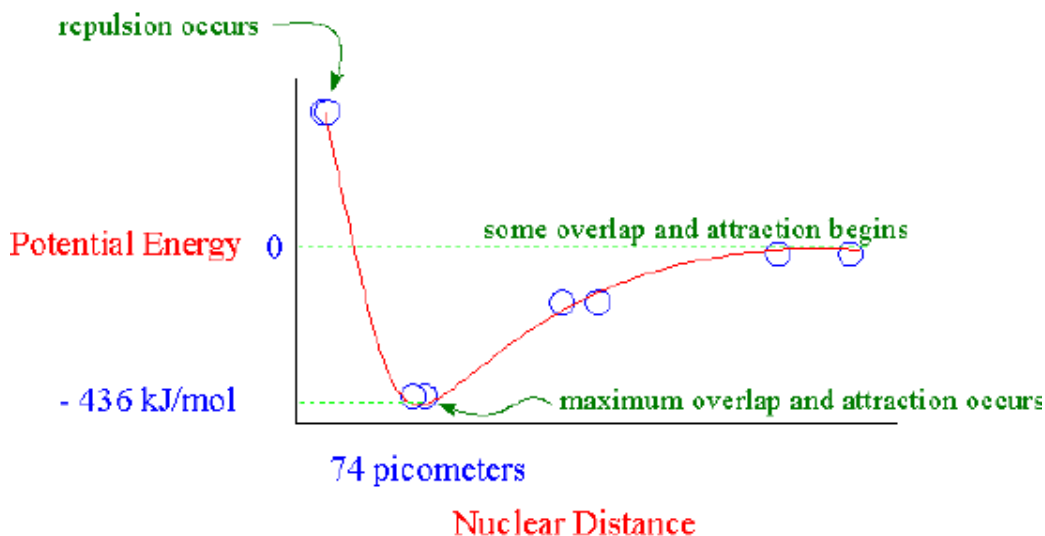
Chemical Bonds

Chemical bonds are the attractive forces that hold atoms together in the form of compounds. They are formed when electrons

are shared between two atoms. There are 3 types of bonds: [covalent bonds](#), [polar covalent bonds](#) and [ionic bonds](#). The simplest example of bonding can be demonstrated by the H_2 molecule. We can see from the [periodic table](#) that each hydrogen atom has a single electron. If 2 hydrogen atoms come together to form a bond, then each hydrogen atom effectively has a share in both electrons and thus each resembles a noble gas and is more stable. The 2 electrons that are shared can be represented either by 2 dots or a single dash between the atoms.



Valence bond theory describes a chemical bond as the overlap of atomic orbitals. In the case of the hydrogen molecule, the 1s orbital of one hydrogen atom overlaps with the 1s orbital of the second hydrogen atom to form a molecular orbital called a sigma bond. Attraction increases as the distance between the atoms gets closer but nuclear-nuclear repulsion becomes important if the atoms approach too close.



There are 3 methods of showing the formulas of molecules. Molecular formulas show only the types and numbers of atoms in the molecule. Structural formulas show the atoms in their correct placement in the molecule and allow for distinguishing [isomers](#). Electron-dot formulas are similar to structural formulas but also include all of the non-bonding outer electrons. Knowledge of electron placement allows us to understand not only the shape of molecules but their chemical character. If we understand the chemical character of a molecule, we can predict how it will react with other molecules without having to blindly memorize reactions.

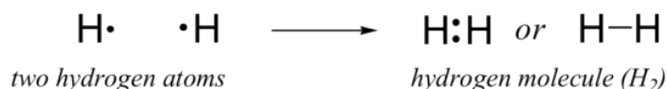
Covalent bonds and Lewis structures [Edit section](#)

Lewis structures, also known as Lewis-dot diagrams, show the bonding relationship between atoms of a molecule and the lone pairs of electrons in the molecule. Lewis structures can also be useful in predicting molecular geometry in conjunction with hybrid orbitals. A compound may have multiple resonance forms that are also all correct Lewis structures. This section will discuss the rules for correctly writing Lewis structures.

Before we begin, there are a few things to know. An electron is represented as a dot. A bond, which is made up of 2 shared electrons, is represented by two dots between the bonded atoms or a line. Double bonds and triple bonds are represented as two and three lines (pairs of electrons), respectively. Lone pairs on the outer rims of an atom are represented as two dots. The electrons represented in a Lewis structure are the outer-shell electrons, which are called valence electrons. This is because they are the ones involved in chemical reactions.

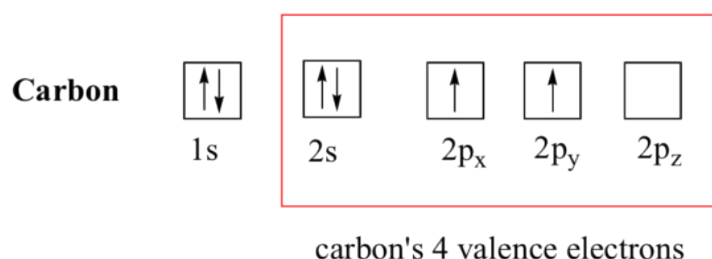
While alkali metals (such as sodium and potassium), alkaline earth metals (such as magnesium and calcium), and halogens (such as fluorine and chlorine) often form ions in order to achieve a full octet, the principle elements of organic chemistry - carbon, hydrogen, nitrogen, and oxygen - instead tend to fill their second shell orbitals by *sharing* electrons with other atoms, forming what we call covalent bonds. Consider the simplest case of hydrogen gas. An isolated hydrogen atom has only one electron, located in the 1s orbital. If two hydrogen atoms come close enough so that their respective 1s orbitals overlap, the two electrons can be

shared between the two nuclei, and a covalently bonded H_2 molecule is formed. In the 'Lewis method', each pair of electrons that is shared between two atoms is drawn as a single line, designating a single covalent bond.

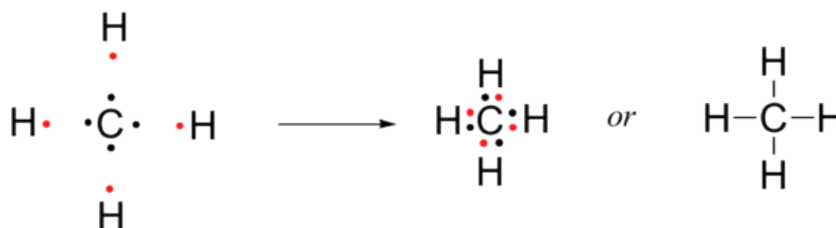


Hydrogen represents is a special case, of course – a hydrogen atom cannot fulfill the octet rule; it needs only two electrons to have a full shell (you could think of this as the 'doublet rule' for hydrogen).

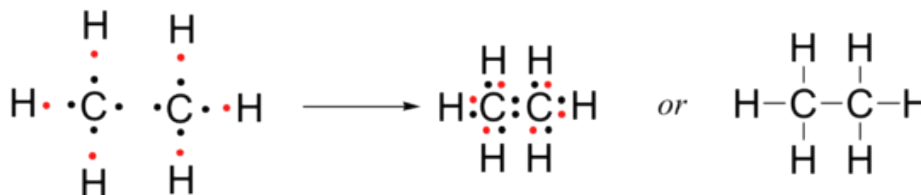
One of the simplest organic molecules is methane with the molecular formula CH_4 . Methane is the 'natural gas' burned in home furnaces and hot water heaters, as well as in electrical power generating plants. To illustrate the covalent bonding in methane using the Lewis method, we first must recognize that, although a carbon atom has a total of six electrons, the two electrons in the inner 1s orbital do not participate in bonding interactions. It is the other four- those in the 2s and 2p orbitals - that form covalent bonds with other atoms. Only the partially occupied, highest energy shell of orbitals - in this case the 2s and 2p orbitals - can overlap with orbitals on other atoms to form covalent bonds. Electrons in these orbitals are termed 'valence electrons'.



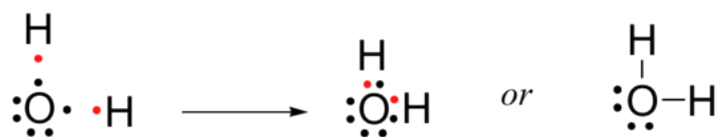
A carbon atom, then, has four valence electrons with which to form covalent bonds. In order to fulfill the octet rule and increase the occupancy of its second shell to eight electrons, it must participate in four electron-sharing interactions - in other words, it must form four covalent bonds. In a methane molecule, the central carbon atom shares its four valence electrons with four hydrogen atoms, thus forming four bonds and fulfilling the octet rule (for the carbon) and the 'doublet rule' (for each of the hydrogens).



The next relatively simple organic molecule to consider is ethane, which has the molecular formula C_2H_6 . If we draw each atom with its valence electron(s) separately, we can see that the octet/doublet rule can be fulfilled for all of them by forming one carbon-carbon bond and six carbon-hydrogen bonds.



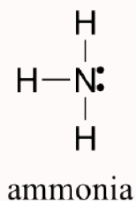
The same approach can be used for molecules in which there is no carbon atom. In a water molecule, two of the six valence electrons on the oxygen atom are used to form bonds to hydrogen atoms, while the remaining four are non-bonding 'lone pairs'.



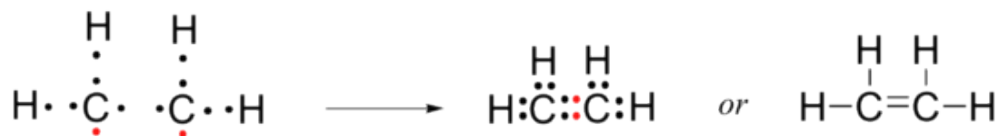
Exercise 1.5.1

Draw the Lewis structure for ammonia, NH_3 .

Answer:

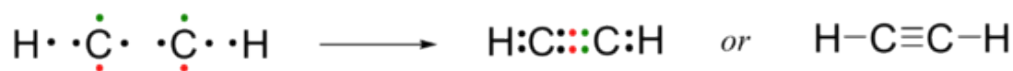


What about multiple bonds? The molecular formula for ethene (also known as ethylene, a compound found in fruits, such as apples, that signals them to ripen) is C_2H_4 . Arranging the atoms and surrounding them with their valence electrons, you can see that the octet/doublet rule can be fulfilled for all atoms only if the two carbons share *two* pairs of electrons between them - in other words, only if a double bond is formed.



Because a hydrogen atom has only a 1s orbital to work with, it cannot form more than one single bond, otherwise it would exceed its doublet rule.

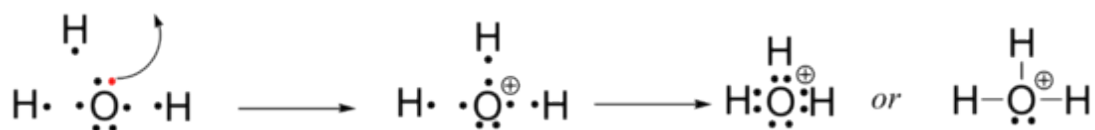
Following this pattern, the triple bond in ethyne molecular formula C_2H_2 , (also known as acetylene, the fuel used in welding torches), is formed when the two carbon atoms share *three* pairs of electrons between them.



What about ions? The hydroxide ion, OH^- , is drawn simply by showing the oxygen atom with its six valence electrons, then adding one more electron to account for the negative charge. Now the oxygen has three non-bonding lone pairs, and can only form one bond to a hydrogen. (Bear in mind that this is merely a description of the *thought process* going into drawing a Lewis structure, and is not meant to describe any actual chemical process).



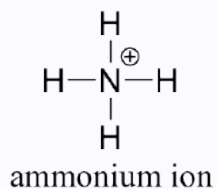
To draw a Lewis structure of the hydronium ion, H_3O^+ , you again start with the oxygen atom with its six valence electrons, then take one away to account for the positive charge (there is now one more proton than there are electrons). The oxygen now can form bonds to three hydrogen atoms.



Exercise 1.5.2

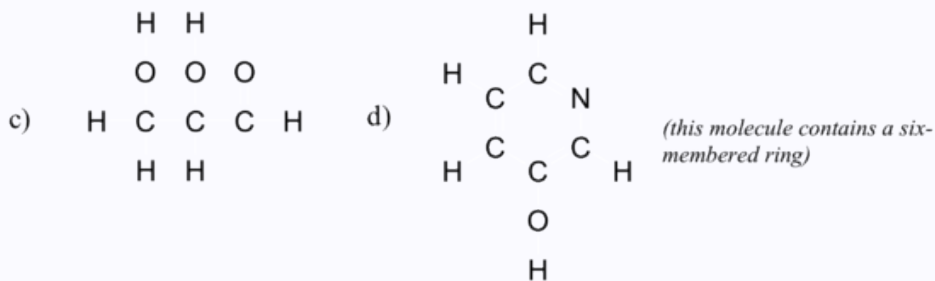
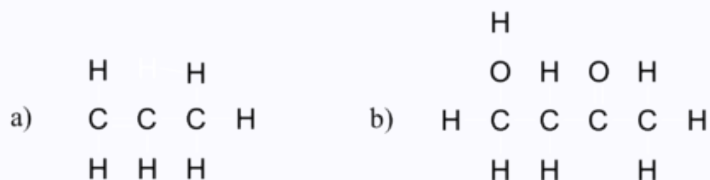
Draw a Lewis structure for the ammonium ion, NH_4^+ .

Answer:

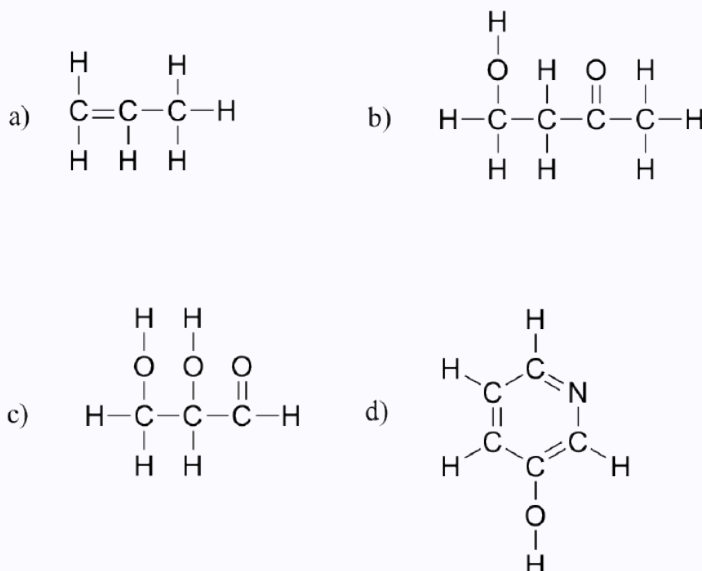


Exercise 1.5.3

Draw Lewis structures for neutral molecules with the connectivity shown below. Show all lone pairs. The octet rule should be fulfilled for all atoms.

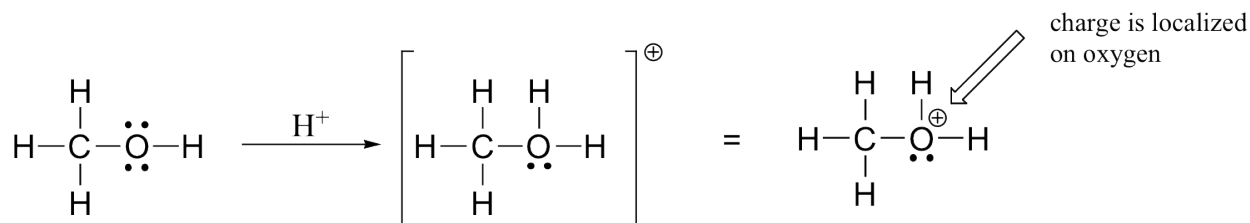


Answer:

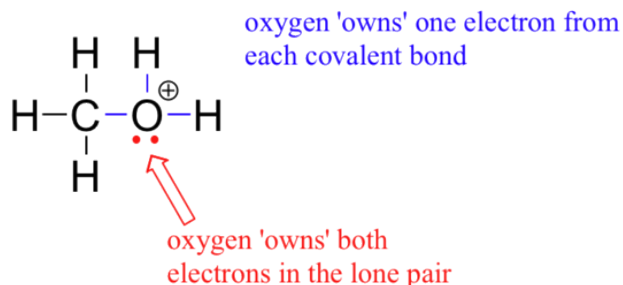


Formal charges

Consider the Lewis structure of methanol, CH_3OH (methanol is the so-called 'wood alcohol' that unscrupulous bootleggers sometimes sold during the Prohibition days, often causing the people who drank it to go blind). Just like in a water molecule, the oxygen atom in a methanol molecule has two non-bonding lone pairs of electrons. And just like a water molecule can be protonated to form the H_3O^+ cation, a methanol molecule can be protonated to form the CH_3OH_2^+ cation.



This polyatomic cation, as you can see, has an overall charge of +1. But we can be more specific than that - we can also state that the positive charge is located specifically on the oxygen atom, rather than on the carbon or any of the hydrogens. When a charge can be located on a particular atom in a polyatomic ion, this atom is said to have a 'formal charge'. Figuring out the formal charge on different atoms of a polyatomic ion is a straightforward process - it's simply a matter of adding up valence electrons. Remember that an oxygen atom needs six valence electrons (in addition to the two electrons in the non-valence 1s orbital) to completely balance the charge of the eight protons in its nucleus. Let's figure out how many electrons the oxygen atom in our CH_3OH_2^+ ion 'owns'.



First, we see that there is one lone pair of electrons that the oxygen is not sharing with any other atom - thus it 'owns' both of these electrons. In addition, the oxygen atom is sharing one *pair* of electrons each with three other atoms - since these electrons are shared, we decide that oxygen 'owns' one electron from each pair, meaning that it owns three bonding electrons. In total then, the oxygen owns five valence electrons: two non-bonding and three bonding. This is one short of the six valence electrons needed to achieve neutrality - thus the oxygen atom has a formal charge of +1.

What is the formal charge, if any, on the other atoms? The carbon needs to 'own' four valence electrons (once again, in addition to the two electrons in its 1s orbital) in order to balance the six protons in its nucleus. Because the carbon atom has four single bonds in this structure, and no lone pairs, it does indeed own four electrons (remember that it owns one of each pair of electrons that it shares in a covalent bond). So the carbon has a formal charge of zero.

Each hydrogen needs to own only one electron to balance the charge of its single proton. Indeed, in the CH_3OH_2^+ structure, each hydrogen atom has one single bond, meaning that each one owns one electron. Thus all of the hydrogen atoms have formal charges of zero. Notice that, as you would expect, the sum of the formal charges of all the atoms in the ion equals the total charge on the ion - this will always be true for every example you encounter, and is a good way to check to make sure you are figuring individual formal charges correctly.

An abbreviated formula for determining formal charges can be expressed as follows:

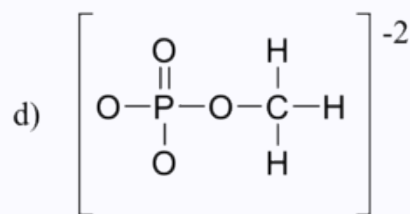
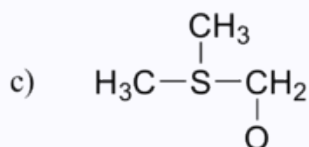
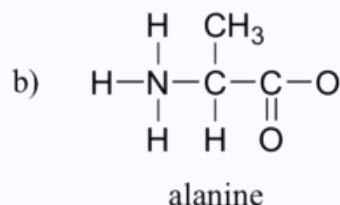
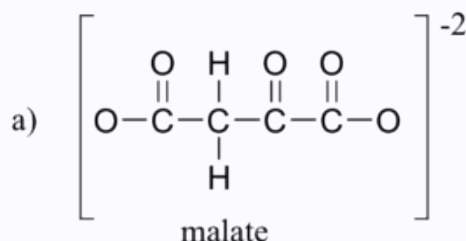
$$\text{formal charge} = (\# \text{ valence electrons}) - (\# \text{ non-bonding electrons}) - (\frac{1}{2} \# \text{ bonding electrons})$$

When drawing structures, it is very important to show all non-zero formal charges, being clear about where the charges are located. When all non-zero formal charges are shown in the structure, the overall charge on an ion does not need to be indicated - that information is obvious from the sum of the formal charges.

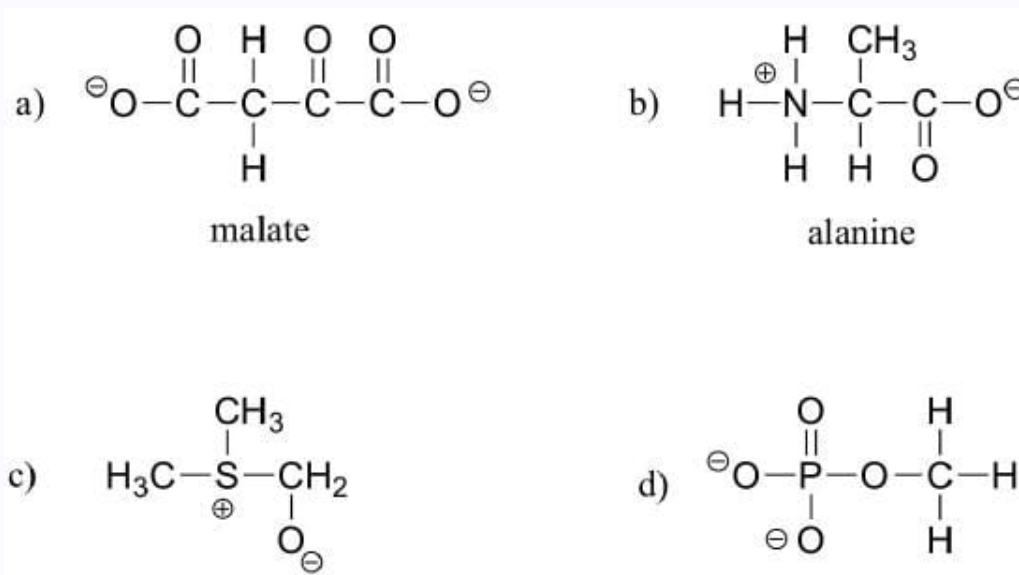
At this point, thinking back to what you learned in general chemistry, you are probably asking "What about dipoles? Doesn't an oxygen atom in an O-H bond 'own' more of the electron density than the hydrogen, because of its greater electronegativity?" You are absolutely correct, and we will be reviewing the concept of dipoles later on. For the purpose of calculating formal charges, however, dipoles don't matter - we always consider the two electrons in a bond to be shared equally, even if that is not an accurate reflection of chemical reality. Formal charges are just that - a formality, a method of electron book-keeping that is tied into the Lewis system for drawing the structures of organic compounds and ions. Later, however, we will see how the concept can help us to visualize how organic molecules react.

Exercise 1.5.4

Label all non-zero formal charges on the molecules/ions below. All atoms have a full octet of electrons (lone pairs are not shown).



Answer:



Hybridization of Atomic Orbitals and the Shape of Molecules

If the four hydrogen atoms in a methane molecule, CH_4 , were bound to the three 2p orbitals and the 2s orbital of the carbon atom, the H-C-H bond angles would be 90° for 3 of the hydrogen atoms and the 4th hydrogen atom would be at 135° from the others. Experimental evidence has shown that the bond angles in methane are not arranged that way but are 109.5° giving the overall shape of a tetrahedron. The tetrahedral structure makes much more sense in that hydrogen atoms would naturally repel each other due to their negative electron clouds and form this shape. If you think electron-electron repulsion isn't significant, try walking through a wall! There is plenty of space for your nuclei to pass through the nuclei of the wall material but ouch, it just doesn't work that way.

Experimental evidence has also shown that the H-N-H bond angles in ammonia (NH_3) are 107° and the H-O-H bond angles in water are 105° . It is clear from these bond angles that the non-bonding pairs of electrons occupy a reasonable amount of space and are pushing the hydrogen atoms closer together compared to the angles found in methane.

The valence shell electron-pair repulsion model (VSEPR) was devised to account for these molecular shapes. In this model, atoms and pairs of electrons will be arranged to minimize the repulsion of these atoms and pairs of electrons. Since the non-bonded electron pairs are held somewhat closer to the nucleus than the attached hydrogen atoms, they tend to crowd the hydrogen atoms. Thus ammonia exists as a distorted tetrahedron (trigonal pyramidal) rather than a trigonal plane and water also exists as a distorted tetrahedron (bent) rather than a linear molecule with the hydrogen atoms at a 180° bond angle.

This concept proposes that since the attached groups are not at the angles of the p orbitals and their atomic orbitals would not have maximum overlap (to form strong bonds) the s and p orbitals will be hybridized to match the bond angles of the attached groups.

The number of these new hybrid orbitals must be equal to the numbers of atoms and non-bonded electron pairs surrounding the central atom!

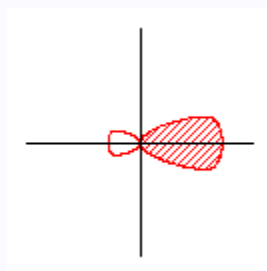
This valence shell repulsion model can be illustrated at home with a very fun experiment!

Example 1.5.5: Methane

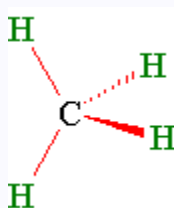
In the case of methane, the three 2p orbitals of the carbon atom are combined with its 2s orbital to form four new orbitals called sp^3 hybrid orbitals. The name is simply a tally of all the orbitals that were blended together to form these new hybrid orbitals. Four hybrid orbitals were required since there are four atoms attached to the central carbon atom. These new orbitals will have an energy slightly above the 2s orbital and below the 2p orbitals as shown in the following illustration. Notice that no change occurred with the 1s orbital.



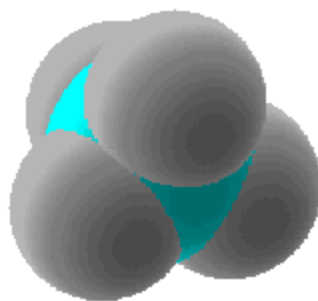
These hybrid orbitals have 75% p-character and 25% s-character which gives them a shape that is shorter and fatter than a p-orbital. The new shape looks a little like...



A stick and wedge drawing of methane shows the tetrahedral angles. The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.



A space-filling model of methane would look like...

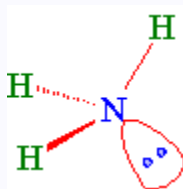


Example 1.5.6: Ammonia

In the case of ammonia, the three 2p orbitals of the nitrogen atom are combined with the 2s orbital to form four sp^3 hybrid orbitals. We need a hybrid orbital for each atom and the pair of non-bonding electrons. Ammonia has three hydrogen atoms and one non-bonded pair of electrons when we draw the electron-dot formula. In order to determine the hybridization of an atom, you must first draw the electron-dot formula.



A stick and wedge drawing of ammonia showing the non-bonding electrons in a probability area for the hybrid orbital...



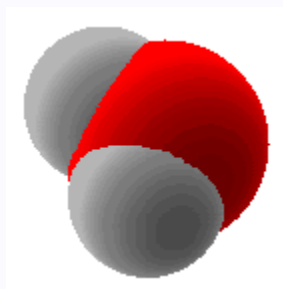
A space-filling model of ammonia would look like...(Note the non-bonded electron pair is not shown in this model.)

Example 1.5.7: Water

In the case of water, the three 2p orbitals of the oxygen atom are combined with the 2s orbital to form four sp^3 hybrid orbitals. The two non-bonded electron pairs will occupy hybrid orbitals. Again we need a hybrid orbital for each atom and each pair of non-bonding electrons. Water has two hydrogen atoms and two non-bonded pairs of electrons when we draw the electron-dot formula.

A stick and wedge drawing of water showing the non-bonding electron pairs in probability areas for the hybrid orbital...

A space-filling model of water would look like...(Note the non-bonded electron pairs are not shown in this model.)

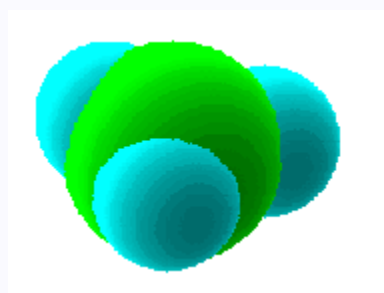


Example 1.5.8: Boron Trifluoride

Now let's look at something a bit different. In the boron trifluoride molecule, only three groups are arranged around the central boron atom. In this case, the 2s orbital is combined with only two of the 2p orbitals (since we only need three hybrid orbitals for the three groups...thinking of groups as atoms and non-bonding pairs) forming three hybrid orbitals called sp^2 hybrid orbitals. The other p-orbital remains non-hybridized and is at right angles to the trigonal planar arrangement of the hybrid orbitals. The trigonal planar arrangement has bond angles of 120° .

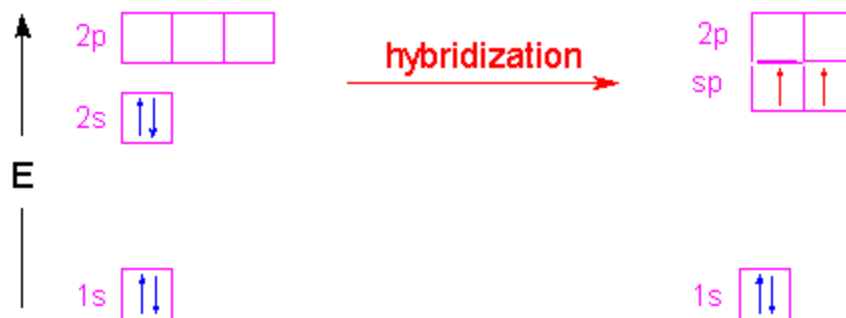
In the following stick model, the empty p orbital is shown as the probability area...one end shaded blue and the other is white...there are no electrons in this orbital!

A space-filling model of boron trifluoride would look like...

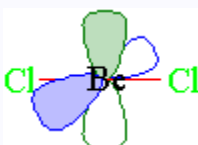


Example 1.5.9: Beryllium Dichloride

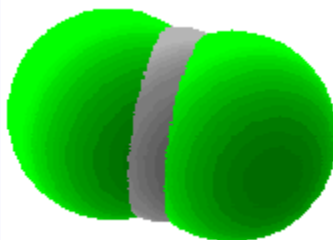
Finally let's look at beryllium dichloride. Since only two groups are attached to beryllium, we only will have two hybrid orbitals. In this case, the 2s orbital is combined with only one of the 2p orbitals to yield two sp hybrid orbitals. The two hybrid orbitals will be arranged as far apart as possible from each other with the result being a linear arrangement. The two non-hybridized p-orbitals stay in their respective positions (at right angles to each other) and perpendicular to the linear molecule.



In the following stick model, the empty p orbitals are shown as the probability areas...one green and one blue.



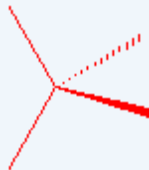
A space-filling model of beryllium dichloride would look like...



Summary of Hybridization

In the following summary, groups are considered to be atoms and/or pairs of electrons and hybrid orbitals are the red lines and wedges. When the octet of an element is exceeded, then hybridization will involve d-orbitals. Non-hybridized p-orbitals are shown as probability areas in blue and green for sp hybridization and blue for sp^2 hybridization. A single electron as found in a radical would occupy a non-hybridized p-orbital.

Number of Groups Attached to a Central Atom	Description and 3-Dimensional Shape	
Two Groups sp	2 groups = sp hybridization 180 degree bond angle linear electron-pair geometry	
Three Groups sp^2	3 groups = sp^2 hybridization 120 degree bond angles trigonal planar electron-pair geometry	

Four Groups sp^3	4 groups = sp^3 hybridization 109.5 degree bond angles tetrahedral electron-pair geometry 
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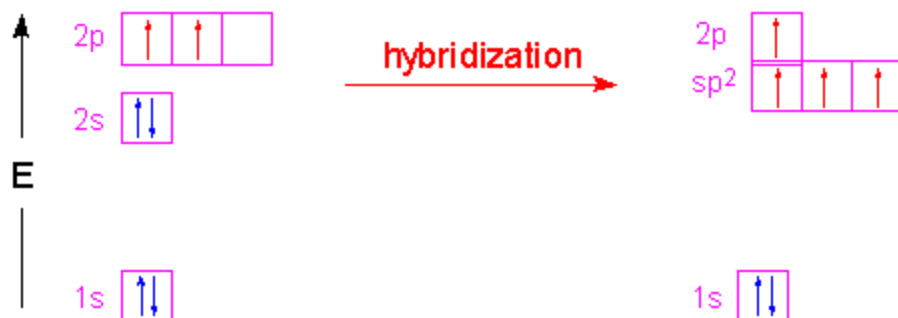
Hybridization Involving Multiple Bonds

Only a maximum of two electrons can occupy any orbital whether it is an atomic orbital or a molecular orbital due to electron-electron repulsion. When we draw a double or a triple-bond between two atoms, we imply that either four or six electrons are directly between these two atoms. Since this is impossible, we must have these extra electrons off to the side in what we refer to as pi bonds. Therefore, all multiple bonds are composed of two different kinds of molecular bonds called pi bonds and sigma bonds.

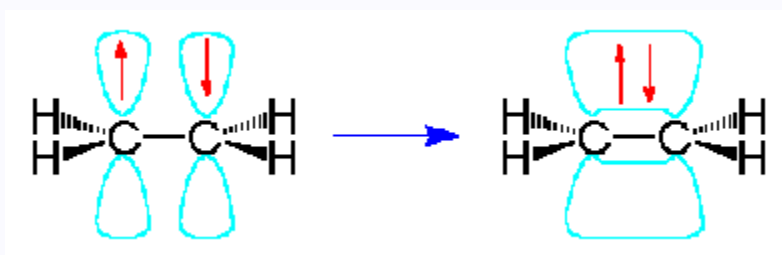
- The sigma (σ) bond is defined as the linear overlap of atomic orbitals in which two electrons are directly between the two bonded nuclei.
- Pi (π) bonds are defined as the parallel overlap of p-orbitals. A double bond has one sigma bond and one pi bond. A triple bond thus consists of a sigma bond and two pi bonds with the pi bonds in different planes.

Example 1.5.10: Ethene

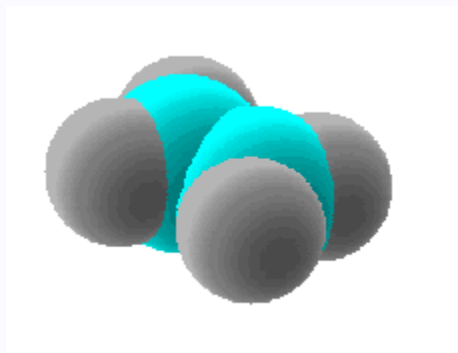
In the ethene molecule, C_2H_4 , both carbon atoms will be sp^2 hybridized and have one unpaired electron in a non-hybridized p-orbital.



These p-orbitals will undergo parallel overlap and form one pi bond with bean-shaped probability areas above and below the plane of the six atoms. This pair of bean-shaped probability areas constitutes one pi bond and the pair of electrons in this bond can be found in either bean-shaped area.

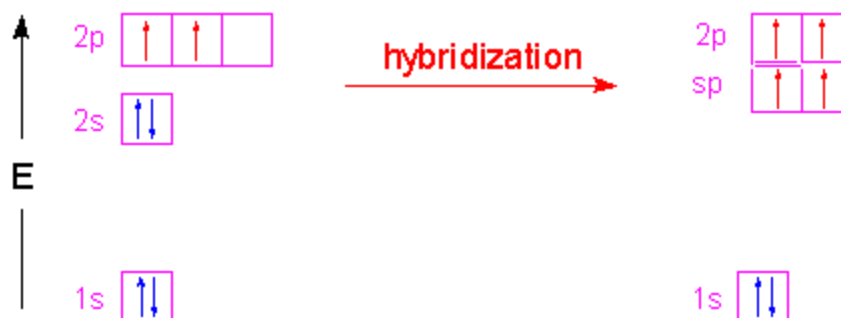


The 3-dimensional model of ethene is planar with H-C-H and H-C-C bond angles of 120° ...the pi bond is not shown in this picture.

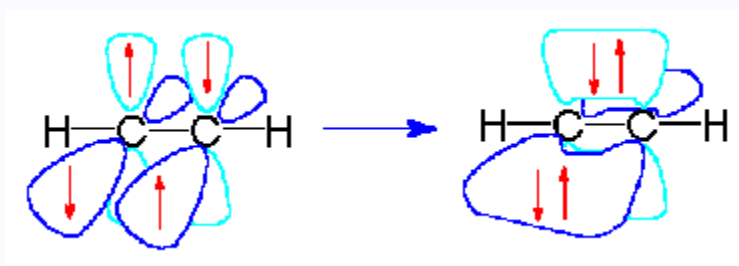


Example 1.5.11: Acetylene

Now let's look at acetylene, C_2H_2 . Both carbon atoms will be sp hybridized and have one electron in each of two non-hybridized p-orbitals.



These p orbitals will undergo parallel overlap to form two pi bonds at right angles to each other.



The 3-dimensional model of acetylene is therefore linear...the pi bonds are not shown in this picture.



The Relationship between Bond Order and Bond Energy [Edit section](#)

Triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 1.5.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

[Edit section](#)

Table 1.5.1: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H-H	432	C-C	346	N-N	≈167	O-O	≈142	F-F	155	C=C	602
H-C	411	C-Si	318	N-O	201	O-F	190	F-Cl	249	C≡C	835
H-Si	318	C-N	305	N-F	283	O-Cl	218	F-Br	249	C=N	615
H-N	386	C-O	358	N-Cl	313	O-Br	201	F-I	278	C≡N	887
H-P	≈322	C-S	272	N-Br	243	O-I	201	Cl-Cl	240	C=O	749

Single Bonds								Multiple Bonds			
H-O	459	C-F	485	P-P	201	S-S	226	Cl-Br	216	C≡O	1072
H-S	363	C-Cl	327			S-F	284	Cl-I	208	N=N	418
H-F	565	C-Br	285			S-Cl	255	Br-Br	190	N≡N	942
H-Cl	428	C-I	213			S-Br	218	Br-I	175	N=O	607
H-Br	362	Si-Si	222					I-I	149	O=O	494
H-I	295	Si-O	452							S=O	532
Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, <i>Inorganic Chemistry</i> , 4th ed. (1993).											

- Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H-F bond is stronger than an H-I bond, H-C is stronger than H-Si, H-N is stronger than H-P, H-O is stronger than H-S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (Figure 1.5.1a)
- Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C-C single bond is stronger than the Si-Si single bond, which is stronger than the Ge-Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller. (Figure 1.5.1b) Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N-N, O-O, and F-F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$Cl-Cl > Br-Br > F-F > I-I \quad (1.2.1)$$

Similar effects are also seen for the O-O versus S-S and for N-N versus P-P single bonds.

Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

- Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

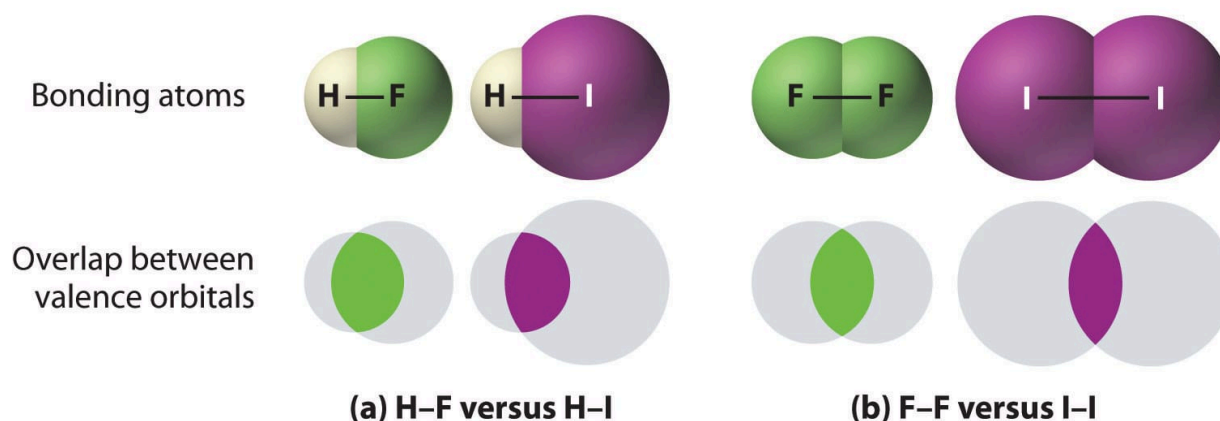


Figure 1.5.1 The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space relative to the size of the bonded atom decreases; that is, the percentage of total orbital volume decreases with increasing size. Hence the

strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6. In contrast, silicon in group 14 has little tendency to form discrete silicon-oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si-O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2 .

Note

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

Table 1.5.2: Average bond energies:

Bond	(kJ/mol)
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

Exercises

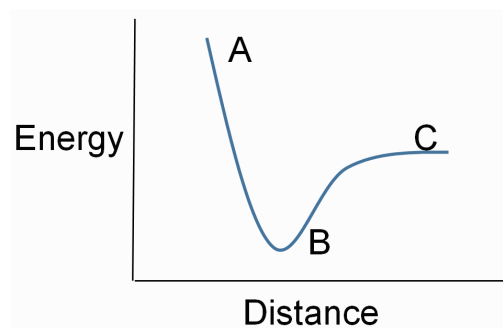
Questions

Q1.5.1

Draw an energy diagram for energy vs. intermolecular distance for a fluorine molecule (F_2) and describe the regions of the graph.

Solutions

S1.5.1



A - Repulsive Forces are present, p-orbitals are too close together

B - Optimal distance between the two p-orbitals to have a bond (the bond length)

C - Cannot form a bond, orbitals are too far away

Contributors

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1.3: Polar Covalent Bonds - Electronegativity

Objectives

After completing this section, you should be able to

1. describe how differences in electronegativity give rise to bond polarity.
2. arrange a given series of the elements most often encountered in organic chemistry (C, H, O, N, S, P and the halogens) in order of increasing or decreasing electronegativity, without referring to a table of electronegativities.
3. predict the partial positive and partial negative ends of a given bond formed between any two of the elements listed in Objective 2, above, without the use of a table of electronegativities or a periodic table.
4. predict the partial positive and partial negative ends of a given bond formed between any two elements not listed in Objective 2, above, using a periodic table.

Key Terms

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

- electronegativity inductive effect
- polar covalent bond

Study Notes

Students often wonder why it is important to be able to tell whether a given bond is polar or not, and why they need to know which atoms carry a partial positive charge and which a partial negative charge. Consider the chloromethane (CH_3Cl) molecule. The carbon atom is shown as carrying a partial positive charge. Now, recall that opposite charges attract. Thus, it seems reasonable that the slightly positive carbon atom in chloromethane should be susceptible to attack by a negatively charged species, such as the hydroxide ion, OH^- . This theory is borne out in practice: hydroxide ions react with chloromethane by attacking the slightly positive carbon atom in the latter. It is often possible to rationalize chemical reactions in this manner, and you will find the knowledge of bond polarity indispensable when you start to write reaction mechanisms.

Note: Because of the small difference in electronegativity between carbon and hydrogen, the **C-H** bond is normally assumed to be nonpolar.

Electronegativity

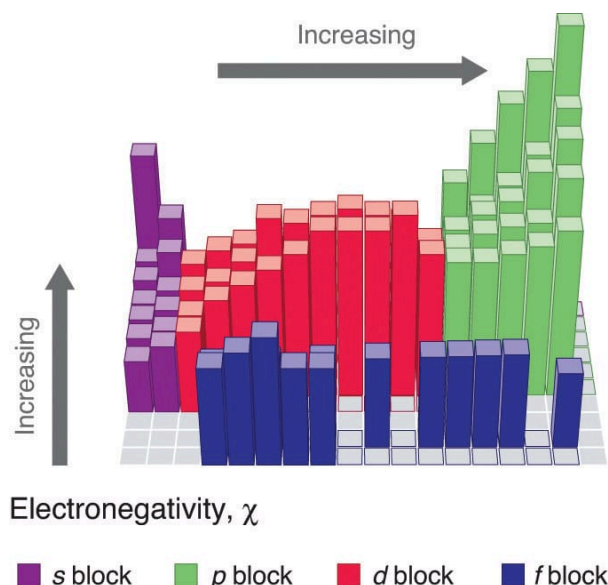
The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table. Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ , pronounced “ky” as in “sky”), which is defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom's electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by the neighboring atoms in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable

elements, which suggests that all the methods are measuring the same fundamental property.

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **larger** the electronegativity value, the **greater** the attraction.



Unfortunately there is no direct way of measuring electronegativity. Dipole-moment measurements tell us about the electrical behavior of *all* electron pairs in the molecule, not just the bonding pair in which we are interested. Also, the polarity of a bond depends on whether the bond is a single, double, or triple bond and on what the other atoms and electron pairs in a molecule are. Therefore the dipole moment cannot tell us quantitatively the difference between the electronegativities of two bonded atoms. Various attempts have been made over the years to derive a scale of electronegativities for the elements, none of which is entirely satisfactory. Nevertheless most of these attempts agree in large measure in telling us which elements are more electronegative than others. The best-known of these scales was devised by the Nobel prize-winning California chemist Linus Pauling (1901 to 1994) and is shown in the periodic table found below. In this scale a value of 4.0 is arbitrarily given to the most electronegative element, fluorine, and the other electronegativities are scaled relative to this value.

Electronegativities of the elements

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →																		
Group (vertical)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period (horizontal)																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60

6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

What if two atoms of equal electronegativity bond together?

Consider a bond between two atoms, A and B. If the atoms are equally electronegative, then both atoms have the same tendency to attract the bonding pair of electrons, and so electrons will be found on average half way between the two atoms.



To get a bond like this, A and B would usually have to be the same element, for example, H₂ or Cl₂ molecules. Note: It's important to realize that this is an average picture. The electrons are actually in a molecular orbital, and are moving around all the time within that orbital. This sort of bond could be thought of as being a "pure" or **non-polar covalent bond** - where the bonding electrons are shared evenly between the two atoms.

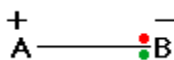
What if B is slightly more electronegative than A?

If B is slightly more electronegative than A, then B will attract the bonding electron pair more than A.



That means that the B end of the bond will have a greater share of the electron density and so becomes slightly negative. At the same time, the A end (rather short of electrons) becomes slightly positive. This unequal sharing of the bonding electrons is indicated in the diagram above using the symbols "δ+" and "δ-". "δ" (read as "delta") means "slightly", so "δ+" means slightly positive, and "δ-" means slightly negative. Because the electrons are shared unequally, the bond between A and B is polarized, and the bond is called a **polar covalent bond**.

A polar covalent bond is a covalent bond in which there is a separation of charge between one end and the other - in other words one end is slightly positive and the other slightly negative. Examples include most covalent bonds, like the hydrogen-chlorine bond in HCl or the hydrogen-oxygen bonds in water.

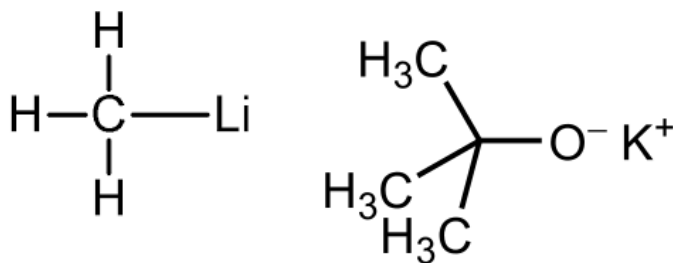


If B is a lot more electronegative than A, then the electron pair is dragged completely over to B's end of the bond. To all intents and purposes, A has lost control of its electron, and B has complete control over both electrons. Ions have been formed. Because the electrons are no longer shared, the bond is an **ionic bond** rather than a covalent bond.

A "spectrum" of bonds

There is no clear-cut division between covalent and ionic bonds. In a pure non-polar covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described

as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do. A general rule in organic chemistry is if the bond is between metal and a non-metal atoms, then the bond should be considered ionic. Examples of this are the lithium - carbon bond in methyl lithium and the potassium - oxygen bond in potassium *tert*-butoxide,



Methyl Lithium potassium *tert*-butoxide

Summary

- No electronegativity difference between two atoms leads to a non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

Exercises

1. Identify the positive and negative ends of each of the bonds shown below.

four simple molecules

Answer:

1. charges on four simple molecules

Questions

Q2.1.1

Rank the following from least polar to most polar using knowledge of electronegativity

$\text{CH}_3\text{CH}_2\text{-Li}$ $\text{CH}_3\text{CH}_2\text{-K}$ $\text{CH}_3\text{CH}_2\text{-F}$ $\text{CH}_3\text{CH}_2\text{-OH}$

Solutions

S2.1.1

(least polar) $\text{OH} < \text{F} < \text{Li} < \text{K}$ (most polar)

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1.4: Polar Covalent Bonds - Dipole Moments

Objectives

After completing this section, you should be able to

1. explain how dipole moments depend on both molecular shape and bond polarity.
2. predict whether a molecule will possess a dipole moment from the molecular formula or structure.
3. use the presence or absence of a dipole moment as an aid to deducing the structure of a given compound.

Key Terms

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

- dipole moment

Study Notes

You must be able to combine your knowledge of molecular shapes and bond polarities to determine whether or not a given compound will have a dipole moment. Conversely, the presence or absence of a dipole moment may also give an important clue to a compound's structure. BCl_3 , for example, has no dipole moment, while NH_3 does. This suggests that in BCl_3 the chlorines around boron are in a trigonal planar arrangement, while the hydrogens around nitrogen in NH_3 have a less symmetrical arrangement - trigonal pyramidal.

Remember that the C-H bond is assumed to be non-polar.

Molecular Dipole Moments

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with more than one polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether the molecule has a net dipole moment.

Example 1.4.1: Polar Bonds vs. Polar Molecules

In a simple diatomic molecule like HCl , if the bond is polar, then the whole molecule is polar. What about more complicated molecules that have more than one bond?

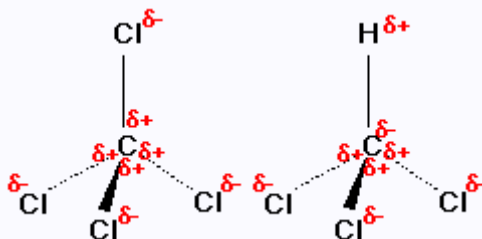


Figure: (left) CCl_4 (right) CHCl_3

Consider CCl_4 , (left panel in figure above), which as a molecule is not polar - in the sense that it doesn't have an end (or a side)

which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right.

In contrast, CHCl_3 is a polar molecule (right panel in figure above). The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

A polar molecule will need to be "lop-sided" in some way.

Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2 , a linear molecule (Figure 1.4.1a). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 1.4.1b); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

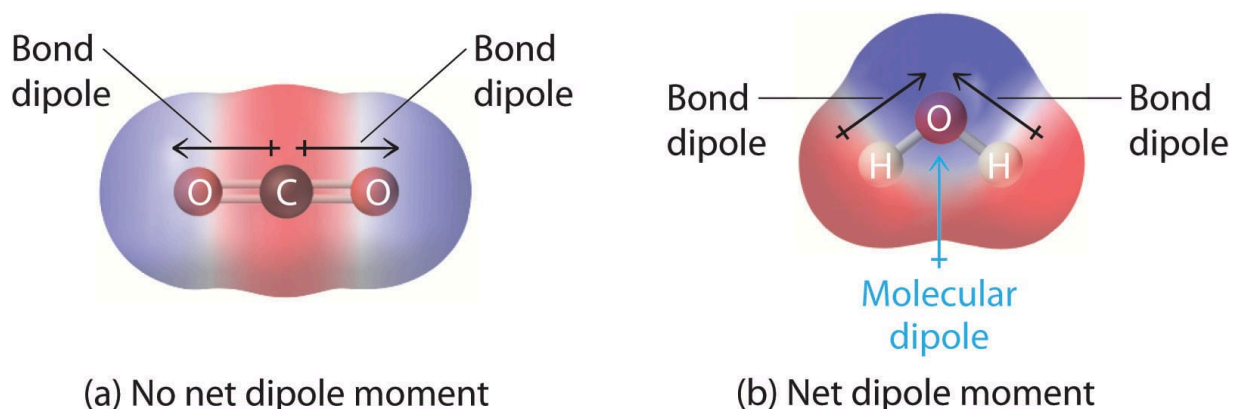


Figure 1.4.1 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2 , the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O , the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment. Edit section

Other examples of molecules with polar bonds are shown in Figure 1.4.2. In molecules like BCl_3 and CCl_4 , that have only one type of bond and a molecular geometries that are highly symmetrical (trigonal planar and tetrahedral), the individual bond dipole moments completely cancel, and there is no net dipole moment. However, although a molecule like CHCl_3 has a tetrahedral geometry, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments do not cancel one another, and the result is a molecule which has a dipole moment.

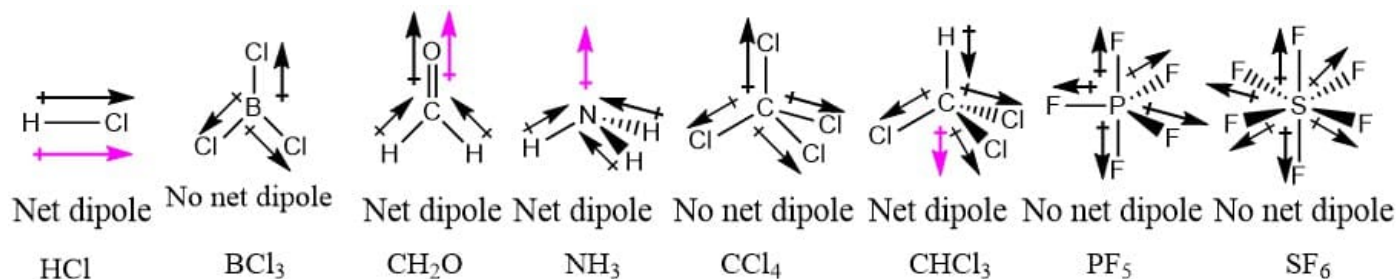


Figure 1.4.2: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl , CH_2O , NH_3 , and CHCl_3), indicated in purple, whereas others do not because the bond dipole moments cancel (BCl_3 , CCl_4 , PF_5 , and SF_6).

Molecules with asymmetrical charge distributions have a net dipole momentEdit section

Example 1.4.1

Which molecule(s) has a net dipole moment?

- H_2S
- NHF_2
- BF_3

Given: three chemical compounds

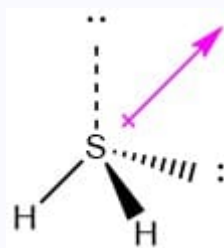
Asked for: net dipole moment

Strategy:

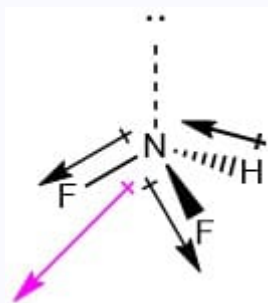
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

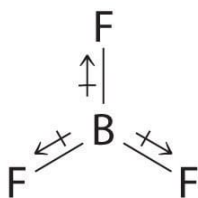
- The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent. The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



- Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater effect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



- The molecular geometry of BF_3 is trigonal planar. Because all the B-F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



Exercise 1.4.1

Which molecule(s) has a net dipole moment?

- a. CH_3Cl
- b. SO_3
- c. XeO_3

Answer: CH_3Cl ; XeO_3

Exercises

1. Determine whether each of the compounds listed below possesses a dipole moment. For the polar compounds, indicate the direction of the dipole moment.
 - a. $\text{O} = \text{C} = \text{O}$
 - b. ICl
 - c. SO_2
 - d. $\text{CH}_3 - \text{O} - \text{CH}_3$
 - e. $\text{CH}_3\text{C}(=\text{O})\text{CH}_3$

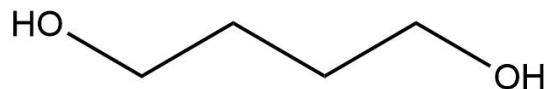
Answers:

1.
 - a. carbon dioxide is nonpolar
 - b. net dipole moment on iodine monochloride
 - c. net dipole moment on sulfur dioxide
 - d. net dipole moment on dimethyl ether
 - e. net dipole moment on 2-propanone

Questions

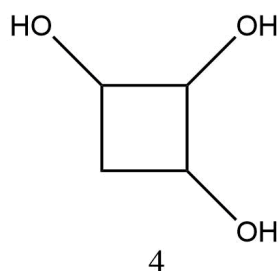
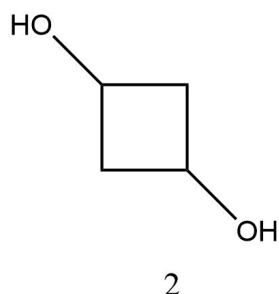
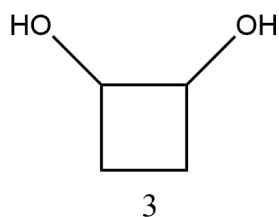
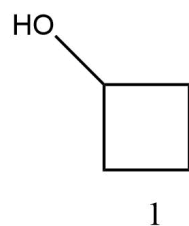
Q2.2.1

The following molecule has no dipole moment in the molecule itself, explain.



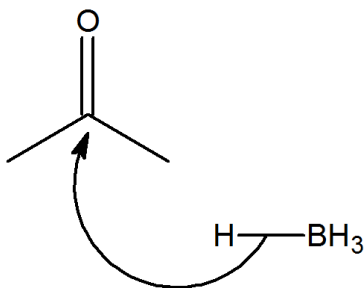
Q2.2.2

Which of the following molecules has a net dipole?



Q2.2.3

Within reactions with carbonyls, such as a reduction reaction, the carbonyl is attacked from the carbon side and not the oxygen side. Using knowledge of electronegativity explain why this happens.



Solutions

S2.2.1

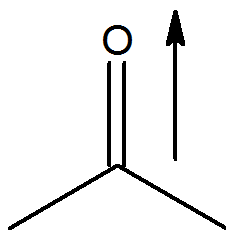
The hydroxyl groups are oriented opposite of one another and therefore the dipole moments would “cancel” one another out. Therefore having a zero net-dipole.

S2.2.2

1, 3, and 4 have a net dipoles.

S2.2.3

The oxygen is more electronegative than the carbon and therefore creates a dipole along the bond. This leads to having a partial positive charge on the carbon and the reduction can take place.



Contributors

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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

1.5: Formal Charges

Objectives

After completing this section, you should be able to

1. calculate the formal charge of an atom in an organic molecule or ion.
2. identify and recognize the bonding patterns for atoms of carbon, hydrogen, oxygen, nitrogen and the halogens that have a formal charge of zero.

Key Terms

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

- valence electrons
- bonding and non-bonding electrons
- formal charge
- carbocations

Study Notes

It is more important that students learn to easily identify atoms that have formal charges of zero, than it is to actually calculate the formal charge of every atom in an organic compound. Students will benefit by memorizing the "normal" number of bonds and non-bonding electrons around atoms whose formal charge is equal to zero.

A **formal charge** compares the number of electrons around a "neutral atom" (an atom not in a molecule) versus the number of electrons around an atom in a molecule. Formal charge is assigned to an atom in a molecule by assuming that electrons in all chemical bonds are shared equally between atoms, regardless of relative electronegativity. To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:[Edit section](#)[Edit section](#)

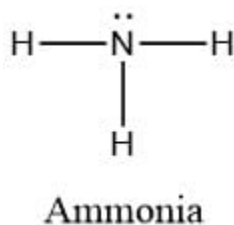
- Non-bonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the two bonded atoms, so one electron from each bond goes to each atom.

The formal charge of each atom in a molecule can be calculated using the following equation:

$$\text{Formal Charge} = (\# \text{ of valence electrons in free atom}) - (\# \text{ of lone-pair electrons}) - (1/2 \# \text{ of bond pair electrons})$$

Eqn. 2.3.1

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH₃) whose Lewis structure is as follows:



A neutral nitrogen atom has five valence electrons (it is in group 15). From the Lewis structure, the nitrogen atom in ammonia has one lone pair and three bonds with hydrogen atoms. Substituting into Equation 2.3.1, we obtain

$$\text{Formal Charge of N} = (5 \text{ valence } e^-) - (2 \text{ lone pair } e^-) - (1/2 \times 6 \text{ bond pair } e^-) = 0$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule has no non-bonding electrons and one bond. Using Equation 2.3.1 to calculate the formal charge on hydrogen, we obtain

$$\text{Formal Charge of H} = (1 \text{ valence } e^-) - (0 \text{ lone pair } e^-) - (1/2 \times 2 \text{ bond pair } e^-) = 0$$

The sum of the formal charges of each atom must be equal to the overall charge of the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall neutral charge of the NH_3 molecule. [Edit section](#)

Typically, the structure with the most formal charges of zero on atoms is the more stable Lewis structure. In cases where there MUST be positive or negative formal charges on various atoms, the most stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges for polyatomic ions.

Example 2.3.1

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

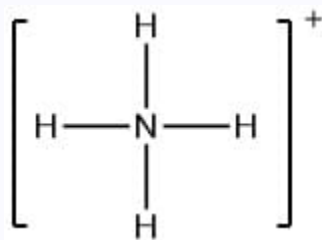
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and non-bonding electrons associated with each atom and then use Equation 2.3.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



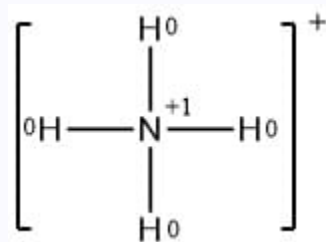
The nitrogen atom in ammonium has zero non-bonding electrons and 4 bonds. Using Equation 2.3.1, the formal charge on the nitrogen atom is therefore

$$\text{Formal Charge of N} = (5 \text{ valence } e^-) - (0 \text{ lone pair } e^-) - (1/2 \times 8 \text{ bond pair } e^-) = +1$$

Each hydrogen atom in has one bond and zero non-bonding electrons. The formal charge on each hydrogen atom is therefore

$$\text{Formal Charge of H} = (1 \text{ valence } e^-) - (0 \text{ lone pair } e^-) - (1/2 \times 2 \text{ bond pair } e^-) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus

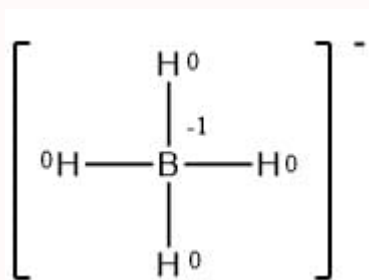


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is $0 + 1 + 0 + 0 + 0 = +1$, which is the same as the overall charge of the ammonium polyatomic ion.

Exercise 1.5.1

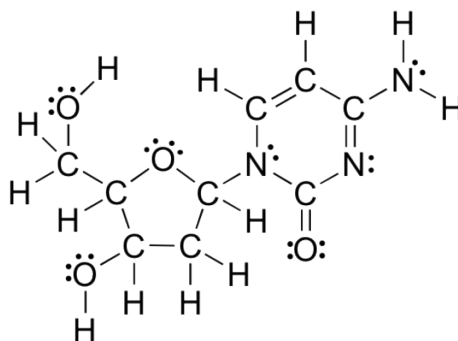
Write the formal charges on all atoms in BH_4^- .

Answer



Common bonding patterns in organic structures

The calculation method reviewed above for determining formal charges on atoms is an essential starting point for a novice organic chemist, and works well when dealing with small structures. But this method becomes unreasonably time-consuming when dealing with larger structures. It would be exceptionally tedious to determine the formal charges on each atom in 2'-deoxycytidine (one of the four nucleoside building blocks that make up DNA) using equation 2.3.1.



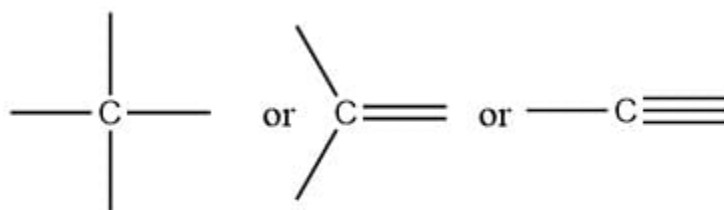
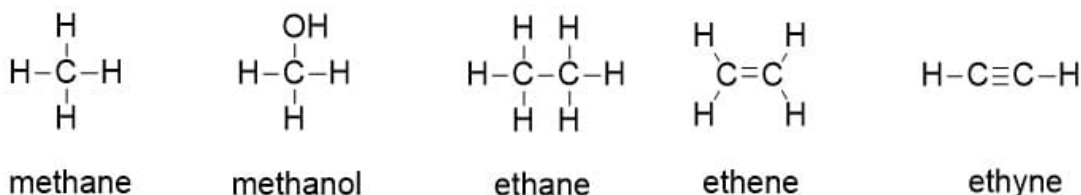
2'-deoxycytidine

And yet, organic chemists, and especially organic chemists dealing with biological molecules, are expected to draw the structure

of large molecules such as this on a regular basis. Clearly, you need to develop the ability to quickly and efficiently draw large structures and determine formal charges. Fortunately, this only requires some practice with recognizing common bonding patterns.

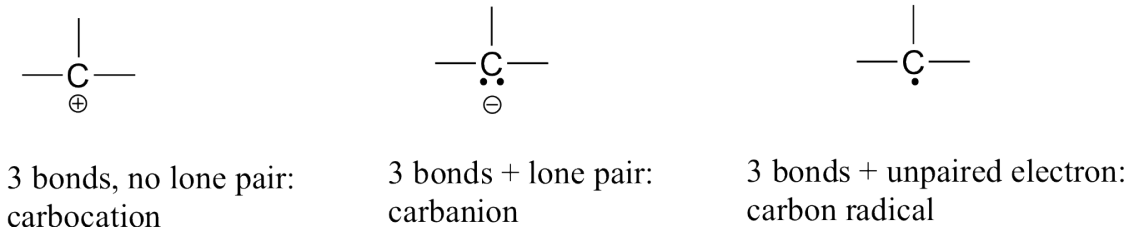
Carbon

Carbon, the most important element for organic chemists. In the structures of methane, methanol, ethane, ethene, and ethyne, there are four bonds to the carbon atom. And each carbon atom has a formal charge of zero. In other words, carbon is **tetravalent**, meaning that it commonly forms four bonds.



Carbon usually has 4 bonds

Carbon is tetravalent in most organic molecules, but there are exceptions. Later in this chapter and throughout this book are examples of organic ions called 'carbocations' and carbanions', in which a carbon atom has a positive or negative formal charge, respectively. **Carbocations** occur when a carbon has only three bonds and no lone pairs of electrons. Carbocations have only 6 valence electrons and a formal charge of +1. **Carbanions** occur when the carbon atom has three bonds plus one lone pair of electrons. Carbanions have 8 valence electrons and a formal charge of -1.



Two other possibilities are carbon radicals and carbenes, both of which have a formal charge of zero. A **carbon radical** has three bonds and a single, unpaired electron. Carbon radicals have 7 valence electrons and a formal charge of zero. **Carbenes** are a highly reactive species, in which a carbon atom has two bonds and one lone pair of electrons, giving it a formal charge of zero. You may encounter carbenes in more advanced chemistry courses, but they will not be discussed any further in this book.

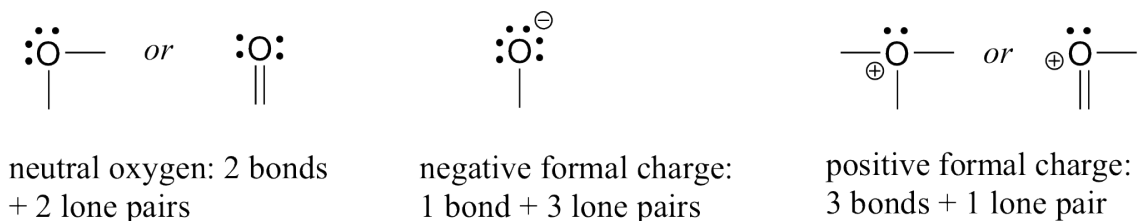
You should certainly use the methods you have learned to check that these formal charges are correct for the examples given above. More importantly, you will need, before you progress much further in your study of organic chemistry, to simply recognize these patterns (and the patterns described below for other atoms) and be able to identify carbons that bear positive and negative formal charges by a quick inspection.

Hydrogen

The common bonding pattern for hydrogen is easy: hydrogen atoms in organic molecules typically have only one bond, no unpaired electrons and a formal charge of zero. The exceptions to this rule are the proton, H^+ , the hydride ion, H^- , and the hydrogen radical, $H^\cdot$. The **proton** is a hydrogen with no bonds and no lone pairs and a formal charge of +1. The **hydride ion** is a hydrogen with no bonds, a pair of electrons, and a formal charge of -1. The **hydrogen radical** is a hydrogen atom with no bonds, a single unpaired electron and a formal charge of 0. Because this book concentrates on organic chemistry as applied to living things, however, we will not be seeing 'naked' protons and hydrides as such, because they are too reactive to be present in that form in aqueous solution. Nonetheless, the *idea* of a proton will be very important when we discuss acid-base chemistry, and the *idea* of a hydride ion will become very important much later in the book when we discuss organic oxidation and reduction reactions. As a rule, though, all hydrogen atoms in organic molecules have one bond, and no formal charge.

Oxygen

The common arrangement of oxygen that has a formal charge of zero is when the oxygen atom has 2 bonds and 2 lone pairs. Other arrangements are oxygen with 1 bond and 3 lone pairs, that has a -1 formal charge, and oxygen with 3 bonds and 1 lone pair that has a formal charge of +1. All three patterns of oxygen fulfill the octet rule.

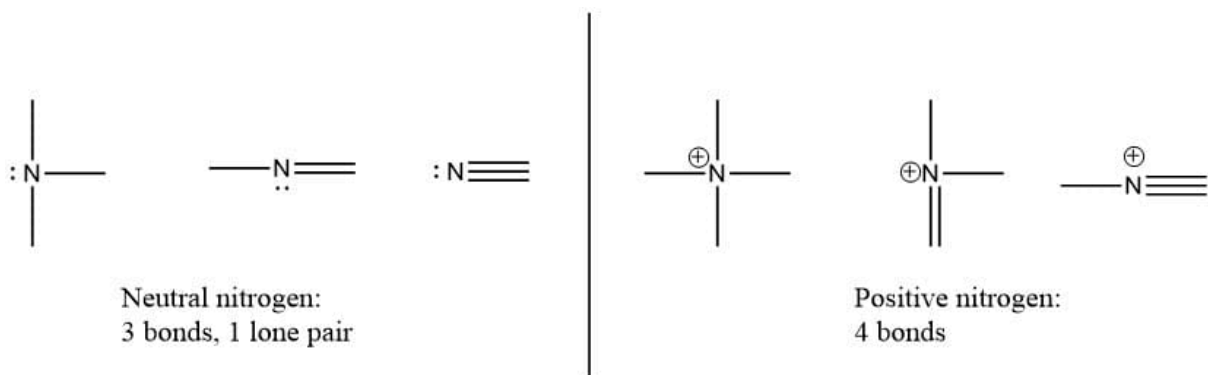


If it has two bonds and two lone pairs, as in water, it will have a formal charge of zero. If it has one bond and three lone pairs, as in hydroxide ion, it will have a formal charge of -1. If it has three bonds and one lone pair, as in hydronium ion, it will have a formal charge of +1.

When we get to our discussion of free radical chemistry in chapter 17, we will see other possibilities, such as where an oxygen atom has one bond, one lone pair, and one unpaired (free radical) electron, giving it a formal charge of zero. For now, however, concentrate on the three main non-radical examples, as these will account for virtually everything we see until chapter 17.

Nitrogen

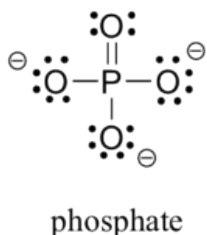
Nitrogen has two major bonding patterns, both of which fulfill the octet rule:



If a nitrogen has three bonds and a lone pair, it has a formal charge of zero. If it has four bonds (and no lone pair), it has a formal charge of +1. In a fairly uncommon bonding pattern, negatively charged nitrogen has two bonds and two lone pairs.

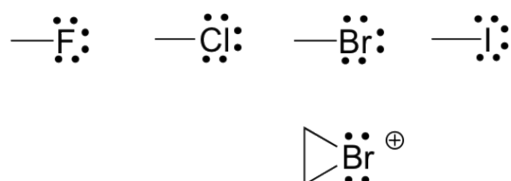
Phosphorus and Sulfur

Two third row elements are commonly found in biological organic molecules: phosphorus and sulfur. Although both of these elements have other bonding patterns that are relevant in laboratory chemistry, in a biological context sulfur almost always follows the same bonding/formal charge pattern as oxygen, while phosphorus is present in the form of phosphate ion (PO_4^{3-}), where it has five bonds (almost always to oxygen), no lone pairs, and a formal charge of zero. Remember that elements in the third row of the periodic table have *d* orbitals in their valence shell as well as *s* and *p* orbitals, and thus are not bound by the octet rule.



Halogens

The halogens (fluorine, chlorine, bromine, and iodine) are very important in laboratory and medicinal organic chemistry, but less common in naturally occurring organic molecules. Halogens in organic compounds usually are seen with one bond, three lone pairs, and a formal charge of zero. Sometimes, especially in the case of bromine, we will encounter reactive species in which the halogen has two bonds (usually in a three-membered ring), two lone pairs, and a formal charge of +1.



These rules, if learned and internalized so that you don't even need to think about them, will allow you to draw large organic structures, complete with formal charges, quite quickly.

Once you have gotten the hang of drawing Lewis structures, it is not always necessary to draw lone pairs on heteroatoms, as you can assume that the proper number of electrons are present around each atom to match the indicated formal charge (or lack thereof). Occasionally, though, lone pairs are drawn if doing so helps to make an explanation more clear.

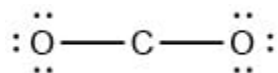
Using Formal Charges to Distinguish between Lewis Structures

Edit section

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2 . Both structures conform to the rules for Lewis electron structures. [Edit section](#)

CO_2

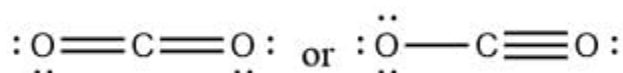
1. C is less electronegative than O, so it is the central atom. [Edit section](#)
2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons. [Edit section](#)
3. Placing one electron pair between the C and each O gives $\text{O}-\text{C}-\text{O}$, with 12 electrons left over. [Edit section](#)
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



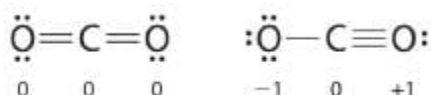
This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.[Edit section](#)

6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO₂ are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.[Edit section](#)

Note

The Lewis structure with the set of formal charges closest to zero is usually the most stable.[Edit section](#)

Example 2.3.2

The thiocyanate ion (SCN[−]), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

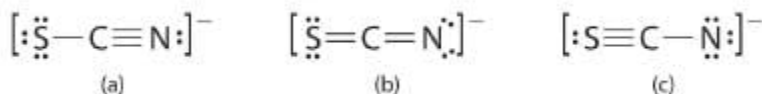
A Use the step-by-step procedure to write two plausible Lewis electron structures for SCN[−].

B Calculate the formal charge on each atom using Equation 2.3.1.

C Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6 - (6 + 2/2) = -1$.

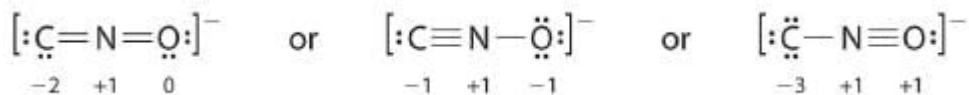
In (b), the sulfur atom has a formal charge of 0. In (c), the sulfur atom has a formal charge of +1. Continuing with the nitrogen, we observe that in (a) the nitrogen atom shares three bonding pairs and has one lone pair and has a total of 5 valence electrons. The formal charge on the nitrogen atom is therefore $5 - (2 + 6/2) = 0$. In (b), the nitrogen atom has a formal charge of -1. In (c), the nitrogen atom has a formal charge of -2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, -1 versus +1, -2.

Exercise 1.5.2

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

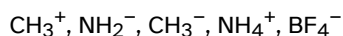
Answer



The second structure is predicted to be the most stable.

Exercises

1. Draw the Lewis structure of each of the molecules listed below.



In each case, use the method of calculating formal charge described to satisfy yourself that the structures you have drawn do in fact carry the charges shown.

Answer:

1. Lewis dot structure of five ions

Questions

Q2.3.1

Give the formal charges for all non-hydrogen atoms in the following molecules: BH_4^- , H_2O , CH_3O^-

Solutions

S2.3.1

BH_4^- (B = -1)

H_2O (O = 0)

CH_3O^- (C = 0, O = -1)

Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

1.6: Resonance

Objective

After completing this section, you should be able to

- draw resonance forms for molecules and ions.

Key Terms

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

- resonance form
- delocalization

Sometimes, even when [formal charges](#) are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. **Resonance** is a way of describing **delocalized** electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5° .

O₃ [Edit section](#)

1. We know that ozone has a V-shaped structure, so one O atom is central:

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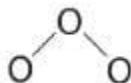


2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

[Edit section](#)

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives

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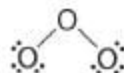


with 14 electrons left over.

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4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

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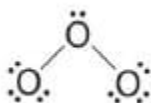


and have 2 electrons left over.

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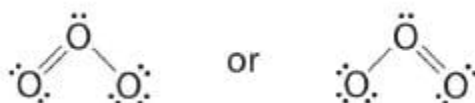
5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

[Edit section](#)



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either

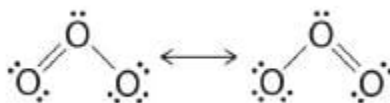
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Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. If the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O₂ (120.7 pm).[Edit section](#)

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:

[Edit section](#)



Before the development of quantum chemistry it was thought that the double-headed arrow indicates that the actual electronic structure is an *average* of those shown, or that the molecule oscillates between the two structures. Today we know that the electrons involved in the double bonds occupy an orbital that extends over all three oxygen molecules, combining *p* orbitals on all three (Figure 2.4.1).

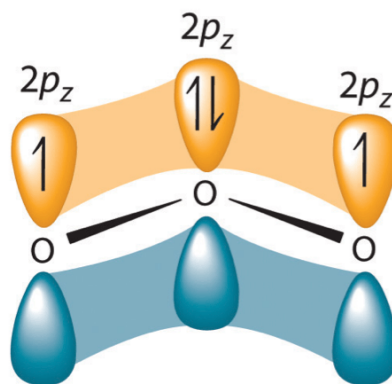


Figure 2.4.1: The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms. In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered p_z orbitals. Similar molecular orbitals are found in every resonance structure. [Edit section](#)

We will discuss the formation of these molecular orbitals in the next chapter but it is important to understand that resonance structures are based on molecular orbitals not averages of different bonds between atoms. We describe the electrons in such molecular orbitals as being **delocalized**, that is they cannot be assigned to a specific bond between two atoms. [Edit section](#)

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure involves a molecular orbital which is a linear combination of atomic orbitals from each of the atoms.

CO₃²⁻ [Edit section](#)

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O₃, though, the Lewis structures describing CO₃²⁻ has *three* equivalent representations. [Edit section](#)

1. Because carbon is the least electronegative element, we place it in the central position:

[Edit section](#)

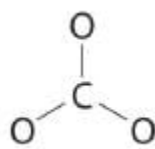


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the -2 charge. This gives $4 + (3 \times 6) + 2 = 24$ valence electrons.

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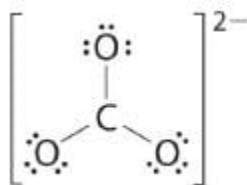
3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

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4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the -2 charge:

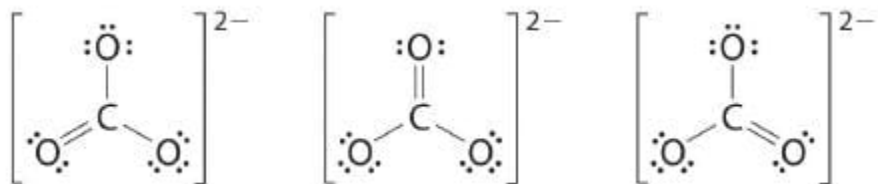
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5. No electrons are left for the central atom. [Edit section](#)

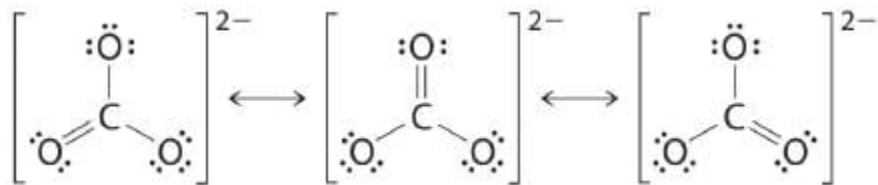
6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:

[Edit section](#)



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:

[Edit section](#)



As the case for ozone, the actual structure involves the formation of a molecular orbital from p_z orbitals centered on each atom and sitting above and below the plane of the CO_3^{2-} ion. [Edit section](#)

Example 2.4.1

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

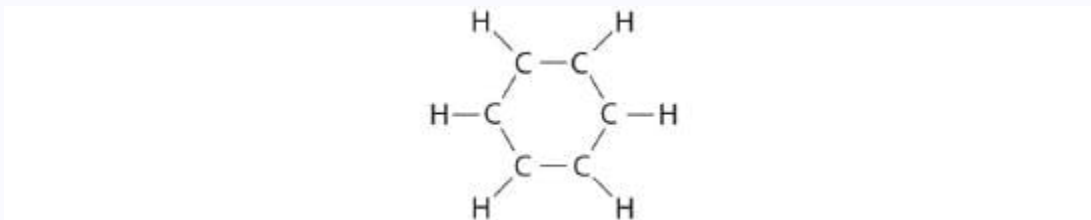
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

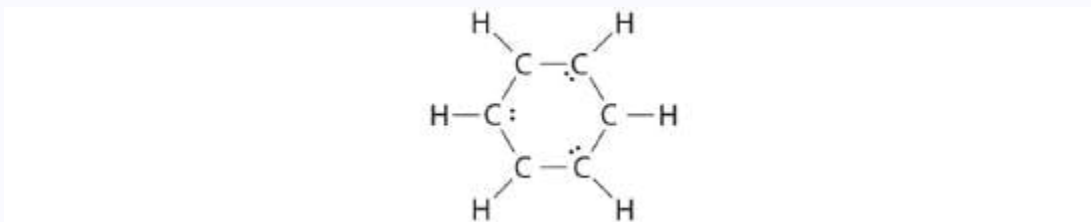
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of $(6 \times 1) + (6 \times 4) = 30$ valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



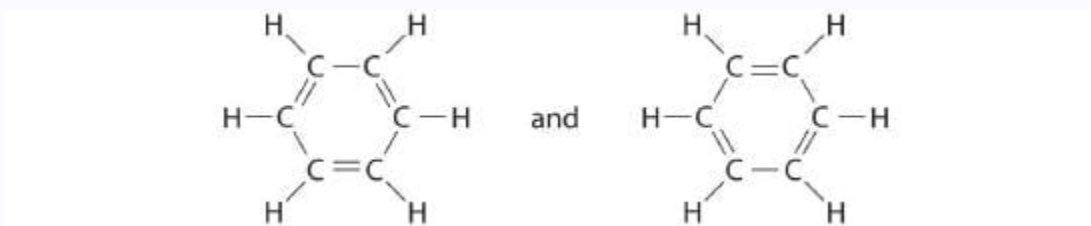
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pair-wise on alternate carbon atoms, we obtain the following:

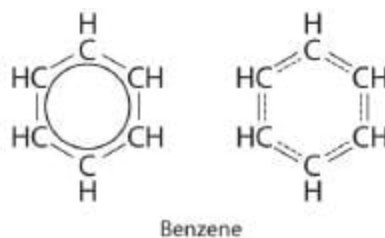


Three carbon atoms now have an octet configuration and a formal charge of -1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon-carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C-C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

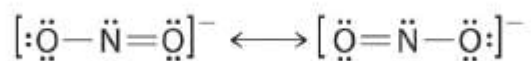


This combination of p orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms.

Exercise 1.6.1

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer



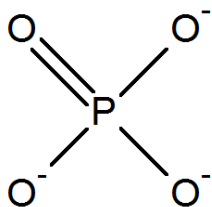
Resonance structures are particularly common in oxyanions of the p -block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.[Edit section](#)

Exercises

Questions

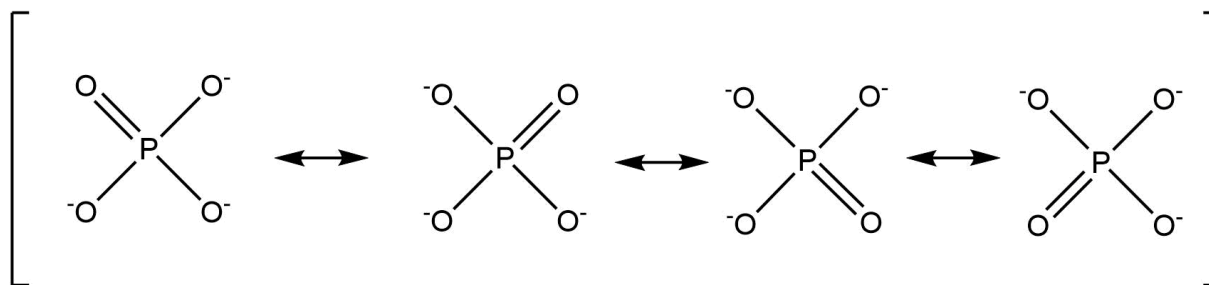
Q2.4.1

Draw the resonance structures for the following molecule:



Solutions

S2.4.1



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

1.7: Rules for Resonance Forms

Objectives

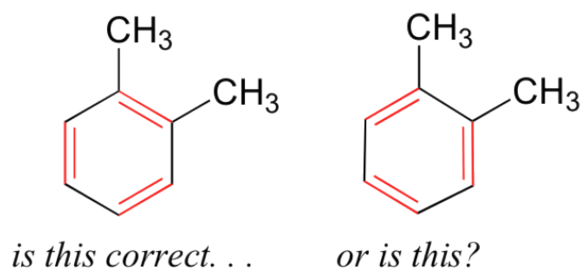
After completing this section, you should be able to

- use the concept of resonance to explain structural features of molecules and ions.
- understand the relationship between resonance and relative stability of molecules and ions.

Recognizing resonance

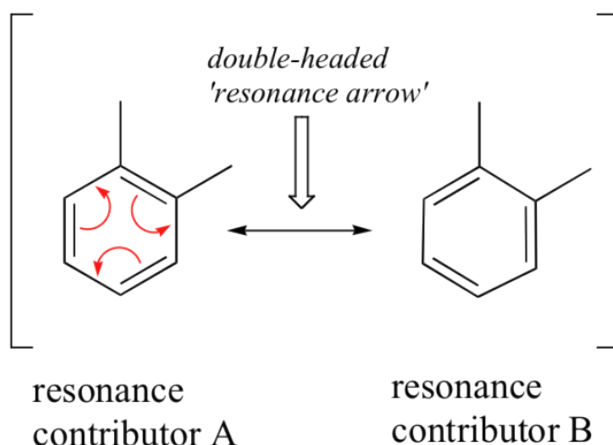
Resonance contributors involve the 'imaginary movement' of pi-bonded electrons or of lone-pair electrons that are adjacent to (i.e. conjugated to) pi bonds. You can never shift the location of electrons in sigma bonds – if you show a sigma bond forming or breaking, you are showing a chemical reaction taking place. Likewise, the positions of atoms in the molecule cannot change between two resonance contributors.

Because benzene will appear throughout this course, it is important to recognize the stability gained through the resonance delocalization of the six pi electrons throughout the six carbon atoms. Benzene also illustrates one way to recognize resonance – when it is possible to draw two or more equivalent Lewis structures. If we were to draw the structure of an aromatic molecule such as 1,2-dimethylbenzene, there are two ways that we could draw the double bonds:



Which way is correct? There are two simple answers to this question: 'both' and 'neither one'. Both ways of drawing the molecule are equally acceptable approximations of the bonding picture for the molecule, but neither one, by itself, is an accurate picture of the delocalized pi bonds. The two alternative drawings, however, *when considered together*, give a much more accurate picture than either one on its own. This is because they imply, together, that the carbon-carbon bonds are not double bonds, not single bonds, but about halfway in between.

When it is possible to draw more than one valid structure for a compound or ion, we have identified **resonance contributors**: two or more different Lewis structures depicting the same molecule or ion that, when considered together, do a better job of approximating delocalized pi-bonding than any single structure. By convention, resonance contributors are linked by a double-headed arrow, and are sometimes enclosed by brackets:

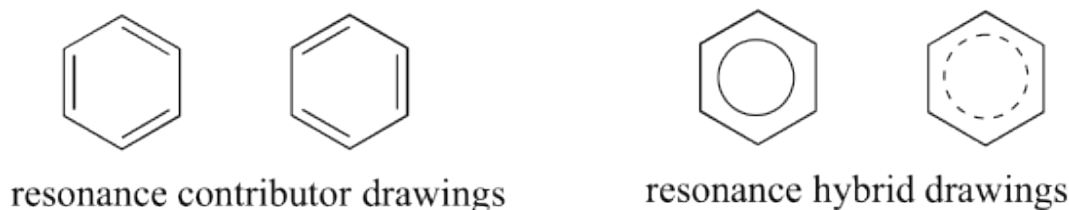


In order to make it easier to visualize the difference between two resonance contributors, small, curved arrows are often used. Each of these arrows depicts the 'movement' of two pi electrons. In the drawing of resonance contributors, however, this electron 'movement' occurs only in our minds, as we try to visualize delocalized pi bonds. Nevertheless, use of the curved arrow notation is an essential skill that you will need to develop in drawing resonance contributors.

The depiction of benzene using the two resonance contributors A and B in the figure above does *not* imply that the molecule at one moment looks like structure A, then at the next moment shifts to look like structure B. Rather, at all moments, the molecule is a combination, or **resonance hybrid** of both A and B.

Caution! It is very important to be clear that in drawing two (or more) resonance contributors, we are not drawing two different molecules: they are simply *different depictions of the exact same molecule*. Furthermore, the double-headed resonance arrow does NOT mean that a chemical reaction has taken place.

Benzene is often drawn as only one of the two possible resonance contributors (it is assumed that the reader understands that resonance hybridization is implied). However, sometimes benzene will be drawn with a circle inside the hexagon, either solid or dashed, as a way of drawing a resonance hybrid.



Resonance Delocalizes Charge to Increase Stability

Resonance is most useful when it delocalizes charge to stabilize reactive intermediates and products. Recognizing, drawing, and evaluating the relative stability of resonance contributors is essential to understanding organic reaction mechanisms.

Rules for drawing and working with resonance contributors

Learning to draw and interpret resonance structures, there are a few basic guidelines to help avoid drawing nonsensical structures. All of these guidelines make perfect sense as long as we remember that resonance contributors are merely a human-invented convention for depicting the delocalization of pi electrons in conjugated systems.

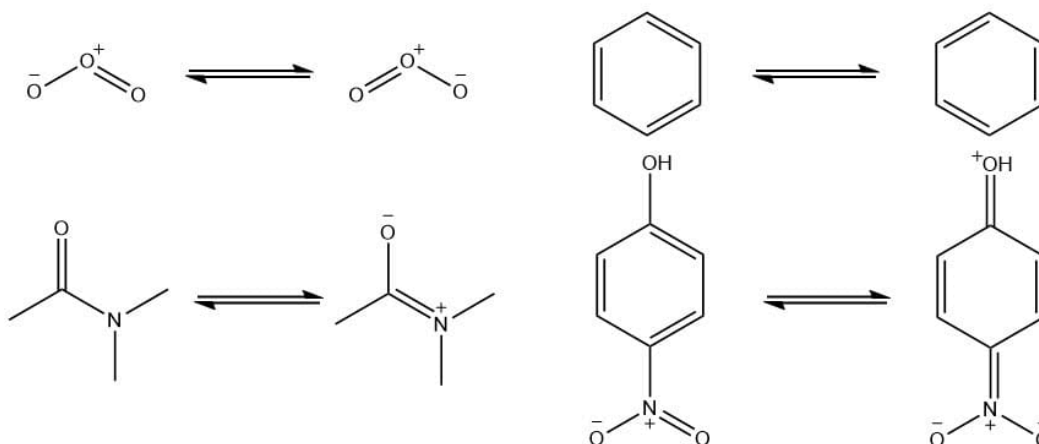
- 1) There is **ONLY ONE REAL STRUCTURE** for each molecule or ion. This real structure (the **resonance hybrid**) takes its character from the average of all the individual **resonance contributors**.
 - When we see two different resonance contributors, we are not seeing a chemical reaction! We are seeing the exact same molecule or ion depicted in two different ways.
- 2) The resonance hybrid is more stable than any individual resonance contributor.
- 3) Resonance forms do not have to contribute equally to the resonance hybrid (explained further in section 4.6).
- 4) All resonance contributors must be correct Lewis structures.
 - Each atom should have a complete valence shell and be shown with correct formal charges.
 - A carbocation (carbon with only 6 valence electrons) is the only allowed exception to the valence shell rules.
- 5) Only delocalizable electrons (pi bond or lone pair electrons) move between one resonance form and another.
 - Sigma bonds are never broken or made, because of this atoms must maintain their same position.
 - All resonance contributors must have the same molecular formula and net charge.

Rules for estimating stability of resonance structures

- The resonance form in which all atoms have complete valence shells is more stable.
- The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
- The structure with the **least number of formal charges** is more stable
- The structure with the **least separation of formal charges** is more stable
- A structure with a **negative charge on the more electronegative atom** will be more stable
- Positive charges on the least electronegative atom** (most electropositive) is more stable
- Resonance forms that are equivalent have no difference in stability and contribute equally.** (eg. benzene)

Examples of Resonance

Single Resonance Configuration

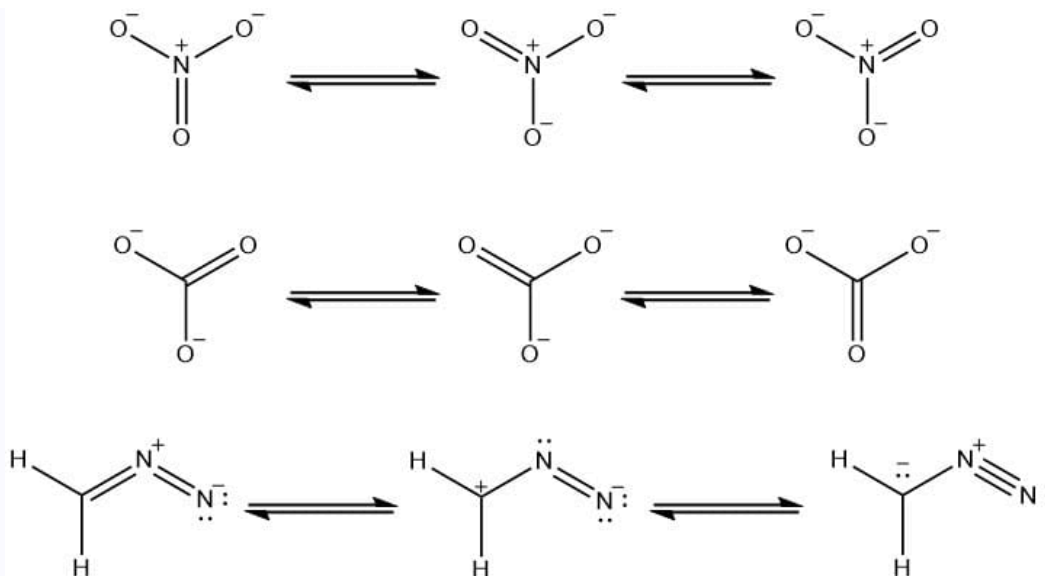


The above resonance structures show that the electrons are delocalized within the molecule and through this process the molecule gains extra stability. Ozone with both of its opposite formal charges creates a neutral molecule and through resonance it is a stable molecule. The extra electron that created the negative charge on one terminal oxygen can be delocalized by resonance through the other terminal oxygen.

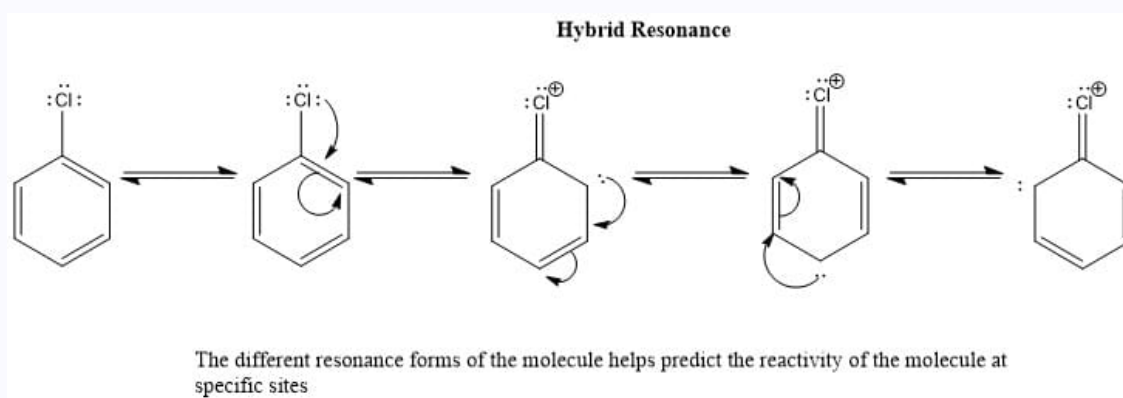
Benzene is an extremely stable molecule due to its geometry and molecular orbital interactions, but most importantly, due to its resonance structures. The delocalized electrons in the benzene ring make the molecule very stable and with its characteristics of a nucleophile, it will react with a strong electrophile only and after the first reactivity, the substituted benzene will depend on its resonance to direct the next position for the reaction to add a second substituent.

Example 2.5.1: Multiple Resonance of other Molecules

Molecules and ions with more than one resonance form



Some structural resonance conformations are the major contributor or the dominant forms that the molecule exists. For example, if we look at the above rules for estimating the stability of a molecule, we see that for the third molecule the first and second forms are the major contributors for the overall stability of the molecule. The nitrogen is more electronegative than carbon so, it can handle the negative charge more than carbon. A carbon with a negative charge is the least favorable conformation for the molecule to exist, so the last resonance form contributes very little for the stability of the Ion.



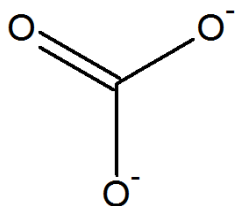
The Hybrid Resonance forms show the different Lewis structures with the electron been delocalized. This is very important for the reactivity of chloro-benzene because in the presence of an electrophile it will react and the formation of another bond will be directed and determine by resonance. The lone pair of electrons delocalized in the aromatic substituted ring is where it can potentially form a new bond with an electrophile, as it is shown there are three possible places that reactivity can take place, the first to react will take place at the *para* position with respect to the chloro substituent and then to either *ortho* position.

Exercises

Questions

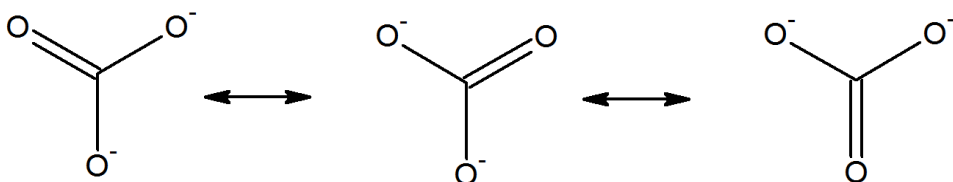
Q2.5.1

Are all the bond lengths the same in the carbonate ion, CO_3^{2-} ?



Solutions

S2.5.1 Yes, the bond lengths in carbonate ion are all the same. Carbonate ion exists as the resonance hybrid of the three resonance forms below.



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

1.8: Drawing Resonance Forms

Objectives

After completing this section, you should be able to

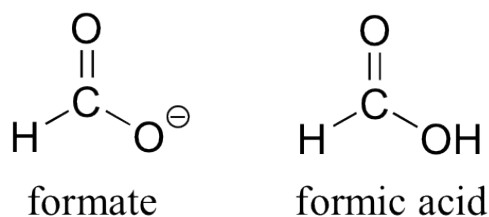
- draw the resonance structures of molecules or ions that exhibit delocalization.
- determine the relative stability of resonance structures using a set of rules.
- use the concept of resonance to explain structural features of molecules and ions.

key words

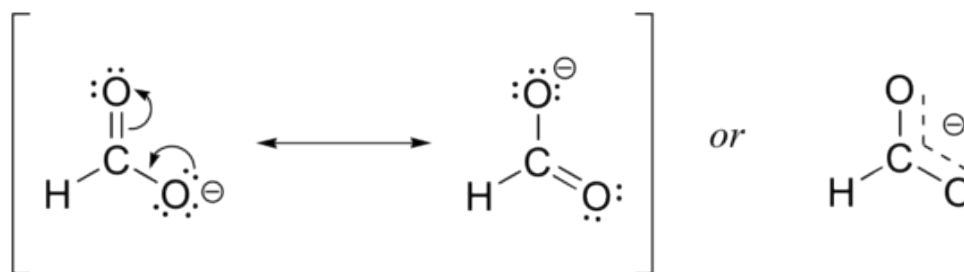
- resonance structure
- resonance hybrid

Resonance Contributors for the Carboxylate Group

The convention of drawing two or more resonance contributors to approximate a single structure may seem a bit clumsy at this point, but the practice is actually very useful when discussing the manner in which many functional groups react. Let's consider formate, the simplest carboxylate ion. The conjugate acid of formate is formic acid, which causes the painful sting you felt if you have ever been bitten by an ant.

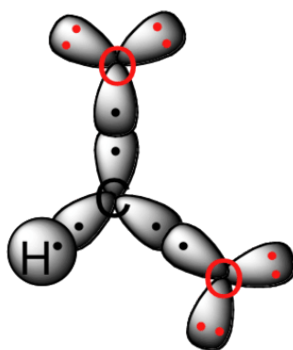


Usually, carboxylate ions are drawn with one carbon-oxygen double bond and one carbon-oxygen single bond, with a negative formal charge located on the single-bonded oxygen. However, the two carbon-oxygen bonds are actually the same length, and although there is indeed an overall negative formal charge on the group, it is shared equally between the two oxygens. Therefore, the carboxylate ion can be more accurately depicted by a *pair* of resonance contributors. Alternatively, a single structure can be used, with a dashed line depicting the resonance-delocalized pi bond and the negative charge located in between the two oxygens.



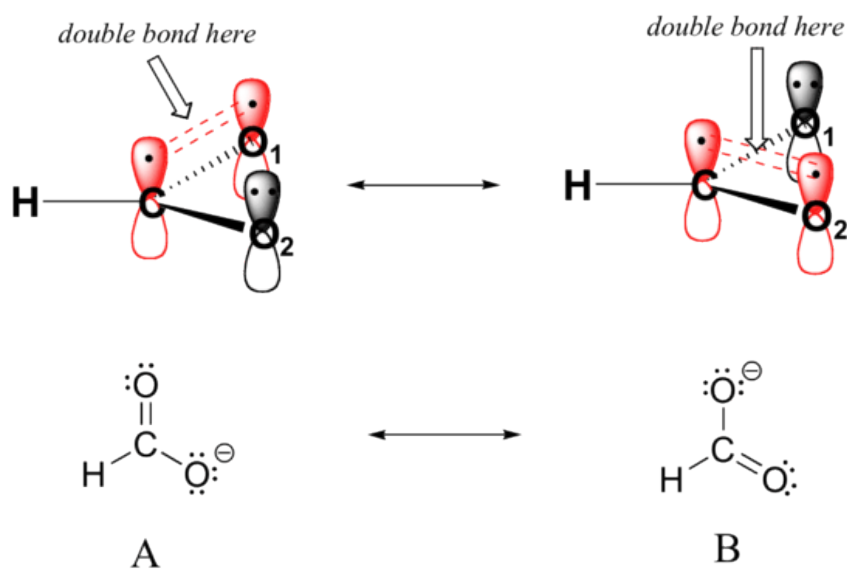
Let's see if we can correlate these drawing conventions to a valence bond theory picture of the bonding in a carboxylate group. We know that the carbon must be sp^2 -hybridized, (the bond angles are close to 120° , and the molecule is planar), and we will treat both oxygens as being sp^2 -hybridized as well. Both carbon-oxygen sigma bonds, then, are formed from the overlap of carbon sp^2

orbitals and oxygen sp^2 orbitals.



the σ -bonding framework of formate

In addition, the carbon and both oxygens each have an unhybridized $2p_z$ orbital situated perpendicular to the plane of the sigma bonds. These three $2p_z$ orbitals are parallel to each other, and can overlap in a side-by-side fashion to form a delocalized pi bond.

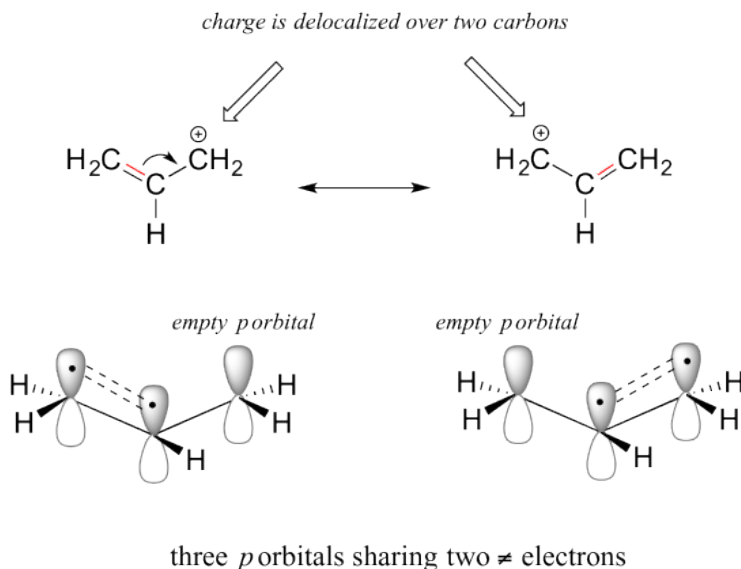


Resonance contributor A shows oxygen #1 sharing a pair of electrons with carbon in a pi bond, and oxygen #2 holding a lone pair of electrons in its $2p_z$ orbital. Resonance contributor B, on the other hand, shows oxygen #2 participating in the pi bond with carbon, and oxygen #1 holding a lone pair in its $2p_z$ orbital. Overall, the situation is one of *three parallel, overlapping $2p_z$ orbitals sharing four delocalized pi electrons*. Because there is one more electron than there are $2p_z$ orbitals, the system has an overall charge of -1 . This is the kind of 3D picture that resonance contributors are used to approximate, and once you get some practice you should be able to quickly visualize overlapping $2p_z$ orbitals and delocalized pi electrons whenever you see resonance structures being used. In this text, carboxylate groups will usually be drawn showing only one resonance contributor for the sake of simplicity, but you should always keep in mind that the two C-O bonds are equal, and that the negative charge is delocalized to both oxygens.

Exercise 2.6.1: There is a third resonance contributor for formate (which we will soon learn is considered a 'minor' contributor). Draw this resonance contributor.

Here's another example, this time with a carbocation. Recall that carbocations are sp^2 -hybridized, with an empty $2p$ orbital oriented perpendicular to the plane formed by three sigma bonds. If a carbocation is adjacent to a double bond, then three $2p$ orbitals can overlap and share the two pi electrons - another kind of conjugated pi system in which the positive charge is shared

over two carbons.

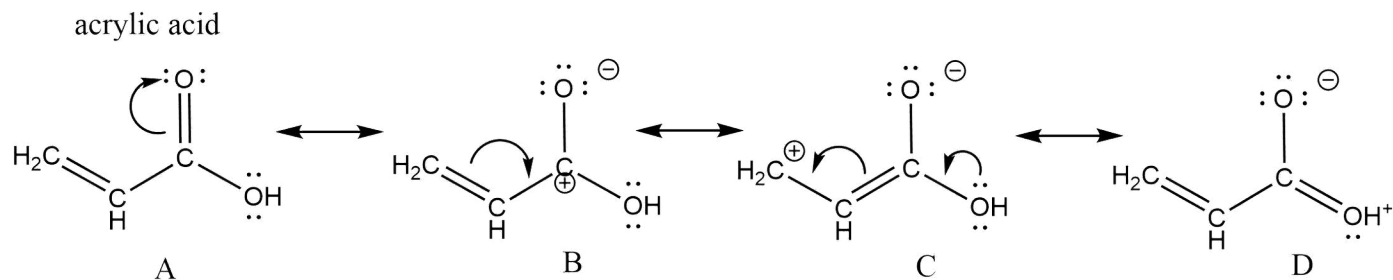


Using Curved Arrows to Show Resonance

There are only three types of electron "motion" in resonance. They are

1. **A lone pair forms a pi bond to an adjacent atom**
2. **A pi bond forms a new pi bond to an adjacent atom**
3. **A pi bond forms a lone pair on adjacent atom**

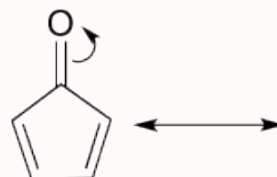
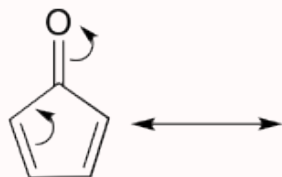
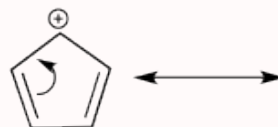
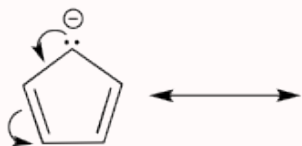
Let's look at the resonance within acrylic acid to demonstrate these three types of resonance.



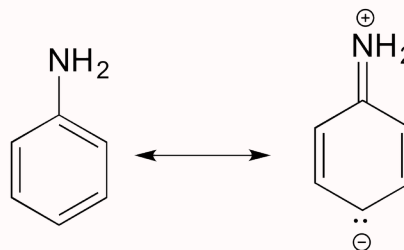
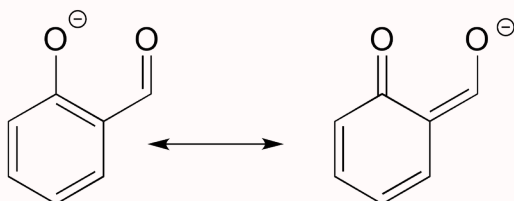
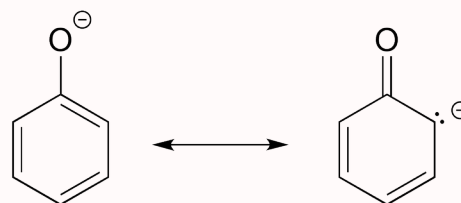
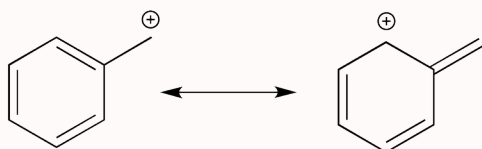
The curved arrow in structure A represents the type 3 resonance "motion" - the pi bond between the carbon and oxygen breaks to form another lone pair on the oxygen. The curved arrow in structure B represents type 2 resonance "motion" - the pi bond breaks to form a new pi bond to the carbocation carbon. In structure C, there are two curved arrows. The curved arrow from the oxygen lone pair is type 1 resonance motion - the lone pairs forms a new pi bond between the oxygen and carbon. The other arrow in structure C moves the pi bond to the end of the chain - what type of resonance is that?

Exercise 2.6.2: Draw the resonance contributors that correspond to the curved, two-electron movement arrows in the

resonance expressions below. Then identify the type of resonance motion in each structure below.



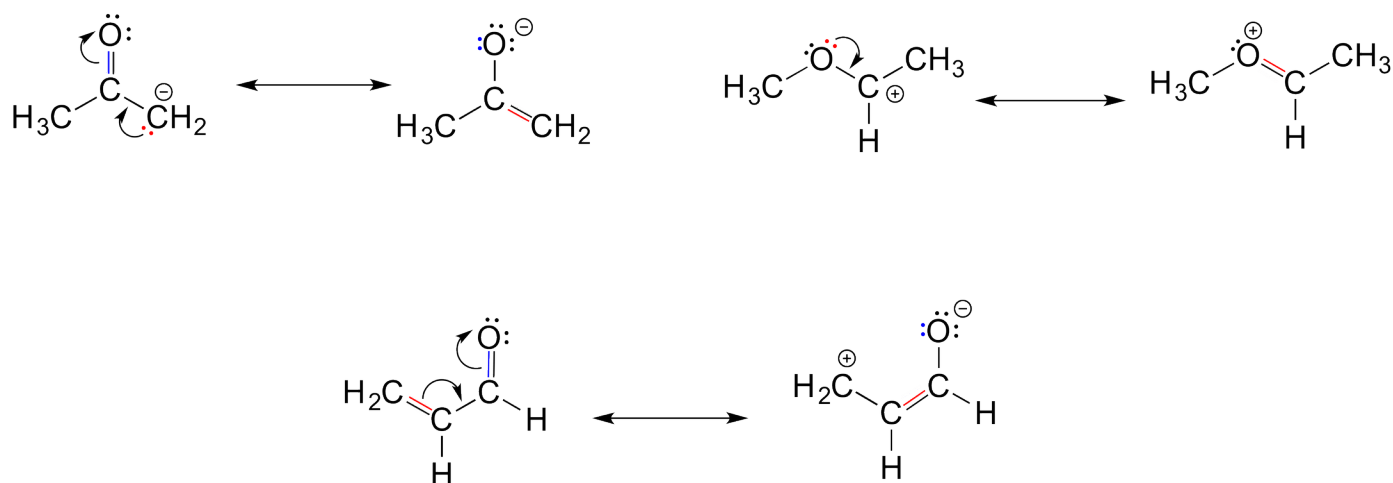
Exercise 2.6.3: In each resonance expression, identify the type of resonance motion. Then draw curved arrows on the left-side contributor that shows how we get to the right-side contributor.



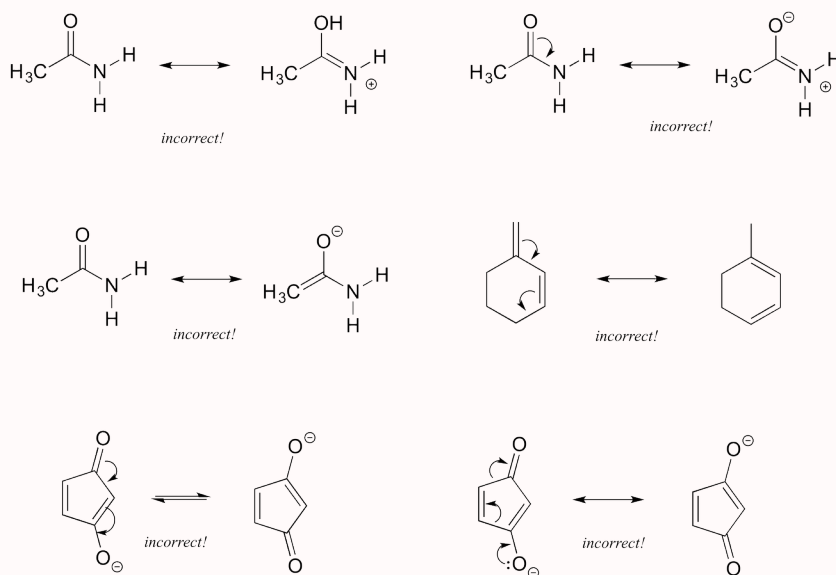
Guided Resonance Practice

[Edit section](#)

Below are a few more examples of 'legal' resonance expressions. Confirm for yourself that the octet rule is not exceeded for any atoms, and that formal charges are correct.



Exercise 2.6.4: Each of the 'illegal' resonance expressions below contains one or more mistakes. Explain what is incorrect in each.



Evaluating Resonance Contributors

1. Identical structures are equally important.
2. Structures with a greater number of bonds are more important.
3. Structures with charge separation are less important.
4. Pay attention to electronegativities.
5. Neutral atoms need to have complete octets

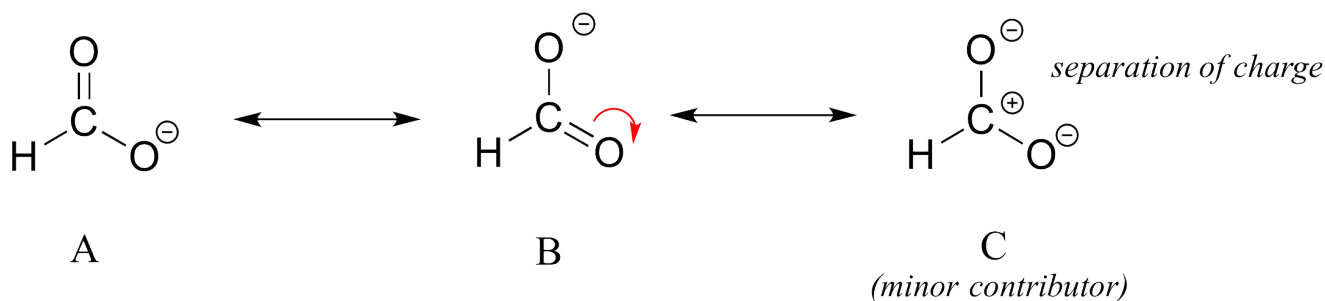
Major vs minor resonance contributors

Different resonance contributors do not always make the same contribution to the overall structure of the hybrid - rather, in many cases one contributor comes closer to depicting the actual bonding picture than another.

Rules for estimating relative stability of resonance structures

1. The structure in which **all atoms have a complete valence shell** is more stable.
2. The structure that has the **greater number of covalent bonds** is more stable.
3. The structure with the **fewest number and/or the least separation of formal charges** is more stable.
4. The structure with **negative charge on the more electronegative atom** is more stable. **Positive charges should be on the less electronegative atom.**
5. Resonance forms that are equivalent have no difference in stability and contribute equally. (eg. benzene)

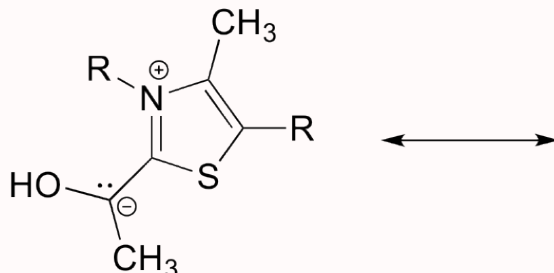
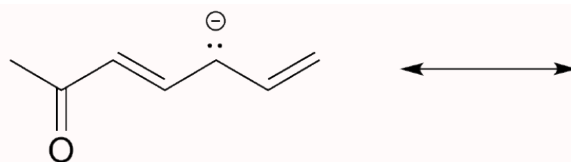
In the case of carboxylates, contributors A and B below are equivalent in terms of their relative contribution to the hybrid structure. However, there is also a third resonance contributor 'C, in which the carbon bears a positive formal charge (a carbocation) and both oxygens are single-bonded and bear negative charges.



Structure C makes a less important contribution to the overall bonding picture of the group relative to A and B. How do we know that structure C is the 'minor' contributor? Apply the rules below

- The carbon in contributor C does not have an octet. In general, resonance contributors in which a carbon does not fulfill the octet rule are relatively less important. (rule #1)
- In structure C, there are only three bonds, compared to four in A and B. In general, a resonance structure with a lower number of total bonds is relatively less important. (rule #2)
- Structure C also has more formal charges than are present in A or B. In general, resonance contributors in which there is more/greater separation of charge are relatively less important. (rule #3)
- Structures A and B are equivalent and will be equal contributors to the resonance hybrid. (rule #5).
- The resonance contributor in which a negative formal charge is located on a more electronegative atom, usually oxygen or nitrogen, is more stable than one in which the negative charge is located on a less electronegative atom such as carbon. An example is in the upper left expression in the next figure. (rule #4)

Solved example: Draw the major resonance contributor of the structure below. Include in your figure the appropriate curved arrows showing how you got from the given structure to your structure. Explain why your contributor is the major one. In what

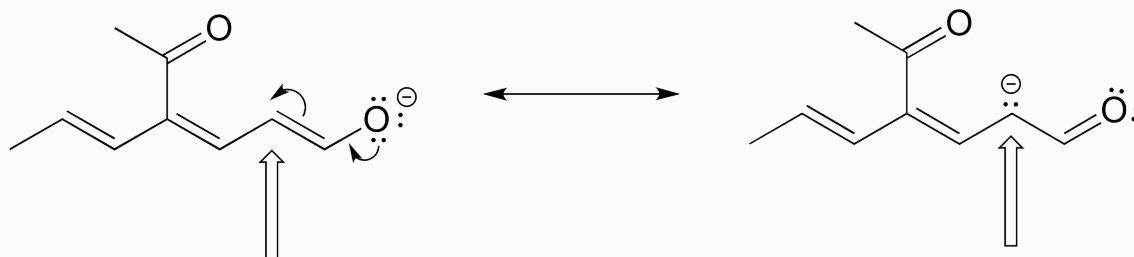


c) Fill in the blanks: the conjugated pi system in part (a) is composed of ____ $2p$ orbitals containing ____ delocalized pi electrons.

Exercise 2.6.7: The figure below shows how the negative formal charge on the oxygen can be delocalized to the carbon indicated by an arrow. More resonance contributors can be drawn in which negative charge is delocalized to three other atoms on the molecule.

a) Circle these atoms.

b) Draw the two most important resonance contributors for the molecule.



A word of advice

Becoming adept at drawing resonance contributors, using the curved arrow notation to show how one contributor can be converted to another, and understanding the concepts of conjugation and resonance delocalization are some of the most challenging but also most important jobs that you will have as a beginning student of organic chemistry. If you work hard now to gain a firm grasp of these ideas, you will have come a long way toward understanding much of what follows in your organic chemistry course. Conversely, if you fail to come to grips with these concepts now, a lot of what you see later in the course will seem like a bunch of mysterious and incomprehensible lines, dots, and arrows, and you will be in for a rough ride, to say the least. More so than many other topics in organic chemistry, *understanding bonding, conjugation, and resonance is something that most students really need to work on 'in person' with an instructor or tutor, preferably using a molecular modeling kit.* Keep working problems, keep asking questions, and keep at it until it all makes sense!

References

1. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. New Jersey: Pearson Prentice Hall, 2007. Print.

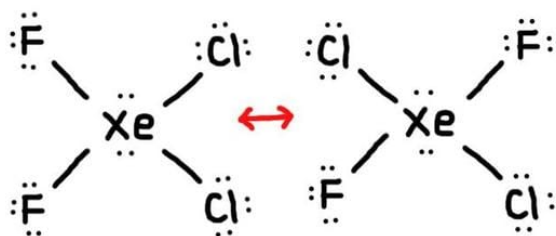
- Ahmad, Wan-Yaacob and Zakaria, Mat B. "Drawing Lewis Structures from Lewis Symbols: A Direct Electron Pairing Approach." Journal of Chemical Education: Journal 77.3: n. pag. Web. March 2000. Link to this journal: http://pkukmweb.ukm.my/~mbz/c_penerb...83%29/p329.pdf

Outside links

- [http://en.wikipedia.org/wiki/Resonance_\(chemistry\)](http://en.wikipedia.org/wiki/Resonance_(chemistry))
- [http://www.absoluteastronomy.com/topics/Resonance_\(chemistry\)#encyclopedia](http://www.absoluteastronomy.com/topics/Resonance_(chemistry)#encyclopedia)
- <http://www.nku.edu/~russellk/tutorial/reson/resonance.html>
- http://en.wikipedia.org/wiki/Formal_charge
- http://commons.wikimedia.org/wiki/Main_Page (for the electronegativity chart)
- <http://misterguch.brinkster.net/PRA037.pdf> (for problem 5)
- <http://commons.wikimedia.org/wiki/File:Phosphite-ion-resonance-structures-2D.png> (for the (HPO_3^{2-}) problem 4 answer)
- <http://commons.wikimedia.org/wiki/File:Sulfate-resonance-2D.png> (for the Sulfate answer)
- http://www.mpcfaculty.net/mark_bishop/resonance.htm
- http://www.chem.ucla.edu/harding/tutorials/resonance/draw_res_str.html

Problems

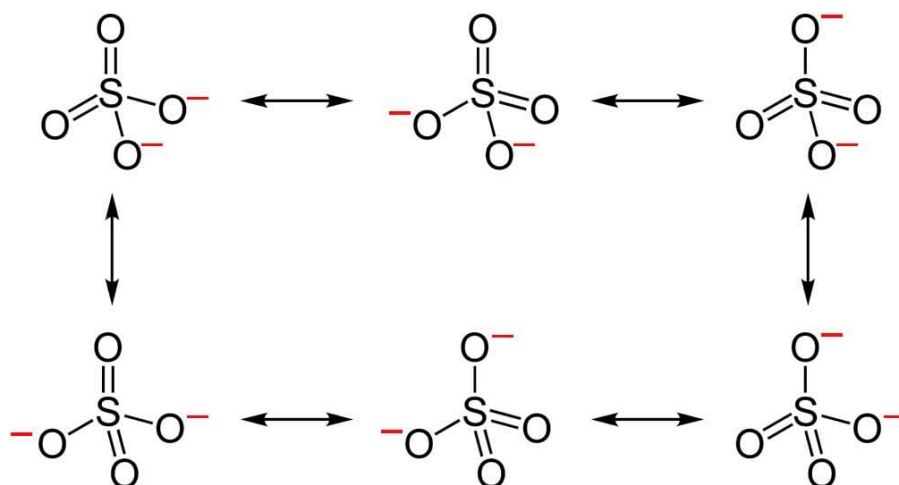
- True or False, The picture below is a resonance structure?



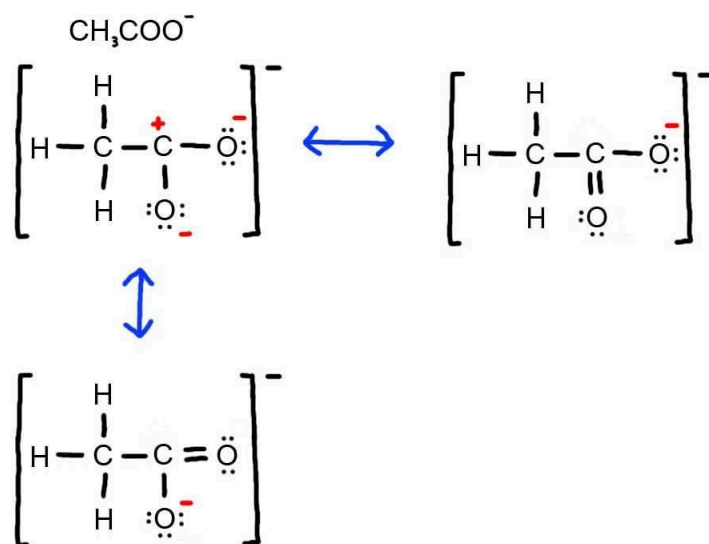
- Draw the Lewis Dot Structure for SO_4^{2-} and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
- Draw the Lewis Dot Structure for CH_3COO^- and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
- Draw the Lewis Dot Structure for HPO_3^{2-} and all possible resonance structures. Assign Formal Charges.
- Draw the Lewis Dot Structure for CHO_2^{1-} and all possible resonance structures. Assign Formal Charges.
- Draw the Resonance Hybrid Structure for PO_4^{3-} .
- Draw the Resonance Hybrid Structure for NO_3^- .

Answers

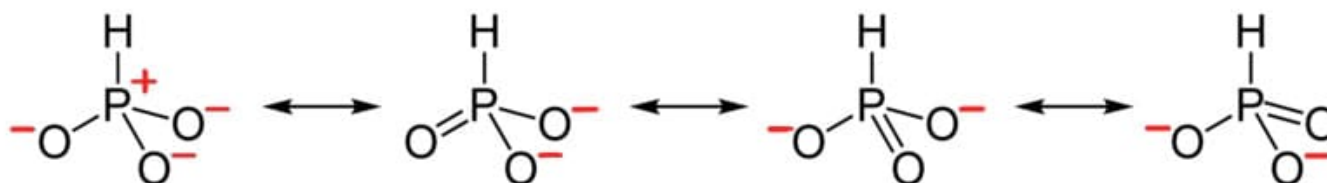
- False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).
- Below are the all Lewis dot structure with formal charges (in red) for Sulfate (SO_4^{2-}). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



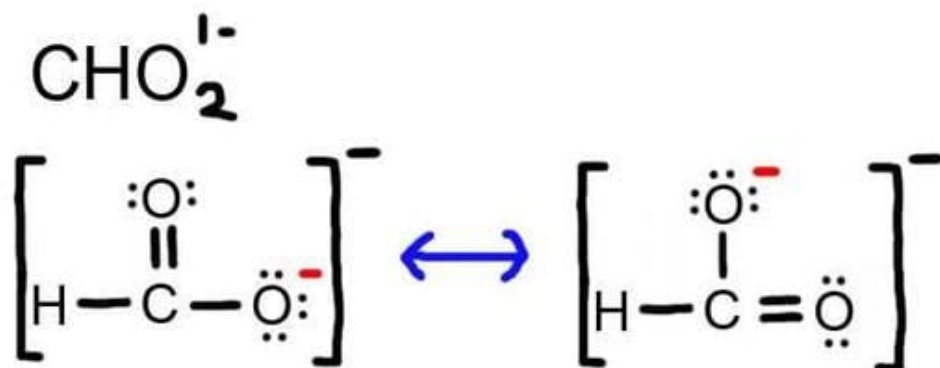
3. Below is the resonance for CH_3COO^- , formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



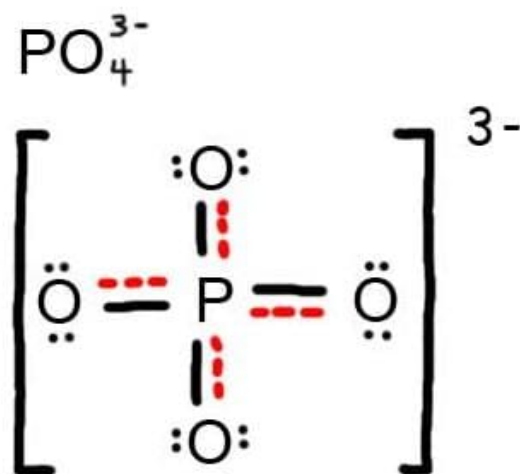
4. The resonance for HPO_3^{2-} , and the formal charges (in red).



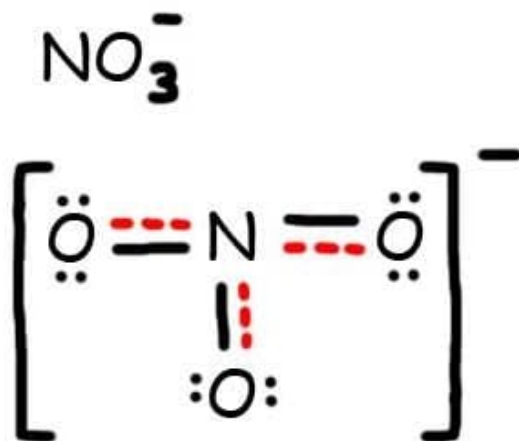
5. The resonance for CHO_2^{1-} , and the formal charges (in red).



6. The resonance hybrid for PO_4^{3-} , hybrid bonds are in red.



7. The resonance hybrid for NO_3^- , hybrid bonds are in red.



Contributors

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1.9: Acids and Bases - The Brønsted-Lowry Definition

Objectives

After completing this section, you should be able to

1. state the Brønsted-Lowry definition of an acid and a base.
2. identify the Brønsted-Lowry acid and base in a given acid-base reaction.
3. identify the conjugate base of an acid and identify the conjugate acid of a base.

Key Terms

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

- Brønsted-Lowry acid
- Brønsted-Lowry base
- conjugate acid
- conjugate base

Study Notes

You should already be familiar with the Brønsted-Lowry concept of acidity and the differences between strong and weak acids. You may wish to review this topic before proceeding.

In 1923, chemists Johannes Brønsted and Martin Lowry independently developed definitions of acids and bases based on compounds abilities to either donate or accept protons (H^+ ions). Here, acids are defined as being able to donate protons in the form of hydrogen ions; whereas bases are defined as being able to accept protons. This took the Arrhenius definition one step further as water is no longer required to be present in the solution for acid and base reactions to occur.

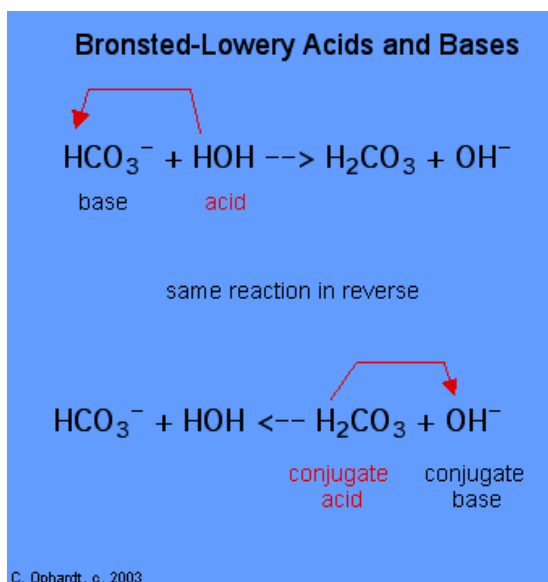
Brønsted-Lowry Definition [Edit section](#)

J.N. Brønsted and T.M. Lowry independently developed the theory of proton donors and proton acceptors in acid-base reactions, coincidentally in the same region and during the same year. The Arrhenius theory where acids and bases are defined by whether the molecule produces hydrogen ion or hydroxide ion when dissolved in water was too limiting, because not all chemical reactions, especially organic reactions, occur in water. The Brønsted-Lowry Theory defines an acid a proton donor, while a base is a proton acceptor. This is illustrated in the following reactions:



Acid	Base	
Donates hydrogen ions	Accepts hydrogen ions.	
HCl	$HOH \rightarrow$	$H_3O^+ + Cl^-$
HOH	$NH_3 \rightarrow$	$NH_4^+ + OH^-$

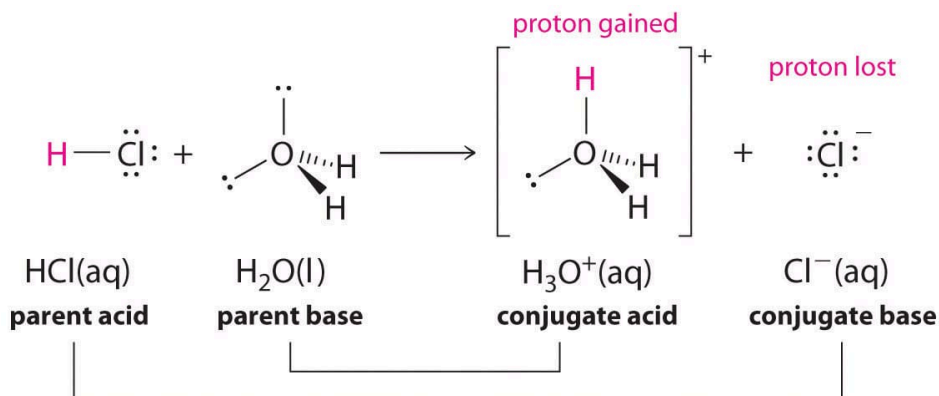
The determination of a substance as a Brønsted-Lowry acid or base can only be done by examining the reaction, since many chemicals can be either an acid or a base. For example, HOH is a base in the first reaction and an acid in the second reaction.



To determine whether a substance is an acid or a base, count the hydrogens on each substance before and after the reaction. If the number of hydrogens has decreased, then that substance is the acid (donates hydrogen ions). If the number of hydrogens has increased, then that substance is the base (accepts hydrogen ions). These definitions are normally applied to the reactants on the left. If the reaction is viewed in reverse a new acid and base can be identified. The substances on the right side of the equation are called the conjugate acid and conjugate base compared to those on the left. Also note that an acid turns into a conjugate base, and the base turns into the conjugate acid after the reaction is over.

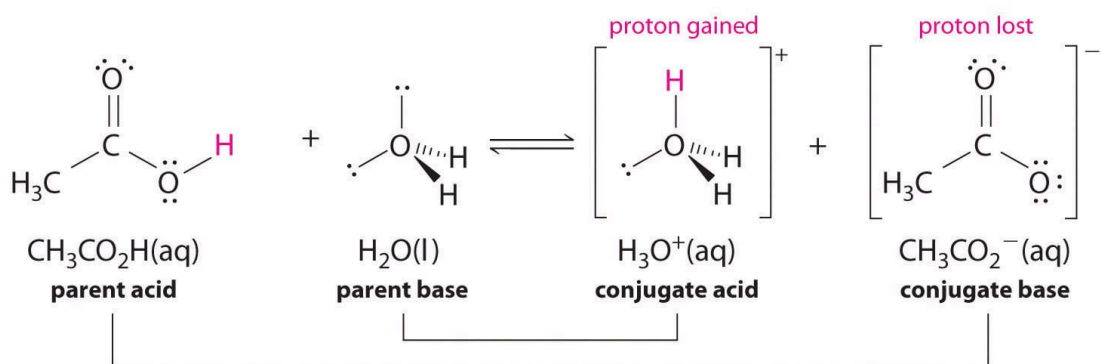
Conjugate Acid-Base Pairs [Edit section](#)

In aqueous solutions, acids and bases can be defined in terms of the transfer of a proton from an acid to a base. Thus for every acidic species in an aqueous solution, there exists a species derived from the acid by the loss of a proton. These two species that differ by only a proton constitute a **conjugate acid-base pair**. For example, in the reaction of HCl with water shown below, HCl , the parent acid, donates a proton to a water molecule, the parent base, thereby forming Cl^- . Thus HCl and Cl^- constitute a conjugate acid-base pair. By convention, we always write a conjugate acid-base pair as the acid followed by its conjugate base. In the reverse reaction, the Cl^- ion in solution acts as a base to accept a proton from H_3O^+ , forming H_2O and HCl . Thus H_3O^+ and H_2O constitute a second conjugate acid-base pair. In general, any acid-base reaction must contain two conjugate acid-base pairs, which in this case are HCl/Cl^- and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.

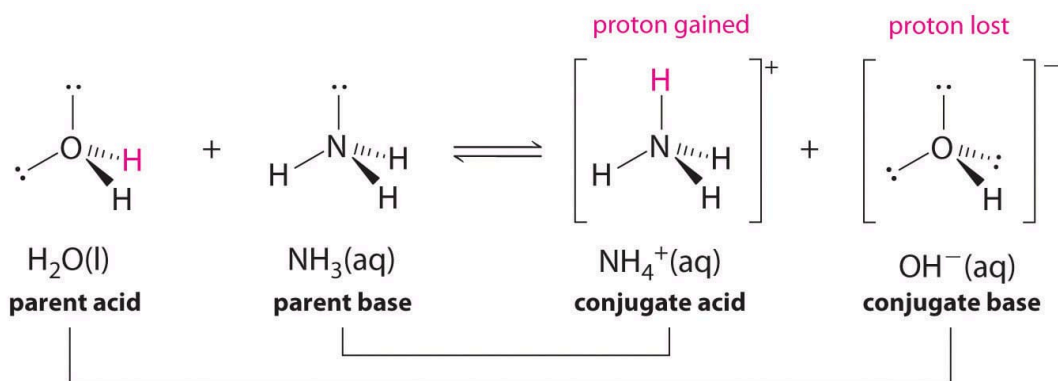


All acid–base reactions contain two conjugate acid–base pairs.

Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$) and the parent base and its conjugate acid ($\text{H}_3\text{O}^+/\text{H}_2\text{O}$).



In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $\text{NH}_4^+/\text{NH}_3$ and $\text{H}_2\text{O}/\text{OH}^-$.



Some common conjugate acid–base pairs are shown in Figure 2.7.1. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Figure 2.7.1 The Relative Strengths of Some Common Conjugate Acid–Base Pairs

ACID		BASE	
←-Relative acid strength increasing	negligible	OH ⁻	O ²⁻
		HS ⁻	S ²⁻
		H ₂ O	OH ⁻
		HPO ₄ ²⁻	PO ₄ ³⁻
		HCO ₃ ⁻	CO ₃ ²⁻
		NH ₄ ⁺	NH ₃
		HCN	CN ⁻
		H ₂ PO ₄ ⁻	HPO ₄ ²⁻
		HSO ₃ ⁻	SO ₃ ²⁻
		H ₂ S	HS ⁻
		H ₂ CO ₃	HCO ₃ ⁻
		C ₅ H ₅ NH ⁺	C ₅ H ₅ N
		CH ₃ CO ₂ H	CH ₃ CO ₂ ⁻
		HF	F ⁻
		H ₃ PO ₄	H ₂ PO ₄ ⁻
Relative base strength increasing →		H ₂ SO ₃	HSO ₃ ⁻
		HSO ₄ ⁻	SO ₄ ²⁻
		H ₃ O ⁺	H ₂ O
		HNO ₃	NO ₃ ⁻
		H ₂ SO ₄	HSO ₄ ⁻
		HCl	Cl ⁻
		HBr	Br ⁻

Exercises

- Identify the Brønsted-Lowry acids and bases in the reactions given below.
 - $\text{CH}_3\text{CH}_2\text{O}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH} + \text{OH}^-$
 - $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}_2^+ + \text{HSO}_4^-$

Answer:

- acids and bases identified in ethoxide reaction with water
 - acids and bases identified in ethanol reaction with sulfuric acid

Questions

Q2.7.1

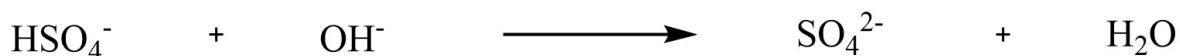
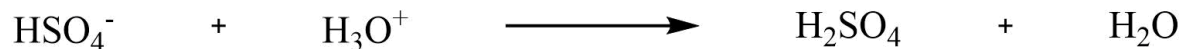
Is the following molecule a Brønsted acid or base?



Solutions

S2.7.1

It can be both, consider the following schemes:



Contributors

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)

- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
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1.10: Acid and Base Strength

Objectives

After completing this section, you should be able to

- write the expression for the K_a of a weak acid.
- convert a given K_a value into a pK_a value, and *vice versa*.
- arrange a series of acids in order of increasing or decreasing strength, given their K_a or pK_a values.
- arrange a series of bases in order of increasing or decreasing strength, given the K_a or pK_a values of their conjugate acids.

Key Terms

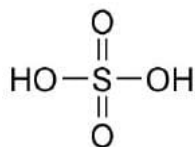
Make certain that you can define, and use in context, the key terms below.

- acidity constant, K_a
- equilibrium constant, K_{eq}

Study Notes

Calculations and expressions involving K_a and pK_a were covered in detail in your first-year general chemistry course. Note that [acidity constant](#) is also known as the acid dissociation constant.

You are no doubt aware that some acids are stronger than others. Sulfuric acid is strong enough to be used as a drain cleaner, as it will rapidly dissolve clogs of hair and other organic material.

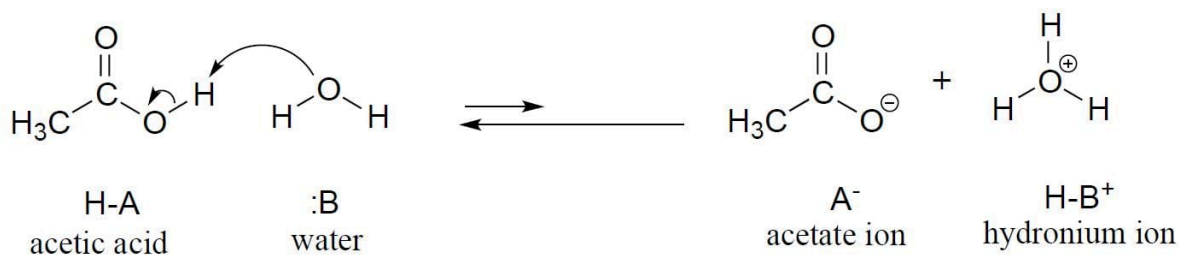


sulfuric acid

Not surprisingly, concentrated sulfuric acid will also cause painful burns if it touches your skin, and permanent damage if it gets in your eyes (there's a good reason for those safety goggles you wear in chemistry lab!). Acetic acid (vinegar), will also burn your skin and eyes, but is not nearly strong enough to make an effective drain cleaner. Water, which we know can act as a proton donor, is obviously not a very strong acid. Even hydroxide ion could *theoretically* act as an acid – it has, after all, a proton to donate – but this is not a reaction that we would normally consider to be relevant in anything but the most extreme conditions.

The relative acidity of different compounds or functional groups – in other words, their relative capacity to donate a proton to a common base under identical conditions – is quantified by a number called the [acid dissociation constant](#), abbreviated **K_a** . The common base chosen for comparison is water.

We will consider acetic acid as our first example. When a small amount of acetic acid is added to water, a proton-transfer event (acid-base reaction) occurs to some extent.



Notice the phrase 'to some extent' – this reaction does *not* run to completion, with all of the acetic acid converted to acetate, its conjugate base. Rather, a *dynamic equilibrium* is reached, with proton transfer going in both directions (thus the two-way arrows) and finite concentrations of all four species in play. The nature of this equilibrium situation, as you recall from General Chemistry, is expressed by an [equilibrium constant](#), K .

The equilibrium constant is actually a ratio of activities (represented by the symbol a), but activities are rarely used in courses other than analytical or physical chemistry. To simplify the discussion for general chemistry and organic chemistry courses, the activities of all of the solutes are replaced with molarities, and the activity of the solvent (usually water) is defined as having the value of 1.

In our example, we added a small amount of acetic acid to a large amount of water: water is the *solvent* for this reaction. Therefore, in the course of the reaction, the concentration of water changes very little, and the water can be treated as a pure solvent, which is always assigned an activity of 1. The acetic acid, acetate ion and hydronium ion are all *solutes*, and so their activities are approximated with molarities. The acid dissociation constant, or K_a , for acetic acid is therefore defined as:

$$K_{eq} = \frac{a_{CH_3COO^-} \cdot a_{H_3O^+}}{a_{CH_3COOH} \cdot a_{H_2O}} \approx \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][1]} \quad (1.10.1)$$

Because dividing by 1 does not change the value of the constant, the "1" is usually not written, and K_a is written as:

$$K_{eq} = K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5} \quad (1.10.2)$$

In more general terms, the dissociation constant for a given acid is expressed as:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \quad (1.10.3)$$

or

$$K_a = \frac{[A][H_3O^+]}{[HA^+]} \quad (1.10.4)$$

Equation 1.10.3 applies to a neutral acid such as like HCl or acetic acid, while Equation 1.10.4 applies to a cationic acid like ammonium (NH_4^+).

The value of $K_a = 1.75 \times 10^{-5}$ for acetic acid is very small - this means that very little dissociation actually takes place, and there is much more acetic acid in solution at equilibrium than there is acetate ion. Acetic acid is a relatively weak acid, at least when compared to sulfuric acid ($K_a = 10^9$) or hydrochloric acid ($K_a = 10^7$), both of which undergo essentially complete dissociation in water.

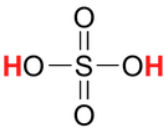
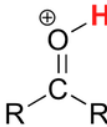
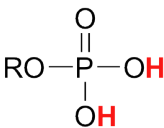
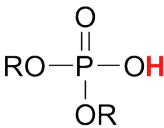
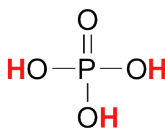
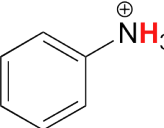
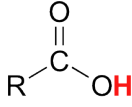
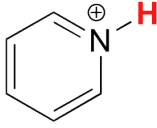
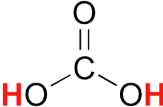
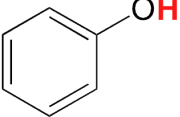
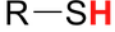
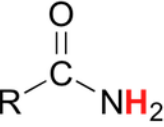
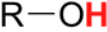
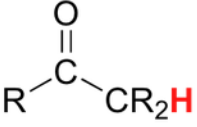
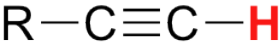
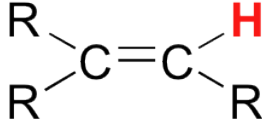
A number like 1.75×10^{-5} is not very easy either to say or to remember. Chemists often use **pK_a** values as a more convenient term to express relative acidity. **pK_a** is related to **K_a** by the following equation

$$pK_a = -\log K_a \quad (1.10.5)$$

Doing the math, we find that the pK_a of acetic acid is 4.8. The use of pK_a values allows us to express the acidity of common compounds and functional groups on a numerical scale of about -10 (very strong acid) to 50 (not acidic at all). Table 1.10.1 at the

end of the text lists exact or approximate pK_a values for different types of protons that you are likely to encounter in your study of organic and biological chemistry. Looking at Table 1.10.1, you see that the pK_a of carboxylic acids are in the 4-5 range, the pK_a of sulfuric acid is -10, and the pK_a of water is 14. Alkenes and alkanes, which are not acidic at all, have pK_a values above 30. *The lower the pK_a value, the stronger the acid.*

Table 1.10.1: Representative acid constants

 sulfuric acid pK_a -10, 2.0	 hydrochloric acid pK_a -7	 hydronium pK_a 0.00	 protonated ketone $pK_a \sim -7$	 protonated alcohol $pK_a \sim -3$
 phosphate monoester ⁽¹⁾ $pK_a \sim 1, 6.5$	 phosphate diester ⁽¹⁾ $pK_a \sim 1.5$	 phosphoric acid $pK_a = 2.2, 7.2, 12.3$	 aniline $pK_a = 4.6$	 carboxylic acid $pK_a \sim 4-5$
 pyridinium pK_a 5.3	 carbonic acid pK_a 6.4, 10.3	 hydrogen cyanide pK_a 9.2	 ammonium pK_a 9.2	 phenol pK_a 9.9
 thiol $pK_a \sim 10-11$	 water pK_a 14.0	 amide $pK_a \sim 17$	 alcohol $pK_a \sim 16-18$	 α-proton $pK_a \sim 18-20$
 terminal alkyne $pK_a \sim 25$	 terminal alkene $pK_a \sim 35$	 ammonia $pK_a \sim 35$		

It is important to realize that pK_a is *not* the same thing as pH: pK_a is an inherent property of a compound or functional group, while pH is the measure of the hydronium ion concentration in a particular aqueous solution:

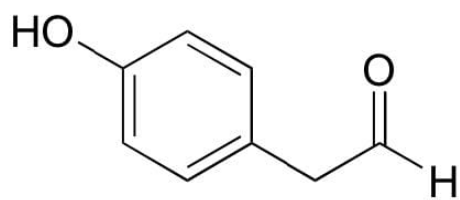
$$pH = -\log[H_3O^+] \quad (1.10.6)$$

Any particular acid will always have the same pK_a (assuming that we are talking about an aqueous solution at room temperature) but different aqueous solutions of the acid could have different pH values, depending on how much acid is added to how much water.

Our table of pK_a values will also allow us to compare the strengths of different bases by comparing the pK_a values of their conjugate acids. The key idea to remember is this: *the stronger the conjugate acid, the weaker the conjugate base*. Sulfuric acid is the strongest acid on our list with a pK_a value of -10 , so HSO_4^- is the weakest conjugate base. You can see that hydroxide ion is a stronger base than ammonia (NH_3), because ammonium (NH_4^+ , $pK_a = 9.2$) is a stronger acid than water ($pK_a = 14.0$).

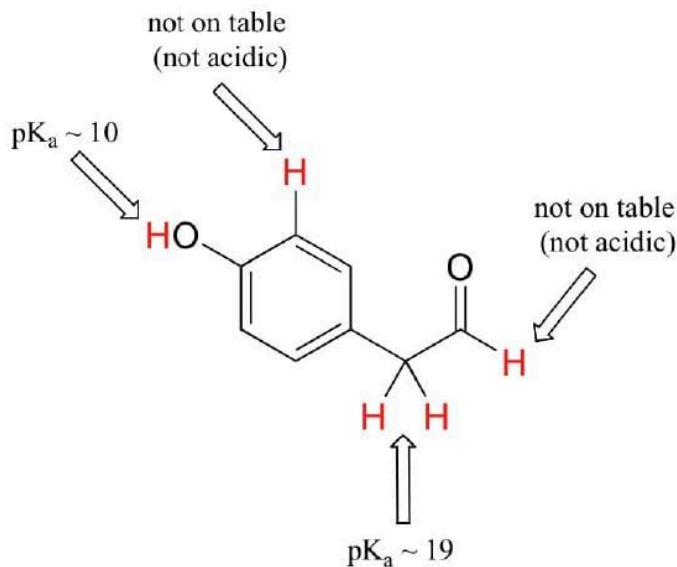
The stronger the conjugate acid, the weaker the conjugate base.

While Table 1.10.1 provides the pK_a values of only a limited number of compounds, it can be very useful as a starting point for estimating the acidity or basicity of just about any organic molecule. Here is where your familiarity with organic functional groups will come in very handy. What, for example, is the pK_a of cyclohexanol? It is not on the table, but as it is an alcohol it is probably somewhere near that of ethanol ($pK_a = 16$). Likewise, we can use Table 1.10.1 to predict that para-hydroxyphenyl acetaldehyde, an intermediate compound in the biosynthesis of morphine, has a pK_a in the neighborhood of 10 , close to that of our reference compound, phenol.



p=hydroxyphenyl acetaldehyde

Notice in this example that we need to evaluate the potential acidity at *four* different locations on the molecule.



Aldehyde and aromatic protons are not at all acidic (pK_a values are above 40 – not on our table). The two protons on the carbon next to the carbonyl are slightly acidic, with pK_a values around 19 - 20 according to the table. The most acidic proton is on the

phenol group, so if the compound were to be reacted with a single molar equivalent of strong base, this is the proton that would be donated first.

As you continue your study of organic chemistry, it will be a very good idea to commit to memory the approximate pK_a ranges of some important functional groups, including water, alcohols, phenols, ammonium, thiols, phosphates, carboxylic acids and carbons next to carbonyl groups (so-called α -carbons). These are the groups that you are most likely to see acting as acids or bases in biological organic reactions.

A word of caution: when using the [pK_a table](#), be absolutely sure that you are considering the correct conjugate acid/base pair. If you are asked to say something about the basicity of ammonia (NH₃) compared to that of ethoxide ion (CH₃CH₂O⁻), for example, the relevant pK_a values to consider are 9.2 (the pK_a of ammonium ion) and 16 (the pK_a of ethanol). From these numbers, you know that ethoxide is the stronger base. Do not make the mistake of using the pK_a value of 38: this is the pK_a of ammonia *acting as an acid*, and tells you how basic the NH₂⁻ ion is (very basic!)

Example 1.10.1: Acidic Groups

Using the pK_a table, estimate pK_a values for the most acidic group on the compounds below, and draw the structure of the conjugate base that results when this group donates a proton. Use the pK_a table above and/or from the [Reference Tables](#).

Answer:

- The most acidic group is the protonated amine, $pK_a \sim 5-9$
- Alpha proton by the C=O group, $pK_a \sim 18-20$
- Thiol, $pK_a \sim 10$
- Carboxylic acid, $pK_a \sim 5$
- Carboxylic acid, $pK_a \sim 5$

Exercises

- Write down an expression for the acidity constant of acetic acid, CH₃COOH.
- The pK_a of acetic acid is 4.72; calculate its K_a .
- The K_a of benzoic acid is 6.5×10^{-5} ; determine its pK_a .
- From your answers to the questions above, determine whether acetic acid or benzoic acid is stronger

Answers

$$1. K_a = \frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} \text{ or } K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$$

$$2. pK_a = -\log_{10} K_a = 4.74$$

$$\text{Thus, } \log_{10} K_a = -4.72 \text{ and } K_a = \text{anti-log}(-4.72) = 1.9 \times 10^{-5}$$

$$3. pK_a = -\log_{10} K_a = -\log_{10} 6.5 \times 10^{-5} = -(-4.19) = 4.19$$

- Benzoic acid is stronger than acetic acid. [Benzoic acid has a higher K_a and a lower pK_a .]

Contributors

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1.11: Predicting Acid-Base Reactions from pKa Values

Template:HideTOC

Objective

After completing this section, you should be able to

- use pK_a values to calculate K_{eq}
- use pK_a values to predict the equilibrium direction of an acid-base reaction.

Key Terms

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

- pK_a

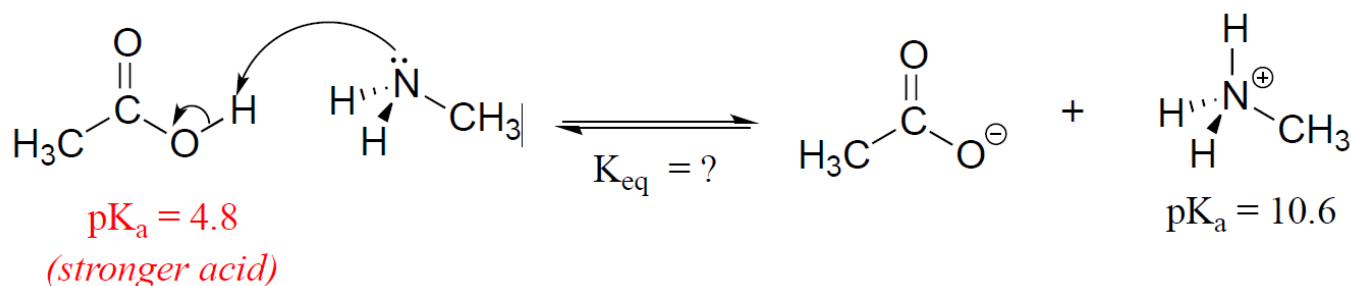
Using pK_a values to predict reaction Equilibria [Edit section](#)

By definition, the pK_a value tells us the extent to which an acid will react with water as the base, but by extension, we can also calculate the equilibrium constant for a reaction between any acid-base pair. Mathematically, it can be shown that:

$$K_{eq} \text{ (for the acid base reaction in question)} = 10^{\Delta pK_a}$$

where ΔpK_a is the pK_a of product acid minus pK_a of reactant acid

Consider a reaction between methylamine and acetic acid:



First, we need to identify the acid species on either side of the equation. On the left side, the acid is of course acetic acid, while on the right side the acid is methyl ammonium. The specific pK_a values for these acids are not on our very generalized pK_a table, but are given in the figure above. Without performing any calculations, you should be able to see that this equilibrium lies far to the right-hand side: acetic acid has a lower pK_a , is a stronger acid, and thus it wants to give up its proton more than methyl ammonium does. Doing the math, we see that

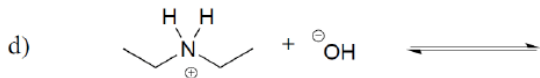
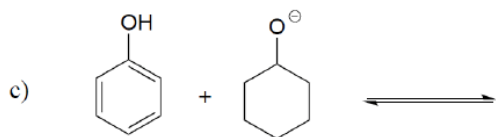
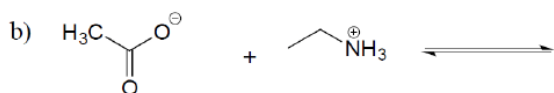
$$K_{eq} = 10^{\Delta pK_a} = 10^{10.6-4.8} = 10^{5.8} = 6.3 \times 10^5 \quad (1.11.1)$$

So K_{eq} is a very large number (much greater than 1) and the equilibrium lies far to the right-hand side of the equation, just as we had predicted.

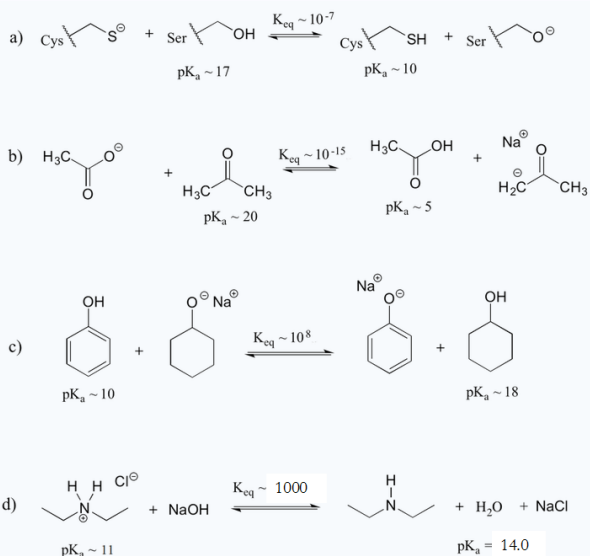
If you had just wanted to approximate an answer without bothering to look for a calculator, you could have noted that the difference in pK_a values is approximately 6, so the equilibrium constant should be somewhere in the order of 10^6 , or one million. Using the pK_a table in this way, and making functional group-based pK_a approximations for molecules for which we don't have exact values, we can easily estimate the extent to which a given acid-base reaction will proceed.

Example 1.11.1

Show the products of the following acid-base reactions, and estimate the value of K_{eq} . Use the pK_a table from [Section 2.8](#) and/or from the [Reference Tables](#).



Answer:

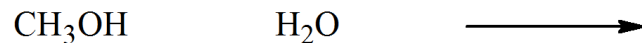


Exercises

Questions

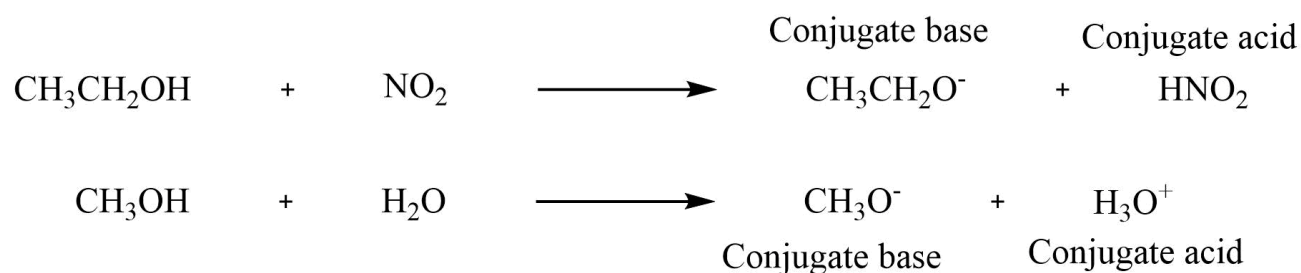
Q2.9.1

In the following reactions give the resulting products and label the conjugate acid and bases.



Solutions

S2.9.1



Contributors

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1.12: Organic Acids and Organic Bases

Objective

After completing this section, you should be able to

- predict the relative acidity of two organic molecules from their structures.
- predict the relative basicity of two organic molecules from their structures.

This page explains the acidity of simple organic acids and looks at the factors which affect their relative strengths.

Organic acids as weak acids

For the purposes of this topic, we are going to take the definition of an acid as "a substance which donates hydrogen ions (protons) to other things". We are going to get a measure of this by looking at how easily the acids release hydrogen ions to water molecules when they are in solution in water.

An acid in solution sets up this equilibrium:



A [hydronium ion](#) is formed together with the anion (negative ion) from the acid. This equilibrium is sometimes simplified by leaving out the water to emphasize the ionization of the acid.

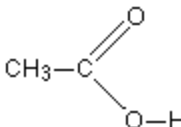
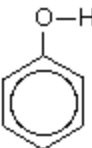


If you write it like this, you must include the state symbols - "(aq)". Writing $H^+_{(aq)}$ implies that the hydrogen ion is attached to a water molecule as H_3O^+ . Hydrogen ions are always attached to something during chemical reactions.

The organic acids are weak in the sense that this ionization is very incomplete. At any one time, most of the acid will be present in the solution as un-ionized molecules. For example, in the case of dilute ethanoic acid, the solution contains about 99% of ethanoic acid molecules - at any instant, only about 1% have actually ionized. The position of equilibrium therefore lies well to the left.

Comparing the strengths of weak acids

The strengths of weak acids are measured on the pK_a scale. The smaller the number on this scale, the stronger the acid is. Three of the compounds we shall be looking at, together with their pK_a values are:

		pK_a
ethanoic acid		4.76
phenol		10.00
ethanol	$\text{CH}_3\text{—CH}_2\text{—O—H}$	about 16

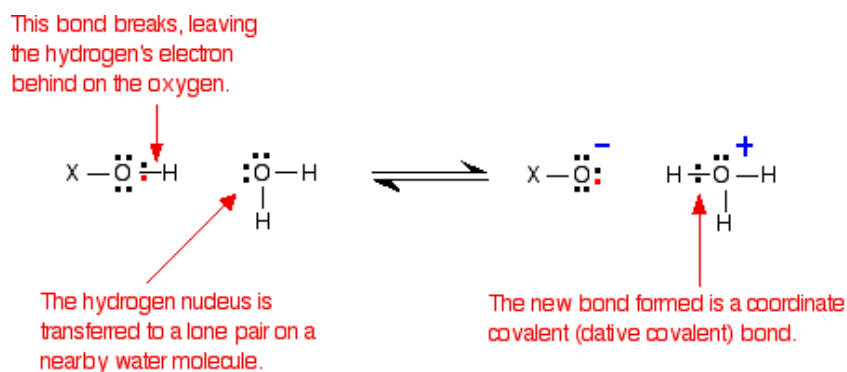
Remember - the smaller the number the stronger the acid. Comparing the other two to ethanoic acid, you will see that phenol is very much weaker with a pK_a of 10.00, and ethanol is so weak with a pK_a of about 16 that it hardly counts as acidic at all!

Note

The smaller the *pK_a*, the stronger the acid

Why are these acids acidic?

In each case, the same bond gets broken - the bond between the hydrogen and oxygen in an -OH group. Writing the rest of the molecule as "X":



If the same bond is being broken in each case, why do these three compounds have such widely different acid strengths?

Differences in acid strengths between carboxylic acids, phenols and alcohols

Two of the factors which influence the ionization of an acid are:

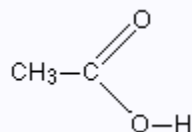
- the strength of the bond being broken,
- the stability of the ions being formed.

In these cases, you seem to be breaking the same oxygen-hydrogen bond each time, and so you might expect the strengths to be

similar. The most important factor in determining the relative acid strengths of these molecules is the nature of the ions formed. You always get a hydronium ion - so that's constant - but the nature of the anion (the negative ion) varies markedly from case to case.

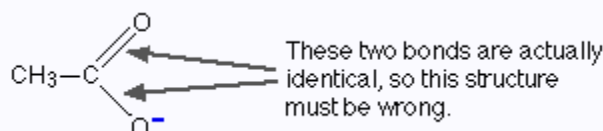
Example 2.10.1: Ethanoic Acid (Acetic Acid)

Ethanoic acid has the structure:



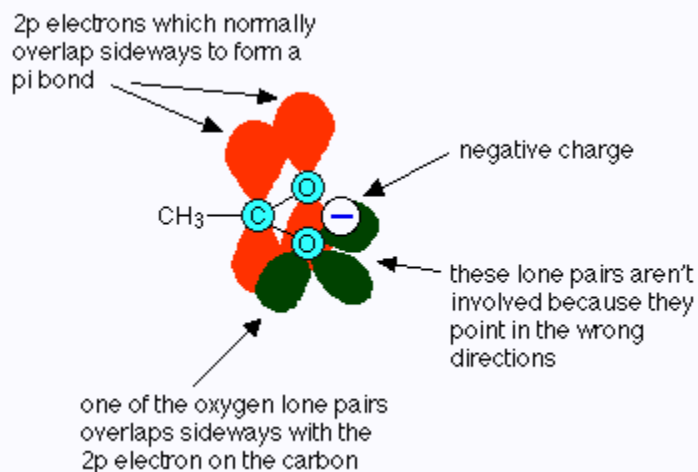
The acidic hydrogen is the one attached to the oxygen. When ethanoic acid ionizes it forms the ethanoate ion, CH_3COO^- .

You might reasonably suppose that the structure of the ethanoate ion was as below, but measurements of bond lengths show that the two carbon-oxygen bonds are identical and somewhere in length between a single and a double bond.

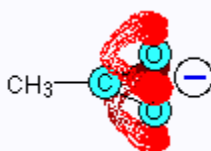


To understand why this is, you have to look in some detail at the bonding in the ethanoate ion. Like any other double bond, a carbon-oxygen double bond is made up of two different parts. One electron pair is found on the line between the two nuclei - this is known as a sigma bond. The other electron pair is found above and below the plane of the molecule in a pi bond. Pi bonds are made by sideways overlap between p orbitals on the carbon and the oxygen.

In an ethanoate ion, one of the lone pairs on the negative oxygen ends up almost parallel to these p orbitals, and overlaps with them

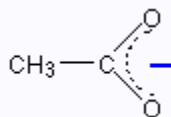


This leads to a delocalized pi system over the whole of the -COO^- group, rather like that in benzene.



All the oxygen lone pairs have been left out of this diagram to avoid confusion. Because the oxygens are more electronegative than the carbon, the delocalized system is heavily distorted so that the electrons spend much more time in the region of the oxygen atoms.

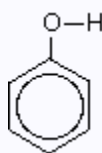
So where is the negative charge in all this? It has been spread around over the whole of the -COO^- group, but with the greatest chance of finding it in the region of the two oxygen atoms. Ethanoate ions can be drawn simply as:



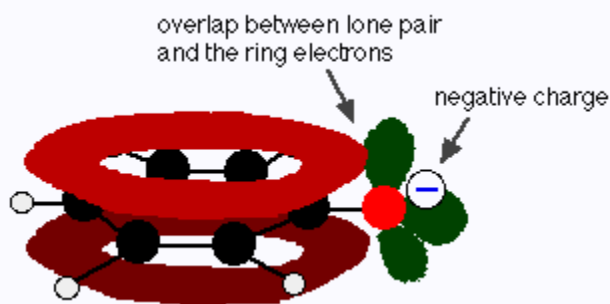
The dotted line represents the delocalization. The negative charge is written centrally on that end of the molecule to show that it isn't localized on one of the oxygen atoms. The more you can spread charge around, the more stable an ion becomes. In this case, if you delocalize the negative charge over several atoms, it is going to be much less attractive to hydrogen ions - and so you are less likely to re-form the ethanoic acid.

Example 2.10.2: Phenol

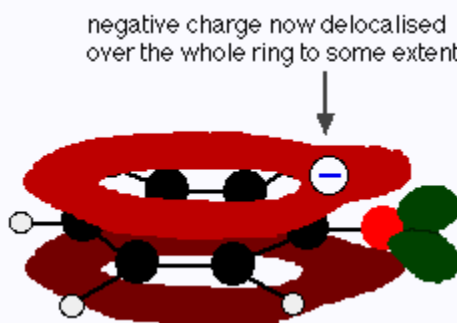
Phenols have an -OH group attached directly to a benzene ring. Phenol itself is the simplest of these with nothing else attached to the ring apart from the -OH group.



When the hydrogen-oxygen bond in phenol breaks, you get a phenoxide ion, $\text{C}_6\text{H}_5\text{O}^-$. Delocalization also occurs in this ion. This time, one of the lone pairs on the oxygen atom overlaps with the delocalized electrons on the benzene ring.

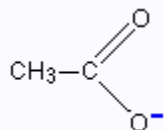


This overlap leads to a delocalization which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localized on the oxygen, but is spread out around the whole ion.

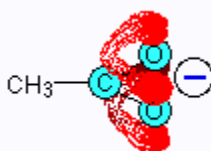


Why then is phenol a much weaker acid than ethanoic acid?

Think about the ethanoate ion again. If there wasn't any delocalization, the charge would all be on one of the oxygen atoms, like this:



But the delocalization spreads this charge over the whole of the COO group. Because oxygen is more electronegative than carbon, you can think of most of the charge being shared between the two oxygens (shown by the heavy red shading in this diagram).



If there wasn't any delocalization, one of the oxygens would have a full charge which would be very attractive towards hydrogen ions. With delocalization, that charge is spread over two oxygen atoms, and neither will be as attractive to a hydrogen ion as if one of the oxygens carried the whole charge.

That means that the ethanoate ion won't take up a hydrogen ion as easily as it would if there wasn't any delocalization. Because some of it stays ionized, the formation of the hydrogen ions means that it is acidic.

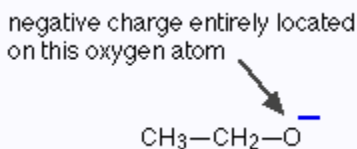
In the phenoxide ion, the single oxygen atom is still the most electronegative thing present, and the delocalized system will be heavily distorted towards it. That still leaves the oxygen atom with most of its negative charge.

What delocalization there is makes the phenoxide ion more stable than it would otherwise be, and so phenol is acidic to an extent.

However, the delocalization hasn't shared the charge around very effectively. There is still lots of negative charge around the oxygen to which hydrogen ions will be attracted - and so the phenol will readily re-form. Phenol is therefore only very weakly acidic.

Example 2.10.3: Ethanol

Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, is so weakly acidic that you would hardly count it as acidic at all. If the hydrogen-oxygen bond breaks to release a hydrogen ion, an ethoxide ion is formed:



This has nothing at all going for it. There is no way of delocalizing the negative charge, which remains firmly on the oxygen atom. That intense negative charge will be highly attractive towards hydrogen ions, and so the ethanol will instantly re-form. Since ethanol is very poor at losing hydrogen ions, it is hardly acidic at all.

Variations in acid strengths between different carboxylic acids

You might think that all carboxylic acids would have the same strength because each depends on the delocalization of the negative charge around the -COO^- group to make the anion more stable, and so more reluctant to re-combine with a hydrogen ion. In fact, the carboxylic acids have widely different acidities. One obvious difference is between methanoic acid, HCOOH , and the other simple carboxylic acids:

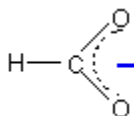
	pK _a
HCOOH	3.75
CH_3COOH	4.76
$\text{CH}_3\text{CH}_2\text{COOH}$	4.87
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	4.82

Note

Remember that the higher the value for pK_a, the weaker the acid is.

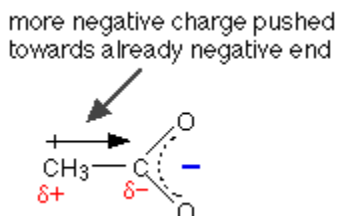
Why is ethanoic acid weaker than methanoic acid? It again depends on the stability of the anions formed - on how much it is possible to delocalize the negative charge. The less the charge is delocalized, the less stable the ion, and the weaker the acid.

The methanoate ion (from methanoic acid) is:



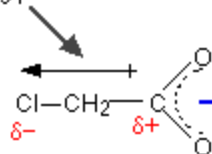
The only difference between this and the ethanoate ion is the presence of the CH_3 group in the ethanoate. But that's important! Alkyl groups have a tendency to "push" electrons away from themselves. That means that there will be a small amount of extra negative charge built up on the -COO^- group. Any build-up of charge will make the ion less stable, and more attractive to hydrogen ions.

Ethanoic acid is therefore weaker than methanoic acid, because it will re-form more easily from its ions.



The other alkyl groups have "electron-pushing" effects very similar to the methyl group, and so the strengths of propanoic acid and butanoic acid are very similar to ethanoic acid. The acids can be strengthened by pulling charge away from the -COO^- end. You can do this by attaching electronegative atoms like chlorine to the chain.

negative charge delocalised even more
by being pulled out onto chlorine atom



As the next table shows, the more chlorines you can attach the better:

	pK _a
CH ₃ COOH	4.76
CH ₂ ClCOOH	2.86
CHCl ₂ COOH	1.29
CCl ₃ COOH	0.65

Trichloroethanoic acid is quite a strong acid.

Attaching different halogens also makes a difference. Fluorine is the most electronegative and so you would expect it to be most successful at pulling charge away from the -COO⁻ end and so strengthening the acid.

	pK _a
CH ₂ FCOOH	2.66
CH ₂ ClCOOH	2.86
CH ₂ BrCOOH	2.90
CH ₂ ICOOH	3.17

The effect is there, but isn't as great as you might expect.

Finally, notice that the effect falls off quite quickly as the attached halogen gets further away from the -COO⁻ end. Here is what happens if you move a chlorine atom along the chain in butanoic acid.

	pK _a
CH ₃ CH ₂ CH ₂ COOH	4.82
CH ₃ CH ₂ CHClCOOH	2.84
CH ₃ CHClCH ₂ COOH	4.06
CH ₂ ClCH ₂ CH ₂ COOH	4.52

The chlorine is effective at withdrawing charge when it is next-door to the -COO⁻ group, and much less so as it gets even one carbon further away.

This page explains why simple organic bases are basic and looks at the factors which affect their relative strengths. For A'level purposes, all the bases we are concerned with are primary amines - compounds in which one of the hydrogens in an ammonia molecule, NH₃, is replaced either by an alkyl group or a benzene ring.

Ammonia as a weak base

All of the compounds we are concerned with are derived from ammonia and so we'll start by looking at the reason for its basic

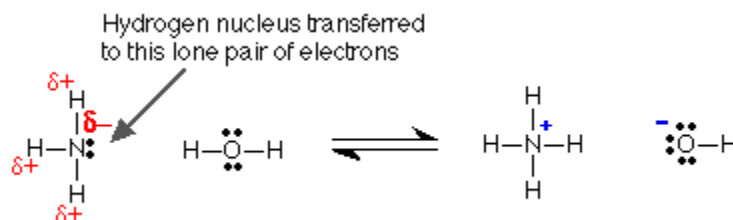
properties. For the purposes of this topic, we are going to take the definition of a base as "a substance which combines with hydrogen ions (protons)". We are going to get a measure of this by looking at how easily the bases take hydrogen ions from water molecules when they are in solution in water.

Ammonia in solution sets up this equilibrium:



An ammonium ion is formed together with hydroxide ions. Because the ammonia is only a weak base, it doesn't hang on to the extra hydrogen ion very effectively and so the reaction is reversible. At any one time, about 99% of the ammonia is present as unreacted molecules. The position of equilibrium lies well to the left.

The ammonia reacts as a base because of the active lone pair on the nitrogen. Nitrogen is more electronegative than hydrogen and so attracts the bonding electrons in the ammonia molecule towards itself. That means that in addition to the lone pair, there is a build-up of negative charge around the nitrogen atom. That combination of extra negativity and active lone pair attracts the new hydrogen from the water.



Comparing the strengths of weak bases

The strengths of weak bases are measured on the pK_b scale. The smaller the number on this scale, the stronger the base is. Three of the compounds we shall be looking at, together with their pK_b values are:

		pK_b
ammonia	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}:\text{H} \\ \\ \text{H} \end{array}$	4.75
methylamine	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3-\text{N}:\text{H} \\ \\ \text{H} \end{array}$	3.36
phenylamine	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}:\text{H} \\ \\ \text{C}_6\text{H}_5 \end{array}$	9.38

Remember - the smaller the number the stronger the base. Comparing the other two to ammonia, you will see that methylamine is a stronger base, whereas phenylamine is very much weaker.

- Methylamine is typical of aliphatic primary amines - where the -NH_2 group is attached to a carbon chain. All aliphatic primary amines are stronger bases than ammonia.
- Phenylamine is typical of aromatic primary amines - where the -NH_2 group is attached directly to a benzene ring. These are very much weaker bases than ammonia.

Explaining the differences in base strengths

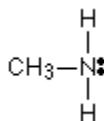
Two of the factors which influence the strength of a base are:

- the ease with which the lone pair picks up a hydrogen ion,
- the stability of the ions being formed.

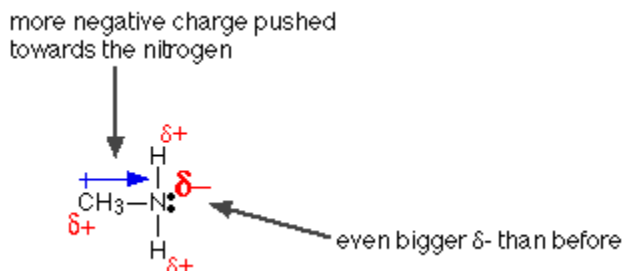
Why are aliphatic primary amines stronger bases than ammonia?

Methylamine

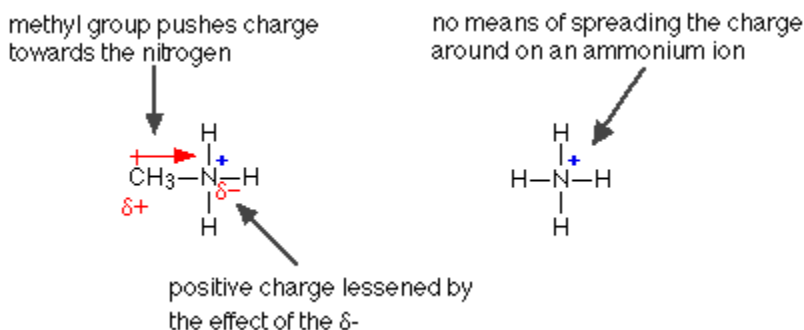
Methylamine has the structure:



The only difference between this and ammonia is the presence of the CH₃ group in the methylamine. But that's important! Alkyl groups have a tendency to "push" electrons away from themselves. That means that there will be a small amount of extra negative charge built up on the nitrogen atom. That extra negativity around the nitrogen makes the lone pair even more attractive towards hydrogen ions.



Making the nitrogen more negative helps the lone pair to pick up a hydrogen ion. What about the effect on the positive methylammonium ion formed? Is this more stable than a simple ammonium ion? Compare the methylammonium ion with an ammonium ion:



In the methylammonium ion, the positive charge is spread around the ion by the "electron-pushing" effect of the methyl group. The more you can spread charge around, the more stable an ion becomes. In the ammonium ion there is not any way of spreading the charge.

To summarize:

- The nitrogen is more negative in methylamine than in ammonia, and so it picks up a hydrogen ion more readily.

- The ion formed from methylamine is more stable than the one formed from ammonia, and so is less likely to shed the hydrogen ion again.

Taken together, these mean that methylamine is a stronger base than ammonia.

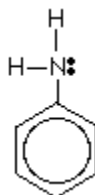
The other aliphatic primary amines

The other alkyl groups have "electron-pushing" effects very similar to the methyl group, and so the strengths of the other aliphatic primary amines are very similar to methylamine. For example:

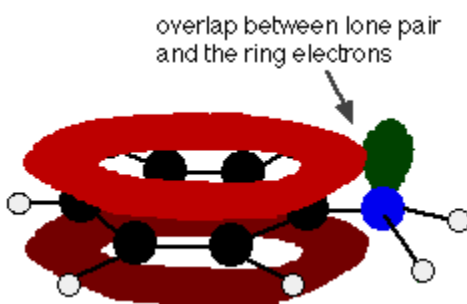
	pK _b
CH ₃ NH ₂	3.36
CH ₃ CH ₂ NH ₂	3.27
CH ₃ CH ₂ CH ₂ NH ₂	3.16
CH ₃ CH ₂ CH ₂ CH ₂ NH ₂	3.39

Why are aromatic primary amines much weaker bases than ammonia?

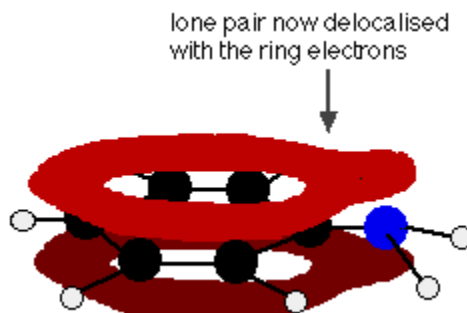
An aromatic primary amine is one in which the -NH₂ group is attached directly to a benzene ring. The only one you are likely to come across is phenylamine. Phenylamine has the structure:



The lone pair on the nitrogen touches the delocalized ring electrons . . .



. . . and becomes delocalized with them:



That means that the lone pair is no longer fully available to combine with hydrogen ions. The nitrogen is still the most electronegative atom in the molecule, and so the delocalized electrons will be attracted towards it, but the intensity of charge around the nitrogen is nothing like what it is in, say, an ammonia molecule.

The other problem is that if the lone pair is used to join to a hydrogen ion, it is no longer available to contribute to the delocalization. That means that the delocalization would have to be disrupted if the phenylamine acts as a base. Delocalization makes molecules more stable, and so disrupting the delocalization costs energy and will not happen easily.

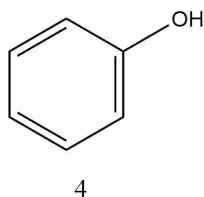
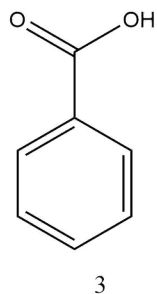
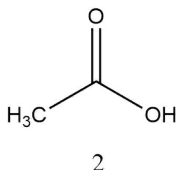
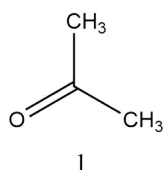
Taken together - the lack of intense charge around the nitrogen, and the need to break some delocalization - this means that phenylamine is a very weak base indeed.

Exercises

Questions

Q2.10.1

Determine which of the one of the molecules is an acid or a base.



Solutions

S2.10.1

1 = Base

2 = Acid

3 = Acid

4 = Acid

Contributors

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1.13: Acids and Bases - The Lewis Definition

Objectives

After completing this section, you should be able to

1. state the Lewis definition of an acid and a base.
2. identify a given compound as being a Lewis acid or Lewis base, given its Lewis structure or its Kekulé structure.
3. identify an organic molecule or ion in a reaction as either an electrophile or nucleophile.

Key Terms

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

- Lewis acid
- Lewis base
- Electrophile
- Nucleophile

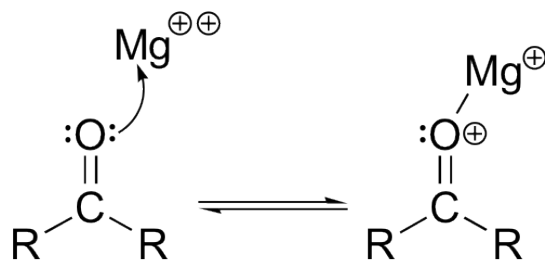
Study Notes

The Lewis concept of acidity and basicity will be of great use to you when you study reaction mechanisms. The realization that an ion such as

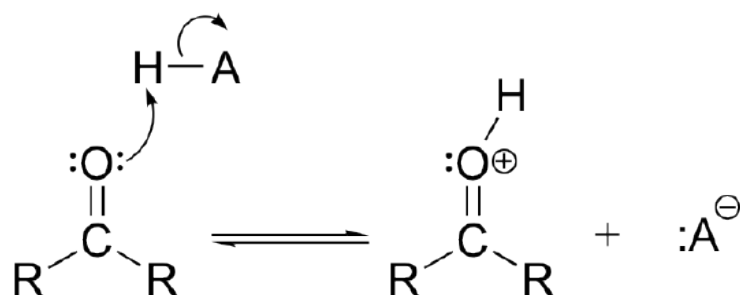
methyl cation

is electron deficient, and is therefore a Lewis acid, should help you understand why this ion reacts with substances which are Lewis bases (e.g., H_2O).

The Brønsted-Lowry picture of acids and bases as proton donors and acceptors is not the only definition in common use. A broader definition is provided by the **Lewis theory** of acids and bases, in which a **Lewis acid** is an electron-pair acceptor and a **Lewis base** is an electron-pair donor. This definition includes not only Brønsted-Lowry proton transfer reactions, but also includes reactions in which no proton transfer is involved. The interaction between a magnesium cation (Mg^{+2}) and a carbonyl oxygen is a common example of a Lewis acid-base reaction. The carbonyl oxygen (the Lewis base) donates a pair of electrons to the magnesium cation (the Lewis acid).



As we will see in [Chapter 19](#) when we begin the study of reactions involving carbonyl groups, this interaction has the very important effect of increasing the polarity of the carbon-oxygen double bond. The Brønsted-Lowry equivalent of the reaction above is simply protonation of the carbonyl group. This, too, has the effect of increasing the polarity of the carbonyl double bond.



While it is important to be familiar with the Lewis definition, the focus throughout the remainder of this chapter will be on acid-base reactions of the Brønsted-Lowry type, where an actual proton transfer event takes place.

Lewis Acids

Borane is unusual because it is a compound without an octet. The central boron atom has only six valence electrons. It needs one more pair of electrons to obtain an octet. The boron is a Lewis acid.

electrons donated to empty orbital on boron

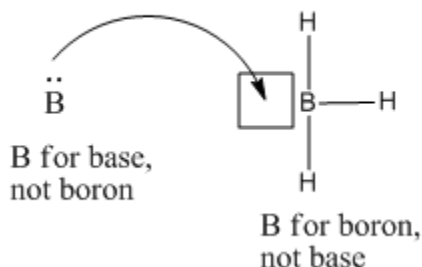


Figure 2.11.1: Borane is a Lewis acid. It can accept electrons from a donor atom. The square drawn beside the boron is used to reinforce the idea that there is a vacant site for electrons there.

- Lewis acids are often short of a complete octet.

In the main group of the periodic table, atoms in the [Group 13 column](#) (including boron and aluminum) have three valence electrons to share in order to make bonds. Sharing these electrons with three electrons from neighbors would make three bonds, and provide six electrons, not eight, in the valence shell. Another pair of electrons must be accepted from a donor to achieve an octet.

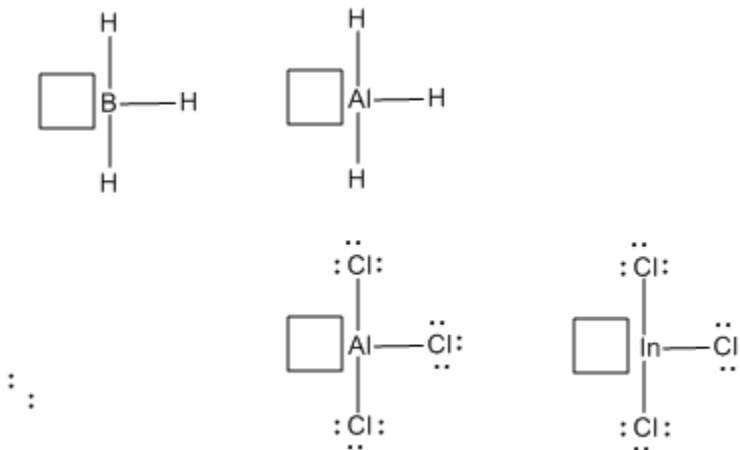


Figure 2.11.2: Boron, aluminum and indium are from the same column of the periodic table. All three are often Lewis acidic;

they can accept electrons from donors.

- Boron, aluminum and indium compounds are often Lewis acids.

The eight-electron rule does not hold throughout the periodic table. In order to obtain noble gas configurations, some atoms may need eighteen electrons in their valence shell. For example, transition metals such as titanium often follow an eighteen-electron rule. Titanium has four valence electrons and can form four bonds in compounds such as titanium tetrakis (isopropoxide), below, or titanium tetrachloride, TiCl_4 . However, the titanium atom in that compound has only eight valence electrons, not eighteen. It can easily accept electrons from donors.

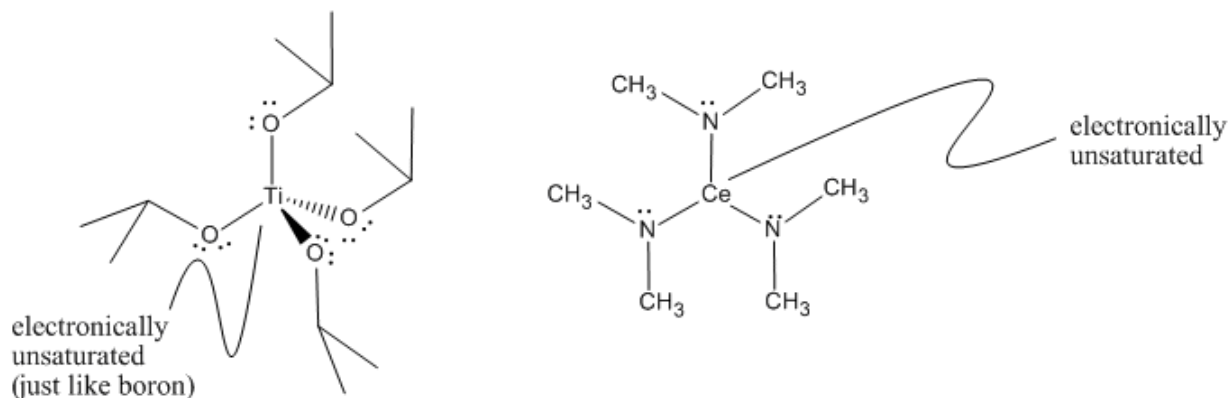


Figure 2.11.3: Although titanium has eight electrons in this molecule, titanium tetrakis(isopropoxide), it can accommodate up to eighteen. It is a Lewis acid. The cerium atom in cerium tris(dimethylamide) comes from a similar part of the periodic table and is also a Lewis acid.

- Transition metals such as titanium, iron and nickel may have up to eighteen electrons and can frequently accept electron pairs from Lewis bases. Transition metals are often Lewis acids.
- Lanthanides such as cerium and samarium could conceivably have up to thirty-two electrons in their valence shells! They never do. However, they are usually strong Lewis acids.

Positive ions are often Lewis acids because they have an electrostatic attraction for electron donors. Examples include alkali and alkaline earth metals in the group IA and IIA columns. K^+ , Mg^{2+} and Ca^{2+} are sometimes seen as Lewis acidic sites in biology, for example. These ions are very stable forms of these elements because of their low electron ionization potentials. However, their positive charges do attract electron donors.



Figure 2.11.4. A calcium ion essentially has a noble gas configuration. Nevertheless, its positive charge can attract electrons from a donor atom.

In a similar way, "early" transition metals -- those that are close to the left hand side of the periodic table, especially in groups IIIB, IVB and VB -- have low ionization potentials and have high positive charges or oxidation states. For example, Sc^{3+} , Zr^{4+} and V^{5+} are common forms of some early transition metals, and they are strong Lewis acids.

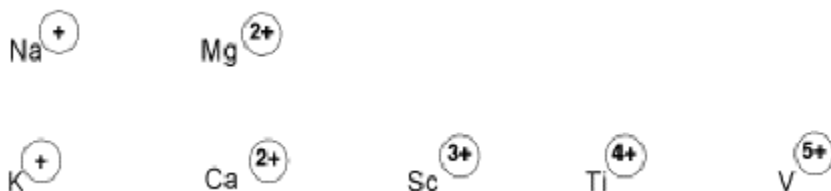


Figure 2.11.5: A few alkali, alkaline earth and transition metals that are commonly found as cations.

- Many cations such as Ca^{2+} or Sc^{3+} are good Lewis acids. Their positive charges attract electrons.

The Proton as a Common Lewis Acid

Perhaps the most common example of a Lewis acid or electrophile is also the simplest. It is the hydrogen cation or proton. It is called a proton because, in most hydrogen atoms, the only particle in the nucleus is a proton. If an electron is removed to make a cation, a proton is all that is left.

- H^+ is a very common Lewis acid or electrophile.

A proton is electrophilic for a couple of reasons. It has a positive charge, and so it will attract electrons, which are negative. Also, it lacks the electron configuration of its noble gas neighbor, helium. Helium has two electrons. If a Lewis base or nucleophile donates a pair of electrons to a proton, the proton will obtain a Noble gas configuration. That's part of the reason why, in some periodic tables, hydrogen is shown in two places: at the very left, illustrating its potential to lose an electron, like sodium and lithium; and at the right, illustrating its potential to take on helium's configuration.

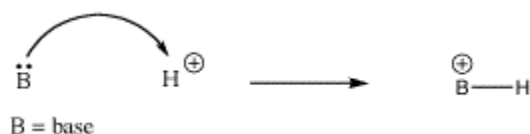


Figure 2.11.6: Proton as Lewis acid.

There is something about hydrogen cations that is not so simple, however. They are actually not so common. Instead, protons are generally always bound to a Lewis base. Hydrogen is almost always covalently (or datively / coordinately) bonded to another atom.

Many of the other elements commonly found in compounds with hydrogen are more electronegative than hydrogen. As a result, hydrogen often has a partial positive charge. Remember, that is one of the reasons that atoms can act as Lewis acids: with a partial positive charge, an atom becomes electrophilic.

Our statement about protons might better be expressed as:

- H^+ is a very common Lewis acid or electrophile.

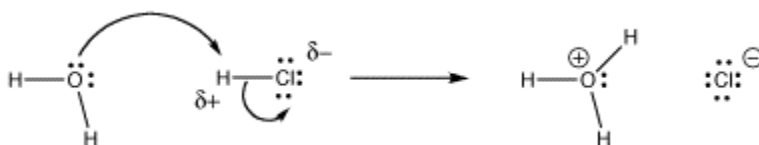


Figure 2.11.7. Proton transfer from one site to another.

If hydrogens are almost always bonded to other atoms, then the Lewis acid-base interactions we have looked at so far are slightly different here. Instead of two compounds coming together and forming a bond, we have one Lewis base replacing another at a proton.

- Protons are transferred from one basic site to another.
- Transfer occurs by donation of a lone pair to the proton.

Lewis Bases

What makes a molecule (or an atom or ion) a Lewis base? It must have a pair of electrons available to share with another atom to form a bond. The most readily available electrons are those that are not already in bonds. Bonding electrons are low in energy. Non-bonding electrons are higher in energy and may be stabilized when they are delocalized in a new bond.

Lewis bases usually have non-bonding electrons or lone pairs.

Note 1: Ammonia

Ammonia, NH_3 , has a lone pair and is a Lewis base. It can donate to compounds that will accept electrons.



Ammonia donating to an electron acceptor or Lewis acid.

Lewis bases may be anionic or neutral. The basic requirement is that they have a pair of electrons to donate. Examples of Lewis bases include halide ions such as bromide or chloride. To the right of the halides in the periodic table are Noble gases such as neon. Noble gases do have lone pairs, but are stable enough that they do not usually react. They are not very good Lewis bases. To the left of the halides, however, are other examples in oxygen and nitrogen compounds. Water also has lone pairs and is a common Lewis base, and so is hydroxide ion, HO^- .

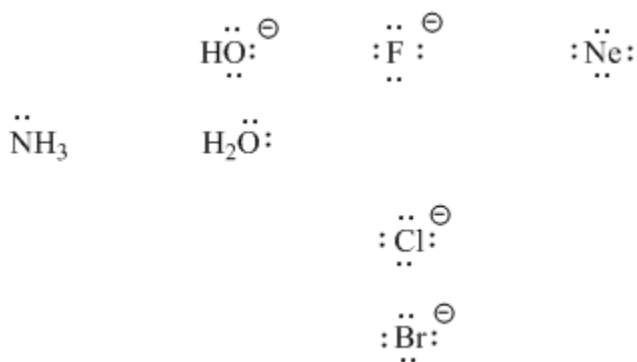


Figure 2.11.8: Some examples of Lewis basic ions and molecules. Note that neon, although it has non-bonding electron pairs or lone pairs, does not usually act as a Lewis base.

- Halides, water, ammonia and hydroxide ion are examples of Lewis bases.

One column further to the left in the periodic table from nitrogen is carbon. Carbon does not normally have a lone pair. For example, methane, CH_4 , has all of its valence electrons in bonding pairs. These bonding pairs are too stable to donate under normal conditions. Methane is not a Lewis base.

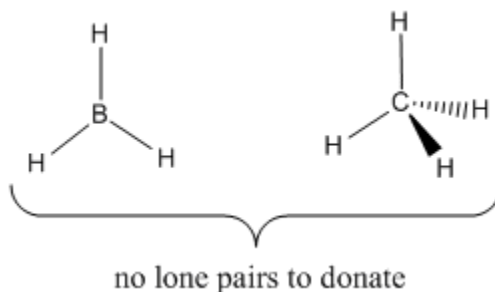


Figure 2.11.9. Carbon and boron "hydrides". Neither of these compounds has a lone pair, and neither is a good Lewis base.

Even further to the left is boron. A simple boron compound is borane, BH_3 . Borane has no lone pairs; all its valence electrons are

in bonds. Boron is not a good Lewis base.

Problem

Which of the following compounds appear to be Lewis bases?

a) SiH_4 b) AlH_3 c) PH_3 d) SH_2 e) SH^-

Lewis Acid-Base Complexes

What happens when a Lewis base donates a pair of electrons to a Lewis acid? The arrow formalism we have been using to illustrate the behaviour of Lewis acids and Lewis bases is meant to show the direction of electron movement from the donor to the acceptor. However, given that a bond can be thought of as a pair of electrons that are shared between two atoms (in this case, between the donor and the acceptor), these arrows also show where bonds are forming.

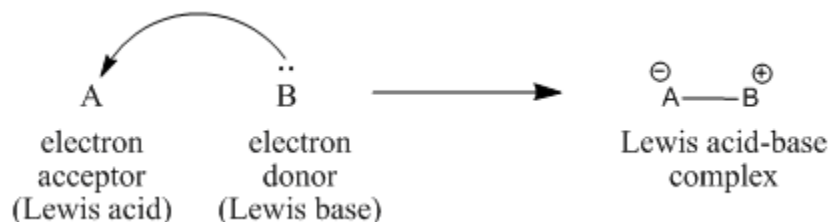


Figure 2.11.10. Donation of electrons from a Lewis base to a Lewis acid.

The electrons donated from a Lewis base to a Lewis acid form a new bond. A new, larger compound is formed from the smaller Lewis acid and Lewis base. This compound is called a Lewis acid-base complex.

A simple example of Lewis acid-base complexation involves ammonia and boron trifluoride. The nitrogen atom has a lone pair and is an electron donor. The boron has no octet and is an electron acceptor. The two compounds can form a Lewis acid-base complex or a coordination complex together.

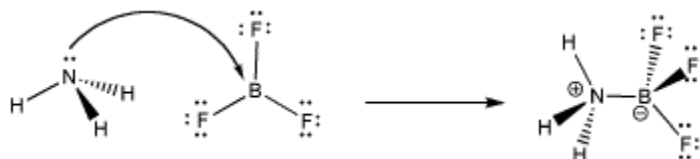


Figure 2.11.11: Formation of a Lewis acid-base complex from ammonia and boron trifluoride.

When the nitrogen donates a pair of electrons to share with the boron, the bond that forms is sometimes called a coordinate bond. Another term for this kind of bond is a dative bond. A coordinate or dative bond is any covalent bond that arose because one atom brought a pair of its electrons and donated them with another.

There is another piece of terminology you should get used to here. Sometimes, the electron donor is called a **nucleophile** and the electron acceptor is called an **electrophile**. Ammonia is a nucleophile and boron trifluoride is an electrophile.

- Because Lewis bases are attracted to electron-deficient atoms, and because positive charge is generally associated with the nucleus of an atom, Lewis bases are sometimes referred to as "nucleophiles". Nucleophile means nucleus-loving.
- Because Lewis acids attract electron pairs, Lewis acids are sometimes called "electrophiles". Electrophile means electron-loving.

Lewis acid-base complexes frequently have very different properties from the separate compounds from which they were formed. For example, titanium tetrachloride is a yellow liquid at room temperature. It is so Lewis acidic that it reacts with moisture in the air, undergoing a reaction that generates HCl gas in the form of white smoke. Tetrahydrofuran (or THF), a mild Lewis base, is a colourless liquid. When THF and TiCl_4 are combined, a Lewis acid-base complex is formed, $\text{TiCl}_4(\text{THF})_2$. $\text{TiCl}_4(\text{THF})_2$ is a yellow solid at room temperature. Although it still reacts with the air, it does so very slowly, and shows no visible change when exposed

to the air for several minutes.

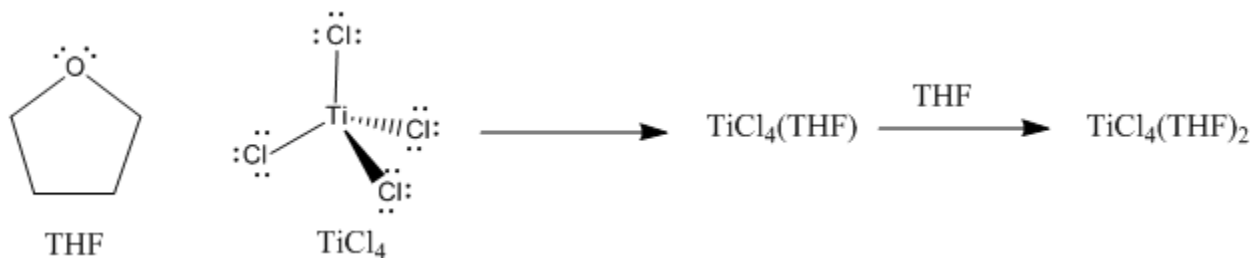


Figure 2.11.12: A Lewis acid-base complex between tetrahydrofuran (THF) and titanium tetrachloride.

Problem 1

Show, using arrow notation, the reaction between THF and titanium tetrachloride to form the Lewis acid-base complex, $\text{TiCl}_4(\text{THF})_2$. Also show the structures of the complexes formed.

Problem 2

A similar Lewis acid-base complex is formed between THF and borane, BH_3 .

1. Which compound is the Lewis acid? Which one is the Lewis base?
2. Which atom in the Lewis acid is the acidic site? Why?
3. Which atom in the Lewis base is the basic site? Why?
4. How many donors would be needed to satisfy the acidic site?
5. Show, using arrow notation, the reaction to form a Lewis acid-base complex.
6. Borane is highly pyrophoric; it reacts violently with air, bursting into flames. Show, using arrow notation, what might be happening when borane contacts the air.
7. Borane-THF complex is much less pyrophoric than borane. Why do you suppose that is so?

Problem 3

When a neutral Lewis acid combines with an anionic Lewis base, the product is called a complex ion. The same is true if a cationic Lewis acid combines with a neutral Lewis base.

Show the formation of the following polyatomic anions from the Lewis acid-base pairs that were combined in each case.

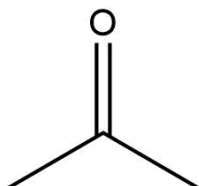
- a) BF_4^- b) PF_6^- c) AlCl_4^- d) AlH_4^- e) $\text{Ag}(\text{NH}_3)^{2+}$

Exercises

Questions

Q2.11.1

For the following molecules state whether they are Lewis acid or base and whether or not they are a Brønsted acid or base.



Solutions

S2.11.1

Acetone is a Lewis base and a Brønsted base. Ammonium cation is both a Lewis acid and a weak Brønsted acid.

Contributors

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1.14: Noncovalent Interactions Between Molecules

Objectives

After completing this section, you should be able to

1. identify the various intermolecular forces that may be at play in a given organic compound.
2. describe how intermolecular forces influence the physical properties, 3-dimensional shape and structure of compounds.

Key Terms

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

- dipole-dipole forces
- London dispersion forces
- hydrogen bond
- intermolecular forces
- noncovalent interaction
- van der Waals forces

Study Notes

Much of the material in this section should be familiar to you from your pre-requisite general chemistry course. Nonetheless, this section is important, as it covers some of the fundamental factors that influence many physical and chemical properties.

Introduction

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intramolecular* forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *intermolecular* forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

Note

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases

only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law,.)

In this section, we explicitly consider three kinds of intermolecular interactions: There are two additional types of electrostatic interaction that you are already familiar with: the ion-ion interactions that are responsible for ionic bonding and the ion-dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole-Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 2.12.1. These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 2.12.1). Hence dipole-dipole interactions, such as those in part (b) in Figure 2.12.1, are *attractive intermolecular interactions*, whereas those in part (d) in Figure 2.12.1 are *repulsive intermolecular interactions*.

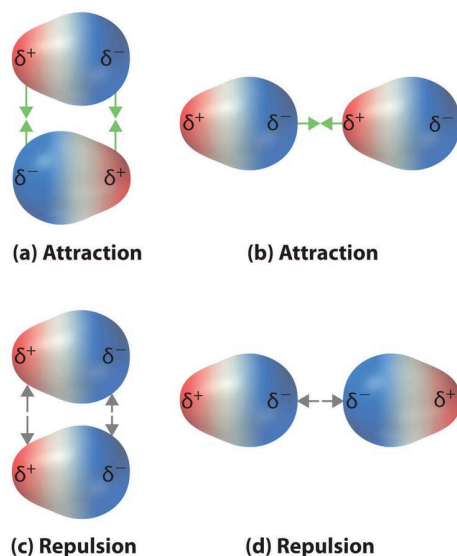


Figure 2.12.1 Attractive and Repulsive Dipole-Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole-dipole interactions simultaneously, as shown in Figure 2.12.2. On average, however, the attractive interactions dominate.

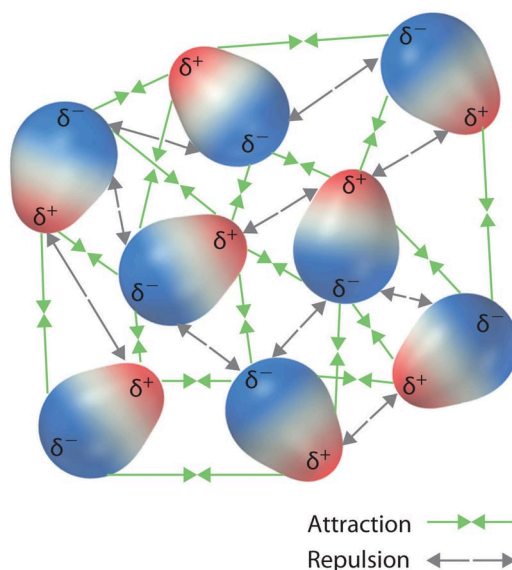


Figure 2.12.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ± 1 , or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6 , or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 2.12.1. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 2.12.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

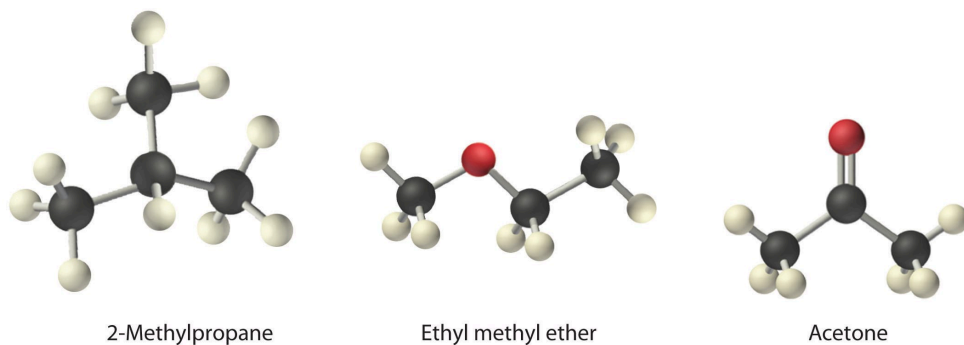
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C ₃ H ₆ (cyclopropane)	42	0	240
CH ₃ OCH ₃ (dimethyl ether)	46	1.30	248
CH ₃ CN (acetonitrile)	41	3.9	355

Note

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 2.12.1

Arrange ethyl methyl ether (CH₃OCH₂CH₃), 2-methylpropane [isobutane, (CH₃)₂CHCH₃], and acetone (CH₃COCH₃) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativity values. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H₂O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = –11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise 2.12.1

Arrange carbon tetrafluoride (CF₄), ethyl methyl sulfide (CH₃SC₂H₅), dimethyl sulfoxide [(CH₃)₂S=O], and 2-methylbutane [isopentane, (CH₃)₂CHCH₂CH₃] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = –128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 11.3).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 2.12.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	-189.4	-185.9
Xe	131	-111.8	-108.1
N ₂	28	-210	-195.8
O ₂	32	-218.8	-183.0
F ₂	38	-219.7	-188.1
I ₂	254	113.7	184.4
CH ₄	16	-182.5	-161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 11.5.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole-induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6 , or 64-fold.

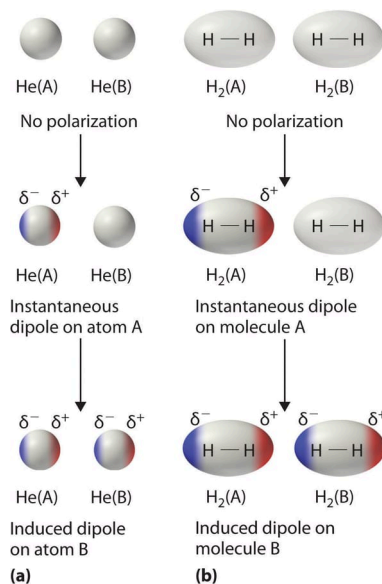


Figure 2.12.3 Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H₂ molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole-induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H₂ molecules in part (b) in Figure 11.5.3, tends to become more pronounced as atomic and molecular masses increase (Table 11.3). For example, Xe boils at -108.1°C, whereas He boils at -269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron-electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light

species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

Note

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 2.12.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 2.12.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12} . Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

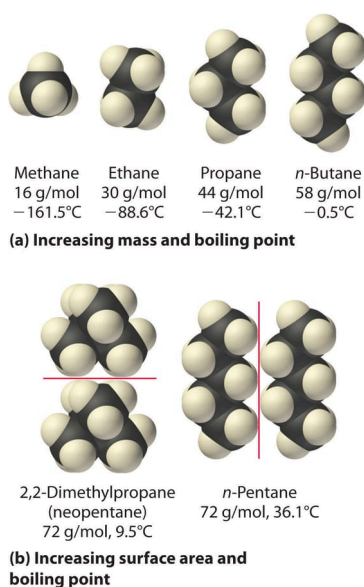


Figure 2.12.4 Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 2.12.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(\text{CH}_3)_2\text{CHCH}_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (-42.1°C) < 2-methylpropane (-11.7°C) < *n*-butane (-0.5°C) < *n*-pentane (36.1°C).

Exercise 2.12.2

Arrange GeH_4 , SiCl_4 , SiH_4 , CH_4 , and GeCl_4 in order of decreasing boiling points.

Answer: GeCl_4 (87°C) > SiCl_4 (57.6°C) > GeH_4 (-88.5°C) > SiH_4 (-111.8°C) > CH_4 (-161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 2.12.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of -130°C for water! Imagine the implications for life on Earth if water boiled at -130°C rather than 100°C .

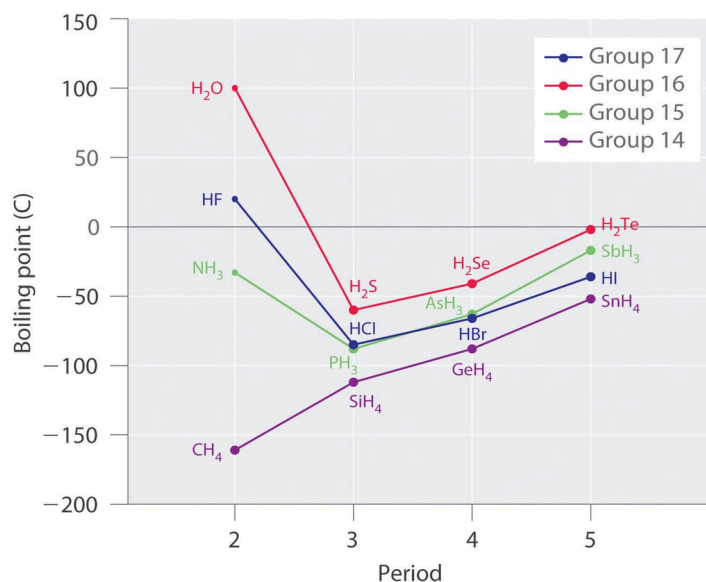


Figure 2.12.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF , NH_3 , and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H-O, H-N, and H-F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole-dipole distances results in very strong dipole-dipole interactions called hydrogen bonds, as shown for ice in Figure 2.12.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O-H covalent bonds and two O ··· H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

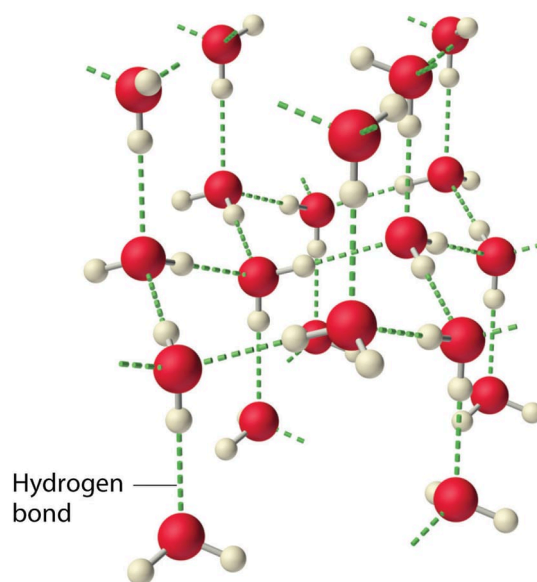


Figure 2.12.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

Note

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH₃. Consequently, even though their molecular masses are similar to that of

water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 2.12.3

Considering CH_3OH , C_2H_6 , Xe, and $(\text{CH}_3)_3\text{N}$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

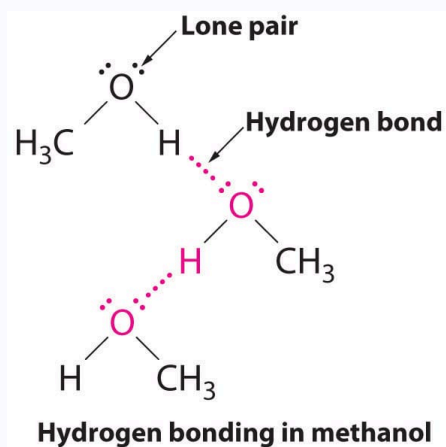
Strategy:

- Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
- Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine $[(\text{CH}_3)_3\text{N}]$ do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

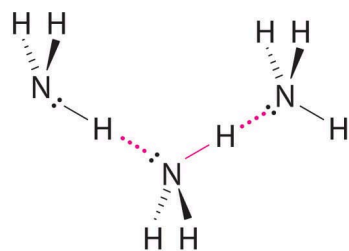
B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



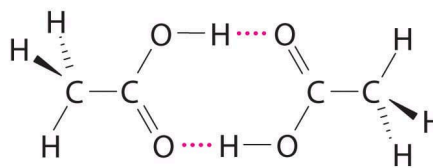
Exercise 2.12.3

Considering $\text{CH}_3\text{CO}_2\text{H}$, $(\text{CH}_3)_3\text{N}$, NH_3 , and CH_3F , which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer: $\text{CH}_3\text{CO}_2\text{H}$ and NH_3 ;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Example 2.12.4

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O . Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (-269°C) < Ar (-185.7°C) < N_2O (-88.5°C) < C_{60} ($>280^\circ\text{C}$) < NaCl (1465°C).

Exercise 2.12.4

Arrange 2,4-dimethylheptane, Ne, CS_2 , Cl_2 , and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (-34.6°C) > Ne (-246°C)

Summary

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because

their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong $O \cdots H$ hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

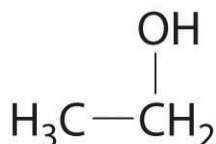
Key Takeaway

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

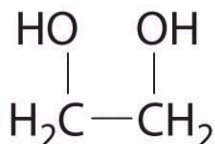
Conceptual Problems

1. What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?
2. Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.
3. Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.
4. Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?
5. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
6. Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.
7. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
8. Using acetic acid as an example, illustrate both attractive and repulsive intermolecular interactions. How does the boiling point of a substance depend on the magnitude of the repulsive intermolecular interactions?
9. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
10. The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, –85°C; HBr, –67°C; and HI, –34°C. Explain any trends in the data, as well as any deviations from that trend.
11. Identify the most important intermolecular interaction in each of the following.
 1. SO_2
 2. HF
 3. CO_2
 4. CCl_4
 5. CH_2Cl_2
12. Identify the most important intermolecular interaction in each of the following.
 1. LiF
 2. I_2
 3. ICl
 4. NH_3
 5. NH_2Cl

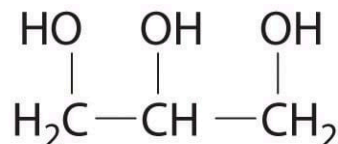
13. Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)
14. Arrange Kr, Cl₂, H₂, N₂, Ne, and O₂ in order of increasing polarizability. Explain your reasoning.
15. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.
16. The structures of ethanol, ethylene glycol, and glycerin are as follows:



Ethanol



Ethylene glycol



Glycerin

Arrange these compounds in order of increasing boiling point. Explain your rationale.

17. Do you expect the boiling point of H₂S to be higher or lower than that of H₂O? Justify your answer.
18. Ammonia (NH₃), methylamine (CH₃NH₂), and ethylamine (CH₃CH₂NH₂) are gases at room temperature, while propylamine (CH₃CH₂CH₂NH₂) is a liquid at room temperature. Explain these observations.
19. Why is it not advisable to freeze a sealed glass bottle that is completely filled with water? Use both macroscopic and microscopic models to explain your answer. Is a similar consideration required for a bottle containing pure ethanol? Why or why not?
20. Which compound in the following pairs will have the higher boiling point? Explain your reasoning.
 1. NH₃ or PH₃
 2. ethylene glycol (HOCH₂CH₂OH) or ethanol
 3. 2,2-dimethylpropanol [CH₃C(CH₃)₂CH₂OH] or *n*-butanol (CH₃CH₂CH₂CH₂OH)
21. Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?
22. Use the melting of a metal such as lead to explain the process of melting in terms of what is happening at the molecular level. As a piece of lead melts, the temperature of the metal remains constant, even though energy is being added continuously. Why?
23. How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the H₂O molecule? What effect does this have on the structure and density of ice?
24.
 1. Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular interactions in liquid HI.
 2. In which substance are the individual hydrogen bonds stronger: HF or H₂O? Explain your reasoning.
 3. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or H₂O? Explain your reasoning.

Answers

- 1.
- 2.
- 3.
- 4.

5. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.
- 6.
- 7.
- 8.
9. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure.
- 10.
11.
 1. The V-shaped SO_2 molecule has a large dipole moment due to the polar $\text{S}=\text{O}$ bonds, so dipole–dipole interactions will be most important.
 2. The $\text{H}-\text{F}$ bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.
 3. Although the $\text{C}=\text{O}$ bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.
 4. This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.
 5. This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.
- 12.
- 13.
- 14.
15. Water has two polar $\text{O}-\text{H}$ bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of *four* hydrogen bonds per H_2O molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors, it only has one $\text{O}-\text{H}$ bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form *two* hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.
- 16.
- 17.
- 18.
- 19.
- 20.
21. Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.

Contributors

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

1.15: Molecular Models

Objective

After completing this section, you should be able to

- use ball-and-stick molecular models to make models of simple organic compounds (e.g., ethane, ethylene, acetylene, ethanol, formaldehyde, acetone, acetic acid), given their Kekulé structures or molecular formulas.

Study Notes

You will have noticed that we have given two names for most of the compounds discussed up to this point. In general we shall be using systematic (i.e., IUPAC—International Union of Pure and Applied Chemistry) names throughout the course. However, simple compounds are often known by their common names, which may be more familiar than their IUPAC counterparts. We shall address the subject of nomenclature (naming) in Chapter 3.

ethanol, ethanol

formaldehyde (methanal), formaldehyde (methanal)

acetone (propanone), acetone (propanone)

acetic (ethanoic) acid, acetic (ethanoic) acid

Exercises

1. Construct a molecular model of each of the compounds listed below.

- $\text{CH}_3\text{-CN}$
- $\text{CH}_3\text{-N=C=O}$
- $\text{CH}_3\text{-CH}_2\text{-O-CH}_3$

Hint: Use the curved sticks to form the multiple bonds and the straight sticks for single bonds.

Answers:

- molecular model of acetonitrile
- molecular model of methyl isocyanate
- molecular model of ethyl methyl ether

Contributors

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1.1 Atoms, Electrons, and Orbitals

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2: CHAPTER 2 ALKANES

- 2.1: Functional Groups
- 2.2: Alkanes and Alkane Isomers
- 2.3: Alkyl Groups
- 2.4: Naming Alkanes
- 2.5: Naming Cycloalkanes
- 2.6: The Nature of Chemical Bonds: Molecular Orbital Theory
- 2.7: sp^3 Hybrid Orbitals and the Structure of Methane
- 2.8: sp^3 Hybrid Orbitals and the Structure of Ethane
- 2.9: sp^2 Hybrid Orbitals and the Structure of Ethylene
- 2.10: sp Hybrid Orbitals and the Structure of Acetylene
- 2.11: Drawing Chemical Structures

2.1: Functional Groups

Objectives

After completing this section, you should be able to

1. explain why the properties of a given organic compound are largely dependent on the functional group or groups present in the compound.
2. identify the functional groups present in each of the following compound types: alkenes, alkynes, arenes, (alkyl and aryl) halides, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, (carboxylic) acid chlorides, amides, amines, nitriles, nitro compounds, sulfides and sulfoxides.
3. identify the functional groups present in an organic compound, given its structure.
4. Given the structure of an organic compound containing a single functional group, identify which of the compound types listed under Objective 2, above, it belongs to.
5. draw the structure of a simple example of each of the compound types listed in Objective 2.

Key Terms

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

- **functional group**

Study Notes

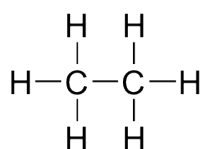
The concept of functional groups is a very important one. We expect that you will need to refer back to tables at the end of Section 3.1 quite frequently at first, as it is not really feasible to learn the names and structures of all the functional groups and compound types at one sitting. Gradually they will become familiar, and eventually you will recognize them automatically.

Functional groups are atoms or small groups of atoms (two to four) that exhibit a characteristic reactivity. A particular functional group will almost always display its characteristic chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have characteristic names that often carry over in the naming of individual compounds incorporating specific groups

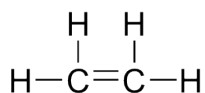
As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

Hydrocarbons and halides

We have already seen some examples of very common functional groups: ethene, for example, contains a carbon-carbon double bond. This double bond is referred to, in the functional group terminology, as an **alkene**.



ethane
(an **alkane**)



ethene
(an **alkene**)



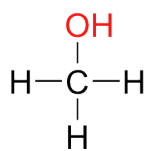
ethyne
(an **alkyne**)

The carbon-carbon triple bond in ethyne is the simplest example of an **alkyne** function group.

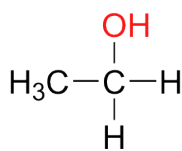
What about ethane? All we see in this molecule is carbon-hydrogen and carbon-carbon single bonds, so in a sense we can think of ethane as lacking a functional group entirely. However, we do have a general name for this 'default' carbon bonding pattern: molecules or parts of molecules containing only carbon-hydrogen and carbon-carbon single bonds are referred to as **alkanes**. If the carbon of an alkane is bonded to a halogen, the group is now referred to as a **haloalkane** (fluoroalkane, chloroalkane, etc.). Chloroform, CHCl_3 , is an example of a simple haloalkane.

Alcohols and Thiols

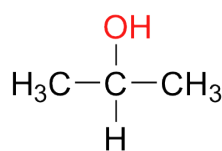
We have already seen the simplest possible example of an **alcohol** functional group in methanol. In the alcohol functional group, a carbon is single-bonded to an OH group (this OH group, by itself, is referred to as a **hydroxyl**). If the central carbon in an alcohol is bonded to only one other carbon, we call the group a primary alcohol. In secondary alcohols and tertiary alcohols, the central carbon is bonded to two and three carbons, respectively. Methanol, of course, is in class by itself in this respect.



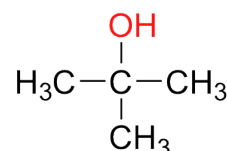
methanol



a primary alcohol

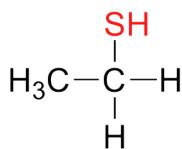


a secondary alcohol

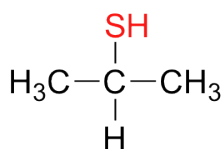


a tertiary alcohol

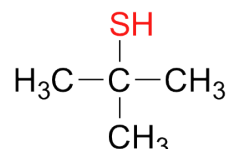
The sulfur analog of an alcohol is called a **thiol** (the prefix *thio*, derived from the Greek, refers to sulfur).



a primary thiol

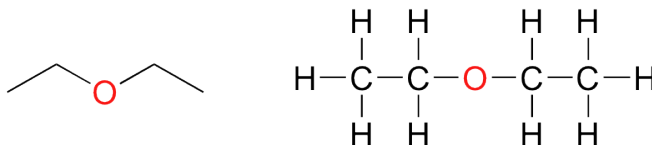


a secondary thiol

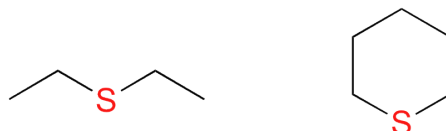


a tertiary thiol

In an **ether** functional group, a central oxygen is bonded to two carbons. Below are the line and Lewis structures of diethyl ether, a common laboratory solvent and also one of the first medical anaesthesia agents.

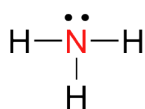


In **sulfides**, the oxygen atom of an ether has been replaced by a sulfur atom.

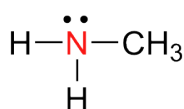


Amines and Phosphates

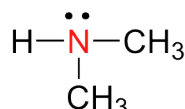
Ammonia is the simplest example of a functional group called **amines**. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines.



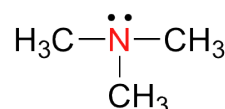
ammonia



a primary amine

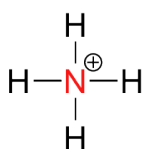


a secondary amine

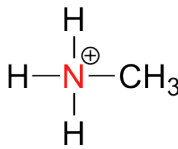


a tertiary amine

One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations.

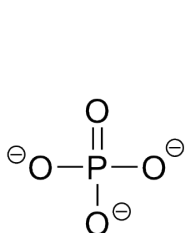


ammonium

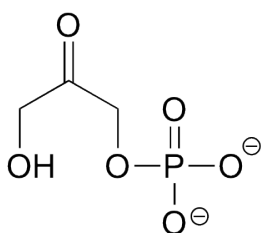


a primary ammonium

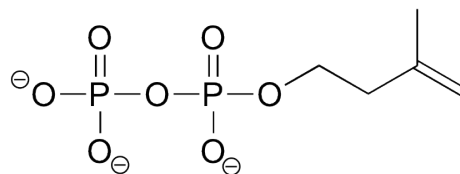
Phosphorus is a very important element in biological organic chemistry, and is found as the central atom in the **phosphate** group. Many biological molecules contain phosphate, diphosphate, and triphosphate groups, which are linked to a carbon atom by the **phosphate ester** functionality.



inorganic phosphate

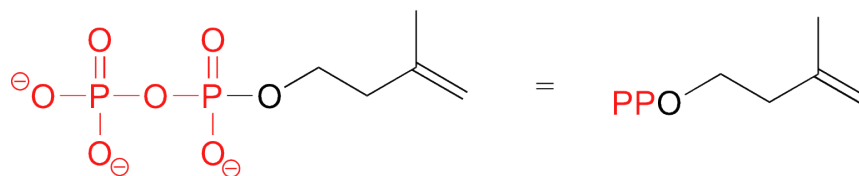
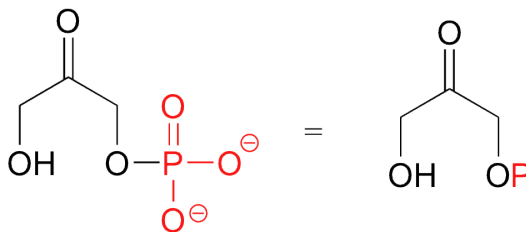


an organic phosphate ester



an organic diphosphate ester

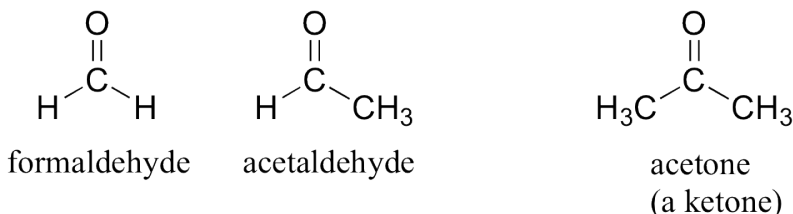
Because phosphates are so abundant in biological organic chemistry, it is convenient to depict them with the abbreviation 'P'. Notice that this 'P' abbreviation includes the oxygen atoms and negative charges associated with the phosphate groups.



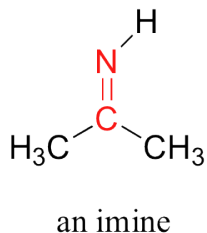
Carbonyl Containing Functional Groups

Aldehydes and Ketones

There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.

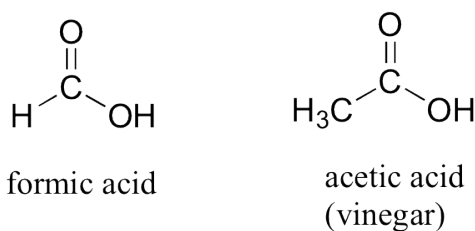


Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.

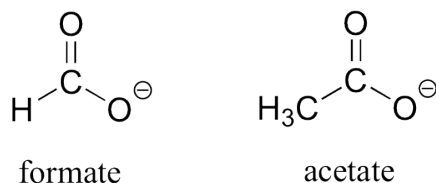


Carboxylic acids and acid derivatives

If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives**', a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.

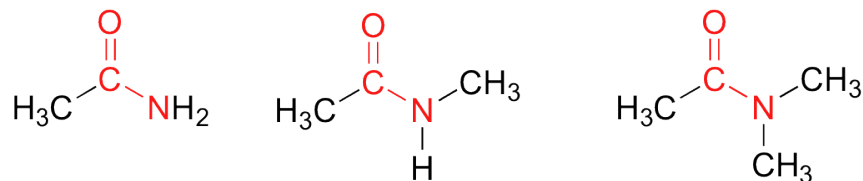


As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).

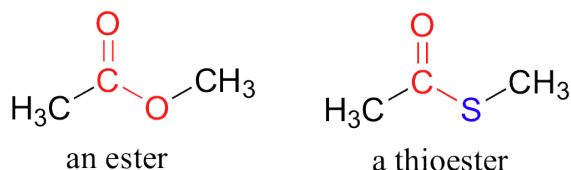


In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons,

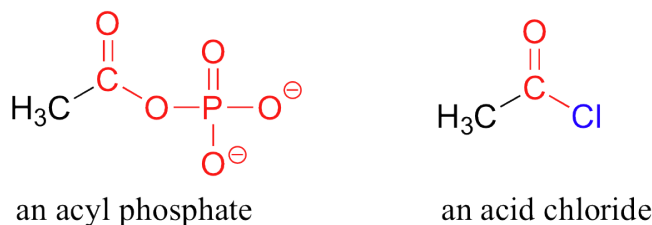
or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.



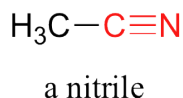
In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.



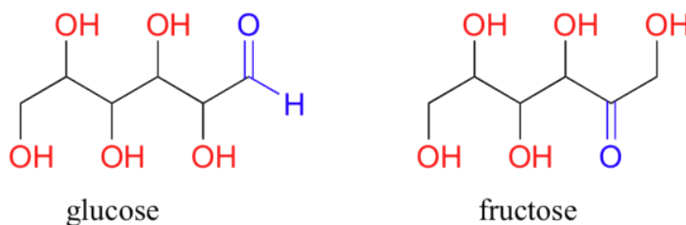
In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.



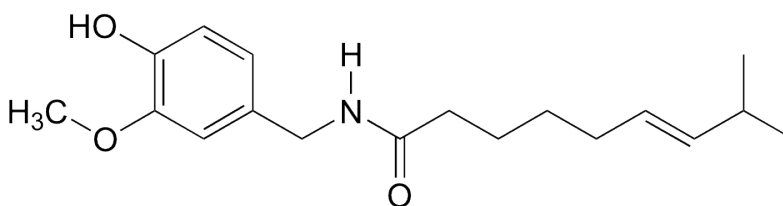
Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.



A single compound may contain several different functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').

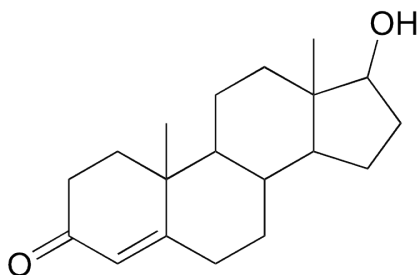


Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.

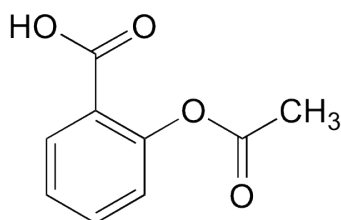


capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.



testosterone

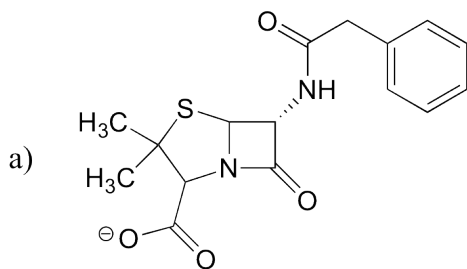


acetylsalicylic acid
(aspirin)

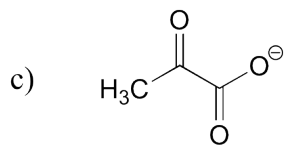
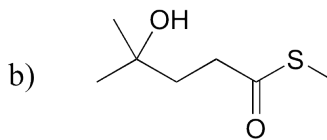
While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table found below provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

Problems

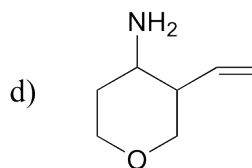
1: Identify the functional groups in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.



penicillin



pyruvate



2: Draw one example each (there are many possible correct answers) of compounds fitting the descriptions below, using line structures. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus

may exceed the octet rule).

a) a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups

b) an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.

c) A compound with molecular formula C_6H_9NO that has an amide functional group, and does *not* have an alkene group.

Solution

1:

a) carboxylate, sulfide, aromatic, two amide groups (one of which is cyclic)

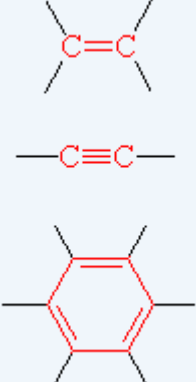
b) tertiary alcohol, thioester

c) carboxylate, ketone

d) ether, primary amine, alkene

Functional Group Tables

Exclusively Carbon Functional Groups

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	Alkene	$H_2C=CH_2$	Ethene	Ethylene
	Alkyne	$HC\equiv CH$	Ethyne	Acetylene
	Arene	C_6H_6	Benzene	Benzene

Functional Groups with Single Bonds to Heteroatoms

Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	Halide	H_3C-I	Iodomethane	Methyl iodide
	Alcohol	CH_3CH_2OH	Ethanol	Ethyl alcohol
	Ether	$CH_3CH_2OCH_2CH_3$	Diethyl ether	Ether

	Amine	$\text{H}_3\text{C}-\text{NH}_2$	Aminomethane	Methylamine
	Nitro Compound	$\text{H}_3\text{C}-\text{NO}_2$	Nitromethane	
	Thiol	$\text{H}_3\text{C}-\text{SH}$	Methanethiol	Methyl mercaptan
	Sulfide	$\text{H}_3\text{C}-\text{S}-\text{CH}_3$	Dimethyl sulfid	

Functional Groups with Multiple Bonds to Heteroatoms

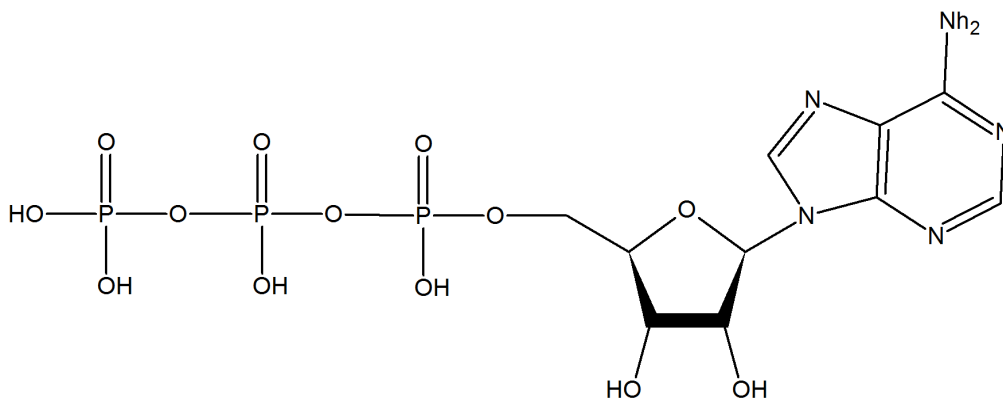
Group Formula	Class Name	Specific Example	IUPAC Name	Common Name
	Nitrile	$\text{H}_3\text{C}-\text{CN}$	Ethanenitrile	Acetonitrile
	Aldehyde	H_3CCHO	Ethanal	Acetaldehyde
	Ketone	H_3CCOCH_3	Propanone	Acetone
	Carboxylic Acid	$\text{H}_3\text{CCO}_2\text{H}$	Ethanoic Acid	Acetic acid
	Ester	$\text{H}_3\text{CCO}_2\text{CH}_2\text{CH}_3$	Ethyl ethanoate	Ethyl acetate
	Acid Halide	H_3CCOCl	Ethanoyl chloride	Acetyl chloride
	Amide	$\text{H}_3\text{CCON}(\text{CH}_3)_2$	N,N-Dimethylethanamide	N,N-Dimethylacetamide
	Acid Anhydride	$(\text{H}_3\text{CCO})_2\text{O}$	Ethanoic anhydride	Acetic anhydride

Exercises

Questions

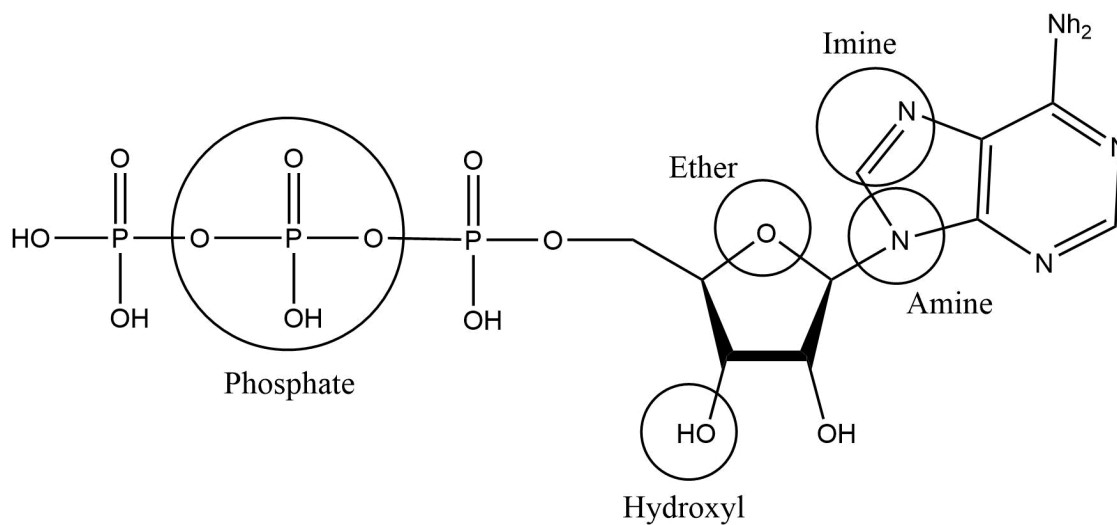
Q3.1.1

The following is the molecule for ATP, or the molecule responsible for energy in human cells. Identify the functional groups for ATP.



Solutions

S3.1.1



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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2.2: Alkanes and Alkane Isomers

Objectives

After completing this section, you should be able to

1. draw the Kekulé structure, condensed structure and shorthand structure of each of the first ten straight-chain alkanes.
2. name each of the first ten straight-chain alkanes, given its molecular formula, Kekulé structure, condensed structure or shorthand structure.
3. explain the difference in structure between a straight- and a branched-chain alkane, and illustrate the difference using a suitable example.
4. explain why the number of possible isomers for a given molecular formula increases as the number of carbon atoms increases.
5. draw all the possible isomers that correspond to a given molecular formula of the type $C_n H_{2n+2}$, where $n \leq 7$.

Key Terms

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

- branched-chain alkane
- constitutional or structural isomer
- homologous series
- isomer
- saturated hydrocarbon
- straight-chain alkane (or normal alkane)

Study Notes

A series of compounds in which successive members differ from one another by a CH_2 unit is called a homologous series. Thus, the series $CH_4, C_2H_6, C_3H_8 \dots C_nH_{2n+2}$, is an example of a homologous series.

It is important that you commit to memory the names of the first 10 straight-chain alkanes (i.e., from CH_4 to $C_{10}H_{22}$). You will use these names repeatedly when you begin to learn how to derive the systematic names of a large variety of organic compounds. You need not remember the number of isomers possible for alkanes containing more than seven carbon atoms. Such information is available in reference books when it is needed. When drawing isomers, be careful not to deceive yourself into thinking that you can draw more isomers than you are supposed to be able to. Remember that it is possible to draw each isomer in several different ways and you may inadvertently count the same isomer more than once.

Alkanes are organic compounds that consist entirely of single-bonded carbon and hydrogen atoms and lack any other functional groups. Alkanes can be subdivided into the following three groups: the straight-chain alkanes, branched alkanes, and cycloalkanes. Alkanes and branched alkanes have the general formula C_nH_{2n+2} . Alkanes are sometimes called saturated hydrocarbons, meaning that all of the carbon atoms that make up the molecule are single bonded to other atoms (no double or triple bonds).

Cycloalkanes are cyclic [hydrocarbons](#), meaning that some or all of the carbons in the molecule are arranged in the form of a ring. Cycloalkanes have the general formula C_nH_{2n} . Cycloalkanes are also saturated. There are also polycyclic alkanes, which are molecules that contain two or more cycloalkanes that are joined, forming multiple rings.

This is an introductory page about alkanes, such as methane, ethane, propane, butane and the remainder of the common alkanes. This page addresses their formula and isomerism, their physical properties, and an introduction to their chemical reactivity.

Molecular Formulas

Alkanes are the simplest family of hydrocarbons - compounds containing carbon and hydrogen only. Alkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds. The first six alkanes are as follows:

methane	CH ₄
ethane	C ₂ H ₆
propane	C ₃ H ₈
butane	C ₄ H ₁₀
pentane	C ₅ H ₁₂
hexane	C ₆ H ₁₄

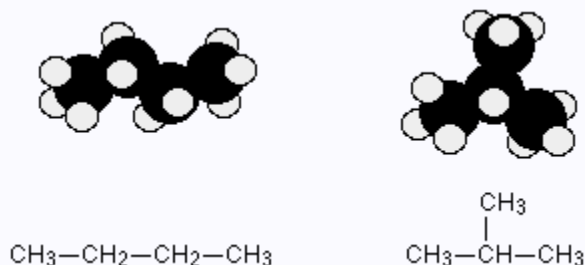
You can work out the formula of any of the alkanes using the general formula C_nH_{2n+2}

Isomerism

All of the alkanes containing 4 or more carbon atoms show structural isomerism, meaning that there are two or more different structural formulae that you can draw for each molecular formula.

Example: Butane or MethylPropane

C₄H₁₀ could be either of these two different molecules:



These are named butane and 2-methylpropane, respectively

What is structural isomerism?

Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. For example, both of the following are the same molecule. They are not isomers; both are butane.



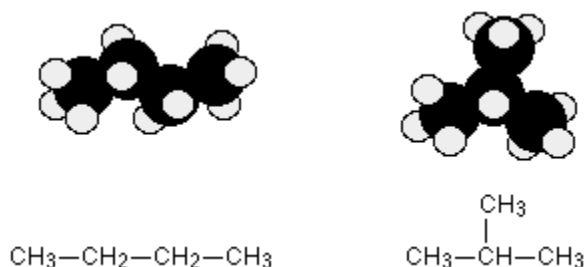
There are also endless other possible ways that this molecule could twist itself. There is completely free rotation around all the carbon-carbon single bonds. If you had a model of a molecule in front of you, you would have to take it to pieces and rebuild it if you wanted to make an isomer of that molecule. If you can make an apparently different molecule just by rotating single bonds,

it's not different - it's still the same molecule.

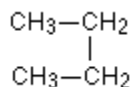
In structural isomerism, the atoms are arranged in a completely different order. This is easier to see with specific examples. What follows looks at some of the ways that structural isomers can arise. The names of the various forms of structural isomerism probably do not matter all that much, but you must be aware of the different possibilities when you come to draw isomers.

Chain isomerism

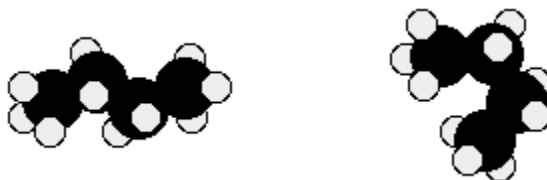
These isomers arise because of the possibility of branching in carbon chains. For example, there are two isomers of butane, C_4H_{10} . In one of them, the carbon atoms lie in a "straight chain" whereas in the other the chain is branched.



Be careful not to draw "false" isomers which are just twisted versions of the original molecule. For example, this structure is just the straight chain version of butane rotated about the central carbon-carbon bond.

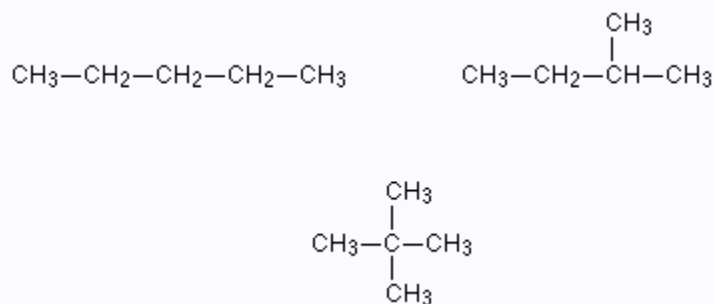


You could easily see this with a model. This is the example we've already used at the top of this page.



Example 2.2.1: Chain Isomers in Pentane

Pentane, C_5H_{12} , has three chain isomers. If you think you can find any others, they are simply twisted versions of the ones below. If in doubt make some models.



Examples of Simple Unbranched Alkanes

Name	Molecular Formula	Structural Formula	Isomers		Name	Molecular Formula	Structural Formula	Isomers
methane	CH ₄	CH ₄	1		hexane	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	5
ethane	C ₂ H ₆	CH ₃ CH ₃	1		heptane	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	9
propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃	1		octane	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	18
butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	2		nonane	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	35
pentane	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	3		decane	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	75

Exercises

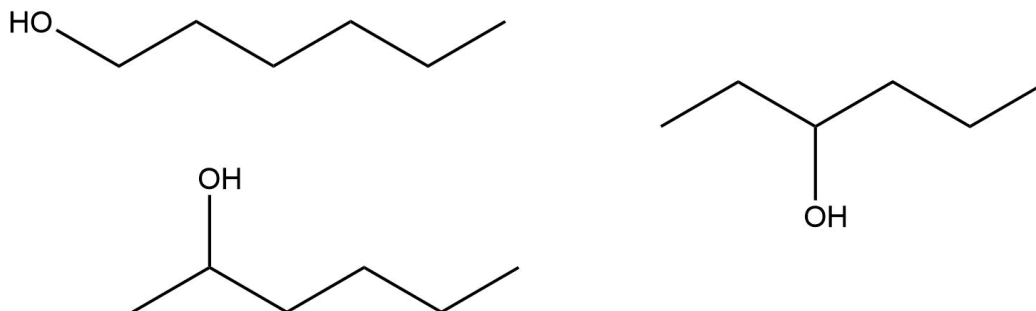
Questions

Q3.2.1

Give all the isomers for a straight chain hexanol.

Solutions

S3.2.1



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

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2.3: Alkyl Groups

Objectives

After completing this section, you should be able to

1. recognize and name any alkyl group that can be considered to have been formed by the removal of a terminal hydrogen atom from a straight-chain alkane containing ten or fewer carbon atoms.
2. explain what is meant by a primary, secondary, tertiary or quaternary carbon atom.
3. represent the various types of organic compounds using the symbol "R" to represent any alkyl group.

Key Terms

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

- alkyl group
- methyl group
- isopropyl group
- sec-butyl group
- isobutyl group
- *tert*-butyl group
- primary carbon
- secondary carbon
- tertiary carbon
- quaternary carbon

Study Notes

The differences among primary, secondary, tertiary and quaternary carbon atoms are explained in the following discussion. A convenient way of memorizing this classification scheme is to remember that a primary carbon atom is attached directly to only one other carbon atom, a secondary carbon atom is attached directly to two carbon atoms, and so on.

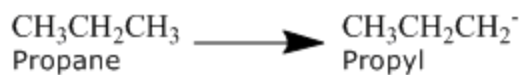
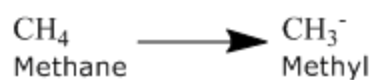
The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

Table 2.3.1: Alkyl Group names

Group	CH ₃ –	C ₂ H ₅ –	CH ₃ CH ₂ CH ₂ –	(CH ₃) ₂ CH–	CH ₃ CH ₂ CH ₂ CH ₂ –	(CH ₃) ₂ CHCH ₂ –	CH ₃ CH ₂ CH(CH ₃)–	(CH ₃) ₃ C–	R–
Name	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	sec-Butyl	tert-Butyl	Alkyl

Alkyl Groups

Alkanes can be described by the general formula C_nH_{2n+2}. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula C_nH_{2n+1}. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.



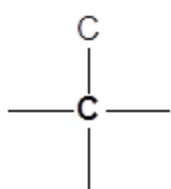
The same concept can be applied to any of the straight chain alkane names provided in Table 2.3.2.

Table 2.3.2: *straight chain alkane*

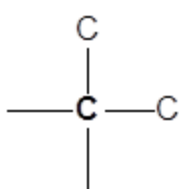
Name	Molecular Formula	Condensed Structural Formula
Methane	CH ₄	CH ₄
Ethane	C ₂ H ₆	CH ₃ CH ₃
Propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃
Butane	C ₄ H ₁₀	CH ₃ (CH ₂) ₂ CH ₃
Pentane	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃
Hexane	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃
Heptane	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃
Octane	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃
Nonane	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃
Decane	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃
Undecane	C ₁₁ H ₂₄	CH ₃ (CH ₂) ₉ CH ₃
Dodecane	C ₁₂ H ₂₆	CH ₃ (CH ₂) ₁₀ CH ₃
Tridecane	C ₁₃ H ₂₈	CH ₃ (CH ₂) ₁₁ CH ₃
Tetradecane	C ₁₄ H ₃₀	CH ₃ (CH ₂) ₁₂ CH ₃
Pentadecane	C ₁₅ H ₃₂	CH ₃ (CH ₂) ₁₃ CH ₃
Hexadecane	C ₁₆ H ₃₄	CH ₃ (CH ₂) ₁₄ CH ₃
Heptadecane	C ₁₇ H ₃₆	CH ₃ (CH ₂) ₁₅ CH ₃
Octadecane	C ₁₈ H ₃₈	CH ₃ (CH ₂) ₁₆ CH ₃
Nonadecane	C ₁₉ H ₄₀	CH ₃ (CH ₂) ₁₇ CH ₃
Eicosane	C ₂₀ H ₄₂	CH ₃ (CH ₂) ₁₈ CH ₃

Classification of carbon atoms

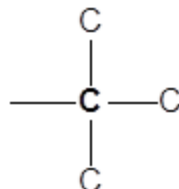
Carbons have a special terminology to describe how many other carbons they are attached to.



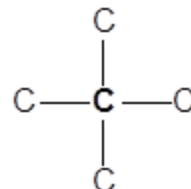
1°



2°



3°

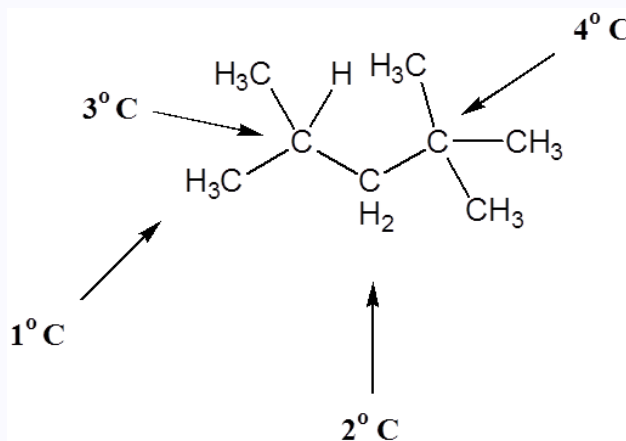


4°

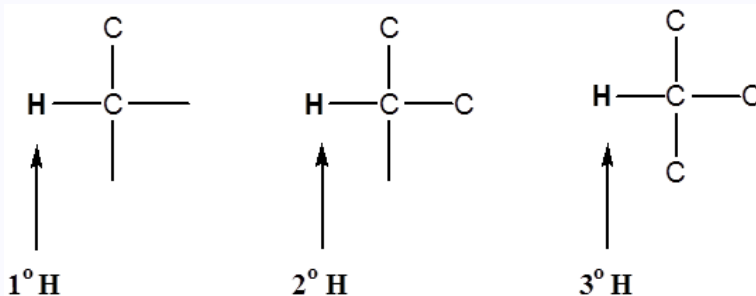
- Primary carbons (1°) attached to one other C atom
- Secondary carbons (2°) are attached to two other C's
- Tertiary carbons (3°) are attached to three other C's
- Quaternary carbons (4°) are attached to four C's

Example 2.3.1

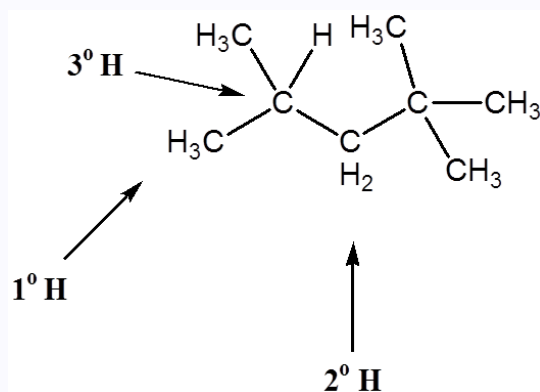
You will find that hydrogen atoms are also classified in this manner. A hydrogen atom attached to a primary carbon atom is called a primary hydrogen; thus, isobutane, has nine primary hydrogens and one tertiary hydrogen.



- Primary hydrogens (1°) are attached to carbons bonded to one other C atom
- Secondary hydrogens (2°) are attached to carbons bonded to two other C's
- Tertiary hydrogens (3°) are attached to carbons bonded to three other C's



Example 2.3.2

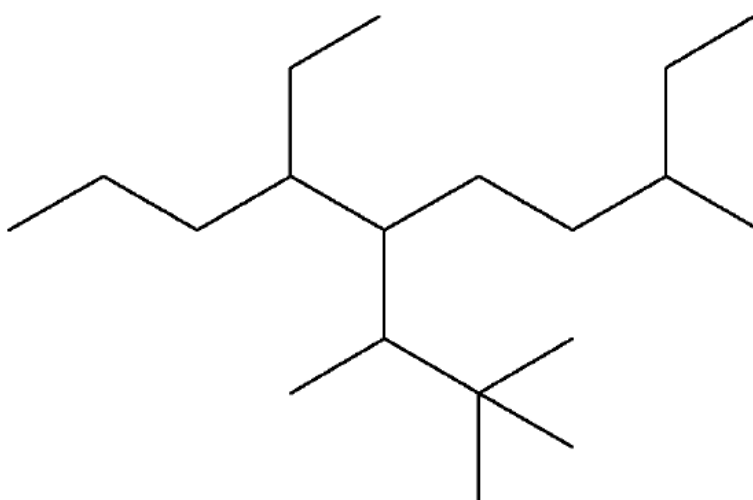


Exercises

Questions

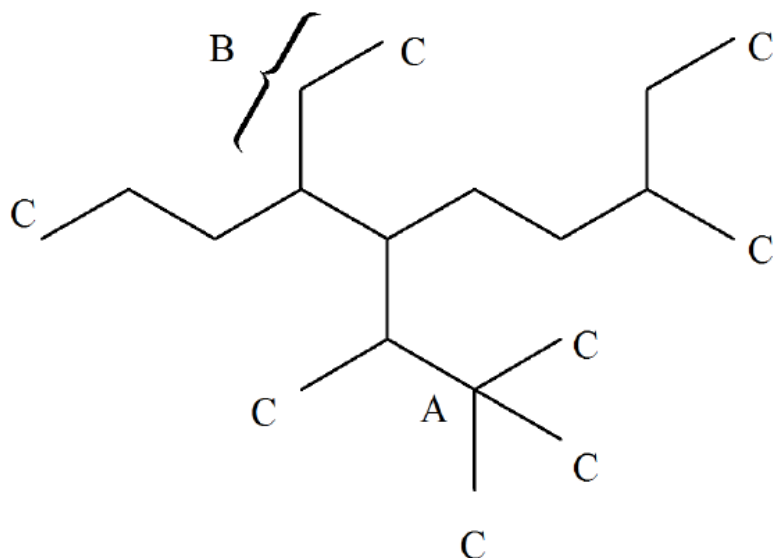
Q3.3.1

Consider the following molecule. How many carbons are in the longest chain? Find a primary and quaternary carbon, and label an ethyl group.



Solutions

S3.3.1



A = 4° Carbon

B = Ethyl Group

C = 1° Carbon

The longest chain is 10 carbons long

Contributors

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- Prof. Steven Farmer ([Sonoma State University](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

2.4: Naming Alkanes

Objectives

After completing this section, you should be able to

1. provide the correct IUPAC name for any given alkane structure (Kekulé, condensed or shorthand).
2. draw the Kekulé, condensed or shorthand structure of an alkane, given its IUPAC name.

Key Terms

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

- IUPAC system

Study Notes

The IUPAC system of nomenclature aims to ensure

1. that every organic compound has a unique, unambiguous name.
2. that the IUPAC name of any compound conveys the structure of that compound to a person familiar with the system.

One way of checking whether the name you have given to an alkane is reasonable is to count the number of carbon atoms implied by the chosen name. For example, if you named a compound 3-ethyl-4-methylheptane, you have indicated that the compound contains a total of 10 carbon atoms—seven carbon atoms in the main chain, two carbon atoms in an ethyl group, and one carbon atom in a methyl group. If you were to check the given structure and find 11 carbon atoms, you would know that you had made a mistake. Perhaps the name you should have written was 3-ethyl-4,4-dimethylheptane!

When naming alkanes, a common error of beginning students is a failure to pick out the longest carbon chain. For example, the correct name for the compound shown below is 3-methylheptane, not 2-ethylhexane.

3-methylheptane

Remember that every substituent must have a number, and do not forget the prefixes: di, tri, tetra, etc.

You must use commas to separate numbers, and hyphens to separate numbers and substituents. Notice that 3-methylhexane is one word.

Hydrocarbons having no double or triple bond functional groups are classified as **alkanes** or **cycloalkanes**, depending on whether the carbon atoms of the molecule are arranged only in chains or also in rings. Although these hydrocarbons have no functional groups, they constitute the framework on which functional groups are located in other classes of compounds, and provide an ideal starting point for studying and naming organic compounds. The alkanes and cycloalkanes are also members of a larger class of compounds referred to as **aliphatic**. Simply put, aliphatic compounds are compounds that do not incorporate any aromatic rings in their molecular structure.

The following table lists the IUPAC names assigned to simple continuous-chain alkanes from C-1 to C-10. A common "**ane**" suffix identifies these compounds as alkanes. Longer chain alkanes are well known, and their names may be found in many reference and text books. The names **methane** through **decane** should be memorized, since they constitute the root of many IUPAC names. Fortunately, common numerical prefixes are used in naming chains of five or more carbon atoms.

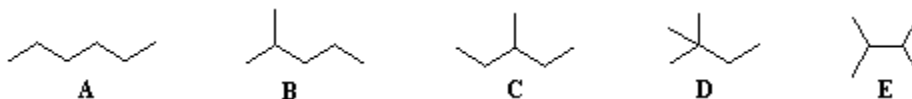
Table 2.4.1: Simple Unbranched Alkanes

Name	Molecular Formula	Structural Formula	Isomers		Name	Molecular Formula	Structural Formula	Isomers
methane	CH ₄	CH ₄	1		hexane	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	5
ethane	C ₂ H ₆	CH ₃ CH ₃	1		heptane	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	9
propane	C ₃ H ₈	CH ₃ CH ₂ CH ₃	1		octane	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	18
butane	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	2		nonane	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	35
pentane	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	3		decane	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	75

Some important behavior trends and terminologies

1. The formulas and structures of these alkanes increase uniformly by a CH₂ increment.
2. A uniform variation of this kind in a series of compounds is called **homologous**.
3. These formulas all fit the **C_nH_{2n+2}** rule. This is also the highest possible H/C ratio for a stable hydrocarbon.
4. Since the H/C ratio in these compounds is at a maximum, we call them **saturated** (with hydrogen).

Beginning with butane (C₄H₁₀), and becoming more numerous with larger alkanes, we note the existence of alkane isomers. For example, there are five C₆H₁₄ isomers, shown below as abbreviated line formulas (**A** through **E**):



Although these distinct compounds all have the same molecular formula, only one (**A**) can be called hexane. How then are we to name the others?

The **IUPAC** system requires first that we have names for simple unbranched chains, as noted above, and second that we have names for simple alkyl groups that may be attached to the chains. Examples of some common **alkyl groups** are given in the following table. Note that the "ane" suffix is replaced by "**yl**" in naming groups. The symbol **R** is used to designate a generic (unspecified) alkyl group.

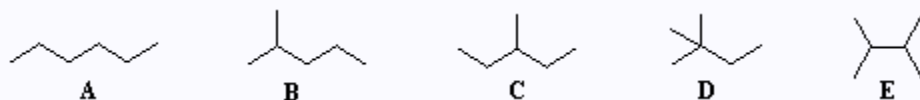
Table 2.4.2: Alkyl Groups Names

Group	CH ₃ –	C ₂ H ₅ –	CH ₃ CH ₂ CH ₂ –	(CH ₃) ₂ CH–	CH ₃ CH ₂ CH ₂ CH ₂ –	(CH ₃) ₂ CHCH ₂ –	CH ₃ CH ₂ CH(CH ₃)–	(CH ₃) ₃ C–	R–
Name	Methyl	Ethyl	Propyl	Isopropyl	Butyl	Isobutyl	sec-Butyl	tert-Butyl	Alkyl

IUPAC Rules for Alkane Nomenclature

1. Find and name the longest continuous carbon chain.
2. Identify and name groups attached to this chain.
3. Number the chain consecutively, starting at the end nearest a substituent group.
4. Designate the location of each substituent group by an appropriate number and name.
5. Assemble the name, listing groups in alphabetical order.
6. The prefixes di, tri, tetra etc., used to designate several groups of the same kind, are not considered when alphabetizing.

Example 2.4.1: Alkanes



The IUPAC names of the isomers of hexane are: **A** hexane **B** 2-methylpentane **C** 3-methylpentane **D** 2,2-dimethylbutane **E** 2,3-dimethylbutane

Alkyl Groups

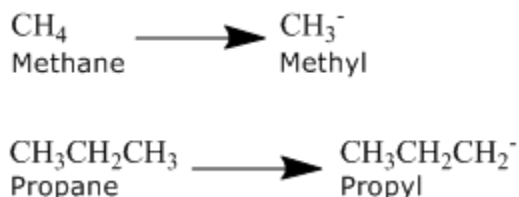
Halogen substituents are easily accommodated, using the names: fluoro (F-), chloro (Cl-), bromo (Br-) and iodo (I-).

Example 2.4.2: Halogen Substitution

For example, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$ would be named 1-bromo-3-methylbutane. If the halogen is bonded to a simple alkyl group an alternative "alkyl halide" name may be used. Thus, $\text{C}_2\text{H}_5\text{Cl}$ may be named chloroethane (no locator number is needed for a two carbon chain) or ethyl chloride.

Alkyl Groups

Alkanes can be described by the general formula $\text{C}_n\text{H}_{2n+2}$. An alkyl group is formed by removing one hydrogen from the alkane chain and is described by the formula $\text{C}_n\text{H}_{2n+1}$. The removal of this hydrogen results in a stem change from **-ane** to **-yl**. Take a look at the following examples.



The same concept can be applied to any of the straight chain alkane names provided in the table above.

Name	Molecular Formula	Condensed Structural Formula
Methane	CH_4	CH_4
Ethane	C_2H_6	CH_3CH_3
Propane	C_3H_8	$\text{CH}_3\text{CH}_2\text{CH}_3$
Butane	C_4H_{10}	$\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Pentane	C_5H_{12}	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$
Hexane	C_6H_{14}	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
Heptane	C_7H_{16}	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$
Octane	C_8H_{18}	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
Nonane	C_9H_{20}	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$
Decane	$\text{C}_{10}\text{H}_{22}$	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$

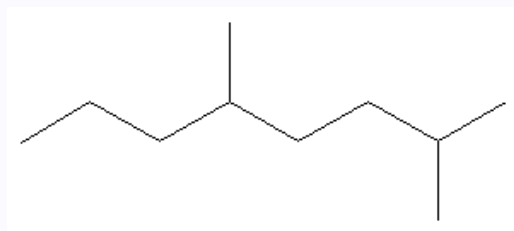
Name	Molecular Formula	Condensed Structural Formula
Undecane	C ₁₁ H ₂₄	CH ₃ (CH ₂) ₉ CH ₃
Dodecane	C ₁₂ H ₂₆	CH ₃ (CH ₂) ₁₀ CH ₃
Tridecane	C ₁₃ H ₂₈	CH ₃ (CH ₂) ₁₁ CH ₃
Tetradecane	C ₁₄ H ₃₀	CH ₃ (CH ₂) ₁₂ CH ₃
Pentadecane	C ₁₅ H ₃₂	CH ₃ (CH ₂) ₁₃ CH ₃
Hexadecane	C ₁₆ H ₃₄	CH ₃ (CH ₂) ₁₄ CH ₃
Heptadecane	C ₁₇ H ₃₆	CH ₃ (CH ₂) ₁₅ CH ₃
Octadecane	C ₁₈ H ₃₈	CH ₃ (CH ₂) ₁₆ CH ₃
Nonadecane	C ₁₉ H ₄₀	CH ₃ (CH ₂) ₁₇ CH ₃
Eicosane	C ₂₀ H ₄₂	CH ₃ (CH ₂) ₁₈ CH ₃

Three Rules for Naming Alkanes

1. Choose the longest, most substituted carbon chain containing a functional group.
2. A carbon bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substituent present must have the lowest possible number.
3. Take the alphabetical order into consideration; that is, after applying the first two rules given above, make sure that your substituents and/or functional groups are written in alphabetical order.

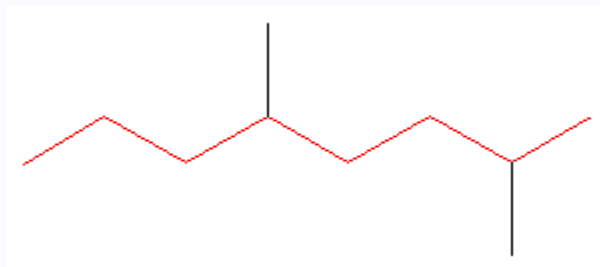
Example 2.4.3

What is the name of the follow molecule?



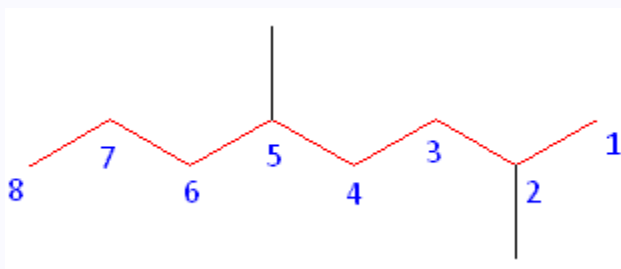
SOLUTION

Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example does not contain any functional groups, so we only need to be concerned with choosing the longest, most substituted carbon chain. The longest carbon chain has been highlighted in red and consists of eight carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional

groups, then any substitute present must have the lowest possible number. Because this example does not contain any functional groups, we only need to be concerned with the two substitutes present, that is, the two methyl groups. If we begin numbering the chain from the left, the methyls would be assigned the numbers 4 and 7, respectively. If we begin numbering the chain from the right, the methyls would be assigned the numbers 2 and 5. Therefore, to satisfy the second rule, numbering begins on the right side of the carbon chain as shown below. This gives the methyl groups the lowest possible numbering.

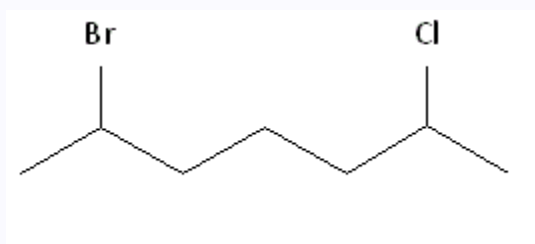


Rule 3: In this example, there is no need to utilize the third rule. Because the two substitutes are identical, neither takes alphabetical precedence with respect to numbering the carbons. This concept will become clearer in the following examples.

The name of this molecule is **2,5-dimethyloctane**

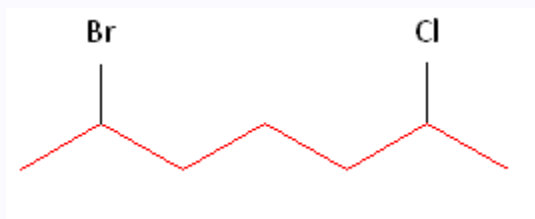
Example 2.4.4

What is the name of the follow molecule?

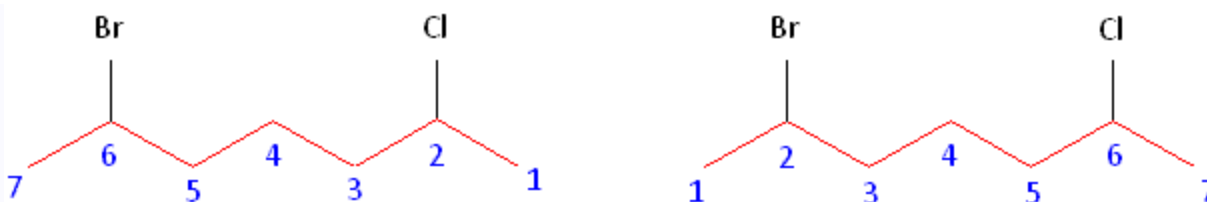


SOLUTION

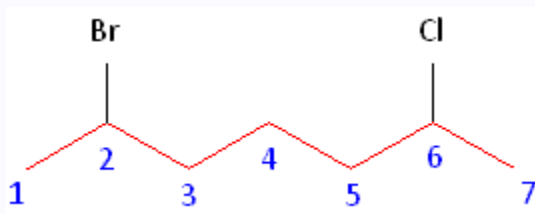
Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine. The longest carbon chain has been highlighted in red and consists of seven carbons.



Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. If there are no functional groups, then any substituent present must have the lowest possible number. In this example, numbering the chain from either the left or the right would satisfy this rule. If we number the chain from the left, bromine and chlorine would be assigned the second and sixth carbon positions, respectively. If we number the chain from the right, chlorine would be assigned the second position and bromine would be assigned the sixth position. In other words, whether we choose to number from the left or right, the functional groups occupy the second and sixth positions in the chain. To select the correct numbering scheme, we need to utilize the third rule.



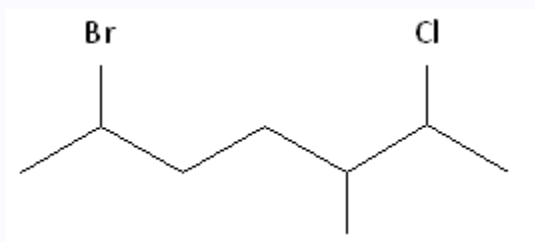
Rule #3: After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.



The name of this molecule is: **2-bromo-6-chloroheptane**

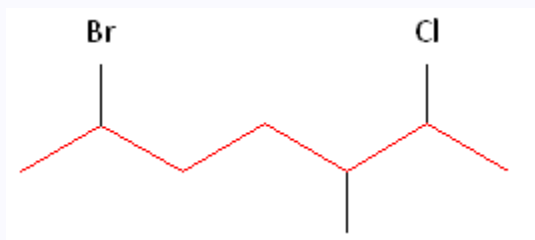
Example 2.4.5

What is the name of the follow molecule?



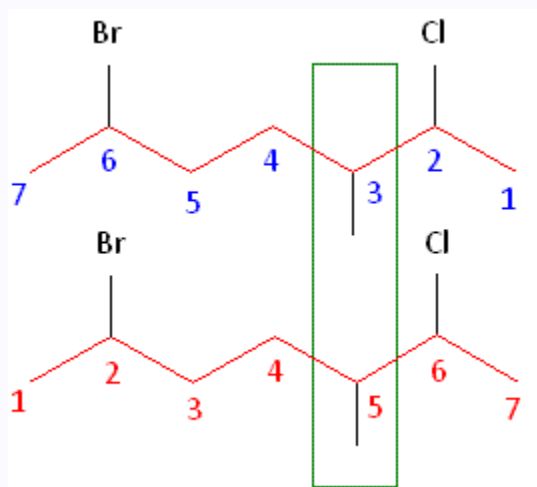
SOLUTION

Rule #1: Choose the longest, most substituted carbon chain containing a functional group. This example contains two functional groups, bromine and chlorine, and one substitute, the methyl group. The longest carbon chain has been highlighted in red and consists of seven carbons.

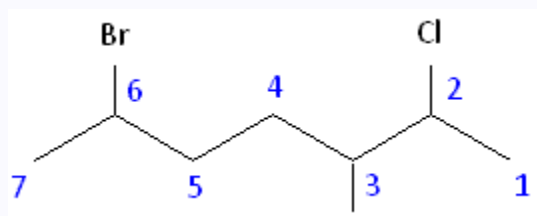


Rule #2: Carbons bonded to a functional group must have the lowest possible carbon number. After taking functional groups into consideration, any substitutes present must have the lowest possible carbon number. This particular example illustrates the **point of difference principle**. If we number the chain from the left, bromine, the methyl group and chlorine would occupy the second, fifth and sixth positions, respectively. This concept is illustrated in the second drawing below. If we number the chain from the right, chlorine, the methyl group and bromine would occupy the second, third and sixth positions, respectively, which is illustrated in the first drawing below. The position of the methyl, therefore, becomes a **point of difference**. In the first drawing, the methyl occupies the third position. In the second drawing, the methyl occupies the fifth position. To satisfy

the second rule, we want to choose the numbering scheme that provides the lowest possible numbering of this substitute. Therefore, the first of the two carbon chains shown below is correct.



Therefore, the first numbering scheme is the appropriate one to use.



Once you have determined the correct numbering of the carbons, it is often useful to make a list, including the functional groups, substitutes, and the name of the parent chain.

Rule #3: After applying the first two rules, take the alphabetical order into consideration. Alphabetically, bromine comes before chlorine. Therefore, bromine is assigned the second carbon position, and chlorine is assigned the sixth carbon position.

Parent chain: heptane Substituents: 2-chloro 3-methyl 6-bromo

The name of this molecule is: **6-bromo-2-chloro-3-methylheptane**

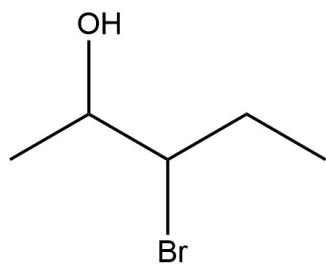
Exercises

3.4 Exercises

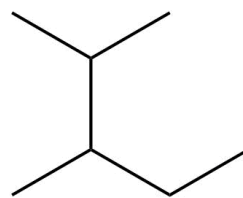
Questions

Q3.4.1

Are the following structures properly named, and if they are not, what is the correct naming?



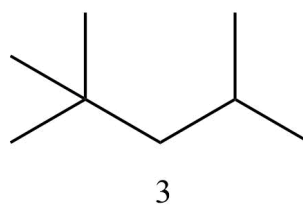
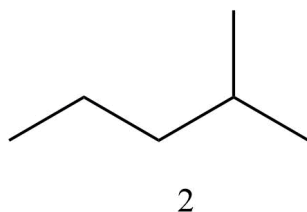
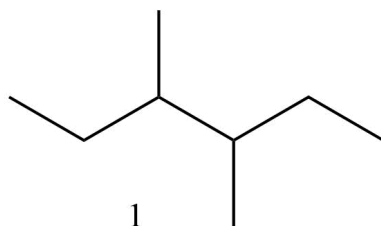
3-bromo-4-hydroxypentane



2-isopropylbutane

Q3.4.2

Give the name of the following molecules:



Solutions

S3.4.1

They are both labeled incorrectly:

3-bromo-2-hydroxypentane

2, 3-dimethylpentane

S3.4.2

1 = 3,4-Dimethyl hexane

2 = 2-methyl pentane

3 = 2,2,4-trimethyl pentane

Contributors

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- Prof. Steven Farmer ([Sonoma State University](#))
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2.5: Naming Cycloalkanes

Objectives

After completing this section, you should be able to

1. name a substituted or unsubstituted cycloalkane, given its Kekulé structure, shorthand structure or condensed structure.
2. draw the Kekulé, shorthand or condensed structure for a substituted or unsubstituted cycloalkane, given its IUPAC name.

Key Terms

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

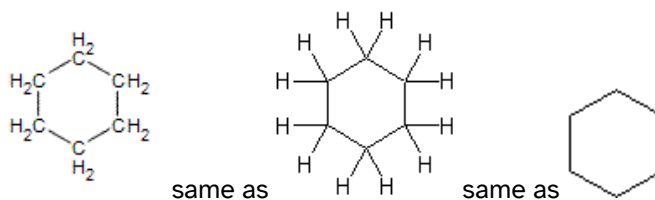
- cycloalkane

Study Notes

Provided that you have mastered the IUPAC system for naming alkanes, you should find that the nomenclature of cycloalkanes does not present any particular difficulties.

Many organic compounds found in nature contain rings of carbon atoms. These compounds are known as cycloalkanes. **Cycloalkanes** have one or more rings of carbon atoms. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds. The simplest examples of this class consist of a single, un-substituted carbon ring, and these form a homologous series similar to the unbranched alkanes.

Like alkanes, cycloalkane molecules are often drawn as skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens. Cyclohexane, one of the most common cycloalkanes is shown below as an example.

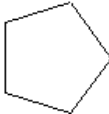
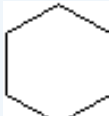
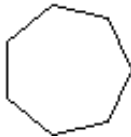
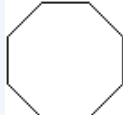
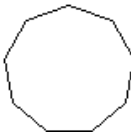
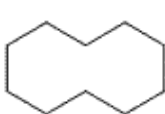


Cyclic hydrocarbons have the prefix "cyclo-". The IUPAC names, molecular formulas, and skeleton structures of the first ten cycloalkanes are given in Table 4.1.1. Note that the general formula for a cycloalkane composed of n carbons is C_nH_{2n} , and not C_nH_{2n+2} as for alkanes. Although a cycloalkane has two fewer hydrogens than the equivalent alkane, each carbon is bonded to four other atoms so are still considered to be **saturated** with hydrogen.

Table 4.1.1: Examples of Simple Cycloalkanes

Cycloalkane	Molecular Formula	Skeleton Structure
Cyclopropane	C_3H_6	

Table 4.1.1: Examples of Simple Cycloalkanes

Cycloalkane	Molecular Formula	Skeleton Structure
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	
Cycloheptane	C_7H_{14}	
Cyclooctane	C_8H_{16}	
Cyclononane	C_9H_{18}	
Cyclodecane	$C_{10}H_{20}$	

IUPAC Rules for Nomenclature

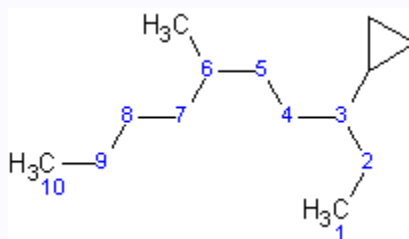
The naming of substituted cycloalkanes follows the same basic steps used in naming alkanes.

1. Determine the parent chain.
2. Number the substituents of the ring so that the sum of the numbers is the lowest possible.
3. Name the substituents and place them in alphabetical order.

More specific rules for naming substituted cycloalkanes with examples are given below.

1. Determine the cycloalkane to use as the parent. If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkanes substituents have an ending "-yl". If there are two cycloalkanes in the molecule, use the cycloalkane with the higher number of carbons as the parent.

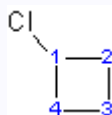
Example 4.1.1



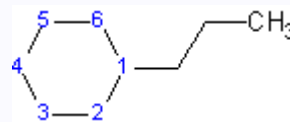
The longest straight chain contains 10 carbons, compared with cyclopropane, which only contains 3 carbons. The parent chain in this molecule is decane and cyclopropane is a substituent, . The name of this molecule is 3-cyclopropyl-3,10-dimethyldecane.

2) When there is only one substituent on the ring, the ring carbon attached to the substituent is automatically carbon #1. Indicating the number of the carbon with the substituent in the name is optional.

Example 4.1.2



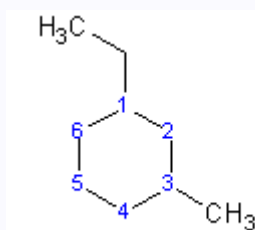
1-chlorocyclobutane or chlorocyclobutane



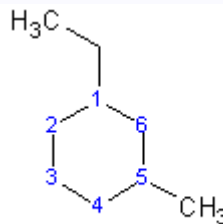
1-propylcyclohexane or propylcyclohexane

If there are multiple substituents on the ring, number the carbons of the cycloalkane so that the carbons with substituents have the lowest possible number. A carbon with multiple substituents should have a lower number than a carbon with only one substituent or functional group. One way to make sure that the lowest number possible is assigned is to number the carbons so that when the numbers corresponding to the substituents are added, their sum is the lowest possible.

Example 4.1.3

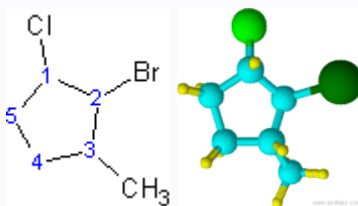


1-ethyl-3-methylcyclohexane (1+3=4) **NOT** 1-ethyl-5-methylcyclohexane (1+5=6)



3) When naming the cycloalkane, the substituents must be placed in alphabetical order. Remember the prefixes di-, tri-, etc. , are not used for alphabetization.

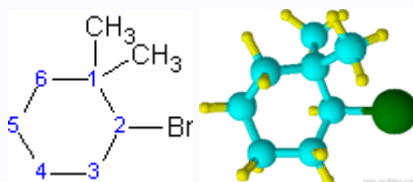
Example 4.1.4



2-bromo-1-chloro-3-methylcyclopentane

Notice that "f" of fluoro alphabetically precedes the "m" of methyl.

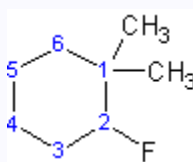
Example 4.1.5



(2-bromo-1,1-dimethylcyclohexane)

Although "di" alphabetically precedes "f", "di" is not used in determining the alphabetical order.

Example 4.1.6



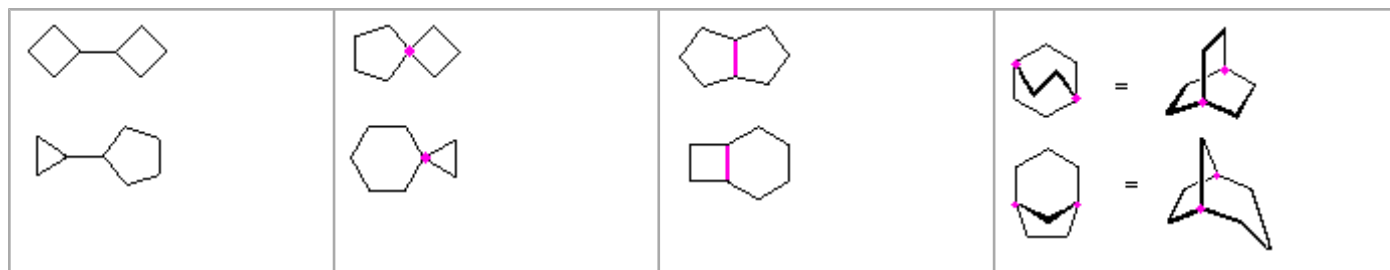
(2-fluoro-1,1-dimethylcyclohexane **NOT** 1,1-dimethyl-2-fluorocyclohexane)

Hydrocarbons having more than one ring are common, and are referred to as **bicyclic** (two rings), **tricyclic** (three rings) and in general, **polycyclic** compounds. The molecular formulas of such compounds have H/C ratios that decrease with the number of rings. In general, for a hydrocarbon composed of **n carbon atoms** associated with **m rings** the formula is: **C_nH_(2n + 2 - 2m)**. The structural relationship of rings in a polycyclic compound can vary. They may be separate and independent, or they may share one or two common atoms. Some examples of these possible arrangements are shown in the following table.

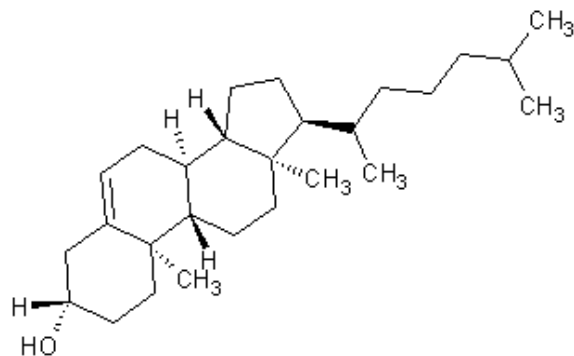
Table
4.1.2:
Examples
of
Isomeric

Bicycloalkanes

Isolated Rings	Spiro Rings	Fused Rings	Bridged Rings
No common atoms	One common atom	One common bond	Two common atoms



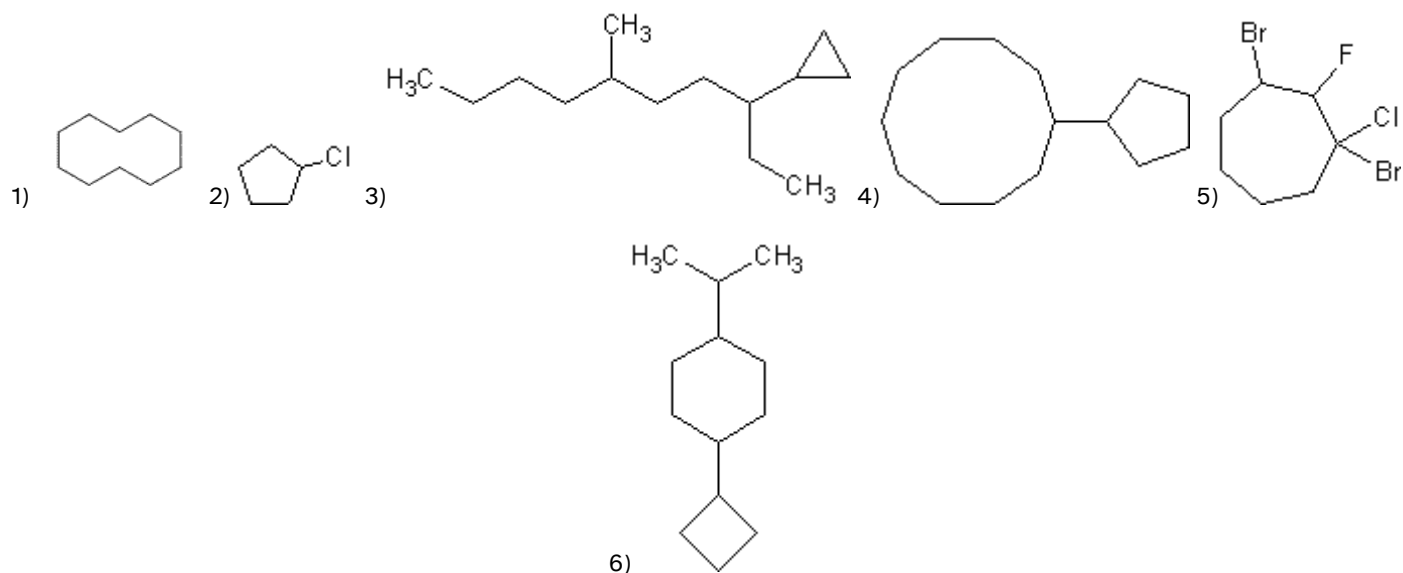
Polycyclic compounds, like cholesterol shown below, are biologically important and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules, and will not be covered here.



Cholesterol (polycyclic)

Problems

Name the following structures. (Note: The structures are complex for practice purposes and may not be found in nature.)

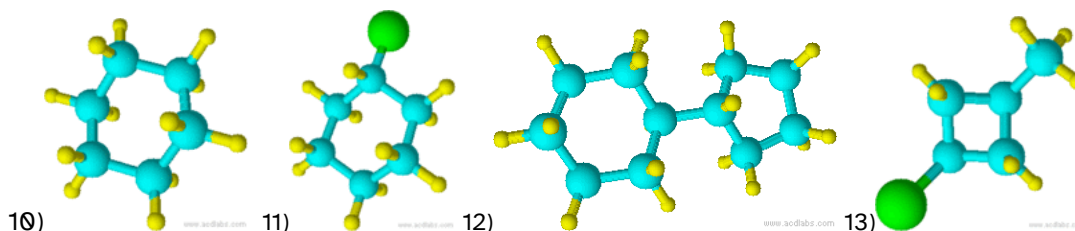


Draw the following structures.

- 7) 1,1-dibromo-3-butyl-5-fluoro-7-methylcyclooctane
- 8) 1,1-dibromo-2,3-dichloro-4-propylcyclobutane
- 9) 1-ethyl-2-methyl-1,3-dipropylcyclopentane

Name the following structures.

Blue=Carbon Yellow=Hydrogen Green=Chlorine

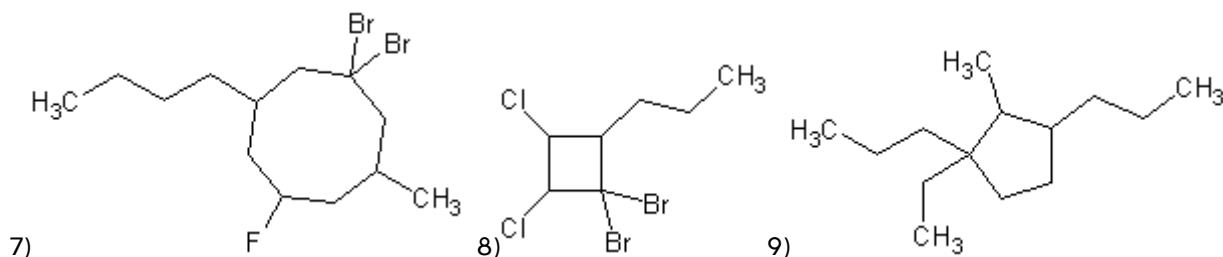


Answers to Practice Problems

1) cyclodecane 2) chlorocyclopentane or 1-chlorocyclopentane

3) 6-methyl-3-cyclopropyldecane 4) cyclopentylcyclodecane or 1-cyclopentylcyclodecane 5) 1,3-dibromo-1-chloro-2-fluorocycloheptane

6) 1-cyclobutyl-4-isopropylcyclohexane



10) cyclohexane 11) chlorocyclohexane 12) cyclopentylcyclohexane 13) 1-chloro-3-methylcyclobutane

Outside links

- [More Practice Problems on Nomenclature of Cycloalkanes](#)
- Vollhardt, Schore. Organic Chemistry. 5th ed.
- Wikipedia: Cycloalkanes
- <http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm>
- <http://www.chemguide.co.uk/organicprops/alkanes/background.html>
- <http://www.cem.msu.edu/~reusch/VirtualText/nomen1.htm>
- <http://science.csustan.edu/nhuy/chem...IVNamecya.htm>
- <http://en.wikibooks.org/wiki/Organic...s/Cycloalkanes>

References

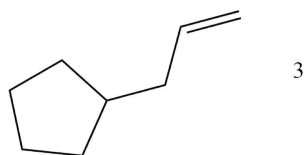
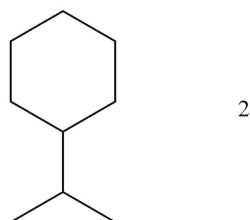
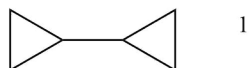
1. ACD/ChemSketch Freeware, version 11.0, Advanced Chemistry Development, Inc., Toronto, ON, Canada, www.acdlabs.com, 2008.
2. Bruice, Paula Yurkanis. Organic Chemistry. 5th. CA. Prentice Hall, 2006.
3. Fryhle, C.B. and G. Solomons. Organic Chemistry. 9th ed. Danvers, MA: Wiley, 2008.
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5. Sadava, Heller, Orians, Purves, Hillis. Life The Science of Biology. 8th ed. Sunderland, MA: W.H. Freeman, 2008.
6. Vollhardt, K. Peter C., and Neil E. Schore. Organic Chemistry. 5th ed. New York: W.H. Freeman, 2007.

Exercises

Questions

Q4.1.1

Name the following compounds:



Q4.1.2

Draw the following structures

1 = 1,2-dimethylcyclohexane

2 = 2-cyclopropyl butane

3 = 1,2,3-trimethyl cyclopentane

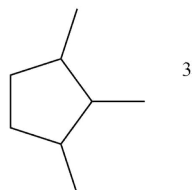
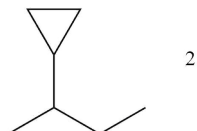
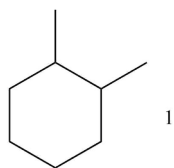
Solutions

S4.1.1

1 = 1-cyclopropyl cyclopropane

2 = 1-isopropyl cyclohexane

3 = 2-propenyl cyclopentane



Contributors

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- Dr. Kelly Matthews (Senior Professor of Chemistry, Harrisburg Area Community College)

2.6: The Nature of Chemical Bonds: Molecular Orbital Theory

Objectives

After completing this section, you should be able to

1. describe the formation of covalent bonds in terms of molecular orbitals.
2. account for differences in bond length and strength in terms of the efficiency with which atomic orbitals overlap.
3. draw simple molecular orbital diagrams (e.g., for the H_2 molecule) showing the formation of bonding and anti-bonding orbitals.

Key Terms

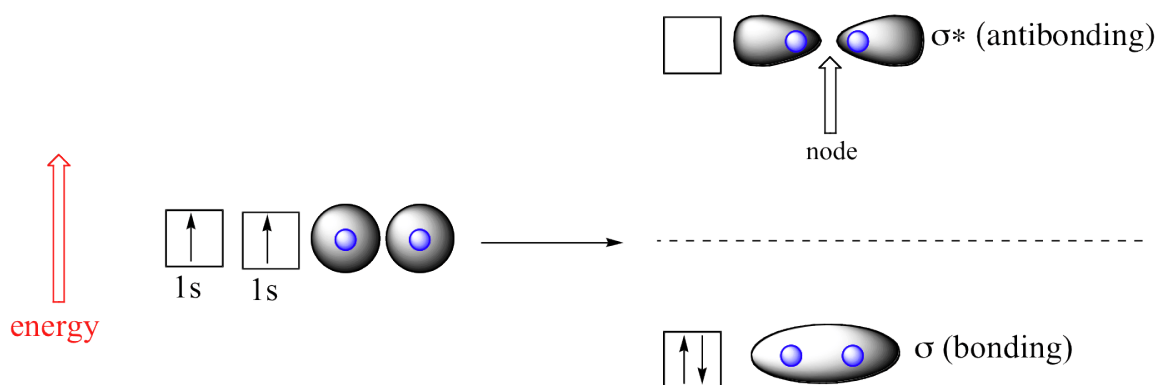
Make certain that you can define, and use in context, the key terms below.

- anti-bonding molecular orbital
- bonding molecular orbital
- molecular orbital (MO) theory

As we have seen, valence bond theory does a remarkably good job of explaining the bonding geometry and properties of many organic compounds. There are some areas, however, where the valence bond theory falls short. It fails to adequately account, for example, for some interesting properties of compounds that contain alternating double and single bonds. In order to understand these properties, we need to think about chemical bonding in a new way, using the ideas of molecular orbital (MO) theory.

Another look at the H_2 molecule: bonding and anti-bonding sigma molecular orbitals

Let's consider again the simplest possible covalent bond: the one in molecular hydrogen (H_2). When we described the hydrogen molecule using valence bond theory, we said that the two $1s$ orbitals from each atom overlap, allowing the two electrons to be shared and thus forming a covalent bond. In molecular orbital theory, we make a further statement: we say that the two atomic $1s$ orbitals don't just overlap, they actually *combine to form two completely new orbitals*. These two new orbitals, instead of describing the likely location of an electron around a single nucleus, describe the location of an electron pair around two or more nuclei. The bonding in H_2 , then, is due to the formation of a new **molecular orbital (MO)**, in which a pair of electrons is delocalized around two hydrogen nuclei. An important principle of quantum mechanical theory is that when orbitals combine, the number of orbitals before the combination takes place must equal the number of new orbitals that result – orbitals don't just disappear! We saw this previously when we discussed hybrid orbitals: one s and three p orbitals make four sp^3 hybrids. When two atomic $1s$ orbitals combine in the formation of H_2 , the result is two molecular orbitals called **sigma (σ) orbitals**. According to MO theory, the first sigma orbital is lower in energy than either of the two isolated atomic $1s$ orbitals – thus this sigma orbital is referred to as a **bonding molecular orbital**. The second, **sigma-star (σ^*) orbital** is higher in energy than the two atomic $1s$ orbitals, and is referred to as an **anti-bonding molecular orbital**. In MO theory, a star (*) sign always indicates an anti-bonding orbital.



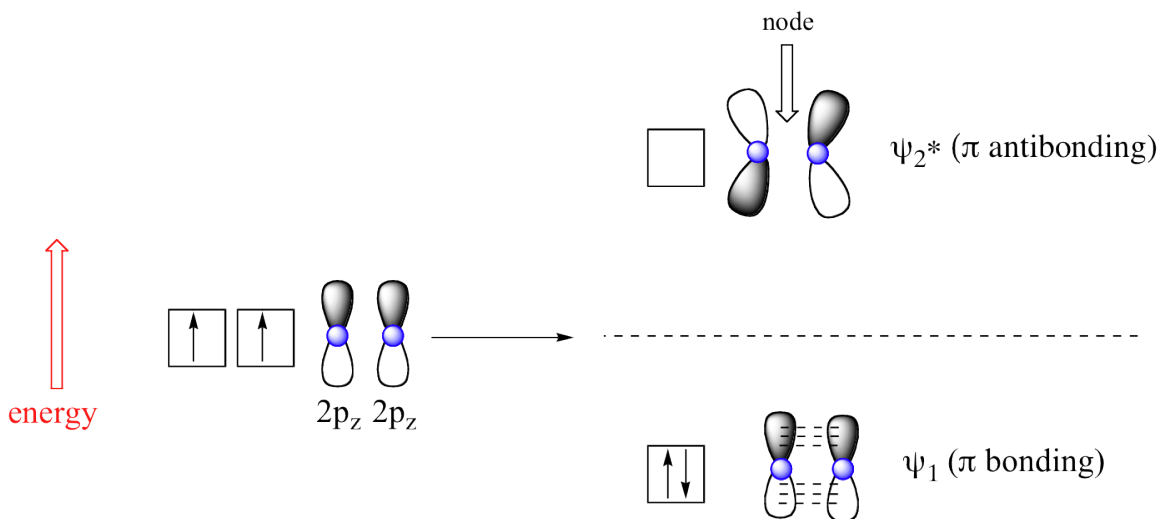
Following the *aufbau* ('building up') principle, we place the two electrons in the H_2 molecule in the lowest energy molecular orbital, which is the (bonding) sigma orbital.

The bonding sigma orbital, which holds both electrons in the ground state of the molecule, is egg-shaped, encompassing the two nuclei, and with the highest likelihood of electrons being in the area between the two nuclei. The high-energy, anti-bonding sigma-star orbital can be visualized as a pair of droplets, with areas of higher electron density near each nucleus and a 'node', (area of zero electron density) midway between the two nuclei.

Remember that we are thinking here about electron behavior as *wave behavior*. When two separate waves combine, they can do so with what is called constructive interference, where the two amplitudes reinforce one another, or destructive interference, where the two amplitudes cancel one another out. Bonding MO's are the consequence of constructive interference between two atomic orbitals which results in an attractive interaction and an increase in electron density between the nuclei. Anti-bonding MO's are the consequence of destructive interference which results in a repulsive interaction and a 'canceling out' of electron density between the nuclei (in other words, a node).

MO theory and pi bonds - conjugation

The advantage of MO theory becomes more apparent when we think about pi bonds, especially in those situations where two or more pi bonds are able to interact with one another. Let's first consider the pi bond in ethene from an MO theory standpoint (in this example we will be disregarding the various sigma bonds, and thinking *only* about the pi bond). According to MO theory, the two atomic $2p_z$ orbitals combine to form two **pi (π) molecular orbitals**, one a low-energy π bonding orbital and one a high-energy **pi-star (π^*) anti-bonding molecular orbital**. These are sometimes denoted, in MO diagrams like the one below, with the Greek letter psi (Ψ) instead of π .



In the bonding ψ_1 orbital, the two shaded lobes of the $2p_z$ orbitals interact constructively with each other, as do the two

unshaded lobes (remember, the shading choice represents mathematical (+) and (-) signs for the wavefunction). Therefore, there is increased electron density between the nuclei in the molecular orbital – this is why it is a bonding orbital.

In the higher-energy anti-bonding Ψ_2^* orbital, the shaded lobe of one $2p_z$ orbital interacts destructively with the unshaded lobe of the second $2p_z$ orbital, leading to a node between the two nuclei and overall repulsion.

By the *aufbau* principle, the two electrons from the two atomic orbitals will be paired in the lower-energy Ψ_1 orbital when the molecule is in the ground state.

Exercises

1. Draw a simple molecular orbital diagram for each of the following molecules
 - a. nitrogen, N_2 .
 - b. oxygen, O_2 .

Answers:

[Answers](#)

Contributors

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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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

Objective

After completing this section, you should be able to describe the structure of methane in terms of the sp^3 hybridization of the central carbon atom.

Key Terms

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

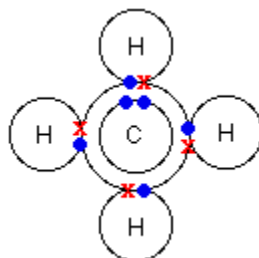
- bond angle
- hybridization
- sp^3 hybrid

Study Notes

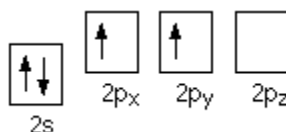
The tetrahedral shape is a very important one in organic chemistry, as it is the basic shape of all compounds in which a carbon atom is bonded to four other atoms. Note that the tetrahedral bond angle of $\angle\text{H-C-H}$ is 109.5° .

Bonding in Methane, CH_4 [Edit section](#)

We are starting with methane because it is the simplest case which illustrates the sort of processes involved. You might remember that the bonding picture of methane looks like this.



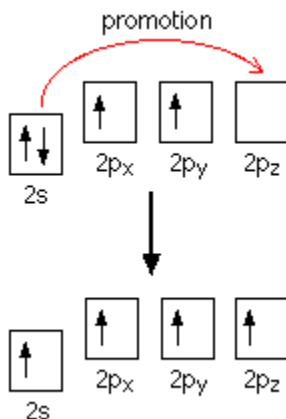
There is a serious mismatch between this structure and the modern electronic structure of carbon, $1s^2 2s^2 2p_x^1 2p_y^1$. The modern structure shows that there are only 2 unpaired electrons to share with hydrogens, instead of the 4 which the bonding picture requires.



You can see this more readily using the electrons-in-boxes notation. Only the 2nd level electrons are shown. The $1s^2$ electrons are too deep inside the atom to be involved in bonding. The only electrons directly available for sharing are the 2p electrons. Why then isn't methane CH_2 ?

Promotion of an electron

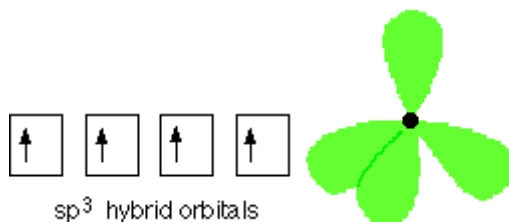
When bonds are formed, energy is released and the system becomes more stable. If carbon forms 4 bonds rather than 2, twice as much energy is released and so the resulting molecule becomes even more stable. There is only a small energy gap between the 2s and 2p orbitals, and so it pays the carbon to provide a small amount of energy to promote an electron from the 2s to the empty 2p to give 4 unpaired electrons. The extra energy released when the bonds form more than compensates for the initial input.



The carbon atom is now said to be in an excited state. Now that we've got 4 unpaired electrons ready for bonding, another problem arises. In methane all the carbon-hydrogen bonds are identical, but our electrons are in two different kinds of orbitals. You aren't going to get four identical bonds unless you start from four identical orbitals.

Hybridization

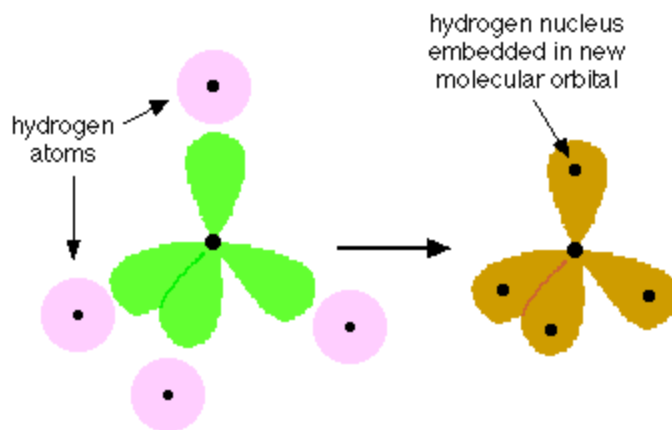
The electrons rearrange themselves again in a process called hybridization. This reorganizes the electrons into four identical hybrid orbitals called sp^3 hybrids (because they are made from one s orbital and three p orbitals). You should read " sp^3 " as "s p three" - not as "s p cubed".



sp^3 hybrid orbitals look a bit like half a p orbital, and they arrange themselves in space so that they are as far apart as possible. You can picture the nucleus as being at the center of a tetrahedron (a triangularly based pyramid) with the orbitals pointing to the corners. For clarity, the nucleus is drawn far larger than it really is.

What happens when the bonds are formed?

Remember that hydrogen's electron is in a 1s orbital - a spherically symmetric region of space surrounding the nucleus where there is some fixed chance (say 95%) of finding the electron. When a covalent bond is formed, the atomic orbitals (the orbitals in the individual atoms) merge to produce a new molecular orbital which contains the electron pair which creates the bond.



Four molecular orbitals are formed, looking rather like the original sp^3 hybrids, but with a hydrogen nucleus embedded in each lobe. Each orbital holds the 2 electrons that we've previously drawn as a dot and a cross. The principles involved - promotion of electrons if necessary, then hybridization, followed by the formation of molecular orbitals - can be applied to any covalently-bound molecule.

Contributors

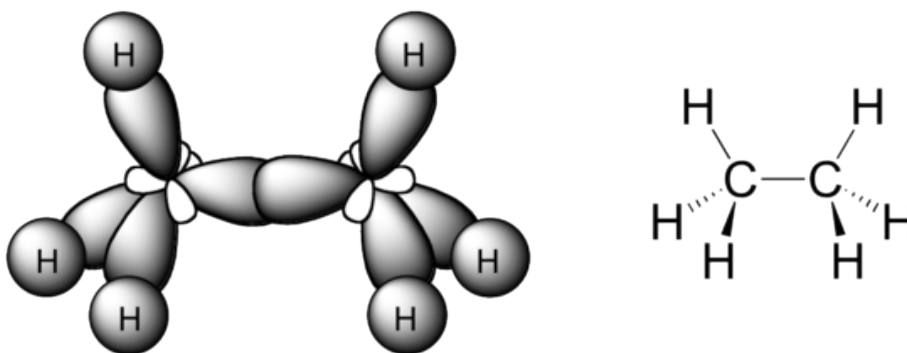
- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

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

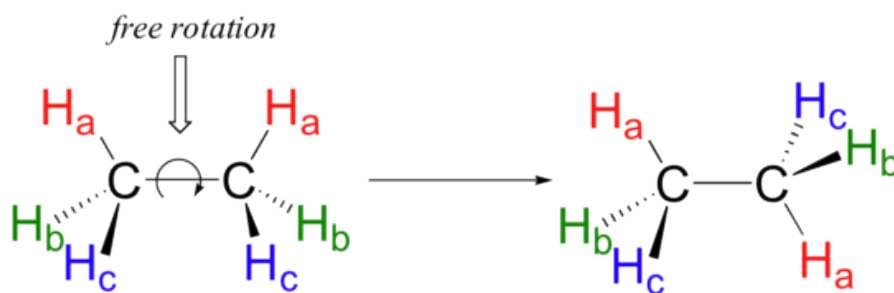
Objective

After completing this section, you should be able to describe the structure of ethane in terms of the sp^3 hybridization of the two carbon atoms present in the molecule ethane.

In the ethane molecule, the bonding picture according to valence orbital theory is very similar to that of methane. Both carbons are sp^3 -hybridized, meaning that both have four bonds arranged with tetrahedral geometry. The carbon-carbon bond, with a bond length of 1.54 Å, is formed by overlap of one sp^3 orbital from each of the carbons, while the six carbon-hydrogen bonds are formed from overlaps between the remaining sp^3 orbitals on the two carbons and the 1s orbitals of hydrogen atoms. All of these are sigma bonds.



Because they are formed from the end-on-end overlap of two orbitals, *sigma bonds are free to rotate*. This means, in the case of ethane molecule, that the two methyl (CH_3) groups can be pictured as two wheels on a hub, each one able to rotate freely with respect to the other.



In chapter 3 we will learn more about the implications of rotational freedom in sigma bonds, when we discuss the ‘conformation’ of organic molecules.

The sp^3 bonding picture is also used to describe the bonding in amines, including ammonia, the simplest amine. Just like the carbon atom in methane, the central nitrogen in ammonia is sp^3 -hybridized. With nitrogen, however, there are five rather than four valence electrons to account for, meaning that three of the four hybrid orbitals are half-filled and available for bonding, while the fourth is fully occupied by a non-bonding pair of electrons.

C_2H_4 , also known as ethylene or ethene, is a gaseous material created synthetically through steam cracking. In nature, it is released in trace amounts by plants to signal their fruits to ripen. Ethene consists of two sp^2 -hybridized carbon atoms, which are sigma bonded to each other and to two hydrogen atoms each. The remaining non-hybridized p orbitals on each carbon overlap to form a pi bond, which gives ethene its reactivity.

Exercise

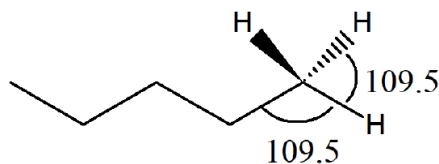
Questions

Q1.7.1

Draw pentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, predict the bond angles within this molecule.

Solutions

S1.7.1



All the bond angles will be the same size.

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

Objectives

After completing this section, you should be able to

1. account for the formation of carbon-carbon double bonds using the concept of sp^2 hybridization.
2. describe a carbon-carbon double bond as consisting of one σ bond and one π bond.
3. explain the difference between a σ bond and a π bond in terms of the way in which p orbitals overlap.

Key Terms

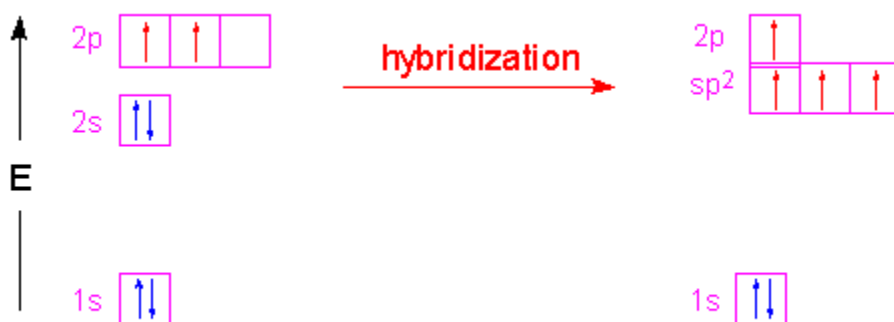
Make certain that you can define, and use in context, the key terms below.

- pi (π) bond
- sp^2 hybrid

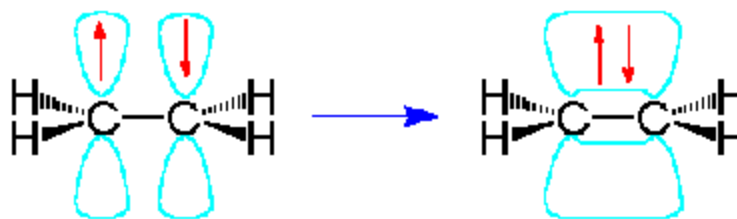
Bonding in Ethylene

A key component of using Valence Bond Theory correctly is being able to draw the Lewis dot diagram correctly. Ethylene, commonly known as ethene, has a double bond between the carbons and single bonds between each hydrogen and carbon: each bond is represented by a pair of dots, which represent electrons. Each carbon requires a full octet and each hydrogen requires a pair of electrons. The correct Lewis structure for ethylene is shown below:

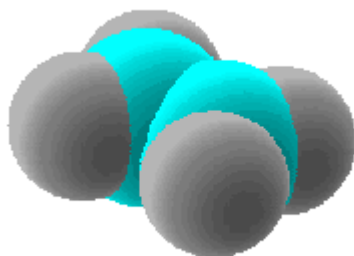
In the molecule ethene, both carbon atoms will be sp^2 hybridized and have one unpaired electron in a non-hybridized p orbital.



These p -orbitals will undergo parallel overlap and form one sigma bond with bean-shaped probability areas above and below the plane of the six atoms. This pair of bean-shaped probability areas constitutes one pi bond and the pair of electrons in this bond can be found in either bean-shaped area.

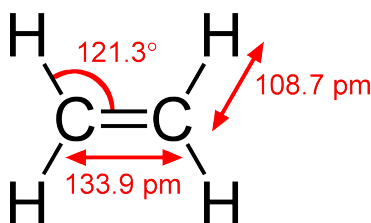


The 3-dimensional model of ethene is therefore planar with H-C-H and H-C-C bond angles of 120° . The pi bond is not shown in this picture.



[Edit section](#)

Valence Shell Electron Pair Repulsion (VSEPR) Theory is used to predict the bond angles and spatial positions of the carbon and hydrogen atoms of ethene and to determine the bond order of the carbon atoms (the number of bonds formed between them). Each carbon atom is of the general arrangement AX_3 , where A is the central atom surrounded by three other atoms (denoted by X); compounds of this form adopt trigonal planar geometry, forming 120° degree bond angles. In order for the non-hybridized p orbitals to successfully overlap, the CH_2 must be coplanar: therefore, C_2H_4 is a planar molecule and each bond angle is about 120° degrees. The diagram below shows the bond lengths and hydrogen-carbon-carbon bond angles of ethene:



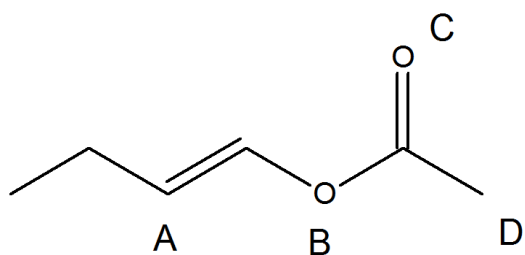
According to valence bond theory, two atoms form a covalent bond through the overlap of individual half-filled valence atomic orbitals, each containing one unpaired electron. In ethene, each hydrogen atom has one unpaired electron and each carbon is sp^2 hybridized with one electron each sp^2 orbital. The fourth electron is in the p orbital that will form the pi bond. The bond order for ethene is simply the number of bonds between each atom: the carbon-carbon bond has a bond order of two, and each carbon-hydrogen bond has a bond order of one.

Exercise

Questions

Q1.8.1

Consider the following molecule:



At each atom, what is the hybridization and the bond angle? At atom A draw the molecular orbital.

Solutions

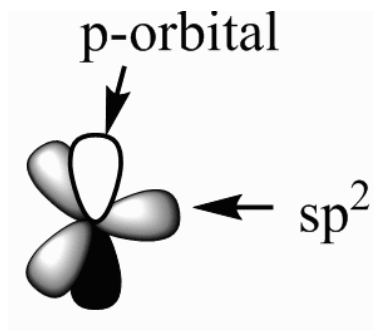
S1.8.1

A - sp^2 , 120°

B - sp^3 , 109°

C - sp^2 , 120° (with the lone pairs present)

D - sp^3 , 109°



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2.10: sp Hybrid Orbitals and the Structure of Acetylene

Objectives

After completing this section, you should be able to

1. use the concept of sp hybridization to account for the formation of carbon-carbon triple bonds, and describe a carbon-carbon triple bond as consisting of one σ bond and two π bonds.
2. list the approximate bond lengths associated with typical carbon-carbon single bonds, double bonds and triple bonds. [You may need to review Sections 1.7 and 1.8.]
3. list the approximate bond angles associated with sp^3 -, sp^2 - and sp -hybridized carbon atoms and predict the bond angles to be expected in given organic compounds. [If necessary, review Sections 1.6, 1.7 and 1.8.]
4. account for the differences in bond length, bond strength and bond angles found in compounds containing sp^3 -, sp^2 - and sp -hybridized carbon atoms, such as ethane, ethylene and acetylene.

Key Terms

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

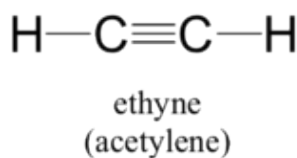
- sp hybrid orbital

Study Notes

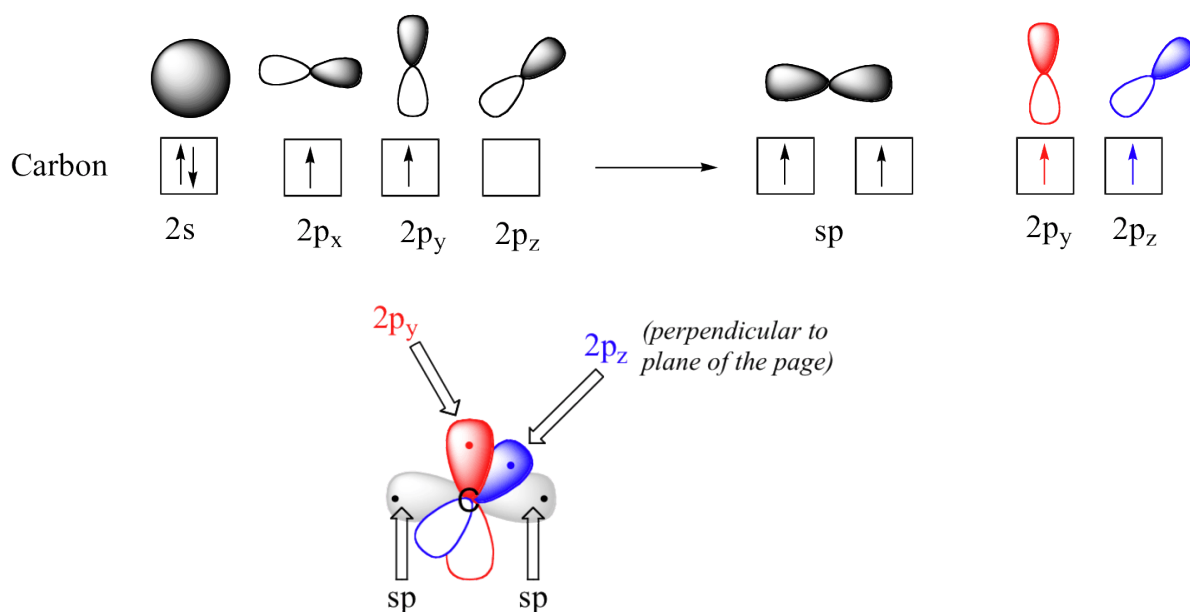
The bond angles associated with sp^3 -, sp^2 - and sp -hybridized carbon atoms are approximately 109.5° , 120° and 180° , respectively.

Bonding in acetylene

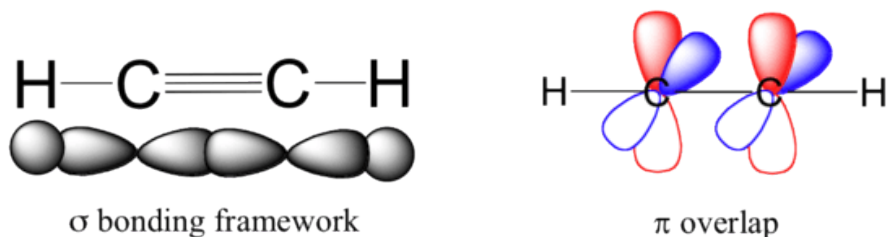
Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (another common name is acetylene), the simplest alkyne.



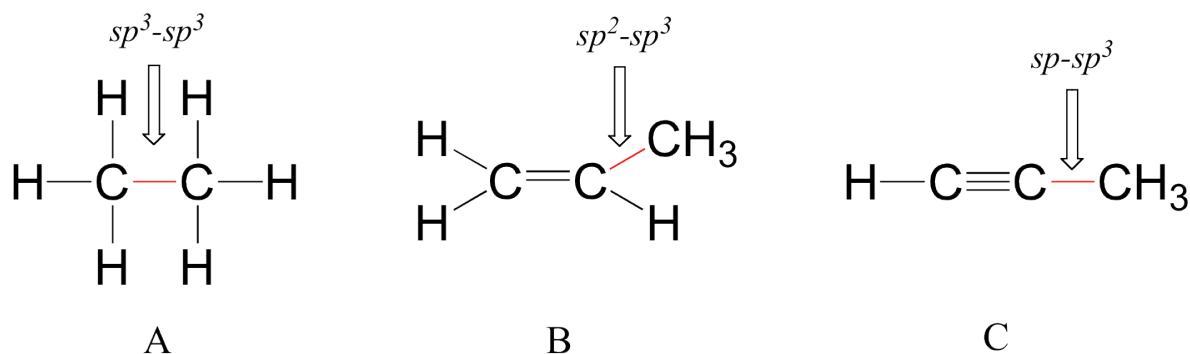
This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only $1.20\text{\AA}$ long. In the hybrid orbital picture of acetylene, both carbons are **sp -hybridized**. In an sp -hybridized carbon, the $2s$ orbital combines with the $2p_x$ orbital to form two sp hybrid orbitals that are oriented at an angle of 180° with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain non-hybridized, and are oriented perpendicularly along the y and z axes, respectively.



The C-C sigma bond is formed by the overlap of one sp orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second sp orbital on each carbon with a $1s$ orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of p orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).



The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two sp^3 orbitals.



In alkene B, however, the carbon-carbon single bond is the result of overlap between an sp^2 orbital and an sp^3 orbital, while in alkyne C the carbon-carbon single bond is the result of overlap between an sp orbital and an sp^3 orbital. These are all single bonds, but the single bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one s orbital and one p orbital, and thus it has 50% s character and 50% p character. sp^2 orbitals, by comparison, have 33% s character and 67% p character, while sp^3 orbitals have 25% s character and 75% p character. Because of their spherical shape, $2s$ orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to $2p$ orbitals. Consequently, bonds involving $sp + sp^3$ overlap (as in alkyne C) are shorter and stronger than bonds involving $sp^2 + sp^3$ overlap (as in alkene B). Bonds involving sp^3-sp^3 overlap (as in alkane A) are the longest and weakest of the group, because of the 75% ' p ' character of the hybrids.

Comparison of C-C bonds Ethane, Ethylene, and Acetylene

Molecule	Bond	Bond Strength (kJ/mol)	Bond Length (pm)
Ethane, CH_3CH_3	$(sp^3) \text{ C-C } (sp^3)$	376	154
Ethylene, $\text{H}_2\text{C=CH}_2$	$(sp^2) \text{ C=C } (sp^2)$	728	134
Acetylene, $\text{HC}\equiv\text{CH}$	$(sp) \text{ C}\equiv\text{C } (sp)$	965	120

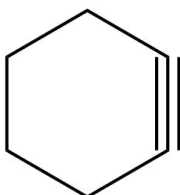
Notice that as the bond order increases the bond length decreases and the bond strength increases.

Exercises

Questions

Q1.9.1

1-Cyclohexyne is a very strained molecule. By looking at the molecule explain why there is such a intermolecular strain using the knowledge of hybridization and bond angles.



Solutions

S1.9.1

The alkyne is a sp hybridized orbital. By looking at a sp orbital, we can see that the bond angle is 180° , but in cyclohexane the regular angles would be 109.5° . Therefore the molecule would be strained to force the 180° to be a 109° .

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2.11: Drawing Chemical Structures

Objectives

After completing this section, you should be able to

1. propose one or more acceptable Kekulé structures (structural formulas) for any given molecular formula
2. write the molecular formula of a compound, given its Kekulé structure.
3. draw the shorthand structure of a compound, given its Kekulé structure.
4. interpret shorthand structures and convert them to Kekulé structures.
5. write the molecular formula of a compound, given its shorthand structure.

Study Notes

When drawing the structure of a neutral organic compound, you will find it helpful to remember that

- each carbon atom has four bonds.
- each nitrogen atom has three bonds.
- each oxygen atom has two bonds.
- each hydrogen atom has one bond.

It is necessary to draw structural formulas for organic compounds because in most cases a molecular formula does not uniquely represent a single compound. Different compounds having the same molecular formula are called **isomers**, and the prevalence of organic isomers reflects the extraordinary versatility of carbon in forming strong bonds to itself and to other elements. When the group of atoms that make up the molecules of different isomers are bonded together in fundamentally different ways, we refer to such compounds as **constitutional isomers**. There are seven constitutional isomers of $C_4H_{10}O$, and structural formulas for these are drawn in the following table. These formulas represent all known and possible $C_4H_{10}O$ compounds, and display a common structural feature. There are no double or triple bonds and no rings in any of these structures.

Table 2.11.1: Structural Formulas for $C_4H_{10}O$ isomers

Kekulé Formula	Condensed Formula	Shorthand Formula
	$CH_3(CH_2)_3OH$	
	$C_2H_5(OH)CH_3$	
	$(CH_3)CHCH_2OH$	
	$(CH_3)_3COH$	
	$CH_3(CH_2)_2OCH_3$	
	$(CH_3)_2CHOCH_3$	

Simplification of structural formulas may be achieved without any loss of the information they convey. In **condensed structural**

formulas the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens. **Shorthand (line) formulas** omit the symbols for carbon and hydrogen entirely (unless the hydrogen is bonded to an atom other than carbon). Each straight line segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogens is calculated from the tetravalency of carbon. Non-bonding valence shell electrons are omitted in these formulas.

Developing the ability to visualize a three-dimensional structure from two-dimensional formulas requires practice, and in most cases the aid of molecular models. As noted earlier, many kinds of model kits are available to students and professional chemists, and the beginning student is encouraged to obtain one.

Kekulé Formula

A Kekulé Formula or structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. Structural formulas are helpful because they explain the properties and structure of the compound which empirical and molecular formulas cannot always represent.

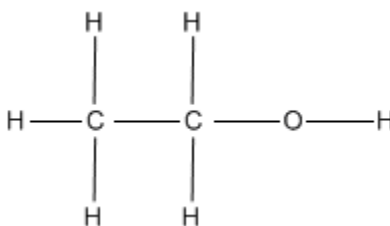


Figure 2.11.1: Kekulé Formula for Ethanol

Condensed Formula

Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together.

Ex. Condensed Structural Formula for Ethanol: $\text{CH}_3\text{CH}_2\text{OH}$ (Molecular Formula for Ethanol $\text{C}_2\text{H}_6\text{O}$).

Shorthand Formula

Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letters with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are then assumed to complete each of carbon's four bonds. All other atoms that are connected to carbon atoms are written out. Line angle formulas help show structure and order of the atoms in a compound making the advantages and disadvantages similar to structural formulas.

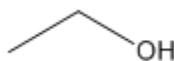


Figure 2.11.2: Shorthand Formula for Ethanol

Exercises

Write down the molecular formula for each of the compounds shown here.

compounds A through D for naming

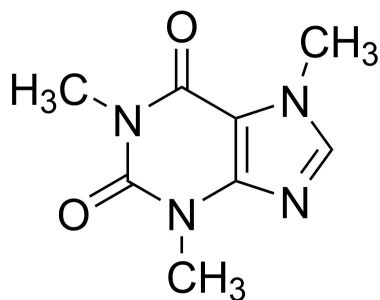
Answers:

- A. C_7H_7N
- B. C_5H_{10}
- C. C_5H_4O
- D. $C_5H_6Br_2$

Questions

Q1.12.1

Below is the molecule for caffeine. Give the molecular formula for it.



Solutions

S1.12.1

$C_8H_{10}O_2N_4$

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3: CHAPTER 3 CONFORMATIONS AND CYCLOALKANES

- 3.1: Conformations of Ethane
- 3.2: Conformations of Other Alkanes
- 3.3: Cis-Trans Isomerism in Cycloalkanes
- 3.4: Stability of Cycloalkanes - Ring Strain
- 3.5: Conformations of Cycloalkanes
- 3.6: Conformations of Cyclohexane
- 3.7: Axial and Equatorial Bonds in Cyclohexane
- 3.8: Conformations of Monosubstituted Cyclohexanes
- 3.9: Conformations of Disubstituted Cyclohexanes
- 3.10: Conformations of Polycyclic Molecules

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3.1: Conformations of Ethane

Objectives

After completing this section, you should be able to

1. explain the concept of free rotation about a carbon-carbon single bond.
2. explain the difference between conformational isomerism and structural isomerism.
3. draw the conformers of ethane using both sawhorse representation and Newman projection.
4. sketch a graph of energy versus bond rotation for ethane, and discuss the graph in terms of torsional strain.

Key Terms

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

- conformation (conformer, conformational isomer)
- dihedral angle
- eclipsed conformation
- Newman projection
- staggered conformation
- strain energy
- torsional strain (eclipsing strain)

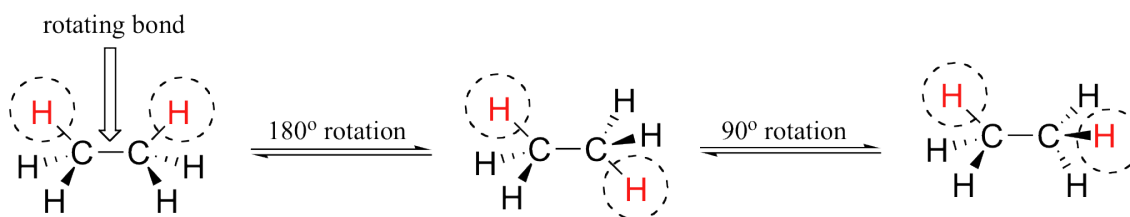
Study Notes

You should be prepared to sketch various conformers using both sawhorse representations and Newman projections. Each method has its own advantages, depending upon the circumstances. Notice that when drawing the Newman projection of the eclipsed conformation of ethane, you cannot clearly draw the rear hydrogens exactly behind the front ones. This is an inherent limitation associated with representing a 3-D structure in two dimensions.

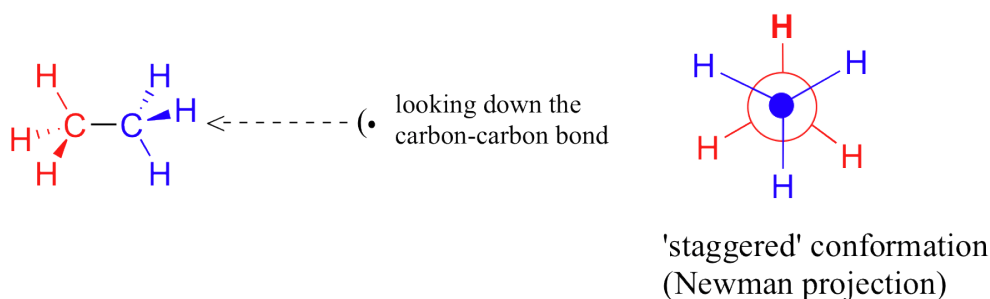
Conformational isomerism involves rotation about sigma bonds, and does not involve any differences in the connectivity of the atoms or geometry of bonding. Two or more structures that are categorized as conformational isomers, or **conformers**, are really just two of the exact same molecule that differ only in rotation of one or more sigma bonds.

Ethane Conformations

Although there are seven sigma bonds in the ethane molecule, rotation about the six carbon-hydrogen bonds does not result in any change in the shape of the molecule because the hydrogen atoms are essentially spherical. Rotation about the carbon-carbon bond, however, results in many different possible molecular conformations.



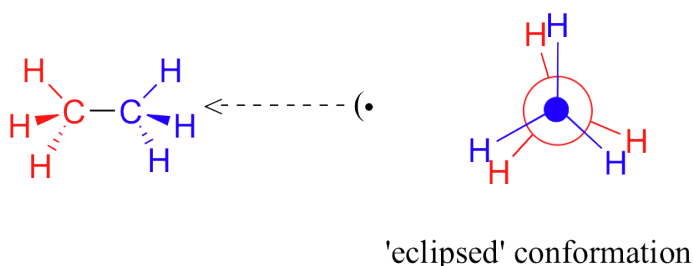
In order to better visualize these different conformations, it is convenient to use a drawing convention called the **Newman projection**. In a Newman projection, we look lengthwise down a specific bond of interest – in this case, the carbon-carbon bond in ethane. We depict the 'front' atom as a dot, and the 'back' atom as a larger circle.



The six carbon-hydrogen bonds are shown as solid lines protruding from the two carbons at 120° angles, which is what the actual tetrahedral geometry looks like when viewed from this perspective and flattened into two dimensions.

The lowest energy conformation of ethane, shown in the figure above, is called the 'staggered' conformation. In the staggered conformation, all of the C-H bonds on the front carbon are positioned at an angle of 60° relative to the C-H bonds on the back carbon. This angle between a sigma bond on the front carbon compared to a sigma bond on the back carbon is called the **dihedral angle**. In this conformation, the distance between the bonds (and the electrons in them) is maximized. Maximizing the distance between the electrons decreases the electrostatic repulsion between the electrons and results in a more stable structure.

If we now rotate the front CH_3 group 60° clockwise, the molecule is in the highest energy 'eclipsed' conformation, and the hydrogens on the front carbon are as close as possible to the hydrogens on the back carbon.



This is the highest energy conformation because of unfavorable electrostatic repulsion between the electrons in the front and back C-H bonds. The energy of the eclipsed conformation is approximately 3 kcal/mol (12 kJ/mol) higher than that of the staggered conformation. **Torsional strain** (or eclipsing strain) is the name given to the energy difference caused by the increased electrostatic repulsion of eclipsing bonds.

Another 60° rotation returns the molecule to a second eclipsed conformation. This process can be continued all around the 360° circle, with three possible eclipsed conformations and three staggered conformations, in addition to an infinite number of variations in between. We will focus on the staggered and eclipsed conformers since they are, respectively, the lowest and highest energy conformers.

Unhindered (Free) Rotations Do Not Exist in Ethane

The carbon-carbon bond is not *completely* free to rotate – the 3 kcal/mol torsional strain in ethane creates a barrier to rotation that must be overcome for the bond to rotate from one staggered conformation to another. This rotational barrier is not large enough to prevent rotation except at extremely cold temperatures. So at normal temperatures, the carbon-carbon bond is constantly rotating. However, at any given moment the molecule is more likely to be in a staggered conformation – one of the rotational 'energy valleys' – than in any other conformer. The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds, as shown in figure 3.6.1.

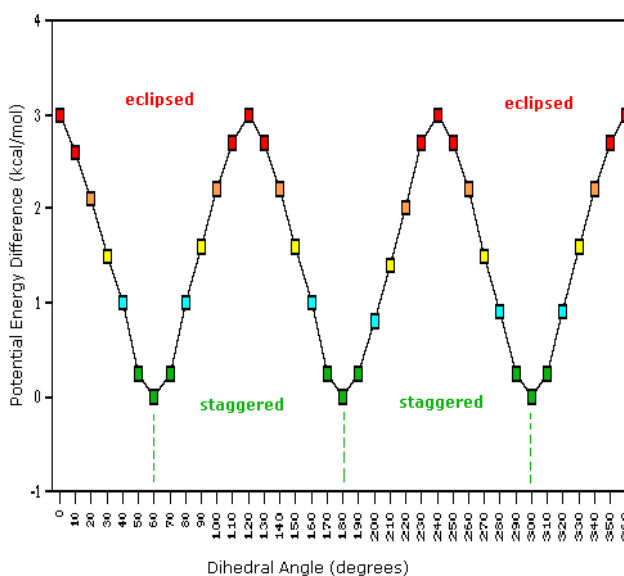


Figure 3.6.1: The potential energy associated with the various conformations of ethane varies with the dihedral angle of the bonds. Valleys in the graph represent the low energy staggered conformers, while peaks represent the higher energy eclipsed conformers.

Although the conformers of ethane are in rapid equilibrium with each other, the 3 kcal/mol energy difference leads to a substantial preponderance of staggered conformers (> 99.9%) at any given time. The animation below illustrates the relationship between ethane's potential energy and its dihedral angle

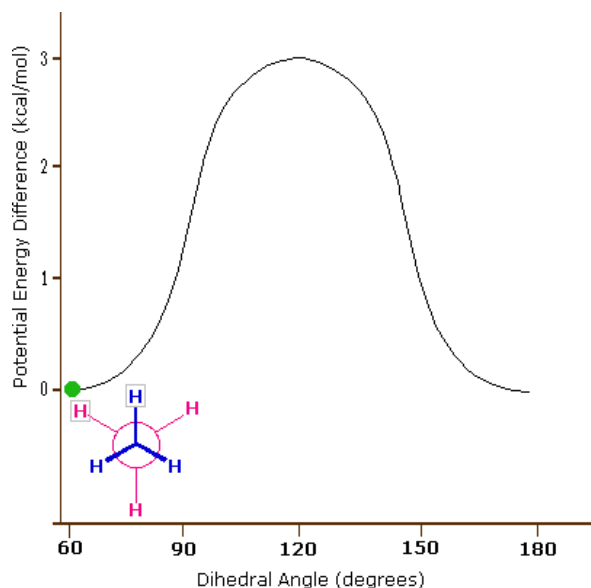


Figure 3.6.2: Animation of potential energy vs. dihedral angle in ethane

Exercises

Questions

Q3.6.1

What is the most stable rotational conformation of ethane and explain why it is preferred over the other conformation?

Solutions

S3.6.1

Staggered, as there is less repulsion between the hydrogen atoms.

Contributors

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3.2: Conformations of Other Alkanes

Objectives

After completing this section, you should be able to

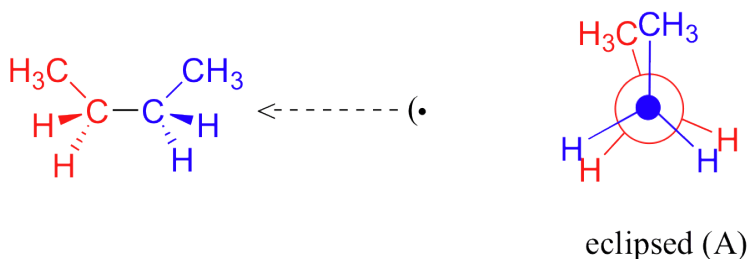
1. depict the staggered and eclipsed conformers of propane (or a similar compound) using sawhorse representations and Newman projections.
2. sketch a graph of energy versus bond rotation for propane (or a similar compound) and discuss the graph in terms of torsional strain.
3. depict the anti, gauche, eclipsed and fully eclipsed conformers of butane (or a similar compound), using sawhorse representations and Newman projections.
4. sketch a graph of energy versus C₂-C₃ bond rotation for butane (or a similar compound), and discuss it in terms of torsional and steric repulsion.
5. assess which of two (or more) conformers of a given compound is likely to predominate at room temperature from a semi-quantitative knowledge of the energy costs of the interactions involved.

Key Terms

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

- anti conformation
- gauche conformation
- eclipsed conformation
- steric repulsion (strain)

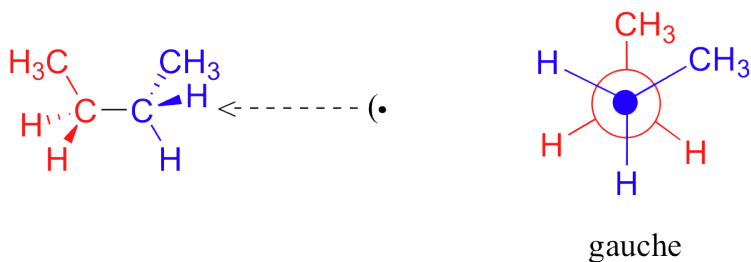
In butane, there are three rotating carbon-carbon sigma bonds to consider, but we will focus on the middle bond between C₂ and C₃. Below are two representations of butane in a conformation which puts the two CH₃ groups (C₁ and C₄) in the eclipsed position.



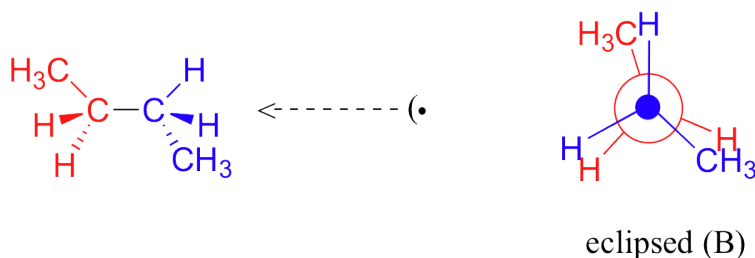
This is the highest energy conformation for butane, due to torsional strain caused by the electrostatic repulsion of electrons in the eclipsed bonds, but also because of another type of strain called '**van der Waals repulsion**', or '**steric repulsion**', between the two rather bulky methyl groups.

What is van der Waals repulsion? In Chapter 2 that the van der Waals force between two nonpolar groups is an *attractive* force? Consider this: you probably like to be near your friends, but no matter how close you are you probably don't want to share a one-room apartment with five of them. When the two methyl groups are brought too close together, the overall resulting non-covalent interaction is repulsive rather than attractive. The result is that their respective electron densities repel one another.

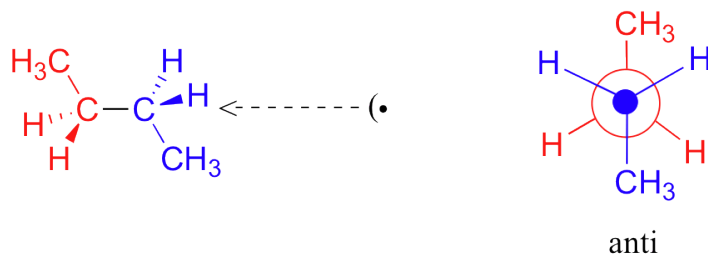
If we rotate the front, (blue) carbon by 60° clockwise, the butane molecule is now in a staggered conformation.



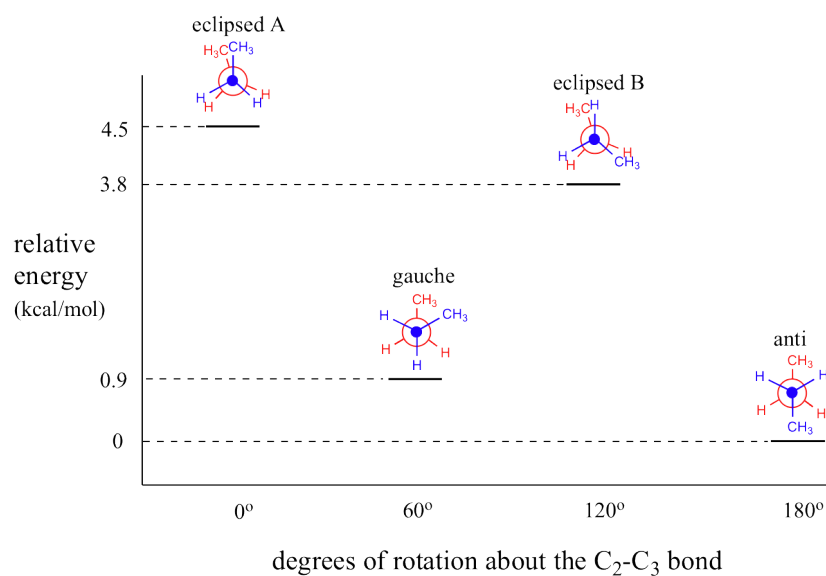
This is more specifically referred to as the '**gauche**' conformation of butane. Notice that although they are staggered, the two methyl groups are not as far apart as they could possibly be. There is still significant steric repulsion between the two bulky groups. A further rotation of 60° gives us a second eclipsed conformation (B) in which both methyl groups are lined up with hydrogen atoms.



Due to steric repulsion between methyl and hydrogen substituents, this eclipsed conformation B is higher in energy than the gauche conformation. However, because there is no methyl-to-methyl eclipsing, it is lower in energy than eclipsed conformation A. One more 60° rotation produces the '**anti**' conformation, where the two methyl groups are positioned opposite each other and steric repulsion is minimized.



The anti conformation is the lowest energy conformation for butane. The diagram below summarizes the relative energies for the various eclipsed, staggered, and gauche conformations.



The following diagram illustrates the change in potential energy that occurs with rotation about the C_2-C_3 bond.

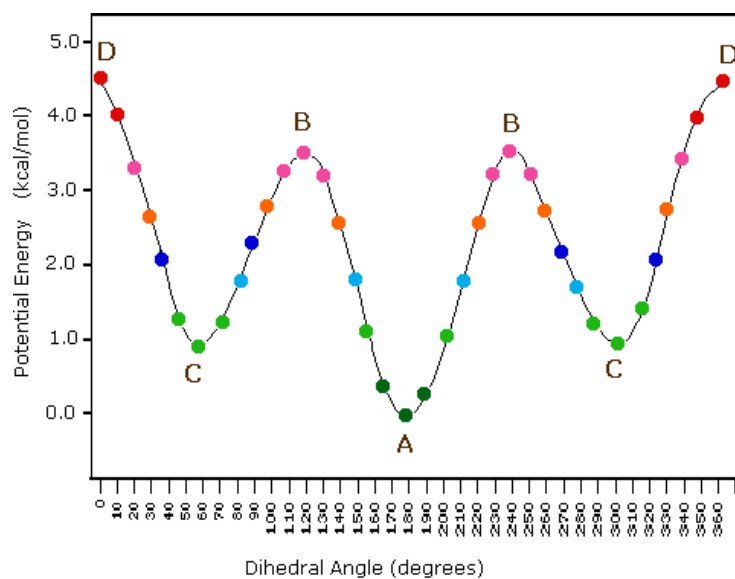


Figure 3.2.1: Potential curve vs dihedral angle of the C_2-C_3 bond of butane.

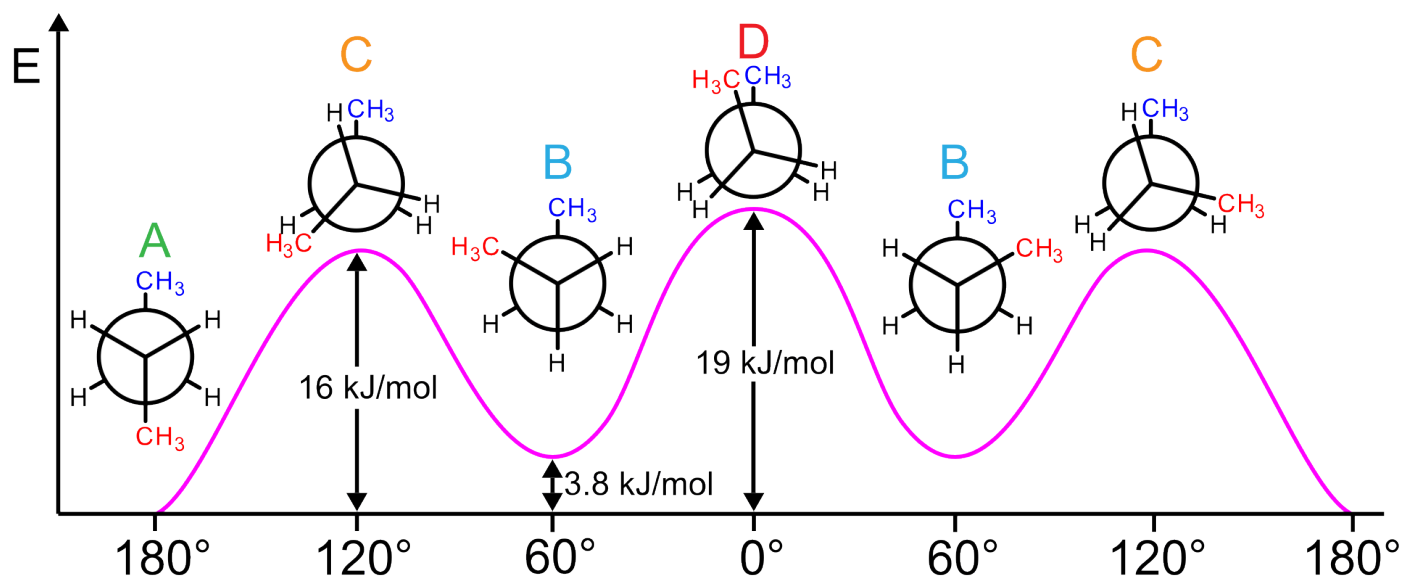
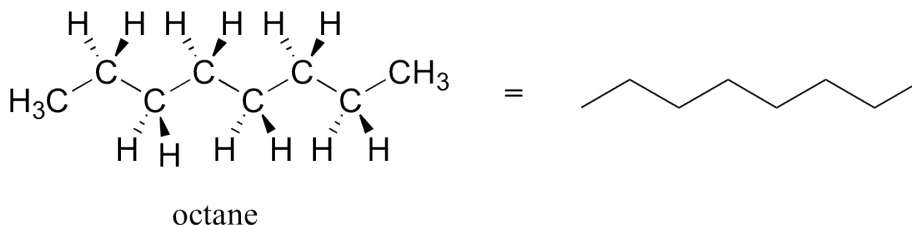


Figure 3.2.2: Newman projections of butane conformations & their relative energy differences (not total energies). Conformations form when butane rotates about one of its single covalent bond. Torsional/dihedral angle is shown on x-axis. Torsional/dihedral angle is shown on x-axis. Conformation names (according to IUPAC): **A**: anti-periplanar, anti or trans **B**: synclinal or gauche **C**: anticlinal or eclipsed **D**: syn-periplanar or cis. Source for conformation names & conformer classification: *Pure & Appl. Chem.*, Vol. 68, No. 12, pp. 2193-2222, 1996. Image used with permission (Public Domain; [Keministi](#)).

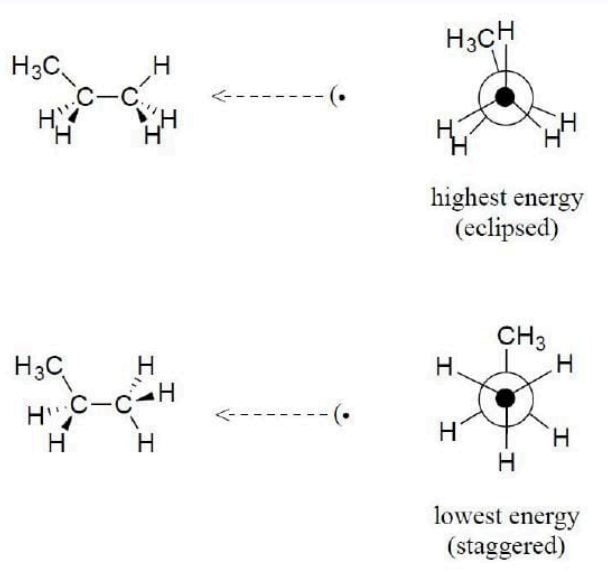
At room temperature, butane is most likely to be in the lowest-energy anti conformation at any given moment in time, although the energy barrier between the anti and eclipsed conformations is not high enough to prevent constant rotation except at very low temperatures. For this reason (and also simply for ease of drawing), it is conventional to draw straight-chain alkanes in a zigzag form, which implies the anti conformation at all carbon-carbon bonds.



Example 3.2.1

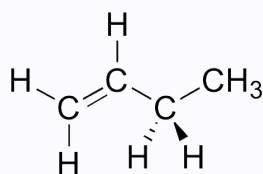
Draw Newman projections of the eclipsed and staggered conformations of propane, as if viewed down the C₁-C₂ bond.

Answer:

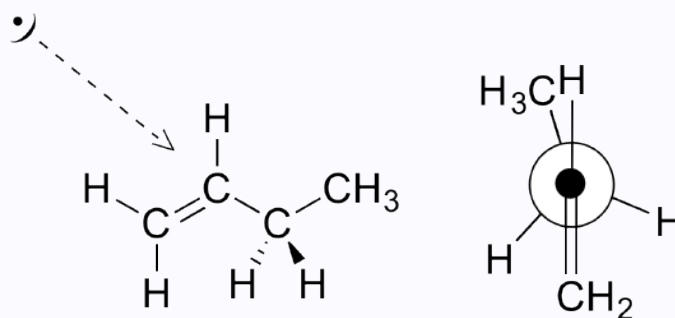


Example 3.2.2

Draw a Newman projection, looking down the C₂-C₃ bond, of 1-butene in the conformation shown below.



Answer:



Exercises

Questions

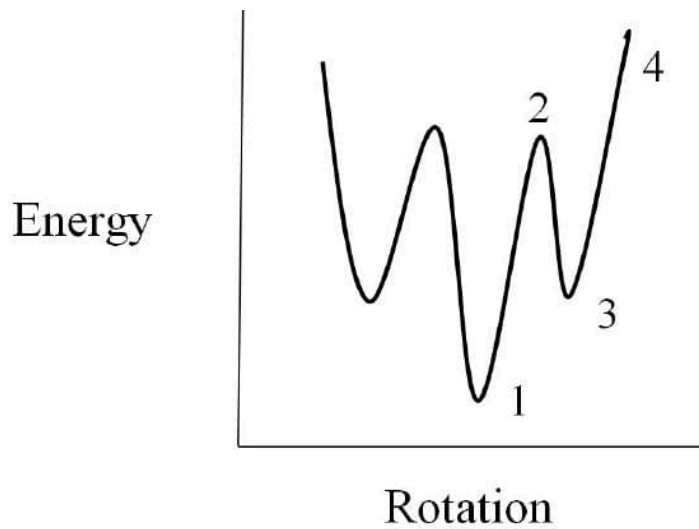
Q3.7.1

Draw the energy diagram for the rotation of the bond highlighted in pentane.

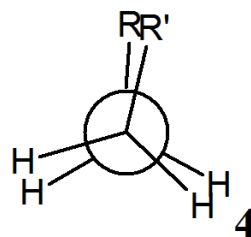
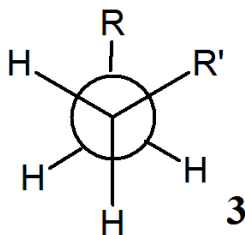
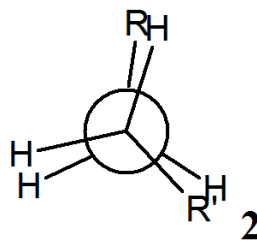
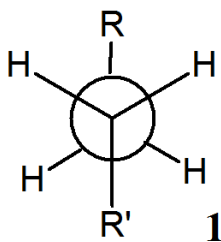


Solutions

S3.7.1



R=Methyl
R'=Ethyl



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
- Jim Clark ([Chemguide.co.uk](#))
- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

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3.3: Cis-Trans Isomerism in Cycloalkanes

Objectives

After completing this section, you should be able to

1. draw structural formulas that distinguish between *cis* and *trans* disubstituted cycloalkanes.
2. construct models of *cis* and *trans* disubstituted cycloalkanes using ball-and-stick molecular models.

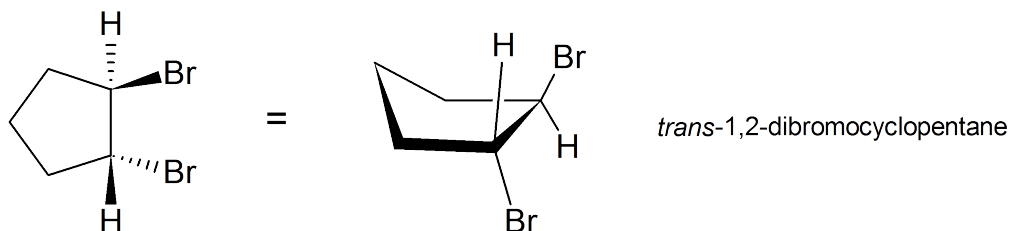
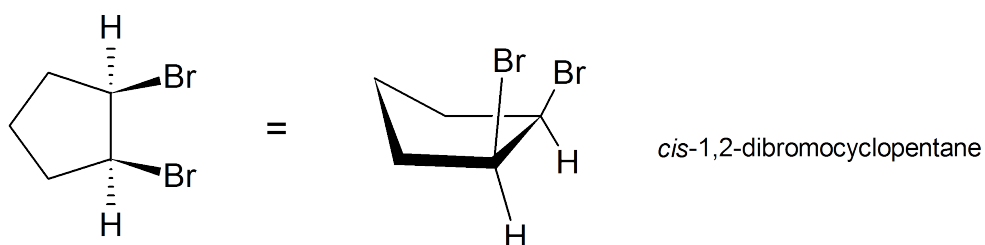
Key Terms

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

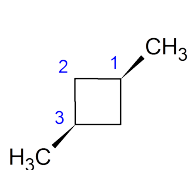
- constitutional isomer
- stereoisomer
- *cis-trans* isomers

Previously, constitutional isomers were defined as molecules that had the same molecular formula, but different atom connectivity. In this section, a new class of isomers, stereoisomers, will be introduced. **Stereoisomers** are molecules that have the same molecular formula, the same atom connectivity, but they differ in the relative spatial orientation of the atoms.

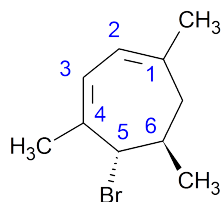
Di-substituted cycloalkanes are one class of molecules that exhibit stereoisomerism. 1,2-dibromocyclopentane can exist as two different stereoisomers: *cis*-1,2-dibromocyclopentane and *trans*-1,2-dibromocyclopentane. The *cis*-1,2-dibromocyclopentane and *trans*-1,2-dibromocyclopentane stereoisomers of 1,2-dibromocyclopentane are shown below. Both molecules have the same molecular formula and the same atom connectivity. They differ only in the relative spatial orientation of the two bromines on the ring. In *cis*-1,2-dibromocyclopentane, both bromine atoms are on the same "face" of the cyclopentane ring, while in *trans*-1,2-dibromocyclopentane, the two bromines are on opposite faces of the ring. Stereoisomers require an additional nomenclature prefix be added to the IUPAC name in order to indicate their spatial orientation. Di-substituted cycloalkane stereoisomers are designated by the nomenclature prefixes ***cis*** (Latin, meaning on this side) and ***trans*** (Latin, meaning across).



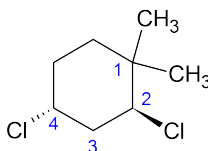
By convention, chemists use heavy, wedge-shaped bonds to indicate a substituent located above the average plane of the ring (coming out of the page), a dashed line for bonds to atoms or groups located below the ring (going back into the page), and solid lines for bonds in the plane of the page.



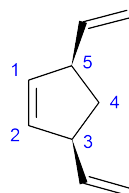
cis-1,3-dimethylcyclobutane



trans-5-bromo-1,4,6-trimethyl-1,3-cycloheptadiene

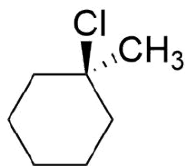


trans-2,4-dichloro-1,1-dimethylcyclohexane



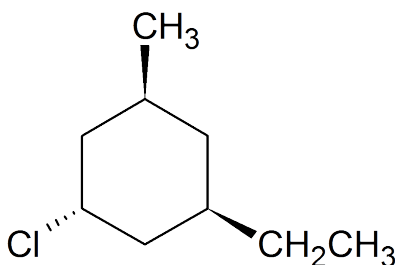
cis-3,5-divinylcyclopentene

In general, if any two sp^3 carbons in a ring have two different substituent groups (not counting other ring atoms) *cis/trans* stereoisomerism is possible. However, the *cis/trans* designations are not used if both groups are on the same carbon. For example, the chlorine and the methyl group are on the same carbon in 1-chloro-1-methylcyclohexane and the *trans* prefix should not be used.



1-chloro-1-methylcyclohexane

If more than two ring carbons have substituents, the stereochemical notation distinguishing the various isomers becomes more complex and the prefixes *cis* and *trans* *cannot be used to formally name the molecule*. However, the relationship of any two substituents can be informally described using *cis* or *trans*. For example, in the tri-substituted cyclohexane below, the methyl group is *cis* to the ethyl group, and also *trans* to the chlorine. However, the entire molecule cannot be designated as either a *cis* or *trans isomer*. Later sections will describe how to name these more complex molecules ([5.5: Sequence Rules for Specifying Configuration](#))



Exercises

Questions

Q4.2.1

Draw the following molecules:

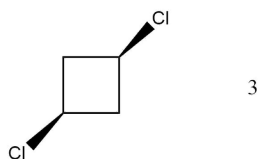
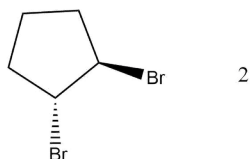
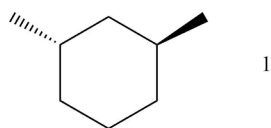
trans-1,3-dimethylcyclohexane

trans-1,2-dibromocyclopentane

cis-1,3-dichlorocyclobutane

Solutions

S4.2.1



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)

3.4: Stability of Cycloalkanes - Ring Strain

Objectives

After completing this section, you should be able to

1. describe the Baeyer strain theory.
2. describe how the measurement of heats of combustion provides information about the amount of strain present in a cycloalkane ring.
3. determine the relative stability of cyclic compounds, by assessing such factors as angle strain, torsional strain and steric strain.

Key Terms

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

- angle strain
- steric strain
- torsional strain
- ring strain
- heat of combustion

Heat of Combustion

The combustion of carbon compounds, especially hydrocarbons, has been the most important source of heat energy for human civilizations throughout recorded history. The practical importance of this reaction cannot be denied, but the massive and uncontrolled chemical changes that take place in combustion make it difficult to deduce mechanistic paths. Using the combustion of propane as an example, we see from the following equation that every covalent bond in the reactants has been broken and an entirely new set of covalent bonds have formed in the products. No other common reaction involves such a profound and pervasive change, and the mechanism of combustion is so complex that chemists are just beginning to explore and understand some of its elementary features.



Since all the covalent bonds in the reactant molecules are broken, the quantity of heat evolved in this reaction, and any other combustion reaction, is related to the strength of these bonds (and, of course, the strength of the bonds formed in the products). Precise heats of combustion measurements can provide useful information about the structure of molecules and their relative stability.

For example, heat of combustion is useful in determining the relative stability of isomers. Pentane has a heat of combustion of -782 kcal/mole, while that of its isomer, 2,2-dimethylpropane (neopentane), is -777 kcal/mole. These values indicate that 2,3-dimethylpentane is 5 kcal/mole more stable than pentane, since it has a lower heat of combustion.

Ring Strain

Table 4.3.1 lists the heat of combustion data for some simple cycloalkanes. These cycloalkanes do not have the same molecular formula, so the heat of combustion per each CH_2 unit present in each molecule is calculated (the fourth column) to provide a useful comparison. From the data, cyclopropane and cyclobutane have significantly higher heats of combustion per CH_2 , while cyclohexane has the lowest heat of combustion. This indicates that cyclohexane is more stable than cyclopropane and

cyclobutane, and in fact, that cyclohexane has a same relative stability as long chain alkanes that are not cyclic. What causes this difference in stability or the strain in these two small cycloalkanes?

Table 4.3.1: Heats of combustion of select hydrocarbons

Cycloalkane (CH ₂) _n	CH ₂ Units n	ΔH ^{25°} kcal/mole	ΔH ^{25°} per CH ₂ Unit	Ring Strain kcal/mole
Cyclopropane	n = 3	468.7	156.2	27.6
Cyclobutane	n = 4	614.3	153.6	26.4
Cyclopentane	n = 5	741.5	148.3	6.5
Cyclohexane	n = 6	882.1	147.0	0.0
Cycloheptane	n = 7	1035.4	147.9	6.3
Cyclooctane	n = 8	1186.0	148.2	9.6
Cyclononane	n = 9	1335.0	148.3	11.7
Cyclodecane	n = 10	1481	148.1	11.0
CH ₃ (CH ₂) _m CH ₃	m = large	—	147.0	0.0

The Baeyer Theory on the Strain in Cycloalkane Rings

In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane are less stable than cyclohexane, because the the smaller rings are more "strained". There are many different types of strain that contribute to the overall ring strain in cycloalkanes, including angle strain, torsional strain, and steric strain. **Torsional strain** and **steric strain** were previously defined in the discussion of conformations of butane. **Angle Strain** occurs when the sp³ hybridized carbons in cycloalkanes do not have the expected ideal bond angle of 109.5°, causing an increase in the potential energy. An example of angle strain can be seen in the diagram of cyclopropane below in which the bond angle is 60° between the carbons.

cyclopropane.bmp

The C-C-C bond angles in cyclopropane (diagram above) (60°) and cyclobutane (90°) are much different than the ideal bond angle of 109.5°. This bond angle causes cyclopropane and cyclobutane to be less stable than molecules such as cyclohexane and cyclopentane, which have a much lower ring strain because the bond angle between the carbons is much closer to 109.5°. Changes in chemical reactivity as a consequence of angle strain are dramatic in the case of cyclopropane, and are also evident for cyclobutane.

In addition to angle strain, there is also steric (transannular) strain and torsional strain in many cycloalkanes. Transannular strain exists when there is steric repulsion between atoms. Torsional (eclipsing) strain exists when a cycloalkane is unable to adopt a staggered conformation around a C-C bond. Torsional strain and steric strain are especially prevalent in small cycloalkanes whose structures are nearly planar.

Larger rings like cyclohexane, deal with torsional strain by forming conformers in which the rings are not planar. A conformer is a stereoisomer in which molecules of the same connectivity and formula exist as different isomers, in this case, to reduce ring strain. The ring strain is reduced in conformers due to the rotations around the sigma bonds, which decreases the angle and torsional strain in the ring. The non-planar structures of cyclohexane are very stable compared to cyclopropane and cyclobutane, and will be discussed in more detail in the next section.

transannular strain.bmp

pentane.bmp

text2.bmp

Exercises

Questions

Q4.3.1

trans-1,2-Dimethylcyclobutane is more stable than *cis*-1,2-dimethylcyclobutane. Explain this observation.

Solutions

S4.3.1

The *trans* form does not have eclipsing methyl groups, therefore lowering the energy within the molecule. It does however have hydrogen-methyl interactions, but are not as high in energy than methyl-methyl interactions.

Contributors

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)
- Kelly Matthews, Senior Professor of Chemistry (Harrisburg Area Community College)

3.5: Conformations of Cycloalkanes

Objectives

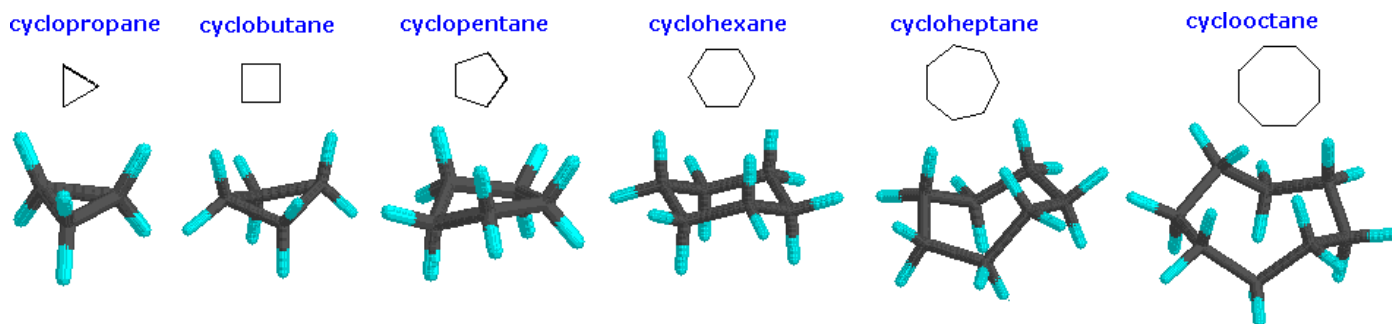
After completing this section, you should be able to

1. describe, and sketch the conformation of, cyclopropane, cyclobutane and cyclopentane.
2. describe the bonding in cyclopropane, and hence account for the high reactivity of this compound.
3. analyse the stability of cyclobutane, cyclopentane and their substituted derivatives in terms of angular strain, torsional strain and steric interactions.

Study Notes

Notice that in both cyclobutane and cyclopentane, torsional strain is reduced at the cost of increasing angular (angle) strain.

Although the customary line drawings of simple cycloalkanes are geometrical polygons, the actual shape of these compounds in most cases is very different.



Cyclopropane is necessarily planar (flat), with the carbon atoms at the corners of an equilateral triangle. The 60° bond angles are much smaller than the optimum 109.5° angles of a normal tetrahedral carbon atom, and the resulting angle strain dramatically influences the chemical behavior of this cycloalkane. Cyclopropane also suffers substantial eclipsing strain, since all the carbon-carbon bonds are fully eclipsed. Cyclobutane reduces some bond-eclipsing strain by folding (the out-of-plane dihedral angle is about 25°), but the total eclipsing and angle strain remains high. Cyclopentane has very little angle strain (the angles of a pentagon are 108°), but its eclipsing strain would be large (about 10 kcal/mol) if it remained planar. Consequently, the five-membered ring adopts non-planar puckered conformations whenever possible.

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

Cyclic systems are a little different from open-chain systems. In an open chain, any bond can be rotated 360° degrees, going through many different conformations. That complete rotation isn't possible in a cyclic system, because the parts that would be trying to twist away from each other would still be connected together. Cyclic systems have fewer "degrees of freedom" than aliphatic systems; they have "restricted rotation".

Because of the restricted rotation of cyclic systems, most of them have much more well-defined shapes than their aliphatic counterparts. Let's take a look at the basic shapes of some common rings.

- Many biologically important compounds are built around structures containing rings, so it's important that we become familiar with them.
- In nature, three- to six-membered rings are frequently encountered, so we'll focus on those.

Cyclopropane

A three membered ring has no rotational freedom whatsoever. A plane is defined by three points, so the three carbon atoms in cyclopropane are all constrained to lie in the same plane.



Furthermore, if you look at a model you will find that the neighboring C-H bonds (C-C bonds, too) are all held in eclipsed conformations.

Cyclopropane is always at maximum torsional strain. This strain can be illustrated in a line drawing of cyclopropane as shown from the side. In this oblique view, the dark lines mean that those sides of the ring are closer to you.



However, the ring isn't big enough to introduce any steric strain, which does not become a factor until we reach six membered rings. Until that point, rings are not flexible enough for two atoms to reach around and bump into each other.

The really big problem with cyclopropane is that the C-C-C bond angles are all too small.

- All the carbon atoms in cyclopropane appear to be tetrahedral.
- These bond angles ought to be 109 degrees.
- The angles in an equilateral triangle are actually 60 degrees, about half as large as the optimum angle.
- This factor introduces a huge amount of strain in the molecule, called angle strain. The large amount of ring strain in cyclopropane weakens the bonds and causes cyclopropane to be significantly more reactive than expected for a hydrocarbon molecule.

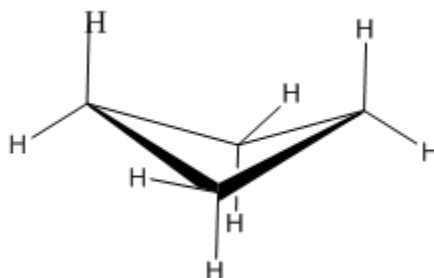
Cyclobutane

Cyclobutane is a four membered ring. In two dimensions, it is a square, with 90 degree angles at each corner.



However, in three dimensions, cyclobutane is flexible enough to buckle into a "butterfly" shape, relieving torsional strain a little bit. When it does that, the bond angles get a little worse, going from 90 degrees to 88 degrees.

In a line drawing, this butterfly shape is usually shown from the side, with the near edges drawn using darker lines.



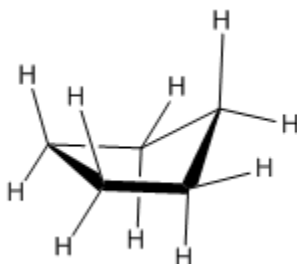
- Angle strain is significant. With bond angles of 88 rather than 109 degrees, cyclobutane has a lot of angle strain, but less than in cyclopropane.
- Torsional strain is still present, but the neighboring bonds are not exactly eclipsed in the butterfly.
- Steric strain is very low. Cyclobutane is still not large enough that the molecule can reach around to cause crowding.
- Cyclobutanes are a slightly more stable than cyclopropanes and are also a little more common in nature.

Cyclopentane

Cyclopentanes are even more stable than cyclobutanes, and they are the second-most common cycloalkane ring in nature, after cyclohexanes. In two dimensions, a cyclopentane appears to be a regular pentagon.



In three dimensions, there is enough freedom of rotation to allow a slight twist out of this planar shape. In a line drawing, this three-dimensional shape is drawn from an oblique view, just like cyclobutane.



- Angle strain is low. The ideal angle in a regular pentagon is about 107 degrees, very close to a tetrahedral bond angle.
- There is still some torsional strain in cyclopentane. Cyclopentane distorts only very slightly into an "envelope" shape in which one corner of the pentagon is lifted up above the plane of the other four. The envelope removes torsional strain along the sides and flap of the envelope. However, the neighboring carbons are eclipsed along the "bottom" of the envelope, away from the flap.
- Again, there is no steric strain in this system.

Exercises

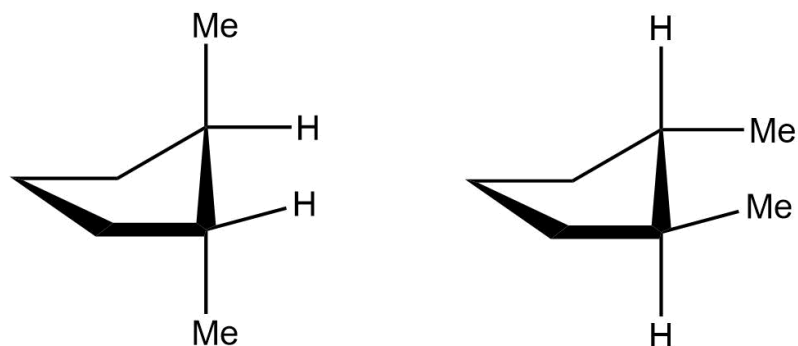
Questions

Q4.4.1

If cyclobutane were to be planar how many H-H eclipsing interactions would there be, and assuming 4 kJ/mol per H-H eclipsing interaction what is the strain on this "planar" molecule?

Q4.4.2

In the two conformations of *trans*-cyclopentane one is more stable than the other. Explain why this is.



Solutions

S4.4.1

There are 8 eclipsing interactions (two per C-C bond). The extra strain on this molecule would be 32 kJ/mol (4 kJ/mol x 8).

S4.4.2

The first conformation is more stable. Even though the methyl groups are *trans* in both models, in the second structure they are eclipsing one another, therefore increasing the strain within the molecule compared to the first structure where the larger methyl groups are anti to one another.

Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
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- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

3.6: Conformations of Cyclohexane

Objectives

After completing this section, you should be able to

1. explain why cyclohexane rings are free of angular strain.
2. draw the structure of a cyclohexane ring in the chair conformation.

Key Terms

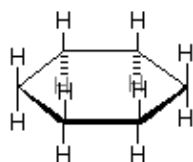
Make certain that you can define, and use in context, the key terms below.

- chair conformation
- twist-boat conformation

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

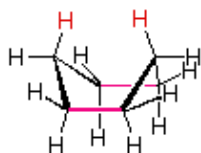
Conformations of Cyclohexane

A planar structure for cyclohexane is clearly improbable. The bond angles would necessarily be 120° , 10.5° larger than the ideal tetrahedral angle. Also, every carbon-carbon bond in such a structure would be eclipsed. The resulting angle and eclipsing strains would severely destabilize this structure. If two carbon atoms on opposite sides of the six-membered ring are lifted out of the plane of the ring, much of the angle strain can be eliminated.



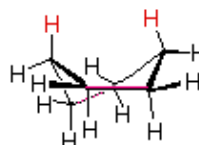
Planar Structure

severe angle strain (120°)
severe eclipsing strain (all bonds)
small steric strain



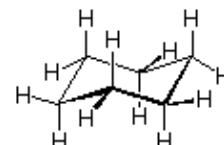
Boat Conformation

slight angle strain
eclipsing strain at **two bonds**
steric crowding of **two hydrogens**



Twist Boat Conformation

slight angle strain
small eclipsing strain
small steric strain



Chair Conformation

no angle strain
no eclipsing strain
small steric strain

This boat structure still has two eclipsed bonds and severe steric crowding of two hydrogen atoms on the "bow" and "stern" of the boat. This steric crowding is often called steric hindrance. By twisting the boat conformation, the steric hindrance can be partially relieved, but the twist-boat conformer still retains some of the strains that characterize the boat conformer. Finally, by lifting one carbon above the ring plane and the other below the plane, a relatively strain-free 'chair' conformer is formed. This is the predominant structure adopted by molecules of cyclohexane.

Exercises

Questions

Q4.5.1

Consider the conformations of cyclohexane, chair, boat, twist boat. Order them in increasing strain in the molecule.

Solutions

S4.5.1

Chair < Twist Boat < Boat (most strain)

Contributors

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3.7: Axial and Equatorial Bonds in Cyclohexane

Objectives

After completing this section, you should be able to

1. Draw the chair conformation of cyclohexane, with axial and equatorial hydrogen atoms clearly shown and identified.
2. identify the axial and equatorial hydrogens in a given sketch of the cyclohexane molecule.
3. explain how chair conformations of cyclohexane and its derivatives can interconvert through the process of ring flip.

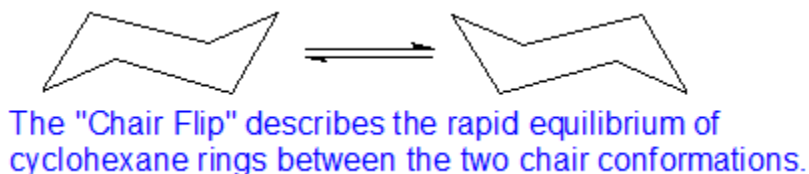
Key Terms

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

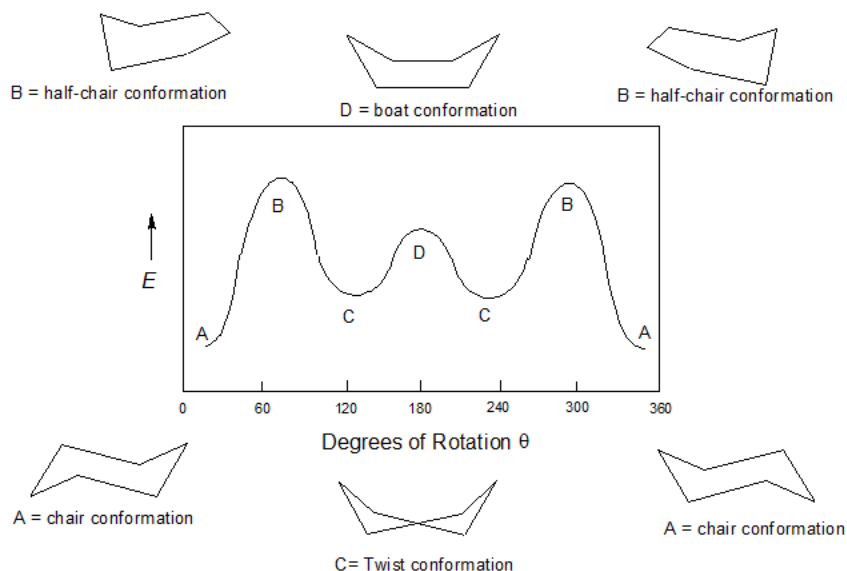
- axial position
- equatorial position
- ring flip

Cyclohexane Conformations (aka Chair Flips)

Cyclohexane is rapidly rotating between the two most stable conformations known as the chair conformations in what is called the "Chair Flip" shown below.

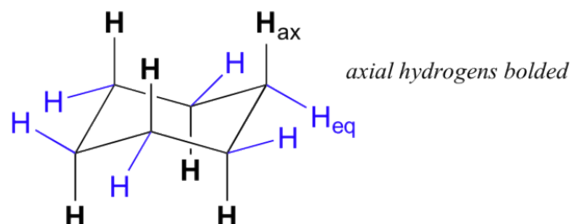


Several other notable cyclohexane conformations occur during the transition from one chair conformer to the other - the boat, the twist, and the half-chair. The relative energies of the conformations is a direct reflection of their relative stabilities. These structural and energetic relationships are summarized in the conformational energy diagram for cyclohexane below.

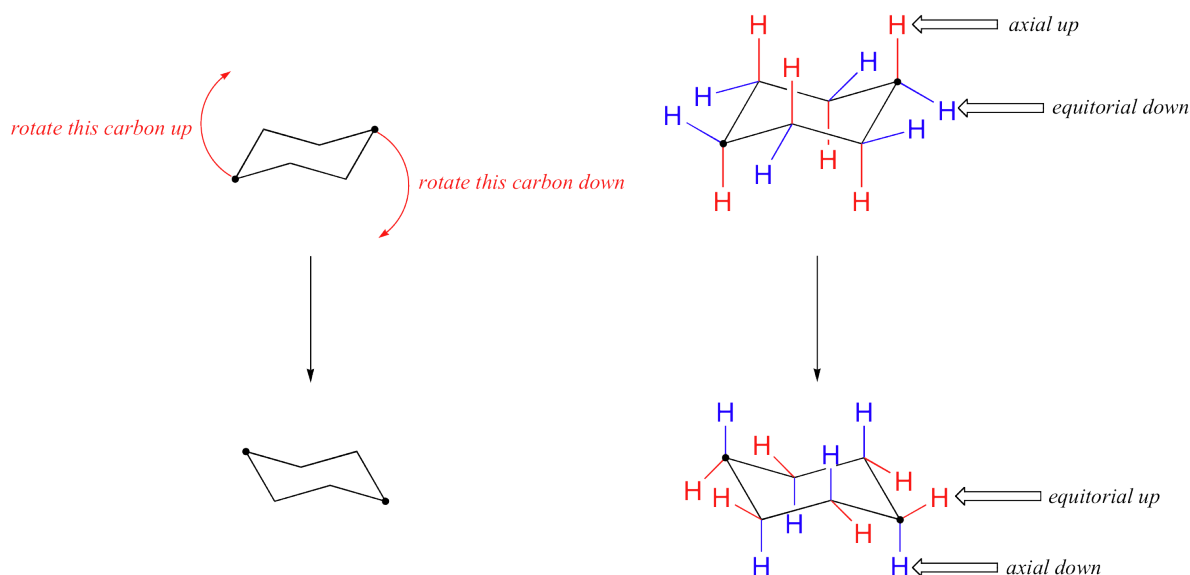


The Chair Conformation - a closer look

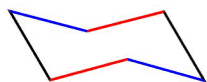
Careful examination of the chair conformation of cyclohexane, shows that the twelve hydrogens are not structurally equivalent. Six of them are located about the periphery of the carbon ring, and are termed **equatorial**. The other six are oriented above and below the approximate plane of the ring (three in each location), and are termed **axial** because they are aligned parallel to the symmetry axis of the ring.



In the figure above, the equatorial hydrogens are colored blue, and the axial hydrogens are black. Since there are two equivalent chair conformations of cyclohexane in rapid equilibrium, all twelve hydrogens have 50% equatorial and 50% axial character. The figure below illustrates how to convert a molecular model of cyclohexane between two different chair conformations - this is something that you should practice with models. Notice that a 'ring flip' causes equatorial hydrogens to become axial, and vice-versa.



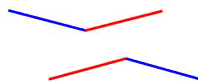
How to Draw chairsEdit section



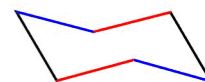
To draw a chair



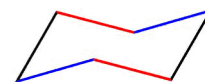
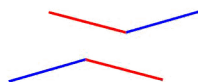
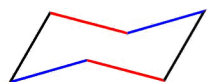
1) Draw two slightly offset parallel lines



2) Draw another pair of parallel lines from the ends of the first pair

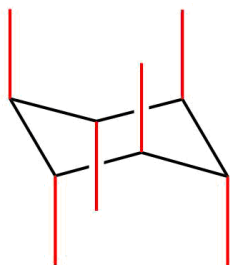


3) Connect with a third set of parallel lines

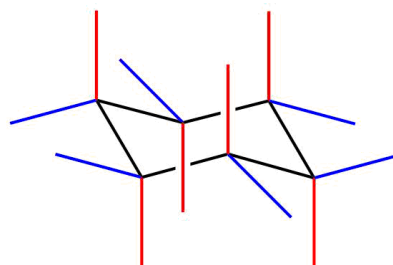


To draw its ring-flip conformer, just start the first pair of lines at the opposite angle

To draw the axial and equatorial bonds



Add axial hydrogens up to every carbon that points up, and add axial hydrogens down to every carbon that point sdown



Draw equatorial bonds at 109.5° angle from the axial bonds. If the axial bond is up, then the equatorial bond will be down, and vice versa

Aside from drawing the basic chair, the key points are:

- Axial bonds alternate up and down, and are shown "vertical".
- Equatorial groups are approximately horizontal, but actually somewhat distorted from that, so that the angle from the axial group is a bit more than a right angle -- reflecting the common 109.5° bond angle.

Exercises

Questions

Q4.6.1

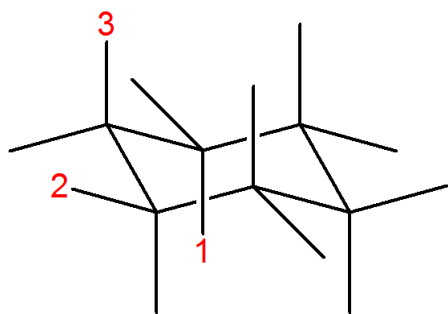
Draw two conformations of cyclohexyl amine ($\text{C}_6\text{H}_{11}\text{NH}_2$). Indicate axial and equatorial positions.

Q4.6.2

Draw the two isomers of 1,4-dihydroxycyclohexane, identify which are equatorial and axial.

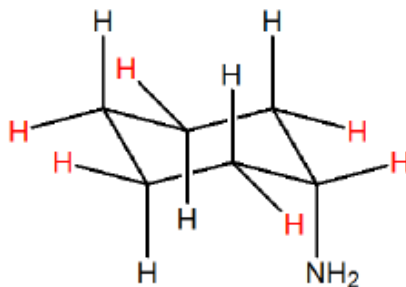
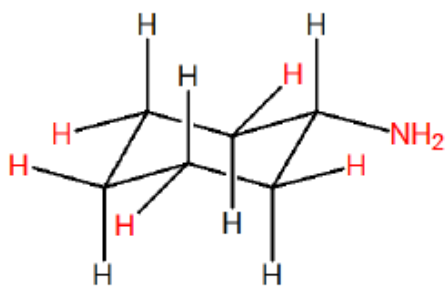
Q4.6.3

In the following molecule, label which are equatorial and which are axial, then draw the chair flip (showing labels 1,2,3).



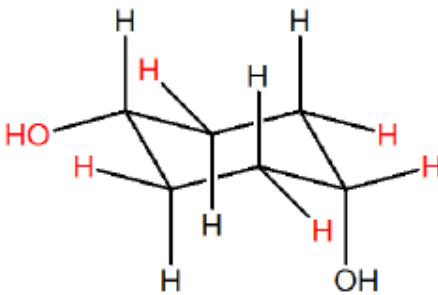
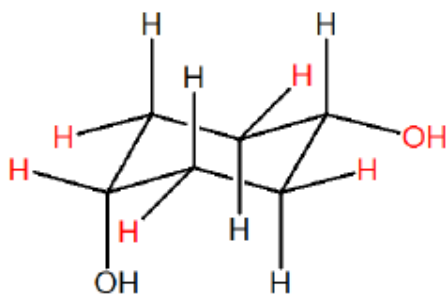
Solutions

S4.6.1



Axial
Equatorial

S4.6.2

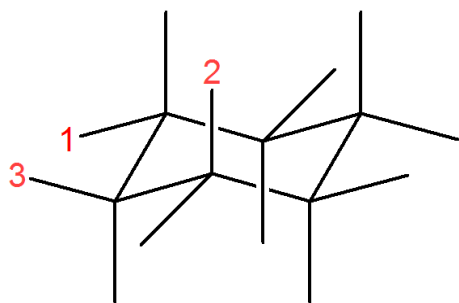


Axial
Equatorial

S4.6.3

Original conformation: 1 = axial, 2 = equatorial, 3 = axial

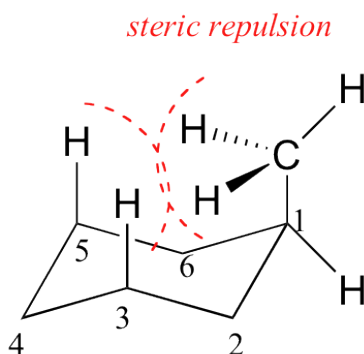
Flipped chair now looks like this.



Contributors

- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
- Dr. Kelly Matthews, Harrisburg Area Community College

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The conformation in which the methyl group is equatorial is more stable, and thus the ring flip equilibrium favors the conformation with the equatorial methyl group.

The relative steric hindrance experienced by different substituent groups oriented in an axial versus equatorial location on cyclohexane may be determined by the conformational equilibrium of the compound. The corresponding equilibrium constant is related to the energy difference between the conformers, and collecting such data allows us to evaluate the relative tendency of substituents to exist in an equatorial or axial location. Table 4.7.1 summarizes some of these free energy values (sometimes referred to as A values).

Looking at the energy values in this table, it is clear that as the size of the substituent increases, the 1,3-diaxial energy tends to increase, also. Note that it is the size and not the molecular weight of the group that is important.

Table 4.7.1: A Selection of ΔG° Values for the Change from Axial to Equatorial Orientation of Substituents for Monosubstituted Cyclohexanes

Substituent	$-\Delta G^\circ$ (kcal/mol)	Substituent	$-\Delta G^\circ$ (kcal/mol)
CH_3-	1.7	$\text{O}_2\text{N}-$	1.1
CH_2H_5-	1.8	$\text{N}\equiv\text{C}-$	0.2
$(\text{CH}_3)_2\text{CH}-$	2.2	$\text{CH}_3\text{O}-$	0.5
$(\text{CH}_3)_3\text{C}-$	≥ 5.0	$\text{HO}_2\text{C}-$	0.7
$\text{F}-$	0.3	$\text{H}_2\text{C}=\text{CH}-$	1.3
$\text{Cl}-$	0.5	C_6H_5-	3.0
$\text{Br}-$	0.5		
$\text{I}-$	0.5		

Chlorocyclohexane

This is an example of the next level of complexity, a mono-substituted cycloalkane.

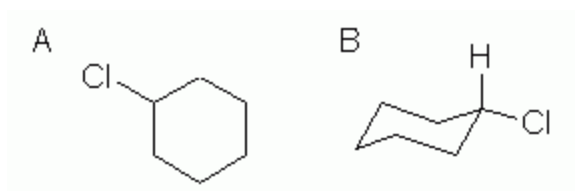


Figure 4.7.3: Chlorocyclohexane: simple hexagon and chair structures

The hexagon structure, Figure 4.7.3A, shows the basic "connectivity" of the atoms. This chemical has one Cl on the ring, and it does not matter where we show it.

The chair structure, Figure 4.7.3B, shows atom connectivity, and also the preferred conformation with the larger chlorine atom in the equatorial position.

Helpful Hints

- Examine a physical model of cyclohexane and chlorocyclohexane, so that you can see the axial and equatorial positions. Common ball and stick models are fine for this. It should be easy to see that the three axial H on one side can get very near each other. If you do not have access to physical models, examining computer models can also be useful. When putting substituents on chair structures, I encourage you to use the four corner positions of the chair as much as possible. It is easier to see the axial and equatorial relationship at the corners.
- Draw both atoms attached to the ring carbons for clarity. In Fig 4.7.3B the H atom that is on the same carbon as the Cl atom is shown. This is not necessary, but showing the H makes it clearer that the chlorine is in the equatorial position.

Exercises

Questions

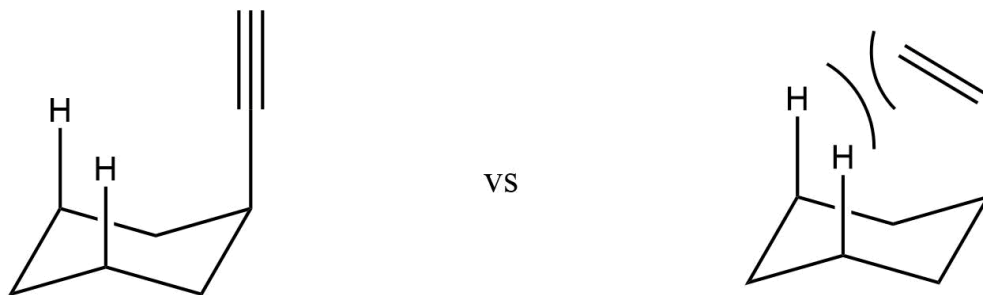
Q4.7.1

In the molecule, cyclohexyl ethyne there is little steric strain, why?

Solutions

S4.7.1

The ethyne group is linear and therefore does not affect the hydrogens in the 1,3 positions to say to the extent as a bulkier or a bent group (e.g. ethene group) would. This leads to less of a strain on the molecule.



Contributors

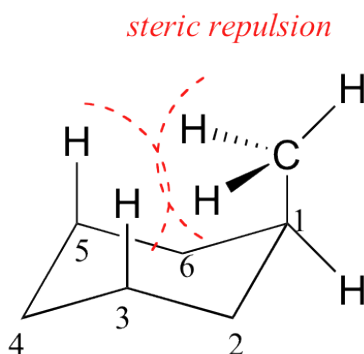
- [Dr. Dietmar Kennepohl](#) FCIC (Professor of Chemistry, [Athabasca University](#))

- Prof. Steven Farmer ([Sonoma State University](#))

>Robert Bruner (<http://bbruner.org>)

- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

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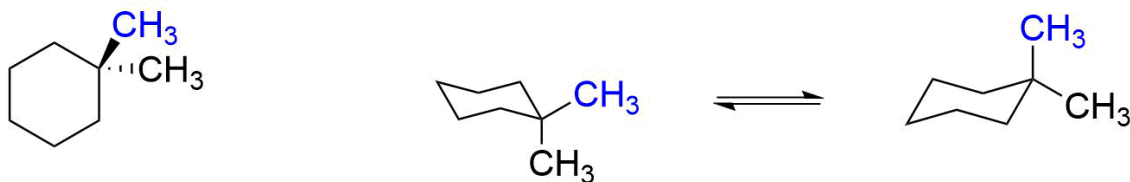


Disubstituted Cyclohexanes

In this section, the effect of conformations on the relative stability of disubstituted cyclohexanes is examined using the two principles:

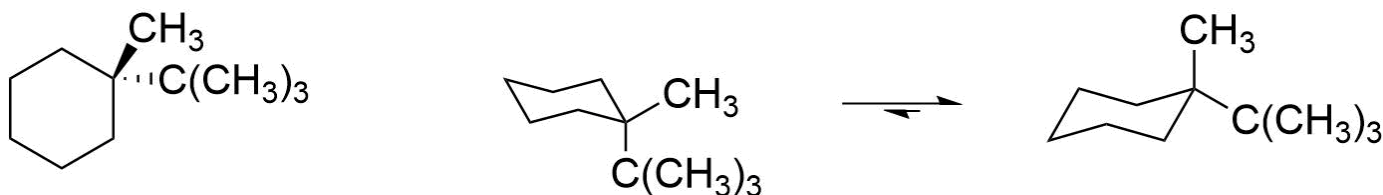
- Chair conformations are generally more stable than other possibilities, so that's all we'll consider.
- Substituents prefer equatorial rather than axial positions in order to minimize the steric hindrance of 1,3-diaxial interactions.

1,1-dimethylcyclohexane does not have *cis* or *trans* isomers, because both methyl groups are on the same ring carbon. Both conformers have one methyl group axial and one methyl group equatorial, and they both have the same energy or relative stability. Therefore, the equilibrium between the two conformers does not favor either one. The energy cost of having one methyl group axial (versus equatorial) is 1.7 kcal/mole (from Table 4.7.1), and both conformers will be equal in energy. Note that both methyl groups cannot be equatorial at the same time without breaking bonds and creating a different molecule.



1,1-dimethylcyclohexane

However, if the two groups are different, as in 1-*tert*-butyl-1-methylcyclohexane, then the equilibrium favors the conformer in which the larger group *tert*-butyl group is in the more stable equatorial position. The energy cost of having one *tert*-butyl group axial (versus equatorial) can be calculated from the values in table 4.7.1 and is approximately 5.0 kcal/mole. That means that the conformer with the *tert*-butyl group axial is approximately 3.3 kcal/mol (5.0 kcal/mol - 1.7 kcal/mole) less stable than the conformer with the *tert*-butyl group equatorial. This means that 1-*tert*-butyl-1-methylcyclohexane will spend the majority of its time in the more stable conformation.

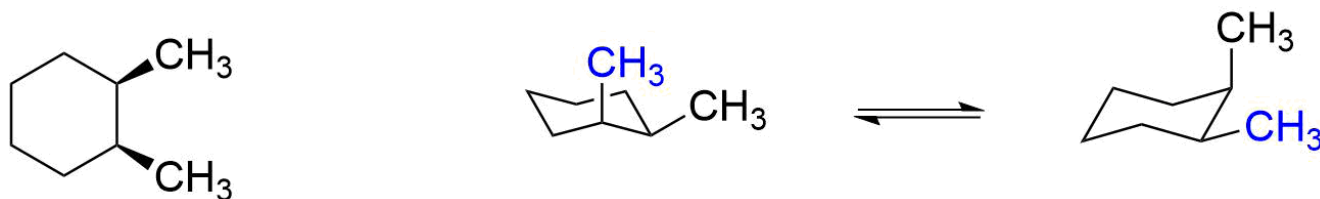


1-*tert*-butyl-1-methylcyclohexane

Disubstituted Cyclohexanes: The Relative Stability of *cis* and *trans* Isomers

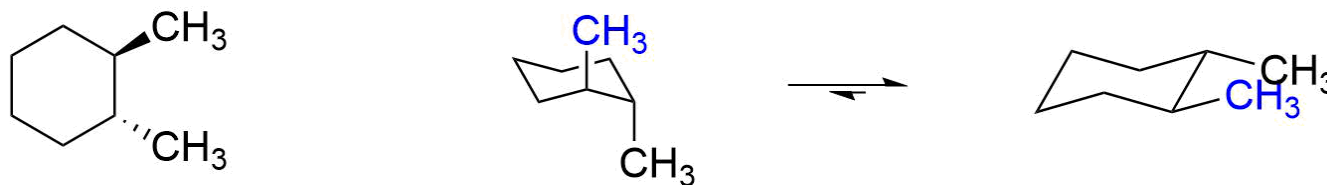
The situation is more complex when the effect of conformations on the relative stability of *cis* and *trans* disubstituted cyclohexanes is analyzed. Remember, configurational stereoisomers do not interconvert without breaking bonds, whereas conformational isomers normally interconvert rapidly by the ring flip process.

Let's apply a similar analysis to the *cis* and *trans* stereoisomers of 1,2-dimethylcyclohexane.



cis-1,2-dimethylcyclohexane

In *cis*-1,2-dimethylcyclohexane, one methyl group is axial and one methyl group is equatorial in both ring flip conformers, so neither conformer is more stable than the other. It is important to note, that this molecule cannot get both methyl groups axial without breaking bonds to make a new molecule.

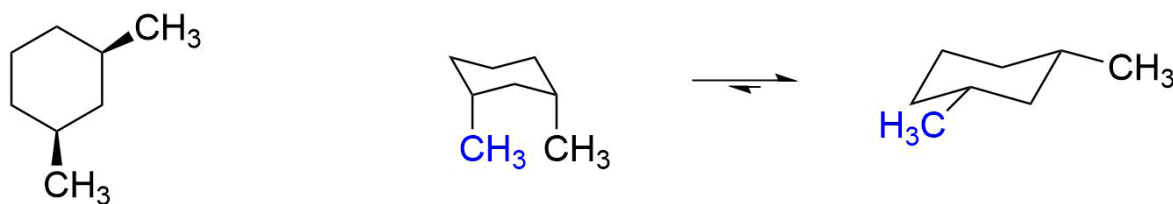


trans-1,2-dimethylcyclohexane

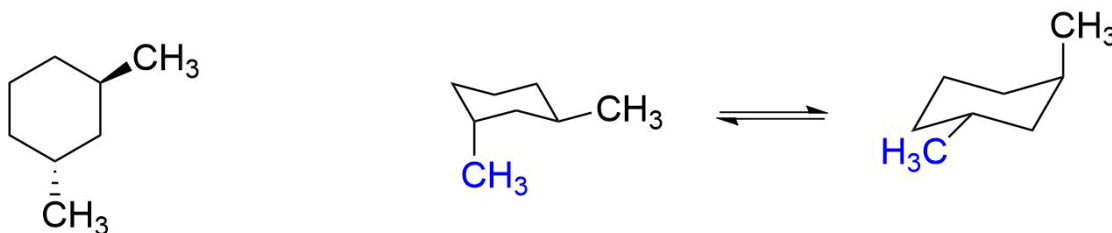
In *trans*-1,2-dimethylcyclohexane, one conformer has both methyl groups axial and the other has both methyl groups equatorial. The conformer with both methyl groups axial is 3.4 kcal/mole (2×1.7 kcal/mol) less stable than the conformer with both methyl groups equatorial. Obviously, the equilibrium will favor the conformer with both methyl groups in the equatorial position.

To decide whether the *cis* or *trans* isomer of 1,2-dimethylcyclohexane is more stable, compare the relative energy of the most stable conformer of *cis*-1,2-dimethylcyclohexane to the most stable conformer of *trans*-1,2-dimethylcyclohexane. The *trans*-1,2-dimethylcyclohexane has the most stable conformer, so it is the more stable isomer.

Does this mean that the *trans* isomer of a disubstituted cyclohexane is always more stable than the *cis* isomer? Let's examine both the *cis* and *trans* isomers of 1,3-dimethylcyclohexane and find out.



cis-1,3-dimethylcyclohexane



trans-1,3-dimethylcyclohexane

As can be seen in the structures above, *cis*-1,3-dimethylcyclohexane's most stable conformer has both methyl groups equatorial, while *trans*-1,3-dimethylcyclohexane always has one methyl group is equatorial and one methyl group axial. This means that the *cis* isomer 1,3-dimethylcyclohexane is more stable than the *trans* isomer. And that is opposite what we found for 1,2-dimethylcyclohexane.

As practice, you should do a similar conformational analysis of the *cis* and *trans* isomers of 1,4-dimethylcyclohexane. You should find that the *trans* isomer of 1,4-dimethylcyclohexane is more stable than the *cis* isomer.

Summary

The relative stabilities of the *cis* and *trans* isomers of disubstituted cyclohexanes depends upon which isomer has the most stable conformer. The most stable isomer for disubstituted cyclohexanes is summarized below.

substitution type	most stable isomer
1,2-disubstituted cyclohexanes	<i>trans</i>
1,3-disubstituted cyclohexanes	<i>cis</i>
1,4-disubstituted cyclohexanes	<i>trans</i>

Exercises

Questions

Q4.8.1

For the following molecules draw the most stable chair conformation and explain why you chose this as an answer

1 = *trans*-1,2-dimethylcyclohexane

2 = *cis*-1,3-dimethylcyclohexane

Solutions

S4.8.1

1 – The most stable conformation would be to have the methyl groups equatorial reducing steric interaction

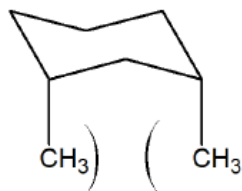
2 – The most stable conformation would be to have the groups equatorial this would reduce the strain if they were axial



1



2



Contributors

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, [Athabasca University](#))
- Prof. Steven Farmer ([Sonoma State University](#))
- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark ([Chemguide.co.uk](#))
- >Robert Bruner (<http://bbruner.org>)
- Kelly Matthews, Senior Professor of Chemistry, Harrisburg Area Community College

3.10: Conformations of Polycyclic Molecules

Objective

After completing this section, you should be able to draw the structures and construct molecular models of *cis*- and *trans*-decalin and of norbornane.

Key Terms

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

- bridgehead carbon atom
- polycyclic molecule

Study Notes

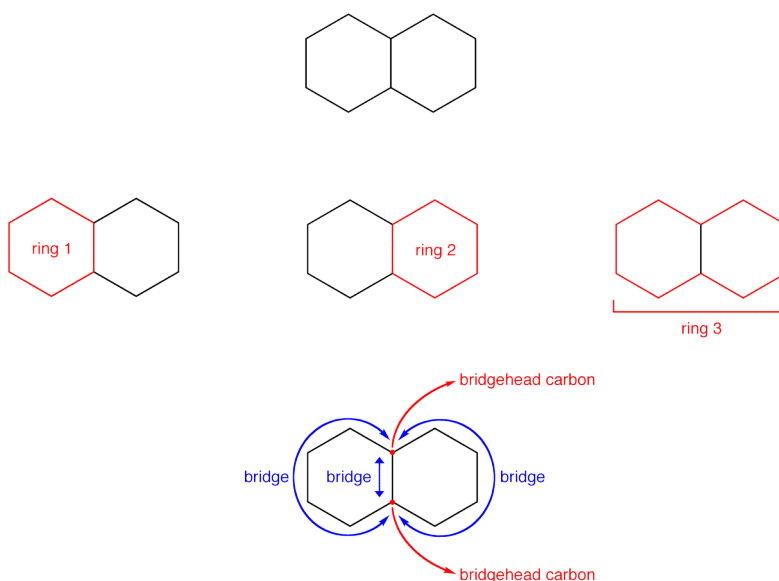
A *bridgehead carbon atom* is a carbon atom which is shared by at least two rings. The hydrogen atom which is attached to a bridgehead carbon may be referred to as a bridgehead hydrogen.

Note that bicyclo[2.2.1]heptane is the systematic name of norbornane. You need not be concerned over the IUPAC name of norbornane. The nomenclature of compounds of this type is beyond the scope of this course.

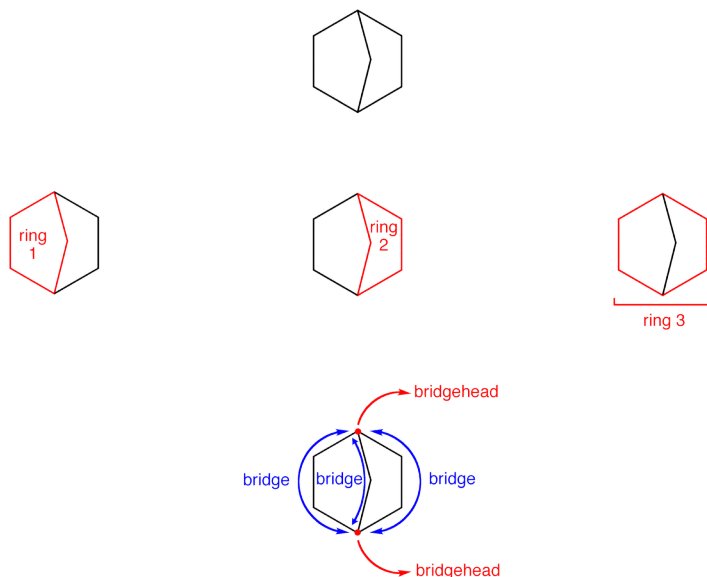
Bicyclic Ring Systems

A bridged bicycloalkane is a bicycloalkane whose molecule has two carbon atoms shared by all three rings identifiable in the molecule. The two carbon atoms shared by the three rings are called bridgehead carbon atoms. A bond or a chain of bonds connecting the bridgehead carbon atoms is called a bridge.

eg. 1: Decalin



eg. 2: bicyclo[2.2.1]heptane

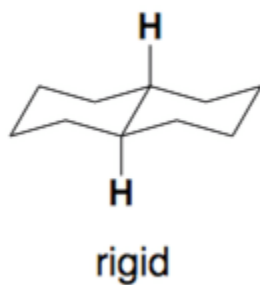


If in a bridged bicycloalkane, the bridgehead carbons are directly bonded to each other, the compound is called a fused bicycloalkane. In other words, in a fused bicycloalkane, the number of carbon atoms in one of the three bridges is zero. eg: decalin

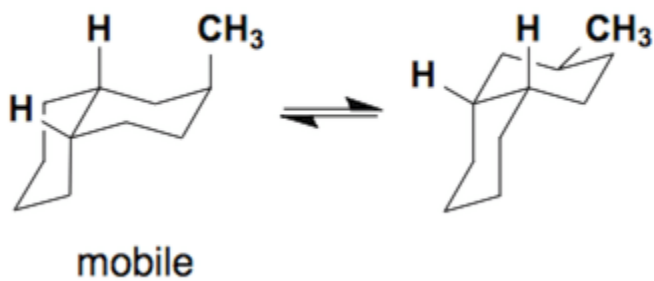
[see also spirobicycloalkane](#)

Decalins can come in two stereoisomers. The *trans*- stereoisomer is a rigid structure which cannot undergo a ring flip. The *cis*- stereoisomer is mobile and can ring flip to allow substituents to sit in the equatorial position.

***trans*-decalin**

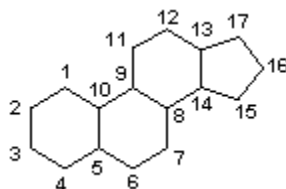


***cis*-decalin**



Steroids

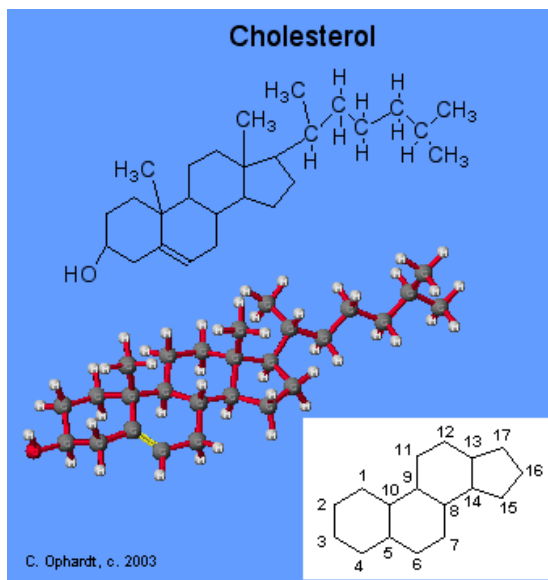
Steroids include such well known compounds as cholesterol, sex hormones, birth control pills, cortisone, and anabolic steroids.



CholesterolEdit section

The best known and most abundant steroid in the body is cholesterol. Cholesterol is formed in brain tissue, nerve tissue, and the blood stream. It is the major compound found in gallstones and bile salts. Cholesterol also contributes to the formation of deposits on the inner walls of blood vessels. These deposits harden and obstruct the flow of blood. This condition, known as atherosclerosis, results in various heart diseases, strokes, and high blood pressure.

Much research is currently underway to determine if a correlation exists between cholesterol levels in the blood and diet. Not only does cholesterol come from the diet, but cholesterol is synthesized in the body from carbohydrates and proteins as well as fat. Therefore, the elimination of cholesterol rich foods from the diet does not necessarily lower blood cholesterol levels. Some studies have found that if certain unsaturated fats and oils are substituted for saturated fats, the blood cholesterol level decreases. The research is incomplete on this problem.

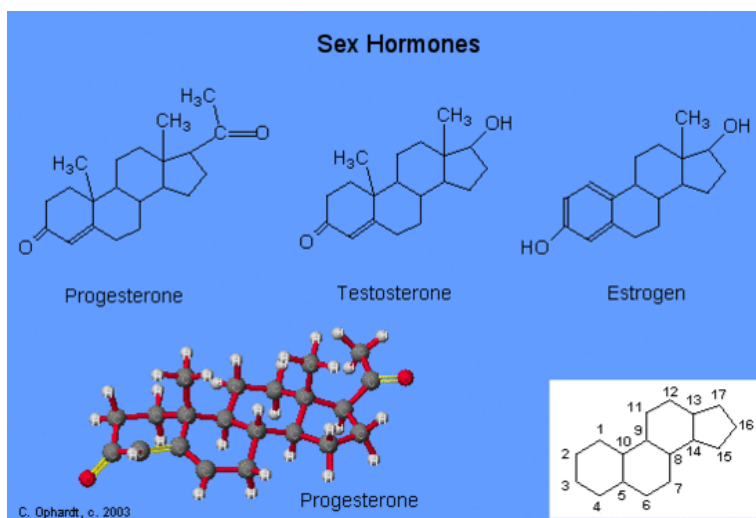


Structures of Sex HormonesEdit section

Sex hormones are also steroids. The primary male hormone, testosterone, is responsible for the development of secondary sex characteristics. Two female sex hormones, progesterone and estrogen or estradiol control the ovulation cycle. Notice that the male and female hormones have only slight differences in structures, but yet have very different physiological effects.

Testosterone promotes the normal development of male genital organs and is synthesized from cholesterol in the testes. It also promotes secondary male sexual characteristics such as deep voice, facial and body hair.

Estrogen, along with progesterone regulates changes occurring in the uterus and ovaries known as the menstrual cycle. For more details see Birth Control. Estrogen is synthesized from testosterone by making the first ring aromatic which results in mole double bonds, the loss of a methyl group and formation of an alcohol group.



Exercises

Questions

Q4.9.1

Someone stated that *trans*-decalin is more stable than *cis*-decalin. Explain why this is incorrect.

Solutions

S4.9.1

Cis-decalin has fewer steric interactions than *trans*-decalin.

Contributors

- Gamini Gunawardena from the [OChemPal](#) site ([Utah Valley University](#))

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INDEX

B

Baeyer theory

3.4: Stability of Cycloalkanes - Ring Strain

D

Disubstituted Cyclohexanes

3.9: Conformations of Disubstituted Cyclohexanes

E

ethylene

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

F

functional group

2.1: Functional Groups

R

ring strain

3.4: Stability of Cycloalkanes - Ring Strain

V

valence bond theory

1.2: The Nature of Chemical Bonds - Valence Bond Theory

values

3.9: Conformations of Disubstituted Cyclohexanes

GLOSSARY

S

Sample Word 1 | Sample Definition 1

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 - 2.2: Alkanes and Alkane Isomers - [CC BY-NC-SA 4.0](#)
 - 2.3: Alkyl Groups - [CC BY-NC-SA 4.0](#)
 - 2.4: Naming Alkanes - [CC BY-NC-SA 4.0](#)
 - 2.5: Naming Cycloalkanes - [CC BY-NC-SA 4.0](#)
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 - 3: Chapter 3 Conformations and Cycloalkanes - [CC BY-NC-SA 4.0](#)
 - 3.1: Conformations of Ethane - [CC BY-NC-SA 4.0](#)
 - 3.2: Conformations of Other Alkanes - [CC BY-NC-SA 4.0](#)
 - 3.3: Cis-Trans Isomerism in Cycloalkanes - [CC BY-NC-SA 4.0](#)
 - 3.4: Stability of Cycloalkanes - Ring Strain - [CC BY-NC-SA 4.0](#)
 - 3.5: Conformations of Cycloalkanes - [CC BY-NC-SA 4.0](#)
 - 3.6: Conformations of Cyclohexane - [CC BY-NC-SA 4.0](#)
 - 3.7: Axial and Equatorial Bonds in Cyclohexane - [CC BY-NC-SA 4.0](#)
 - 3.8: Conformations of Monosubstituted Cyclohexanes - [CC BY-NC-SA 4.0](#)
 - 3.9: Conformations of Disubstituted

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