Chapter 1 – Structure and Bonding

Chapter Outline

I. Atomic Structure (Sections 1.1–1.3).
   A. Introduction to atomic structure (Section 1.1).
      1. An atom consists of a dense, positively charged nucleus surrounded by negatively charged electrons.
         a. The nucleus is made up of positively charged protons and uncharged neutrons.
         b. The nucleus contains most of the mass of the atom.
         c. Electrons move about the nucleus at a distance of about 2 \times 10^{-10} \text{ m} (200 \text{ pm}).
      2. The atomic number \( (Z) \) gives the number of protons in the nucleus.
      3. The mass number \( (A) \) gives the total number of protons and neutrons.
      4. All atoms of a given element have the same value of \( Z \).
         a. Atoms of a given element can have different values of \( A \).
         b. Atoms of the same element with different values of \( A \) are called isotopes.
   B. Orbitals (Section 1.2).
      1. The distribution of electrons in an atom can be described by a wave equation.
         a. The solution to a wave equation is an orbital, represented by \( \Psi \).
         b. \( \Psi^2 \) predicts the volume of space in which an electron is likely to be found.
      2. There are four different kinds of orbitals \( (s, p, d, f) \).
         a. The \( s \) orbitals are spherical.
         b. The \( p \) orbitals are dumbbell-shaped.
         c. Four of the five \( d \) orbitals are cloverleaf-shaped.
      3. An atom's electrons are organized into electron shells.
         a. The shells differ in the numbers and kinds of orbitals they contain.
         b. Electrons in different orbitals have different energies.
         c. Each orbital can hold up to a maximum of two electrons.
      4. The two lowest-energy electrons are in the \( 1s \) orbital.
         a. The \( 2s \) orbital is the next higher in energy.
         b. The next three orbitals are \( 2p_x, 2p_y \), and \( 2p_z \), which have the same energy.
            i. Each \( p \) orbital has a region of zero density, called a node.
         c. The lobes of a \( p \) orbital have opposite algebraic signs.
   C. Electron Configuration (Section 1.3).
      1. The ground-state electron configuration of an atom is a listing of the orbitals occupied by the electrons of the atom in the lowest energy configuration.
      2. Rules for predicting the ground-state electron configuration of an atom:
         a. Orbitals with the lowest energy levels are filled first.
            i. The order of filling is \( 1s, 2s, 2p, 3s, 3p, 4s, 3d \).
         b. Only two electrons can occupy each orbital, and they must be of opposite spin.
         c. If two or more orbitals have the same energy, one electron occupies each until all are half-full (Hund's rule). Only then does a second electron occupy one of the orbitals.
            i. All of the electrons in half-filled shells have the same spin.
   II. Chemical Bonding Theory (Sections 1.4–1.5).
    A. Development of chemical bonding theory (Section 1.4).
       1. Kekulé and Couper proposed that carbon has four "affinity units"; carbon is tetravalent.
       2. Kekulé suggested that carbon can form rings and chains.
3. Van't Hoff and Le Bel proposed that the 4 atoms to which carbon forms bonds sit at the corners of a regular tetrahedron.

4. In a drawing of a tetrahedral carbon, a wedged line represents a bond pointing toward the viewer, a dashed line points behind the plane of the page, and a solid line lies in the plane of the page.

B. Covalent bonds.

1. Atoms bond together because the resulting compound is more stable than the individual atoms.
   a. Atoms tend to achieve the electron configuration of the nearest noble gas.
   b. Atoms in groups 1A, 2A and 7A either lose electrons or gain electrons to form ionic compounds.
   c. Atoms in the middle of the periodic table share electrons by forming covalent bonds.
   d. The neutral collection of atoms held together by covalent bonds is a molecule.

2. Covalent bonds can be represented two ways.
   a. In electron-dot structures, bonds are represented as pairs of dots.
   b. In line-bond structures, bonds are represented as lines drawn between two bonded atoms.

3. The number of covalent bonds formed by an atom depends on the number of electrons it has and on the number it needs to achieve an octet.

4. Valence electrons not used for bonding are called lone-pair (nonbonding) electrons.
   a. Lone-pair electrons are often represented as dots.

C. Valence bond theory (Section 1.5).

1. Covalent bonds are formed by the overlap of two atomic orbitals, each of which contains one electron. The two electrons have opposite spins.

2. Bonds formed by the head-on overlap of two atomic orbitals are cylindrically symmetrical and are called \( \sigma \) bonds.

3. Bond strength is the measure of the amount of energy needed to break a bond.

4. Bond length is the optimum distance between nuclei.

5. Every bond has a characteristic bond length and bond strength.

III. Hybridization (Sections 1.6–1.10).

A. \( sp^3 \) Orbitals (Sections 1.6, 1.7).

1. Structure of methane (Section 1.6).
   a. When carbon forms 4 bonds with hydrogen, one 2s orbital and three 2p orbitals combine to form four equivalent atomic orbitals (\( sp^3 \) hybrid orbitals).
   b. These orbitals are tetrahedrally oriented.
   c. Because these orbitals are unsymmetrical, they can form stronger bonds than unhybridized orbitals can.
   d. These bonds have a specific geometry and a bond angle of 109.5°.

2. Structure of ethane (Section 1.7).
   a. Ethane has the same type of hybridization as occurs in methane.
   b. The C–C bond is formed by overlap of two \( sp^3 \) orbitals.
   c. Bond lengths, strengths and angles are very close to those of methane.

B. \( sp^2 \) Orbitals (Section 1.8).

1. If one carbon 2s orbital combines with two carbon 2p orbitals, three hybrid \( sp^2 \) orbitals are formed, and one \( p \) orbital remains unchanged.

2. The three \( sp^2 \) orbitals lie in a plane at angles of 120°, and the unhybridized \( p \) orbital is perpendicular to them.

3. Two different types of bonds form between two carbons.
   a. A \( \sigma \) bond forms from the overlap of two \( sp^2 \) orbitals.
   b. A \( \pi \) bond forms by sideways overlap of two \( p \) orbitals.
   c. This combination is known as a carbon–carbon double bond.
4. Ethylene is composed of a carbon–carbon double bond and four $\sigma$ bonds formed between the remaining four $sp^2$ orbitals of carbon and the 1s orbitals of hydrogen.
   a. The double bond of ethylene is both shorter and stronger than the C–C bond of ethane.

C. $sp$ Orbitals (Section 1.10).
   1. If one carbon 2s orbital combines with one carbon 2p orbital, two hybrid $sp$ orbitals are formed, and two p orbitals are unchanged.
   2. The two $sp$ orbitals are 180° apart, and the two p orbitals are perpendicular to them and to each other.
   3. Two different types of bonds form.
      a. A $\sigma$ bond forms from the overlap of two $sp$ orbitals.
      b. Two $\pi$ bonds form by sideways overlap of four unhybridized p orbitals.
      c. This combination is known as a carbon–carbon triple bond.
   4. Acetylene is composed of a carbon–carbon triple bond and two $\sigma$ bonds formed between the remaining two $sp$ orbitals of carbon and the 1s orbitals of hydrogen.
      a. The triple bond of acetylene is the strongest carbon–carbon bond.

D. Hybridization of nitrogen and oxygen (Section 1.10).
   1. Covalent bonds between other elements can be described by using hybrid orbitals.
   2. Both the nitrogen atom in ammonia and the oxygen atom in water form $sp^3$ hybrid orbitals.
      a. The lone-pair electrons in these compounds occupy $sp^3$ orbitals.
   3. The bond angles between hydrogen and the central atom is often less than 109° because the lone-pair electrons take up more room than the $\sigma$ bond.
   4. Because of their positions in the third row, phosphorus and sulfur can form more than the typical number of covalent bonds.

IV. Molecular orbital theory (Section 1.11).
   A. Molecular orbitals arise from a mathematical combination of atomic orbitals and belong to the entire molecule.
   1. Two 1s orbitals can combine in two different ways.
      a. The additive combination is a bonding MO and is lower in energy than the two hydrogen 1s atomic orbitals.
      b. The subtractive combination is an antibonding MO and is higher in energy than the two hydrogen 1s atomic orbitals.
   2. Two p orbitals in ethylene can combine to form two $\pi$ MOs.
      a. The bonding MO has no node; the antibonding MO has one node.
   3. A node is a region between nuclei where electrons aren't found.
      a. If a node occurs between two nuclei, the nuclei repel each other.

V. Chemical structures (Section 1.12).
   A. Drawing chemical structures.
   1. Condensed structures don't show C–H bonds and don't show the bonds between CH$_2$, CH$_2$ and CH units.
   2. Skeletal structures are simpler still.
      a. Carbon atoms aren't usually shown.
      b. Hydrogen atoms bonded to carbon aren't usually shown.
      c. Other atoms (O, N, Cl, etc.) are shown.
Solutions to Problems

1.1 (a) To find the ground-state electron configuration of an element, first locate its atomic number. For oxygen, the atomic number is 8; oxygen thus has 8 protons and 8 electrons. Next, assign the electrons to the proper energy levels, starting with the lowest level. Fill each level completely before assigning electrons to a higher energy level.

Notice that the \(2p\) electrons are in different orbitals. According to Hund's rule, we must place one electron into each orbital of the same energy level until all orbitals are half-filled.

\[
\begin{align*}
\text{Oxygen} & \\
1s & \uparrow \downarrow \\
2s & \uparrow \\
2p & \uparrow \uparrow \uparrow \uparrow \\
\end{align*}
\]

Remember that only two electrons can occupy the same orbital, and that they must be of opposite spin.

A different way to represent the ground-state electron configuration is to simply write down the occupied orbitals and to indicate the number of electrons in each orbital. For example, the electron configuration for oxygen is \(1s^2 \ 2s^2 \ 2p^4\).

(b) Nitrogen, with an atomic number of 7, has 7 electrons. Assigning these to energy levels:

\[
\begin{align*}
\text{Nitrogen} & \\
1s & \uparrow \downarrow \\
2s & \uparrow \\
2p & \uparrow \uparrow \uparrow \uparrow \\
\end{align*}
\]

The more concise way to represent ground-state electron configuration for nitrogen:
\(1s^2 \ 2s^2 \ 2p^3\)

(c) Sulfur has 16 electrons,
\(1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^4\)

\[
\begin{align*}
\text{Sulfur} & \\
1s & \uparrow \downarrow \\
2s & \uparrow \uparrow \\
2p & \uparrow \uparrow \uparrow \uparrow \\
3s & \uparrow \uparrow \\
3p & \uparrow \uparrow \uparrow \uparrow \\
\end{align*}
\]
1.2 The elements of the periodic table are organized into groups that are based on the number of outer-shell electrons each element has. For example, an element in group 1A has one outer-shell electron, and an element in group 5A has five outer-shell electrons. To find the number of outer-shell electrons for a given element, use the periodic table to locate its group.

(a) Magnesium (group 2A) has two electrons in its outermost shell.
(b) Cobalt is a transition metal, which has two electrons in the 4s subshell, plus seven electrons in its 3d subshell.
(c) Selenium (group 6A) has six electrons in its outermost shell.

1.3 A solid line represents a bond lying in the plane of the page, a wedged bond represents a bond pointing out of the plane of the page toward the viewer, and a dashed bond represents a bond pointing behind the plane of the page.

1.4

1.5 Identify the group of the central element to predict the number of covalent bonds the element can form.

(a) Carbon (Group 4A) has four electrons in its valence shell and forms four bonds to achieve the noble-gas configuration of neon. A likely formula is $\text{CCl}_4$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Group</th>
<th>Likely Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b) Al</td>
<td>3A</td>
<td>$\text{AlH}_3$</td>
</tr>
<tr>
<td>(c) C</td>
<td>4A</td>
<td>$\text{CH}_2\text{Cl}_2$</td>
</tr>
<tr>
<td>(d) Si</td>
<td>4A</td>
<td>$\text{SiF}_4$</td>
</tr>
<tr>
<td>(e) N</td>
<td>5A</td>
<td>$\text{CH}_3\text{NH}_2$</td>
</tr>
</tbody>
</table>
1.6 Start by drawing the electron-dot structure of the molecule.

(1) Determine the number of valence, or outer-shell electrons for each atom in the molecule. For chloroform, we know that carbon has four valence electrons, hydrogen has one valence electron, and each chlorine has seven valence electrons.

\[
\begin{align*}
\cdot & \cdot & \text{4 x 1} = 4 \\
\text{H} & \cdot & \text{1 x 1} = 1 \\
\ddots & \ddots & \text{7 x 3} = 21 \\
\therefore & \text{26 total valence electrons}
\end{align*}
\]

(2) Next, use two electrons for each single bond.

\[
\begin{align*}
\text{H} \\
\text{Cl : C : Cl} \\
\text{Cl}
\end{align*}
\]

(3) Finally, use the remaining electrons to achieve an noble gas configuration for all atoms. For a line-bond structure, replace the electron dots between two atoms with a line.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Electron-dot structure</th>
<th>Line-bond structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) CHCl₃</td>
<td>:Cl : C : Cl :</td>
<td>:Cl -- C -- Cl :</td>
</tr>
<tr>
<td>(b) H₂S</td>
<td>H : S :</td>
<td>H -- S --</td>
</tr>
<tr>
<td>8 valence electrons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) CH₃NH₂</td>
<td>:H : C : N : H</td>
<td>H -- C -- N -- H</td>
</tr>
<tr>
<td>14 valence electrons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(d) CH₃Li</td>
<td>H : C : Li</td>
<td>H -- C -- Li</td>
</tr>
<tr>
<td>8 valence electrons</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.7 Each of the two carbons has 4 valence electrons. Two electrons are used to form the carbon–carbon bond, and the 6 electrons that remain can form bonds with a maximum of 6 hydrogens. Thus, the formula C₂H₇ is not possible.
1.8 Connect the carbons and add hydrogens so that all carbons are bonded to four different atoms.

The geometry around all carbon atoms is tetrahedral, and all bond angles are approximately 109°.

1.9

The C3–H bonds are σ bonds formed by overlap of an \( sp^3 \) orbital of carbon 3 with an \( s \) orbital of hydrogen.

The C2–H and C1–H bonds are σ bonds formed by overlap of an \( sp^2 \) orbital of carbon with an \( s \) orbital of hydrogen.

The C2–C3 bond is a σ bond formed by overlap of an \( sp^3 \) orbital of carbon 3 with an \( sp^2 \) orbital of carbon 2.

There are two C1–C2 bonds. One is a σ bond formed by overlap of an \( sp^2 \) orbital of carbon 1 with an \( sp^2 \) orbital of carbon 2. The other is a \( \pi \) bond formed by overlap of a \( p \) orbital of carbon 1 with a \( p \) orbital of carbon 2. All four atoms connected to the carbon–carbon double bond lie in the same plane, and all bond angles between these atoms are 120°. The bond angle between hydrogen and the \( sp^3 \)-hybridized carbon is 109°.

1.10

The C3–H bonds are σ bonds formed by overlap of an \( sp^3 \) orbital of carbon 3 with an \( s \) orbital of hydrogen.

The C2–H and C1–H bonds are σ bonds formed by overlap of an \( sp^2 \) orbital of carbon with an \( s \) orbital of hydrogen.

The C2–C3 bond is a σ bond formed by overlap of an \( sp^3 \) orbital of carbon 3 with an \( sp^2 \) orbital of carbon 2.

There are two C1–C2 bonds. One is a σ bond formed by overlap of an \( sp^2 \) orbital of carbon 1 with an \( sp^2 \) orbital of carbon 2. The other is a \( \pi \) bond formed by overlap of a \( p \) orbital of carbon 1 with a \( p \) orbital of carbon 2. All four atoms connected to the carbon–carbon double bond lie in the same plane, and all bond angles between these atoms are 120°. The bond angle between hydrogen and the \( sp^3 \)-hybridized carbon is 109°.

1.11

All atoms lie in the same plane, and all bond angles are approximately 120°.

1,3-Butadiene
1.12

Aspirin.

All carbons are \( sp^2 \) hybridized, with the exception of the indicated carbon. All oxygen atoms have two lone pairs of electrons.

1.13

The C3-H bonds are \( \sigma \) bonds formed by overlap of an \( sp^3 \) orbital of carbon 3 with an \( s \) orbital of hydrogen.

The C1-H bond is a \( \sigma \) bond formed by overlap of an \( sp \) orbital of carbon 1 with an \( s \) orbital of hydrogen.

The C2-C3 bond is a \( \sigma \) bond formed by overlap of an \( sp \) orbital of carbon 2 with an \( sp^3 \) orbital of carbon 3.

There are three C1-C2 bonds. One is a \( \sigma \) bond formed by overlap of an \( sp \) orbital of carbon 1 with an \( sp \) orbital of carbon 2. The other two bonds are \( \pi \) bonds formed by overlap of two \( p \) orbitals of carbon 1 with two \( p \) orbitals of carbon 2.

The three carbon atoms of propyne lie in a straight line: the bond angle is 180°. The H–C1≡C2 bond angle is also 180°. The bond angle between hydrogen and the \( sp^3 \)-hybridized carbon is 109°.

1.14

(a) The \( sp^3 \)-hybridized oxygen atom has tetrahedral geometry.

(b) Tetrahedral geometry at nitrogen and carbon.

(c) Like nitrogen, phosphorus has five outer-shell electrons. \( PH_3 \) has tetrahedral geometry.
The $sp^3$-hybridized sulfur atom has tetrahedral geometry.

1.15 Remember that the end of a line represents a carbon atom with 3 hydrogens, a two-way intersection represents a carbon atom with 2 hydrogens, a three-way intersection represents a carbon with 1 hydrogen and a four-way intersection represents a carbon with no hydrogens.

Adrenaline – $C_{9}H_{13}NO_{3}$

Estrone – $C_{18}H_{22}O_{2}$

1.16 Several possible skeletal structures can satisfy each molecular formula.

(a) $C_{5}H_{12}$

(b) $C_{2}H_{7}N$

(c) $C_{3}H_{6}O$

(d) $C_{4}H_{9}Cl$
1.17

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{O} \\
\text{PABA} & \\
\end{align*}
\]

**Visualizing Chemistry**

1.18

(a)

(b)

1.19 Citric acid (C\(_6\)H\(_8\)O\(_7\)) contains seven oxygen atoms, each of which has two electron lone pairs. Three of the oxygens form double bonds with carbon.
1.20

All carbons are $sp^2$ hybridized, except for the carbon indicated as $sp^3$. The two oxygen atoms and the nitrogen atom have lone pair electrons, as shown.

1.21

Additional Problems

Electron Configuration

1.22

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Number of valence electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Zinc</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>(b) Iodine</td>
<td>53</td>
<td>7</td>
</tr>
<tr>
<td>(c) Silicon</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>(d) Iron</td>
<td>26</td>
<td>2 (in 4s subshell), 6 (in 3d subshell)</td>
</tr>
</tbody>
</table>

1.23

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Ground-state electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Potassium</td>
<td>19</td>
<td>$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^1$</td>
</tr>
<tr>
<td>(b) Arsenic</td>
<td>33</td>
<td>$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^3$</td>
</tr>
<tr>
<td>(c) Aluminum</td>
<td>13</td>
<td>$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^1$</td>
</tr>
<tr>
<td>(d) Germanium</td>
<td>32</td>
<td>$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^2$</td>
</tr>
</tbody>
</table>

Electron-Dot and Line-Bond Structures

1.24

(a) NH$_2$OH  (b) AlCl$_3$  (c) CF$_2$Cl$_2$  (d) CH$_2$O
1.25 (a) The 4 valence electrons of carbon can form bonds with a maximum of 4 hydrogens. Thus, it is not possible for the compound CH$_5$ to exist.

(b) If you try to draw a molecule with the formula C$_2$H$_6$N, you will see that it is impossible for both carbons and nitrogen to have a complete octet of electrons. Therefore, C$_2$H$_6$N is unlikely to exist.

(c) A compound with the formula C$_3$H$_5$Br$_2$ doesn't have filled outer shells for all atoms and is thus unlikely to exist.

1.26

\[
\begin{align*}
&\text{H} \\
&\text{H:C:C:::N:} \\
&\text{H} \\
&\text{Acetonitrile}
\end{align*}
\]

In the compound acetonitrile, nitrogen has eight electrons in its outer electron shell. Six are used in the carbon-nitrogen triple bond, and two are a nonbonding electron pair.

1.27

\[
\begin{align*}
&\text{H} \\
&\text{C=C\text{\vdots\vdots}} \\
&\text{H} \\
&\text{Vinyl chloride}
\end{align*}
\]

Vinyl chloride has 18 valence electrons: Eight electrons are used for 4 single bonds, 4 electrons are used in the carbon–carbon double bond, and 6 electrons are in the 3 lone pairs that surround chlorine.

1.28

(a) (b) (c)

\[
\begin{align*}
&\text{H}_3\text{C-S-S-CH}_3 \\
&\text{H}_3\text{C-C-\text{NH}_2} \\
&\text{H}_3\text{C-C-O-}
\end{align*}
\]

1.29 In molecular formulas of organic molecules, carbon is listed first, followed by hydrogen. All other elements are listed in alphabetical order.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Aspirin</td>
<td>C$_9$H$_8$O$_4$</td>
</tr>
<tr>
<td>(b) Vitamin C</td>
<td>C$_6$H$_8$O$_6$</td>
</tr>
<tr>
<td>(c) Nicotine</td>
<td>C$<em>{10}$H$</em>{14}$N$_2$</td>
</tr>
<tr>
<td>(d) Glucose</td>
<td>C$<em>6$H$</em>{12}$O$_6$</td>
</tr>
</tbody>
</table>
1.30 To work a problem of this sort, you must draw all possible structures consistent with the rules of valence. You must systematically consider all possible attachments, including those that have branches, rings and multiple bonds.

(a) \( \text{H} - \text{H} - \text{H} \)
\( \text{H} \quad \text{C} \quad \text{C} \quad \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \)

(b) \( \text{H} - \text{N} - \text{H} \)
\( \text{H} \quad \text{C} \quad \text{C} \quad \text{O} - \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \)

(c) \( \text{H} - \text{O} - \text{C} - \text{H} \)
\( \text{H} \quad \text{C} \quad \text{C} \quad \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \)

(d) \( \text{H} - \text{C} - \text{C} - \text{Br} \)
\( \text{H} \quad \text{H} \quad \text{H} \)

1.31 Ethanol

\( \text{CH}_3 \quad \text{H} \quad \text{C} \quad \cdot \quad \text{H} \quad \text{OH} \)

1.32

(a) \( \text{H} - \text{O} - \text{C} - \text{C} - \text{C} - \text{O} - \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)

(b) \( \text{H} - \text{O} - \text{C} - \text{C} - \text{C} - \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)

1.33

(a) \( \text{H} - \text{C} \equiv \text{N} \cdot \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)

(b) \( \text{H} - \text{C} - \text{O} - \text{C} - \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)

(c) \( \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)

(d) \( \text{H} - \text{C} - \text{H} \quad \text{C} = \text{C} - \text{H} \)
\( \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \)
1.34

All other bonds are covalent.

Hybridization

1.35 The H₃C– carbon is \( sp^3 \) hybridized, and the –CN carbon is \( sp \) hybridized.

1.36

(a) \( sp^3 \) \( sp^3 \) \( sp^3 \)

(b) \( sp^3 \)

(c) \( sp^2 \) \( sp^2 \) \( sp \) \( sp \)

(d) \( sp^3 \) \( sp^2 \)

1.37

All carbon atoms of benzene are \( sp^2 \) hybridized, and all bond angles of benzene are 120°. Benzene is a planar molecule.

1.38

(a) Glycine

(b) Pyridine

(c) Lactic acid

1.39 Examples:

(a) \( CH_3CH_2CH=CH_2 \)  (b) \( H_2C=CH-C=CH_2 \)  (c) \( H_2C=CH-C≡CH \)
The bond angles formed by atoms having $sp^3$ hybridization are approximately 109°.
The bond angles formed by atoms having $sp^2$ hybridization are approximately 120°.
1.44

Quetiapine (Seroquel) \(\text{C}_{21}\text{H}_{25}\text{N}_{3}\text{O}_{2}\text{S}\)

1.45

Oseltamivir (Tamiflu) \(\text{C}_{16}\text{H}_{28}\text{N}_{2}\text{O}_{4}\)

Clopidogrel (Plavix) \(\text{C}_{16}\text{H}_{16}\text{Cl}\text{N}\text{O}_{2}\text{S}\)

General Problems

1.46 In a compound containing a carbon–carbon triple bond, atoms bonded to the \(sp\)-hybridized carbons must lie in a straight line. It is not possible to form a five-membered ring if four carbons must have a linear relationship.
1.47

The central carbon of allene forms two $\sigma$ bonds and two $\pi$ bonds. The central carbon is $sp$-hybridized, and the two terminal carbons are $sp^2$-hybridized. The bond angle formed by the three carbons is 180°, indicating linear geometry for the carbons of allene.

1.48

Carbon dioxide is a linear molecule.

1.49

All of the indicated atoms are $sp^2$-hybridized.

1.50

(a) The positively charged carbon atom is surrounded by six valence electrons; carbon has three valence electrons, and each hydrogen brings three valence electrons.

(b) The positively charged carbon is $sp^2$-hybridized.

(c) A carbocation is planar about the positively charged carbon.
1.51

(a) A carbanion is isoelectronic with (has the same number of electrons as) a trivalent nitrogen compound.

(b) The negatively charged carbanion carbon has eight valence electrons.

(c) The carbon atom is $sp^3$-hybridized.

(d) A carbanion is tetrahedral.

1.52

According to the Pauli Exclusion Principle, two electrons in the same orbital must have opposite spins. Thus, the two electrons of triplet (spin-unpaired) methylene must occupy different orbitals. In triplet methylene, $sp$-hybridized carbon forms one bond to each of two hydrogens. Each of the two unpaired electrons occupies a $p$ orbital. In singlet (spin-paired) methylene the two electrons can occupy the same orbital because they have opposite spins. Including the two C–H bonds, there are a total of three occupied orbitals. We predict $sp^2$ hybridization and planar geometry for singlet methylene.

1.53

The two compounds differ in the way that the carbon atoms are connected.

1.54

One compound has a double bond, and one has a ring.
1.55

\[ \text{CH}_3\text{CH}_2\text{OH} \quad \text{CH}_3\text{OCH}_3 \]

The two compounds differ in the location of the oxygen atom.

1.56

\[ \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 \quad \text{CH}_3\text{CH}==\text{CHCH}_3 \quad \text{H}_2\text{C}==\text{C}_\text{CH}_3 \]

The compounds differ in the way that the carbon atoms are connected and in the location of the double bond.

1.57

\[ \text{Ibuprofen} \quad \text{Naproxen} \]

\[ \text{Acetaminophen} \]

\[ * = \text{sp}^3\text{-hybridized carbon} \]
\[ # = \text{sp}^2\text{-hybridized carbon} \]

(a), (b)

<table>
<thead>
<tr>
<th>Compound</th>
<th>\text{sp}^3\text{-Hybridized carbons}</th>
<th>\text{sp}^2\text{-Hybridized carbons}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ibuprofen</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Naproxen</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

(c) Each of the structures has a six-membered ring containing three double bonds, each has a methyl group, and each has a C=O group.
Chapter 2 – Polar Covalent Bonds; Acids and Bases

Chapter Outline

I. Polar covalent bonds (Sections 2.1–2.3).
   A. Electronegativity (Section 2.1).
      1. Although some bonds are totally ionic and some are totally covalent, most chemical bonds are polar covalent bonds.
         a. In these bonds, electrons are attracted to one atom more than to the other atom.
      2. Bond polarity is due to differences in electronegativity (EN).
         a. Elements on the right side of the periodic table are more electronegative than elements on the left side.
         b. Carbon has an EN of 2.5.
         c. Elements with EN > 2.5 are more electronegative than carbon.
         d. Elements with EN < 2.5 are less electronegative than carbon.
      3. The difference in EN between two elements can be used to predict the polarity of a bond.
         a. If $\Delta$EN < 0.4, a bond is nonpolar covalent.
         b. If $\Delta$EN is between 0.4 and 2.0, a bond is polar covalent.
         c. If $\Delta$EN > 2.0, a bond is ionic.
         d. The symbols $\delta^+$ and $\delta^-$ are used to indicate partial charges.
         e. A crossed arrow is used to indicate bond polarity.
            i. The tail of the arrow is electron poor, and the head of the arrow is electron rich.
      4. Electrostatic potential maps are also used to show electron-rich (red) and electron-poor (blue) regions of molecules.
   B. Dipole moment (Section 2.2).
      1. Dipole moment is the measure of a molecule's overall polarity.
      2. Dipole moment ($\mu$) = $Q \times r$, where $Q =$ charge and $r =$ distance between charges.
         a. Dipole moment is measured in debyes (D).
      3. Dipole moment can be used to measure charge separation.
      4. Water and ammonia have large values of D; methane and ethane have D = 0.
   C. Formal charge (Section 2.3).
      1. Formal charge (FC) indicates electron "ownership" in a molecule.
      2. \[ FC = \left\lfloor \frac{\text{# of valence electrons}}{2} \right\rfloor - \left\lfloor \frac{\text{# of bonding electrons}}{2} \right\rfloor - \left\lfloor \text{# nonbonding electrons} \right\rfloor \]

II. Resonance (Sections 2.4–2.6).
   A. Chemical structures and resonance (Section 2.4).
      1. Some molecules (acetate ion, for example) can be drawn as two (or more) different electron-dot structures.
         a. These structures are called resonance structures.
         b. The true structure of the molecule is intermediate between the resonance structures.
         c. The true structure is called a resonance hybrid.
      2. Resonance structures differ only in the placement of $\pi$ and nonbonding electrons.
         a. All atoms occupy the same positions.
      3. Resonance is an important concept in organic chemistry.
B. Rules for resonance forms (Section 2.5).
1. Individual resonance forms are imaginary, not real.
2. Resonance forms differ only in the placement of their \( \pi \) or nonbonding electrons.
   a. A curved arrow is used to indicate the movement of electrons, not atoms.
3. Different resonance forms of a molecule don't have to be equivalent.
   a. If resonance forms are nonequivalent, the structure of the actual molecule resembles the more stable resonance form(s).
4. Resonance forms must obey normal rules of valency.
5. The resonance hybrid is more stable than any individual resonance form.

C. A useful technique for drawing resonance forms (Section 2.6).
1. Any three-atom grouping with a multiple bond adjacent to a nonbonding \( p \) orbital has two resonance forms.
2. One atom in the grouping has a lone electron pair, a vacant orbital or a single electron.
3. By recognizing these three-atom pieces, resonance forms can be generated.

III. Acids and bases (Sections 2.7–2.11).

A. Brønsted–Lowry definition (Section 2.7).
1. A Brønsted–Lowry acid donates an \( H^+ \) ion; a Brønsted–Lowry base accepts \( H^+ \).
2. The product that results when a base gains \( H^+ \) is the conjugate acid of the base; the product that results when an acid loses \( H^+ \) is the conjugate base of the acid.
3. Water can act either as an acid or as a base.

B. Acid and base strength (Section 2.8–2.10).
1. A strong acid reacts almost completely with water (Section 2.8).
2. The strength of an acid in water is indicated by \( K_a \), the acidity constant.
3. Strong acids have large acidity constants, and weaker acids have smaller acidity constants.
4. The \( pK_a \) is normally used to express acid strength.
   a. \( pK_a = -\log K_a \)
   b. A strong acid has a small \( pK_a \), and a weak acid has a large \( pK_a \).
   c. The conjugate base of a strong acid is a weak base, and the conjugate base of a weak acid is a strong base.
5. Predicting acid–base reactions from \( pK_a \) (Section 2.9).
   a. An acid with a low \( pK_a \) (stronger acid) reacts with the conjugate base of an acid with a high \( pK_a \) (stronger base).
   b. In other words, the products of an acid–base reaction are more stable than the reactants.
6. Organic acids and organic bases (Section 2.10).
   a. There are two main types of organic acids:
      i. Acids that contain hydrogen bonded to oxygen.
      ii. Acids that have hydrogen bonded to the carbon next to a \( C=O \) group.
   b. The main type of organic base contains a nitrogen atom with a lone electron pair.

C. Lewis acids and bases (Section 2.11).
1. A Lewis acid accepts an electron pair.
   a. A Lewis acid may have either a vacant low-energy orbital or a polar bond to hydrogen.
   b. Examples include metal cations, halogen acids, group 3 compounds and transition-metal compounds.
2. A Lewis base has a pair of nonbonding electrons.
   a. Most oxygen- and nitrogen-containing organic compounds are Lewis bases.
   b. Many organic Lewis bases have more than one basic site.
3. A curved arrow shows the movement of electrons from a Lewis base to a Lewis acid.
IV. Noncovalent interactions in molecules (Section 2.12).
   A. Dipole–dipole interactions occur between polar molecules as a result of electrostatic interactions among dipoles.
      1. These interactions may be either attractive or repulsive.
      2. The attractive geometry is lower in energy and predominates.
   B. Dispersion forces result from the constantly changing electron distribution within molecules.
      1. These forces are transient and weak, but their cumulative effect may be important.
   C. Hydrogen bonds.
      1. Hydrogen bonds form between a hydrogen bonded to an electronegative atom and an unshared electron pair on another electronegative atom.
      2. Hydrogen bonds are extremely important in living organisms.
      3. Hydrophilic substances dissolve in water because they are capable of forming hydrogen bonds.
      4. Hydrophobic substances don't form hydrogen bonds and usually don't dissolve in water.

**Answers to Problems**

2.1 After solving this problem, use Figure 2.2 to check your answers. The larger the number, the more electronegative the element.

<table>
<thead>
<tr>
<th>More electronegative</th>
<th>Less electronegative</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) H (2.1)</td>
<td>Li (1.0)</td>
</tr>
<tr>
<td>(b) Br (2.8)</td>
<td>B (2.0)</td>
</tr>
<tr>
<td>(c) Cl (3.0)</td>
<td>I (2.5)</td>
</tr>
<tr>
<td>(d) C (2.5)</td>
<td>H (2.1)</td>
</tr>
</tbody>
</table>

Carbon is slightly more electronegative than hydrogen.

2.2 As in Problem 2.1, use Figure 2.2. The partial negative charge is placed on the more electronegative atom, and the partial positive charge is placed on the less electronegative atom.

(a) $\delta^+ \delta^-$  
H$_3$C$\cdash$Cl

(b) $\delta^+ \delta^-$  
H$_3$C$\cdash$NH$_2$

(c) $\delta^- \delta^+$  
H$_2$N$\cdash$H

(d) $\delta^- \delta^-$  
H$_3$C$\cdash$SH

(e) $\delta^- \delta^+$  
H$_3$C$\cdash$MgBr

(f) $\delta^+ \delta^-$  
H$_3$C$\cdash$F

Carbon and sulfur have identical electronegativities.

2.3 Use Figure 2.2 to find the electronegativities of each element. Calculate $\Delta$EN and rank the answers in order of increasing $\Delta$EN.

<table>
<thead>
<tr>
<th>Element</th>
<th>EN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>2.5</td>
</tr>
<tr>
<td>Lithium</td>
<td>1.0</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.8</td>
</tr>
<tr>
<td>Fluorine</td>
<td>4.0</td>
</tr>
<tr>
<td>Carbon</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbon</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbon</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$\Delta$EN = 1.5  $\Delta$EN = 1.7  $\Delta$EN = 1.5
Carbon: \( \text{EN} = 2.5 \)  \hspace{1cm} \text{Oxygen:} \ \text{EN} = 3.5 \\
\text{Magnesium:} \ \text{EN} = 1.2 \hspace{1cm} \text{Carbon:} \ \text{EN} = 2.5 \\
\Delta \text{EN} = 1.3 \hspace{1cm} \Delta \text{EN} = 1.0 \\

The most polar bond has the largest \( \Delta \text{EN} \). Thus, in order of increasing bond polarity:

\[
\text{H}_3\text{C—OH} < \text{H}_3\text{C—MgBr} < \text{H}_3\text{C—Li,} \ \text{H}_3\text{C—F} < \text{H}_3\text{C—K}
\]

2.4 In an electrostatic potential map, the color red indicates regions of a molecule that are electron-rich. The map shows that chlorine is the most electronegative atom in chloromethane, and the direction of polarity of the C–Cl bond is:

Chloromethane

2.5

The dipole moment of ethylene glycol is zero because the bond polarities of the two carbon–oxygen bonds cancel.

2.6 For each bond, identify the more electronegative element, and draw an arrow that points from the less electronegative element to the more electronegative element. Estimate the sum of the individual dipole moments to arrive at the dipole moment for the entire molecule.

(a) \( \text{0 dipole moment} \)  \\
(b) \( \text{net dipole moment} \)  \\
(c) \( \text{net dipole moment} \)  \\
(d) \( \text{net dipole moment} \)
To find the formal charge of an atom in a molecule, follow these two steps:

1. Draw an electron-dot structure of the molecule.

2. Use the formula in Section 2.3 (shown below) to determine formal charge for each atom. The periodic table shows the number of valence electrons of the element, and the electron-dot structure shows the number of bonding and nonbonding electrons.

\[
\text{Formal charge (FC)} = \left( \frac{\text{# of valence electrons}}{2} \right) - \left( \frac{\text{# of bonding electrons}}{2} \right) - \text{# nonbonding electrons}
\]

(a) \[\text{H}_2\text{C}≡\text{N}≡\text{N}: \quad \text{H}:\text{C} \\
\text{For carbon: FC} = 4 - \frac{8}{2} - 0 = 0\]

\[\text{For nitrogen 1: FC} = 5 - \frac{8}{2} - 0 = +1\]

\[\text{For nitrogen 2: FC} = 5 - \frac{4}{2} - 4 = -1\]

(b) \[\text{H}_3\text{C}≡\text{N}≡\text{O}: \quad \text{H}:\text{C} \\
\text{For carbon 1: FC} = 4 - \frac{8}{2} - 0 = 0\]

\[\text{For carbon 2: FC} = 4 - \frac{8}{2} - 0 = 0\]

\[\text{For nitrogen: FC} = 5 - \frac{8}{2} - 0 = +1\]

\[\text{For oxygen: FC} = 6 - \frac{2}{2} - 6 = -1\]

Remember: Valence electrons are the electrons characteristic of a specific element. Bonding electrons are those electrons involved in bonding to other atoms. Nonbonding electrons are those electrons in lone pairs.
(c) \[ \text{H}_3\text{C} - \text{N} \equiv \text{C} : = \text{H} \text{:} \text{C} : \text{N} \text{:} \text{:} \text{C} : \text{H} \]

For carbon 1: \( FC = 4 - \frac{8}{2} - 0 = 0 \)

For carbon 2: \( FC = 4 - \frac{6}{2} - 2 = -1 \)

For nitrogen: \( FC = 5 - \frac{8}{2} - 0 = +1 \)

2.8

Formal charge (FC) = \( \left[ \frac{\text{# of valence electrons}}{2} \right] - \left[ \frac{\text{# of bonding electrons}}{2} \right] - \left[ \frac{\text{# nonbonding electrons}}{2} \right] \)

Methyl phosphate

For oxygen 1: \( FC = 6 - \frac{4}{2} - 4 = 0 \)

For oxygen 2: \( FC = 6 - \frac{4}{2} - 4 = 0 \)

For oxygen 3: \( FC = 6 - \frac{2}{2} - 6 = -1 \)

For oxygen 4: \( FC = 6 - \frac{2}{2} - 6 = -1 \)

Oxygen atoms 3 and 4 each have a formal charge of \(-1\), and oxygen atoms 1 and 2 have a formal charge of 0.

2.9

Try to locate the three-atom groupings that are present in resonance forms.

(a) These two structures represent resonance forms. The three-atom grouping (C–C double bond and an adjacent vacant \( p \) orbital) is pictured on the right.

(b) These two structures represent different compounds, not resonance structures.
2.10 Look for three-atom groupings that contain a multiple bond next to an atom with a \( p \) orbital. Exchange the positions of the bond and the electrons in the \( p \) orbital to draw the resonance form of each grouping.

(a) Methyl phosphate anion has 3 three-atom groupings and thus has 3 resonance forms.

Recall from Chapter 1 that phosphorus, a third-row element, can form more than four covalent bonds

(b)

(c)

(d)

2.11 When an acid loses a proton, the product is the conjugate base of the acid. When a base gains a proton, the product is the conjugate acid of the base.

2.12 Recall from Section 2.8 that a stronger acid has a smaller \( pK_a \) and a weaker acid has a larger \( pK_a \). Accordingly, phenylalanine (\( pK_a = 1.83 \)) is a stronger acid than tryptophan (\( pK_a = 2.83 \)).

2.13 HO–H is a stronger acid than H\(_2\)N–H. Since H\(_2\)N\(^{-}\) is a stronger base than HO\(^{-}\), the conjugate acid of H\(_2\)N\(^{-}\) (H\(_2\)N–H) is a weaker acid than the conjugate acid of HO\(^{-}\) (HO–H).
2.14 Use Table 2.3 to find the strength of each acid. A reaction takes place as written if the stronger acid is the reactant.

(a) \[ \text{H} - \text{CN} + \text{CH}_3\text{CO}_2^- \text{Na}^+ \xrightarrow{?} \text{Na}^+ - \text{CN} + \text{CH}_3\text{CO}_2\text{H} \]

\[ pK_a = 9.3 \quad \text{Weaker acid} \quad pK_a = 4.7 \quad \text{Stronger acid} \]

Remember that the lower the pKₐ, the stronger the acid. Thus CH₃CO₂H, not HCN, is the stronger acid, and the above reaction will not take place to a significant extent in the direction written.

(b) \[ \text{CH}_3\text{CH}_2\text{O}^- - \text{H} + \text{Na}^+ - \text{CN} \xrightarrow{?} \text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+ + \text{HCN} \]

\[ pK_a = 16 \quad \text{Weaker acid} \quad pK_a = 9.3 \quad \text{Stronger acid} \]

Using the same reasoning as in part (a), we can see that the above reaction will not occur to a significant extent.

2.15

\[ \text{O} \]

\[ \text{H}_3\text{C} \quad \text{C} \quad \text{H}_3\text{C} \]

\[ \text{H}_3\text{C} \quad \text{C} \quad \text{H}_3\text{C} \]

\[ + \text{Na}^+ : \text{NH}_2 \xrightarrow{?} \quad \text{H}_3\text{C} \quad \text{C} \quad \text{H}_2\text{Na}^+ + : \text{NH}_3 \]

\[ pK_a = 19 \quad \text{Stronger acid} \quad pK_a = 36 \quad \text{Weaker acid} \]

As written, the above reaction will take place to virtual completion due to the large difference in pKₐ values.

2.16 Enter −9.31 into a calculator and use the INV LOG function to arrive at the answer \( K_a = 4.9 \times 10^{-10} \).

2.17 Locate the electron pair(s) of the Lewis base and draw a curved arrow from the electron pair to the Lewis acid. The electron pair moves from the atom at the tail of the arrow (Lewis base) to the atom at the point of the arrow (Lewis acid). (Note: electron dots have been omitted from Cl⁻ to reduce clutter.)

(a) \[ \text{CH}_3\text{CH}_2\text{OH} + \text{H} - \text{Cl} \xleftrightarrow{\text{H} +} \text{CH}_3\text{CH}_2\text{OH} + \text{Cl}^- \]

\[ \text{HN(CH}_3\text{)}_2 + \text{H} - \text{Cl} \xleftrightarrow{\text{H} +} \text{HN(CH}_3\text{)}_2 + \text{Cl}^- \]

\[ \text{P(CH}_3\text{)}_3 + \text{H} - \text{Cl} \xleftrightarrow{\text{H} +} \text{H} - \text{P(CH}_3\text{)}_3 + \text{Cl}^- \]
2.18 (a) The nitrogen on the left is more electron-rich and more basic. The indicated hydrogen is most electron-poor (bluest) and is most acidic.

![Diagram of chemical reactions]

2.19

Vitamin C is water-soluble (hydrophilic) because it has several polar –OH groups that can form hydrogen bonds with water. Vitamin A is fat-soluble (hydrophobic) because most of its atoms can't form hydrogen bonds with water.

![Diagram of chemical structures]
Visualizing Chemistry

2.20 Naphthalene has three resonance forms.

\[ \text{Resonance forms of naphthalene} \]

2.21 Ibuprofen

\[ \text{Ibuprofen structure} \]

2.22 Electrostatic potential maps show that the electron-rich regions of the cis isomer lie on the same side of the double bond, leading to a net dipole moment. Because the electron-rich regions of the trans isomer are symmetrical about the double bond, the individual bond dipole moments cancel, and the isomer has no overall dipole moment.

\[ \text{Net dipole moment} \quad \text{Zero dipole moment} \]

\[ \text{cis-1,2-Dichloroethylene} \quad \text{trans-1,2-Dichloroethylene} \]

2.23

(a) Adenine

\[ \text{Adenine structure} \]

(b) Cytosine

\[ \text{Cytosine structure} \]
Additional Problems

Electronegativity and Dipole Moments

2.24 Use Figure 2.2 if you need help. The most electronegative element is starred.

(a) \( \text{CH}_2\text{FCl} \)  (b) \( \text{FCH}_2\text{CH}_2\text{CH}_2\text{Br} \)  (c) \( \text{HOCH}_2\text{CH}_2\text{NH}_2 \)  (d) \( \text{CH}_3\text{OCH}_2\text{Li} \)

2.25

\[ \begin{array}{c|c}
\text{More polar} & \text{Less polar} \\
\hline
\text{(a)} & \text{Cl–Cl} \\
\text{(b)} & \text{CH}_3\text{Cl} \\
\text{(c)} & \text{HO–CH}_3 \\
\text{(d)} & \text{Li–OH} \\
\end{array} \]

2.26

(a)  (b)  (c)  (d) no dipole moment

2.27 (a) In Section 2.2, we found that \( \mu = Q \times r \). For a proton and an electron separated by 100 pm, \( \mu = 4.80 \text{D} \). If the two charges are separated by 136 pm, \( \mu = 6.53 \text{D} \).

(b) Since the observed dipole moment is 1.08 D, the H–Cl bond has \( (1.08 \text{D} / 6.53 \text{D}) \times 100 \% = 16.5 \% \) ionic character.

2.28 In phosgene, the individual bond polarities tend to cancel, but in formaldehyde, the bond polarities add to each other. Thus, phosgene has a smaller dipole moment than formaldehyde.

2.29 The magnitude of a dipole moment depends on both charge and distance between atoms. Fluorine is more electronegative than chlorine, but a C–F bond is shorter than a C–Cl bond. Thus, the dipole moment of CH\(_3\)F is smaller than that of CH\(_3\)Cl.
2.30 The observed dipole moment is due to the lone pair electrons on sulfur.

\[
\begin{array}{c}
\text{H}_3\text{C}--\text{S} \\
\uparrow \\
\downarrow
\end{array}
\]

Formal Charges

2.31 To save space, molecules are shown as line-bond structures with lone pairs, rather than as electron-dot structures.

(a) \((\text{CH}_3)_2\text{O}--\text{BF}_3\)

Oxygen: \(\text{FC} = 6 - \frac{6}{2} - 2 = +1\)

Boron: \(\text{FC} = 3 - \frac{8}{2} - 0 = -1\)

(b) \(\text{H}_2\text{C}--\text{N}≡\text{N}:\)

Carbon: \(\text{FC} = 4 - \frac{6}{2} - 2 = -1\)

Nitrogen 1: \(\text{FC} = 5 - \frac{8}{2} - 0 = +1\)

Nitrogen 2: \(\text{FC} = 5 - \frac{6}{2} - 2 = 0\)

(c) \(\text{H}_2\text{C}--\text{N}≡\text{N}:\)

Carbon: \(\text{FC} = 4 - \frac{8}{2} - 0 = 0\)

Nitrogen 1: \(\text{FC} = 5 - \frac{8}{2} - 0 = +1\)

Nitrogen 2: \(\text{FC} = 5 - \frac{4}{2} - 4 = -1\)

(d) \(\text{O}=\text{O}--\text{O}:\)

Oxygen 1: \(\text{FC} = 6 - \frac{4}{2} - 4 = 0\)

Oxygen 2: \(\text{FC} = 6 - \frac{6}{2} - 2 = +1\)

Oxygen 3: \(\text{FC} = 6 - \frac{2}{2} - 6 = -1\)

(e) \(\text{CH}_3\)

Carbon: \(\text{FC} = 4 - \frac{6}{2} - 2 = -1\)

Phosphorus: \(\text{FC} = 5 - \frac{8}{2} - 0 = +1\)

(f) \(\text{N}--\text{O}:\)

Nitrogen: \(\text{FC} = 5 - \frac{8}{2} - 0 = +1\)

Oxygen: \(\text{FC} = 6 - \frac{2}{2} - 6 = -1\)
2.32 As in Problem 2.31, molecules are shown as line-bond structures with lone-pair electrons indicated. Only calculations for atoms with non-zero formal charge are shown.

(a) Oxygen: $\text{FC} = 6 - \frac{2}{2} - 6 = -1$

N: $\text{FC} = 5 - \frac{8}{2} - 0 = +1$

(b) Nitrogen 1: $\text{FC} = 5 - \frac{4}{2} - 4 = -1$

Nitrogen 2: $\text{FC} = 5 - \frac{8}{2} - 0 = +1$

Nitrogen 3: $\text{FC} = 5 - \frac{6}{2} - 2 = 0$

(c) Nitrogen 1: $\text{FC} = 5 - \frac{6}{2} - 2 = 0$

Nitrogen 2: $\text{FC} = 5 - \frac{8}{2} - 0 = +1$

Nitrogen 3: $\text{FC} = 5 - \frac{4}{2} - 4 = -1$

Resonance

2.33 Resonance forms do not differ in the position of nuclei. The two structures in (a) are not resonance forms because the positions of the carbon and hydrogen atoms outside the ring are different in the two forms.

\[ \text{not resonance structures} \]

The pairs of structures in parts (b), (c), and (d) represent resonance forms.

2.34

(a)

(b)

(c)

The last resonance structure is a minor contributor because its carbon lacks a complete electron octet.
2.35 The two structures are not resonance forms because the positions of the carbon atoms are
different in the two forms.

Acids and Bases

2.36

\[
\begin{align*}
\text{CH}_3\text{OH} & + \text{HCl} \quad \leftrightarrow \quad \text{CH}_3\text{OH}^+ + \text{Cl}^- \\
\text{CH}_3\text{OH} & + \text{Na}^+ \text{NH}_2 \quad \leftrightarrow \quad \text{CH}_3\text{O}^- \text{Na}^+ + \text{NH}_3
\end{align*}
\]

2.37

The O–H hydrogen of acetic acid is more acidic than the C–H hydrogens. The –OH
oxxygen is electronegative, and, consequently, the –O–H bond is more strongly polarized
than the –C–H bonds. In addition, the acetate anion is stabilized by resonance.

2.38

(a) Br : Al : Br \\
(b) H : C : C : N : H \\
(c) H : B : H

(d) H : F \\
(e) H : C : S : C : H \\
(f) Cl : Ti : Cl

The Lewis acids shown below can accept an electron pair either because they have a vacant
orbital or because they can donate H⁺. The Lewis bases have nonbonding electron pairs.

Lewis acids: AlBr₃, BH₃, HF, TiCl₄

Lewis bases: CH₃CH₂NH₂, H₃C–S–CH₃

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2.39

(a) \[
\text{CH}_3\text{OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CH}_3\text{OH}_2^+ + \text{HSO}_4^- \]

+ CH3OH stronger base \quad + H2SO4 stronger acid \quad CH3OH2+ weaker acid \quad + HSO4– weaker base

(b) \[
\text{CH}_3\text{OH} + \text{NaNH}_2 \rightleftharpoons \text{CH}_3\text{O}^- \text{Na}^+ + \text{NH}_3
\]

+ CH3OH stronger acid \quad + NaNH2 weaker base \quad \text{CH}_3\text{O}^- \text{Na}^+ weaker acid \quad + \text{NH}_3 weaker base

(c) \[
\text{CH}_3\text{NH}_3^+ \text{Cl}^- + \text{NaOH} \rightleftharpoons \text{CH}_3\text{NH}_2^- + \text{H}_2\text{O} + \text{NaCl}
\]

+ CH3NH3+ stronger acid \quad + Cl– weaker base \quad \text{CH}_3\text{NH}_2^- weaker acid \quad + \text{H}_2\text{O} weaker base \quad + NaCl weaker acid

2.40

The substances with the largest values of pKₐ are the least acidic.

![Least acidic](image1) ![Most acidic](image2)

pKₐ = 19.3 \quad pKₐ = 9.9 \quad pKₐ = 9 \quad pKₐ = 4.76

2.41

To react completely (> 99.9%) with NaOH, an acid must have a pKₐ at least 3 units smaller than the pKₐ of H₂O. Thus, all substances in the previous problem except acetone react completely with NaOH.

2.42

The stronger the acid (smaller pKₐ), the weaker its conjugate base. Since NH₄⁺ is a stronger acid than CH₃NH₃⁺, CH₃NH₂ is a stronger base than NH₃.

2.43

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{O}^- \quad \text{K}^+ \quad + \quad \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{H}_3\text{C} \quad \text{C} \quad \text{OH}^- \quad + \quad \text{K}^+ \quad \text{OH}^-
\]

\[
pK_a = 15.7 \quad \text{stronger acid} \quad \text{pK}_a \approx 18 \quad \text{weaker acid}
\]

The reaction takes place as written because water is a stronger acid than tert-butyl alcohol. Thus, a solution of potassium tert-butoxide in water can't be prepared.

2.44

2.45

(a) Acetone: \( K_a = 5 \times 10^{-20} \)  
(b) Formic acid: \( K_a = 1.8 \times 10^{-4} \)

2.46

(a) Nitromethane: \( pK_a = 10.30 \)  
(b) Acrylic acid: \( pK_a = 4.25 \)

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2.47
Formic acid + H₂O $\overset{K_a}{\leftrightarrow}$ Formate$-^-$ + H₃O$^+$
[0.050 M] [x] [x]

$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.050 - x}$

If you let $0.050 - x = 0.050$, then $x = 3.0 \times 10^{-3}$ and pH = 2.52. If you calculate $x$ exactly using the quadratic equation, then $x = 2.9 \times 10^{-3}$ and pH = 2.54.

2.48 Only acetic acid will react with sodium bicarbonate. Acetic acid is the only substance in Problem 2.40 that is a stronger acid than carbonic acid.

**General Problems**

2.49 In maleic acid, the individual dipole moments add to produce a net dipole moment for the whole molecule. The individual dipole moments in fumaric acid cancel, resulting in a zero dipole moment.

![Maleic acid and Fumaric acid](image)

2.50 Sodium bicarbonate reacts with acetic acid to produce carbonic acid, which breaks down to form CO₂. Thus, bubbles of CO₂ indicate the presence of an acid stronger than carbonic acid, in this case acetic acid, as the $pK_a$ values indicate. Phenol does not react with sodium bicarbonate.

2.51 Reactions (a) and (c) are reactions between Brønsted–Lowry acids and bases; the stronger acid and stronger base are identified. Reactions (b) and (d) occur between Lewis acids and bases.

(a)

\[
\text{CH}_3\text{OH} + H^+ \rightarrow \text{CH}_3\text{OH}^+
\]

(base) (acid)

(b)

\[
\text{CH}_3\text{CCH}_3 + \text{TiCl}_4 \rightarrow \text{CH}_3\text{CCH}_3^+\text{TiCl}_4^-
\]

(base) (acid)
2.52 Pairs (a) and (d) represent resonance structures; pairs (b) and (c) do not. For two structures to be resonance forms, all atoms must be in the same positions in all resonance forms.

2.53

(a) H₃C–N=O: ↔ H₃C–N:O⁻
(b) O=O:O⁻ ↔ O:O⁺
(c) H₂C=N=⁺N⁻ ↔ H₂C=N=N⁻

2.54 The cation pictured can be represented by two resonance forms. Reaction with water can occur at either positively charged carbon, resulting in two products.
2.55
(a) \[ \delta^+ \text{O} \hspace{1cm} \delta^- \text{C} \]
(b) \[ \delta^+ \text{C} \hspace{1cm} \delta^- \text{OH} \]
(c) \[ \delta^- \text{O} \hspace{1cm} \delta^+ \text{C} \]
(d) \[ \delta^+ \text{C} \equiv \delta^- \text{N} \]

2.56
\[ \text{Resonance structures for phenyl azide and phenyl nitrite.} \]

2.57
When phenol loses a proton, the resulting anion is stabilized by resonance. The methanol anion is not stabilized by resonance.

2.58
\[ \begin{array}{c}
\text{Phosphorylcholine} \\
\text{(PO\textsubscript{3}H\textsubscript{2})}
\end{array} \]

\[ \to \]
\[ \begin{array}{c}
\text{Phosphatidylethanolamine} \\
\text{(PO\textsubscript{3}H\textsubscript{2})}
\end{array} \]

\[ \text{and} \]
\[ \begin{array}{c}
\text{Phosphatidylglycerol} \\
\text{(PO\textsubscript{3}H\textsubscript{2})}
\end{array} \]

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Chapter 3 – Organic Compounds: 
Alkanes and Their Stereochemistry

Chapter Outline

I. Functional Groups (Section 3.1).
   A. Functional groups are groups of atoms within a molecule that have a characteristic chemical behavior.
   B. The chemistry of every organic molecule is determined by its functional groups.
   C. Functional groups described in this text can be grouped into three categories:
      1. Functional groups with carbon–carbon multiple bonds.
      2. Groups in which carbon forms a single bond to an electronegative atom.

II. Alkanes (Sections 3.2–3.5).
   A. Alkanes and alkane isomers (Section 3.2).
      1. Alkanes are formed by overlap of carbon \( sp^3 \) orbitals.
      2. Alkanes are described as saturated hydrocarbons.
         a. They are hydrocarbons because they contain only carbon and hydrogen.
         b. They are saturated because all bonds are single bonds.
         c. The general formula for alkanes is \( C_n H_{2n+2} \).
      3. For alkanes with four or more carbons, the carbons can be connected in more than one way.
         a. If the carbons are in a row, the alkane is a straight-chain alkane.
         b. If the carbon chain has a branch, the alkane is a branched-chain alkane.
      4. Alkanes with the same molecular formula can exist in different forms known as isomers.
         a. Isomers whose atoms are connected differently are constitutional isomers.
            i. Constitutional isomers are always different compounds with different properties but with the same molecular formula.
         b. Most alkanes can be drawn in many ways.
      5. Straight-chain alkanes are named according to the number of carbons in their chain.
   B. Alkyl groups (Section 3.3).
      1. An alkyl group is the partial structure that results from the removal of a hydrogen atom from an alkane.
         a. Alkyl groups are named by replacing the -ane of an alkane name by -yl.
         b. \( n \)-Alkyl groups are formed by removal of an end hydrogen atom of a straight-chain alkane.
         c. Branched-chain alkyl groups are formed by removal of a hydrogen atom from an internal carbon.
            i. The prefixes \( sec \)- and \( tert \)- refer to the degree of substitution at the branching carbon atom.
      2. There are four possible degrees of alkyl substitution for carbon.
         a. A primary carbon is bonded to one other carbon.
         b. A secondary carbon is bonded to two other carbons.
         c. A tertiary carbon is bonded to three other carbons.
         d. A quaternary carbon is bonded to four other carbons.
         e. The symbol \( R \) refers to the rest of the molecule.
      3. Hydrogens are also described as primary, secondary and tertiary.
         a. Primary hydrogens are bonded to primary carbons (RCH\(_3\)).
         b. Secondary hydrogens are bonded to secondary carbons (R\(_2\)CH\(_2\)).
         c. Tertiary hydrogens are bonded to tertiary carbons (R\(_3\)CH).
C. Naming alkanes (Section 3.4).
   1. The system of nomenclature used in this book is the IUPAC system.
      In this system, a chemical name has a locant, a prefix, a parent and a suffix.
      i. The locant shows the location of substituents and functional groups.
      ii. The prefix indicates the type of substituent or functional group.
      iii. The parent shows the number of carbons in the principal chain.
      iv. The suffix identifies the functional group family.
   2. Naming an alkane:
      a. Find the parent hydrocarbon.
         i. Find the longest continuous chain of carbons, and use its name as the parent name.
         ii. If two chains have the same number of carbons, choose the one with more branch points.
      b. Number the atoms in the parent chain.
         i. Start numbering at the end nearer the first branch point.
         ii. If branching occurs an equal distance from both ends, begin numbering at the end nearer the second branch point.
      c. Identify and number the substituents.
         i. Give each substituent a number that corresponds to its position on the parent chain.
         ii. Two substituents on the same carbon receive the same number.
      d. Write the name as a single word.
         i. Use hyphens to separate prefixes and commas to separate numbers.
         ii. Use the prefixes, di-, tri-, tetra- if necessary, but don't use them for alphabetizing.
      e. Name a complex substituent as if it were a compound, and set it off within parentheses.
         i. Some simple branched-chain alkyl groups have common names.
         ii. The prefix iso is used for alphabetizing, but sec- and tert- are not.

D. Properties of alkanes (Section 3.5).
   1. Alkanes are chemically inert to most laboratory reagents.
   2. Alkanes react with \( \text{O}_2 \) (combustion) and \( \text{Cl}_2 \) (substitution).
   3. The boiling points and melting points of alkanes increase with increasing molecular weight.
      a. This effect is due to weak dispersion forces.
      b. The strength of these forces increases with increasing molecular weight.
   4. Increased branching lowers an alkane's boiling point.

III. Conformations of straight-chain alkanes (Sections 3.6–3.7).
   A. Conformations of ethane (Section 3.6).
      1. Rotation about a single bond produces isomers that differ in conformation.
         a. These isomers (conformers) have the same connections of atoms and can't be isolated.
      2. These isomers can be represented in two ways:
         a. Sawhorse representations view the C–C bond from an oblique angle.
         b. Newman projections view the C–C bond end-on and represent the two carbons as a circle.
      3. There is a barrier to rotation that makes some conformers of lower energy than others.
         a. The lowest energy conformer (staggered conformation) occurs when all C–H bonds are as far from each other as possible.
         b. The highest energy conformer (eclipsed conformation) occurs when all C–H bonds are as close to each other as possible.
         c. Between these two conformations lie an infinite number of other conformations.
4. The staggered conformation is 12 kJ/mol lower in energy than the eclipsed conformation.
   a. This energy difference is due to torsional strain from interactions between C–H bonding orbitals on one carbon and C–H antibonding orbitals on an adjacent carbon, which stabilize the staggered conformer.
   b. The torsional strain resulting from a single C–H interaction is 4.0 kJ/mol.
   c. The barrier to rotation can be represented on a graph of potential energy vs. angle of rotation (dihedral angle).

B. Conformations of other alkanes (Section 3.7).
1. Conformations of propane.
   a. Propane also shows a barrier to rotation that is 14 kJ/mol.
   b. The eclipsing interaction between a C–C bond and a C–H bond is 6.0 kJ/mol.
2. Conformations of butane.
   a. Not all staggered conformations of butane have the same energy; not all eclipsed conformations have the same energy.
      i. In the lowest energy conformation (anti) the two large methyl groups are as far from each other as possible.
      ii. The eclipsed conformation that has two methyl–hydrogen interactions and a H–H interaction is 16 kJ/mol higher in energy than the anti conformation.
      iii. The conformation with two methyl groups 60° apart (gauche conformation) is 3.8 kJ/mol higher in energy than the anti/conformation.
         (a). This energy difference is due to steric strain – the repulsive interaction that results from forcing atoms to be closer together than their atomic radii allow.
      iv. The highest energy conformations occur when the two methyl groups are eclipsed.
         (a). This conformation is 19 kJ/mol less stable than the anti conformation.
         The value of a methyl–methyl eclipsing interaction is 11 kJ/mol.
   b. The most favored conformation for any straight-chain alkane has carbon–carbon bonds in staggered arrangements and large substituents anti to each other.
   c. At room temperature, bond rotation occurs rapidly, but a majority of molecules adopt the most stable conformation.
Solutions to Problems

3.1 Notice that certain functional groups have different designations if other functional groups are also present in a molecule. For example, a molecule containing a carbon–carbon double bond and no other functional group is an alkene; if other groups are present, the group is referred to as a carbon–carbon double bond. Similarly, a compound containing a benzene ring, and only carbon- and hydrogen-containing substituents, is an arene; if other groups are present, the ring is labeled an aromatic ring.

(a) sulfide carboxylic acid
    CH₃SCH₂CH₂CHCOH
    NH₂ amine
    Methionine

(b) aromatic ring carboxylic acid
    CO₂H
    CH₃
    Ibuprofen

(c) ether amide C–C double bond
    HO aromatic ring
    O
    H₃C
    alcohol
    N
    HO
    aromatic ring
    Capsaicin

3.2

(a) Methanol
    CH₃OH

(b) Toluene
    CH₃
    CH₃COH

(c) Acetic acid
    CH₃COH

(d) Methylamine
    CH₃NH₂

(e) Aminoacetone
    CH₃CH₂NH₂

(f) 1,3-Butadiene

3.3

(a) amine ester
    H₃C
    N
    C–C double bond
    O
    CH₃
    Arecoline C₈H₁₃NO₂
3.4 We know that carbon forms four bonds and hydrogen forms one bond. Thus, draw all possible six-carbon skeletons and add hydrogens so that all carbons have four bonds. To draw all possible skeletons in this problem: (1) Draw the six-carbon straight-chain skeleton. (2) Draw a five-carbon chain, identify the different types of carbon atoms on the chain, and add a –CH₃ group to each of the different types of carbons, generating two skeletons. (3) Repeat the process with the four-carbon chain to give rise to the last two skeletons. Add hydrogens to the remaining carbons to complete the structures.

CH₃CH₂CH₂CH₂CH₂CH₃  CH₃CH₂CH₂CHCH₃  CH₃CH₂CH₂CH₂CH₃

3.5 (a) Nine isomeric esters of formula C₅H₁₀O₂ can be drawn. The procedure is described in Problem 3.4.

O   O   O
CH₃CH₂CH₂COCH₃  CH₃CH₂COCH₃  CH₃CH₂COCH₂CH₃

O   O   O
CH₃COCH₂CH₂CH₃  CH₃COCHCH₃  HCOCH₂CH₂CH₂CH₃

O   O   O
HCOCH₂CH₂CH₃  HCOCH₂CHCH₃  HCOCH₃

(b) Two isomers can be drawn.

CH₃CH₂CH₂C≡N  and  CH₃CHC≡N

(c) Three isomers can be drawn.

CH₃CH₂SSCH₂CH₃  CH₃SSCH₂CH₂CH₃  CH₃SSCHCH₃
3.6  (a) Two alcohols have the formula C\textsubscript{3}H\textsubscript{8}O.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{and} \quad \text{CH}_3\text{CHCH}_3
\]

(b) Four bromoalkanes have the formula C\textsubscript{4}H\textsubscript{9}Br.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 \quad \text{CH}_3\text{CHCH}_2\text{Br} \quad \text{CH}_3\text{CCH}_3
\]

(c) Four thioesters have the formula C\textsubscript{4}H\textsubscript{8}OS.

\[
\text{CH}_3\text{CH}_2\text{CSCH}_3 \quad \text{CH}_3\text{CH}_2\text{SCCH}_3 \quad \text{HCSCHCH}_3 \quad \text{HCSCH}_2\text{CH}_2\text{CH}_3
\]

3.7

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2
\]

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2 \quad \text{CH}_3\text{CHCH}_2\text{CH}_2 \quad \text{CH}_3\text{CHCH}_2\text{CH}_2 \quad \text{CH}_3\text{CHCH}_2\text{CH}_2
\]

3.8

(a) \(p\) \(\text{CH}_3\) \(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3\) \(p\) \(t\) \(s\) \(p\)

(b) \(p\) \(t\) \(p\) \(\text{CH}_3\text{CHCH}_3\)

(c) \(p\) \(\text{CH}_3\) \(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3\) \(p\) \(t\) \(s\) \(q\) \(p\)

\(p\) = primary; \(s\) = secondary; \(t\) = tertiary; \(q\) = quaternary

3.9  The carbons and the attached hydrogens have the same classification.

(a) \(p\) \(\text{CH}_3\) \(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3\) \(p\) \(t\) \(s\) \(s\) \(p\)

(b) \(p\) \(t\) \(p\) \(\text{CH}_3\text{CHCH}_3\)

(c) \(p\) \(\text{CH}_3\) \(\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3\) \(p\) \(t\) \(s\) \(p\)

3.10

(a) \(t\) \(\text{CH}_3\) \(\text{CH}_3\text{CHCH}_3\)

(b) \(\text{CH}_3\text{CHCH}_3\)

(c) \(q\) \(\text{CH}_3\) \(\text{CH}_3\text{CH}_2\text{CH}_3\) \(s\) \(\text{CH}_3\)
3.11

(a)

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 & \quad \text{CH}_3\text{CCH}_3 \\
\text{Pentane} & \quad \text{2-Methylbutane} & \quad \text{2,2-Dimethylpropane}
\end{align*}
\]

(b)  
Step 1: Find the longest continuous carbon chain and use it as the parent name. In (b), the longest chain is a pentane.  
Step 2: Identify the substituents. In (b), both substituents are methyl groups.  
Step 3: Number the substituents. In (b), the methyl groups are in the 2- and 3- positions.  
Step 4: Name the compound. Remember that the prefix \textit{di-} must be used when two substituents are the same. The IUPAC name is 2,3-dimethylpentane.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{5} & \quad \text{4} & \quad \text{3} \quad \text{2} \quad \text{1} \quad \text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CHCH}_3 & \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 & \quad \text{CH}_3\text{CCH}_3 \\
\text{2,3-Dimethylpentane} & \quad \text{2,3-Dimethylpentane} & \quad \text{2,2-Dimethylpropane}
\end{align*}
\]

(c)  
\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{CHCH}_2\text{CHCH}_3 & \quad \text{(CH}_3\text{)}_3\text{CCH}_2\text{CH}_2\text{CH}_3\text{CH}_3 \\
\text{2,4-Dimethylpentane} & \quad \text{2,2,5-Trimethylhexane}
\end{align*}
\]

3.12 When you are asked to draw the structure corresponding to a given name, draw the parent carbon chain, attach the specified groups to the proper carbons, and fill in the remaining hydrogens.

(a)  
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHHCHCH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{CHHCHCH}_2\text{CH}_3 \\
\text{3,4-Dimethylnonane} & \quad \text{3-Ethyl-4,4-dimethylheptane}
\end{align*}
\]

(b)  
\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CCHCH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\
\text{2,2-Dimethyl-4-propyloctane} & \quad \text{2,2,4-Trimethylpentane}
\end{align*}
\]
3.13

- Pentyl
- 1-Methylbutyl
- 2-Methylbutyl
- 3-Methylbutyl
- 1,1-Dimethylpropyl
- 1,2-Dimethylpropyl
- 2,2-Dimethylpropyl
- 1-Ethylpropyl

3.14

3,3,4,5-Tetramethylheptane

3.15 The graph shows the energy of a conformation as a function of angle of rotation.

Energy vs. Angle of Rotation
3.16

(a) The *most stable* conformation is staggered and occurs at 60°, 180°, and 300°.

(b) The *least stable* conformation is eclipsed and occurs at 0°, 120°, 240°, and 360°.

(c),(d)

3.17

This conformation of 2,3-dimethylbutane is the most stable because it is staggered and has the fewest CH₃↔CH₃ gauche interactions.

3.18

The conformation is a staggered conformation in which the hydrogens on carbons 2 and 3 are 60° apart. Draw the Newman projection.

The Newman projection shows three gauche interactions, each of which has an energy cost of 3.8 kJ/mol. The total strain energy is 11.4 kJ/mol (3 x 3.8 kJ/mol).
Visualizing Chemistry

3.19

(a) Phenylalanine \( \text{C}_9\text{H}_{11}\text{NO}_2 \)

(b) Lidocaine \( \text{C}_{14}\text{H}_{22}\text{N}_2\text{O} \)

3.20

(a) 3,3,5-Trimethylheptane

(b) 3-Ethyl-2-methylpentane

(c) 2,2,4-Trimethylpentane

(d) 4-Isopropyl-2-methylheptane

3.21

In this conformation, all groups are staggered and the two methyl groups are 180° apart.

Additional Problems

Functional Groups

3.22

(a) Alcohol

(b) Ketone

(c) Amide

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**3.23** Different answers to this problem and to Problem 3.24 are acceptable.

(a) \[ \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3 \]
(b) \[ \text{CH}_3\text{CNHCH}_2\text{CH}_3 \]
(c) \[ \text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3 \]
(d) \[ \text{C} = \text{C} \text{Cl} \]
(e) \[ \text{C} - \text{C} \text{ double bond} \]
(f) \[ \text{C} - \text{C} \text{ triple bond} \]

**3.24** For (a) and (h), only one structure is possible.

(a) \[ \text{C}_4\text{H}_6\text{O}: \text{C}_5\text{H}_9\text{N}: \text{CH}_3\text{CCH}_2\text{CH}_3 \]
(b) \[ \text{C}_5\text{H}_9\text{N}: \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}=\text{N} \]
(c) \[ \text{C}_4\text{H}_6\text{O}: \text{C}_6\text{H}_{11}\text{Br}: \text{HCCH}_2\text{CH}_2\text{CH} \]
(d) \[ \text{C}_6\text{H}_{11}\text{Br}: \text{CH}_3\text{CH}_2\text{CH} = \text{CHCH}_2\text{CH}_2\text{Br} \]
(e) \[ \text{C}_6\text{H}_{14}: \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]
(f) \[ \text{C}_6\text{H}_{12}: \]
(g) \[ \text{C}_5\text{H}_8: \text{CH}_3\text{CH} = \text{CHCH} = \text{CH}_2 \]
(h) \[ \text{C}_5\text{H}_8\text{O}: \text{H}_2\text{C} = \text{CHCH}_2\text{CH}_3 \]

**3.25**

(a) \[ \text{sp}^2 \]
(b) \[ \text{sp} \]
(c) \[ \text{sp}^2 \]
3.26  (a) Although it is stated that biacetyl contains no rings or carbon–carbon double bonds, it is obvious from the formula for biacetyl that some sort of multiple bond must be present. The structure for biacetyl contains two carbon–oxygen double bonds.
(b) Ethyleneimine contains a three-membered ring.
(c) Glycerol contains no multiple bonds or rings.

Isomers
3.27  (a) Eighteen isomers have the formula C₈H₁₈. Three are pictured.

(b) Structures with the formula C₄H₈O₂ may represent esters, carboxylic acids or many other complicated molecules. Three possibilities:

3.28  Heptane  2-Methylhexane  3-Methylhexane

2,2-Dimethylpentane  2,3-Dimethylpentane  2,4-Dimethylpentane

3,3-Dimethylpentane  3-Ethylpentane  2,2,3-Trimethylbutane
3.29

(a) 
\[
\begin{align*}
\text{Br} & \quad \text{CH}_3\text{CHCHCH}_3 \\
\text{CH}_3 & \quad \text{same} \\
\text{CH}_3 & \quad \text{same} \\
\end{align*}
\]

(b) 
\[
\begin{align*}
\text{OH} & \quad \text{HO} \\
\text{HO} & \quad \text{same} \\
\end{align*}
\]

(c) 
\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 \\
\text{CH}_3 & \quad \text{same} \\
\text{CH}_3 & \quad \text{same} \\
\end{align*}
\]

Give the number "1" to the carbon bonded to –OH, and count to find the longest chain containing the –OH group.

3.30 The isomers may be either alcohols or ethers.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 \\
\text{CH}_3\text{CHCH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{OCH}_3 \\
\end{align*}
\]

3.31 First, draw all straight-chain isomers. Then proceed to the simplest branched structure.

(a) There are four alcohol isomers with the formula C₄H₁₀O.
(b) There are 17 isomers of C₅H₁₃N. Nitrogen can be bonded to one, two or three alkyl groups.

\[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 & \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 & \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
&\text{CH}_3\text{CH}_2\text{CHCH}_2\text{NH}_2 & \text{CH}_3\text{CH}_2\text{CH}_3 & \text{CH}_3\text{CHCHCH}_3 & \text{H}_2\text{NCH}_2\text{CH}_2\text{CHCH}_3 \\
&\text{CH}_3\text{CCH}_2\text{NH}_2 & \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3 & \text{CH}_3\text{CH}_2\text{CHNNHCH}_3 \\
&\text{CH}_3\text{CHCH}_2\text{NHCH}_3 & \text{CH}_3\text{CNHCH}_3 & \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2\text{CH}_3 & \text{CH}_3\text{CHNNHCH}_2\text{CH}_3 \\
&\text{CH}_3\text{CH}_2\text{CH}_2\text{NCH}_3 & \text{CH}_3\text{CHNCH}_3 & \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2\text{CH}_3 \\
&\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3 & \text{CH}_3\text{CH}_2\text{CHNH}_2\text{CH}_3 & \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3 & \text{CH}_3\text{CHNNHCH}_2\text{CH}_3 \\
\end{align*}
\]

(c) There are 3 ketone isomers with the formula C₅H₁₀O.

\[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{CH}_2\text{CCH}_3 & \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_3 & \text{CH}_3\text{CHCCH}_3 \\
\end{align*}
\]

(d) There are 4 isomeric aldehydes with the formula C₅H₁₀O. Remember that the aldehyde functional group can occur only at the end of a chain.

\[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH} & \text{CH}_3\text{CHCH}_2\text{CH} & \text{CH}_3\text{CH}_2\text{CHCH} \\
&\text{CH}_3\text{CH}_2\text{COCH}_3 & \text{CH}_3\text{COCH}_2\text{CH}_3 & \text{HCOCH}_2\text{CH}_2\text{CH}_3 & \text{HCOCHCH}_3 \\
\end{align*}
\]

(e) There are 4 esters with the formula C₄H₈O₂.

\[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{COCH}_3 & \text{CH}_3\text{COCH}_2\text{CH}_3 & \text{HCOCH}_2\text{CH}_2\text{CH}_3 & \text{HCOCHCH}_3 \\
\end{align*}
\]

(f) There are 3 ethers with the formula C₄H₁₀O.

\[
\begin{align*}
&\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 & \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 & \text{CH}_3\text{OCHCH}_3 \\
\end{align*}
\]
3.32

(a) \( \text{CH}_3\text{CH}_2\text{OH} \)

(b) \( \text{CH}_3\text{C}≡\text{N} \)

(c) \( \text{CH}_3\text{CHCH}_3 \)

(d) \( \text{CH}_3\text{CHCH}_2\text{OH} \)

(e) \( \text{CH}_3\text{CHOCH}_3 \)

(f) \( \text{CH}_3\text{CCH}_3 \)

3.33

Naming Compounds

3.33

\( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \)

1-Bromopentane 2-Bromopentane 3-Bromopentane

3.34

\( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CHCH}_2\text{Cl} \) \( \text{CH}_3\text{CHCH}_2\text{CH}_{2}\text{CCH}_3 \) \( \text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{CHCH}_3 \)

1-Chloro-2,5-dimethylhexane 2-Chloro-2,5-dimethylhexane 3-Chloro-2,5-dimethylhexane

3.35

(a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3 \)

2-Methylheptane

(b) \( \text{CH}_3\text{CHCH}_3\text{CH}_2\text{CHCH}_3 \)

4-Ethyl-2,2-dimethylhexane

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3 \)

4-Ethyl-3,4-dimethyloctane

(d) \( \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CHCH}_3 \)

2,4,4-Trimethylheptane

(e) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CHCH}_3 \)

3,3-Diethyl-2,5-dimethylnonane

(f) \( \text{CH}_3\text{CHCH}_3\text{CH}_2\text{CHCH}_3 \)

4-Isopropyl-3-methylheptane

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3.36
(a) \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_3 \)
2-Methylpropane
(b) \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_3 \)
2,2-Dimethylpropane
(c) \( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
Hexane

3.37
(a) \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_3 \)
2-Methylpropane
(b) \( \text{CH}_3 \text{CH}_3 \)
Ethane

3.38
(a) \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2-Methylpentane
(b) \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2,2-Dimethylbutane
(c) \( \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2,3,3-Trimethylhexane
(d) \( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
5-Ethyl-2-methylheptane
(e) \( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
3,3,5-Trimethylheptane
(f) \( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2,2,3,3-Tetramethylhexane

3.39
\( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
Hexane
\( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2-Methylpentane
\( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
3-Methylpentane
\( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2,2-Dimethylbutane
\( \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 \)
2,3-Dimethylbutane
3.40

**Structure and Correct Name**

(a) \[ \text{CH}_3\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_3 \]

Correct name: 2,2,6-Trimethyloctane

(b) \[ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \]

Correct name: 3-Ethyl-2-methylhexane

(c) \[ \text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3 \]

Correct name: 4-Ethyl-3,3-dimethylhexane

(d) \[ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \]

Correct name: 3,4,4-Trimethyloctane

(e) \[ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CHCH}_3 \]

Correct name: 2,3,5-Trimethyloctane

**Error**

The longest chain is an octane and has only methyl branches.

The longest chain is a hexane. Numbering should start from the opposite end of the carbon chain, nearer the first branch.

Numbering should start from the opposite end of the carbon chain. See step 2(b) in Section 3.4.

Numbering should start from the opposite end of the carbon chain.

The longest chain is an octane.

3.41

(a) \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_2\text{CH}_3 \]

4,4-Diethyl-2,2-dimethylhexane

(b) \[ \text{CH}_3\text{CH}_2\text{CHCH}_3 \]

6-(3-Methylbutyl)-undecane

Remember that you must choose an alkane whose principal chain is long enough so that the substituent does not become part of the principal chain.
Conformations

3.42

(a), (b) 3.8 kJ/mol 4.0 kJ/mol 11.0 kJ/mol

CH₃CH₂-CHCH₃

H H
C₂–C₃ bond

CH₃

2-Methylbutane Most stable conformation Least stable conformation

The energy difference between the two conformations is \((11.0 + 6.0 + 4.0) \text{ kJ/mol} - 3.8 \text{ kJ/mol} = 17.2 \text{ kJ/mol}\).

(c) Consider the least stable conformation to be at zero degrees. Keeping the front of the projection unchanged, rotate the back by 60° to obtain each conformation.

3.8 kJ/mol 6.0 kJ/mol 6.0 kJ/mol

at 60°: energy = 3.8 kJ/mol at 120°: energy = 18.0 kJ/mol at 180°: energy = 3.8 kJ/mol

6.0 kJ/mol 6.0 kJ/mol 11.0 kJ/mol

at 240°: energy = 21.0 kJ/mol at 300°: energy = 7.6 kJ/mol

Use the lowest energy conformation as the energy minimum. The highest energy conformation is 17.2 kJ/mol higher in energy than the lowest energy conformation.
3.43 Each CH₃↔CH₃ gauche interaction has a value of 3.8 kJ/mol.

\[
\begin{align*}
2 \text{ CH}_3 \leftrightarrow \text{CH}_3 \text{ gauche} & = 2 \times 3.8 \text{ kJ/mol} = 7.6 \text{ kJ/mol} \\
3 \text{ CH}_3 \leftrightarrow \text{CH}_3 \text{ gauche} & = 3 \times 3.8 \text{ kJ/mol} = 11.4 \text{ kJ/mol} \\
3 \text{ CH}_3 \leftrightarrow \text{CH}_3 \text{ gauche} & = 3 \times 3.8 \text{ kJ/mol} = 11.4 \text{ kJ/mol}
\end{align*}
\]

3.44 Since we are not told the values of the interactions for 1,2-dibromoethane, the diagram can only be qualitative.

The anti conformation is at 180°. The gauche conformations are at 60°, 300°.

3.45 The eclipsed conformation at 0° rotation has the largest dipole moment but is a high energy conformation that is present in low abundance. The anti conformation has no net dipole moment because the polarities of the individual bonds cancel. The gauche conformation, however, has a dipole moment. Because the observed dipole moment is 1.0 D at room temperature, a mixture of gauche and anti conformations must be present.
3.46 The best way to draw pentane is to make a model and to copy it onto the page. A model shows the relationship among atoms, and its drawing shows how these relationships appear in two dimensions. From your model, you should be able to see that all atoms are staggered in the drawing.

![Pentane model]

3.47

![Cl-substituted pentane]

General Problems

3.48

(a) CH₃CH₂CH₂CH₂CH₂Br

(b) CH₂OCH₃

(c) CH₃CHC≡N

(d) CH₂OH

(e) There are no aldehyde isomers. However, the structure below is a ketone isomer.

(f) CO₂H

CH₃CCH₃

3.49

(a) Because malic acid has two –CO₂H groups, the formula for the rest of the molecule is C₂H₄O. Possible structures for malic acid are:

- Primary alcohol
- Secondary alcohol
- Tertiary alcohol

(b) Because only one of these compounds (the second one) is also a secondary alcohol, it must be malic acid.
To solve this type of problem, read the problem carefully, word for word. Then try to interpret parts of the problem. For example:

1) Formaldehyde is an aldehyde, \( \text{CHO} \).

2) It trimerizes – that is, 3 formaldehydes come together to form a compound \( \text{C}_3\text{H}_6\text{O}_3 \). Because no atoms are eliminated, all of the original atoms are still present.

3) There are no carbonyl groups. This means that trioxane cannot contain any \(-\text{C}=\text{O}\) functional groups. If you look back to Table 3.1, you can see that the only oxygen-containing functional groups that can be present are either ethers or alcohols.

4) A monobromo derivative is a compound in which one of the \(-\text{H}\)'s has been replaced by a \(-\text{Br}\). Because only one monobromo derivative is possible, we know that there can only be one type of hydrogen in trioxane. The only possibility for trioxane is:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{O} \\
\text{O} & \quad \text{CH}_2
\end{align*}
\]

Trioxane

The highest energy conformation of bromoethane has a strain energy of 15 kJ/mol. Because this includes two \(\text{H}--\text{H}\) eclipsing interactions of 4.0 kJ/mol each, the value of an \(\text{H}--\text{Br}\) eclipsing interaction is 15 kJ/mol – 2(4.0 kJ/mol) = 7.0 kJ/mol.
3.52

<table>
<thead>
<tr>
<th>Most stable</th>
<th>Strain energy</th>
<th>Least stable</th>
<th>Strain energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>* 3.8 kJ/mol</td>
<td></td>
<td>21 kJ/mol</td>
</tr>
<tr>
<td>(b)</td>
<td>7.6 kJ/mol</td>
<td></td>
<td>23 kJ/mol</td>
</tr>
<tr>
<td>(c)</td>
<td>7.6 kJ/mol</td>
<td></td>
<td>26 kJ/mol</td>
</tr>
<tr>
<td>(d)</td>
<td>15.2 kJ/mol</td>
<td>** 28 kJ/mol</td>
<td></td>
</tr>
</tbody>
</table>

*most stable overall (least strain)
**least stable overall (most strain)
The carboxylic acid and alcohol groups in Pravachol are an ester (lactone) group in Zocor. The alcohol at the bottom left of Pravachol is a methyl group in Zocor.

3.54 A puckered ring allows all the bonds in the ring to have a nearly tetrahedral bond angle. (If the ring were flat, C–C–C bond angles would be 120°.) Also, a puckered conformation relieves strain due to eclipsed hydrogens.

3.55 In one of the 1,2-dimethylcyclohexanes the two methyl groups are on the same side of the ring, and in the other isomer the methyl groups are on opposite sides.
Review Unit 1: Bonds and Bond Polarity

Major Topics Covered (with vocabulary:)

Atomic Structure:
atomic number  mass number  wave equation  orbital  shell  node  electron configuration

Chemical Bonding Theory:
covalent bond  Lewis structure  lone-pair electrons  line-bond structure  valence-bond theory
sigma (σ) bond  bond strength  bond length  molecular orbital theory  bonding MO  antibonding MO

Hybridization:
sp³ hybrid orbital  bond angle  sp² hybrid orbital  π (π) bond  sp hybrid orbital

Polar covalent bonds:
polar covalent bond  electronegativity (EN)  electrostatic potential maps  inductive effect
dipole moment  formal charge  dipolar molecule

Resonance:
resonance form  resonance hybrid

Acids and Bases:
Brønsted-Lowry acid  Brønsted-Lowry base  conjugate acid  conjugate base  acidity constant
Kₐ  pKₐ  organic acid  organic base  Lewis acid  Lewis base

Chemical Structures:
condensed structure  skeletal structure  space-filling models  ball-and-stick models

Types of Problems:

After studying these chapters you should be able to:

– Predict the ground state electronic configuration of atoms.
– Draw Lewis electron-dot structures of simple compounds.
– Predict and describe the hybridization of bonds in simple compounds.
– Predict bond angles and shapes of molecules.

– Predict the direction of polarity of a chemical bond, and predict the dipole moment of a simple compound.
– Calculate formal charge for atoms in a molecule.
– Draw resonance forms of molecules.
– Predict the relative acid/base strengths of Brønsted acids and bases.
– Predict the direction of Brønsted acid/base reactions.
– Calculate: pKₐ from Kₐ, and vice versa.
  pH of a solution of a weak acid.
– Identify Lewis acids and bases.
– Draw chemical structures from molecular formulas, and vice versa.
Points to Remember:

* In order for carbon, with valence shell electron configuration of $2s^22p^2$, to form four $sp^3$ hybrid orbitals, it is necessary that one electron be promoted from the $2s$ subshell to the $2p$ subshell. Although this promotion requires energy, the resulting hybrid orbitals are able to form stronger bonds, and compounds containing these bonds are more stable.

* Assigning formal charge to atoms in a molecule is helpful in showing where the electrons in a bond are located. Even if a bond is polar covalent, in some molecules the electrons "belong" more to one of the atoms than the other. This "ownership" is useful for predicting the outcomes of chemical reactions, as we will see in later chapters.

* Resonance structures are representations of the distribution of π and nonbonding electrons in a molecule. Electrons don't move around in the molecule, and the molecule doesn't change back and forth, from structure to structure. Rather, resonance structures are an attempt to show, by conventional line-bond drawings, the electron distribution of a molecule that can't be represented by any one structure.

* As in general chemistry, acid-base reactions are of fundamental importance in organic chemistry. Organic acids and bases, as well as inorganic acids and bases, occur frequently in reactions, and large numbers of reactions are catalyzed by Brønsted acids and bases and Lewis acids and bases.

Self-Test:

For **A** (ricinine) and **B** (oxaflozane): Add all missing electron lone pairs. Identify the hybridization of all carbons. Indicate the direction of bond polarity for all bonds with $\Delta EN \geq 0.5$. In each compound, which bond is the most polar? Convert **A** and **B** to molecular formulas.

Draw a resonance structure for **B**. Which atom (or atoms) of **B** can act as a Lewis base?

Add missing electron lone pairs to **C**. Is it possible to draw resonance forms for **C**? If so, draw at least one resonance form, and describe it.
Multiple Choice:

1. Which element has $4s^24p^2$ as its valence shell electronic configuration?
   (a) Ca  (b) C  (c) Al  (d) Ge

2. Which compound (or group of atoms) has an oxygen with a +1 formal charge?
   (a) NO$_3^-$  (b) O$_3$  (c) acetone anion  (d) acetate anion

The following questions involve these acids: (i) HW ($pK_a = 2$); (ii) HX ($pK_a = 6$); (iii) HY ($pK_a = 10$); (iv) HZ ($pK_a = 20$).

3. Which of the above acids react almost completely with water to form hydroxide ion?
   (a) none of them  (b) all of them  (c) HY and HZ  (d) HZ

4. The conjugate bases of which of the above acids react almost completely with water to form hydroxide ion?
   (a) none of them  (b) all of them  (c) HZ  (d) HY and HZ

5. If you want to convert HX to $X^-$, which bases can you use?
   (a) W$^-$  (b) Y$^-$  (c) Z$^-$  (d) Y$^-$ or Z$^-$

6. If you add equimolar amounts of HW, X$^-$ and HY to a solution, what are the principal species in the resulting solution?
   (a) HW, HX, HY  (b) W$^-$, HX, HY  (c) HW, X$^-$, HY  (d) HW, HX, Y$^-$

7. What is the approximate pH difference between a solution of 1 M HX and a solution of 1 M HY?
   (a) 2  (b) 3  (c) 4  (d) 6

8. If you wanted to write the structure of a molecule that shows carbon and hydrogen atoms as groups, without indicating many of the carbon-hydrogen bonds, you would draw a:
   (a) molecular formula  (b) Kekulé structure  (c) skeletal structure  (d) condensed structure

9. Which of the following molecules has zero net dipole moment?
   (a) 
   (b) 
   (c) 
   (d) 

10. In which of the following bonds is carbon the more electronegative element?
    (a) C—Br  (b) C—I  (c) C—P  (d) C—S
Chapter 4 – Organic Compounds:
Cycloalkanes and Their Stereochemistry

Chapter Outline

I. Cycloalkanes – alicyclic compounds – (Sections 4.1–4.2).
   A. Cycloalkanes have the general formula \( \text{C}_n\text{H}_{2n} \), if they have one ring.
   B. Naming cycloalkanes (Section 4.1).
      1. Find the parent.
         a. If the number of carbon atoms in the ring is larger than the number in the largest
            substituent, the compound is named as an alkyl-substituted cycloalkane.
         b. If the number of carbon atoms in the ring is smaller than the number in the
            largest substituent, the compound is named as an cycloalkyl-substituted alkane.
   2. Number the substituents.
      a. Start at a point of attachment and number the substituents so that the second
         substituent has the lowest possible number.
      b. If necessary, proceed to the next substituent until a point of difference is found.
      c. If two or more substituents might potentially receive the same number, number
         them by alphabetical priority.
      d. Halogens are treated in the same way as alkyl groups.
   C. Cis–trans isomerism in cycloalkanes (Section 4.2).
      1. Unlike open-chain alkanes, cycloalkanes have much less rotational freedom.
         a. Very small rings are rigid.
         b. Large rings have more rotational freedom.
      2. Cycloalkanes have a "top" side and a "bottom" side.
         a. If two substituents are on the same side of a ring, the ring is cis-disubstituted.
         b. If two substituents are on opposite sides of a ring, the ring is trans-disubstituted.
      3. Substituents in the two types of disubstituted cycloalkanes are connected in the
         same order but differ in spatial orientation.
         a. These cycloalkenes are stereoisomers that are known as cis–trans isomers.
         b. cis–trans isomers are stable compounds that can't be interconverted.

II. Conformations of cycloalkanes (Sections 4.3–4.9).
   A. General principles (Section 4.3).
      1. Ring strain.
         a. A. von Baeyer suggested that rings other than those of 5 or 6 carbons were too
            strained to exist.
         b. This concept of angle strain is true for smaller rings, but larger rings can be
            easily prepared.
      2. Heats of combustion of cycloalkanes.
         a. To measure strain, it is necessary to measure the total energy of a compound
            and compare it to a strain-free reference compound.
         b. Heat of combustion measures the amount of heat released when a compound is
            completely burned in oxygen.
            i. The more strained the compound, the higher the heat of combustion.
            ii. Strain per \( \text{CH}_2 \) unit can be calculated and plotted as a function of ring size.
         c. Graphs show that only small rings have serious strain.
3. The nature of ring strain.
   a. Rings tend to adopt puckered conformations.
   b. Several factors account for ring strain.
      i. Angle strain occurs when bond angles are distorted from their normal 
         values.
      ii. Torsional strain is due to eclipsing of bonds.
      iii. Steric strain results when atoms approach too closely.

B. Conformations of small rings (Section 4.4).
   1. Cyclopropane.
      a. Cyclopropane has bent bonds.
      b. Because of bent bonds, cyclopropane is more reactive than other cycloalkanes.
   2. Cyclobutane.
      a. Cyclobutane has less angle strain than cyclopropane but has more torsional 
         strain.
      b. Cyclobutane has almost the same total strain as cyclopropane.
      c. Cyclobutane is slightly bent to relieve torsional strain, but this increases angle 
         strain.
   3. Cyclopentane
      a. Cyclopentane has little angle strain but considerable torsional strain.
      b. To relieve torsional strain, cyclopentane adopts a puckered conformation.
         i. In this conformation, one carbon is bent out of plane; hydrogens are nearly 
            staggered.

C. Conformations of cyclohexane (Sections 4.5–4.8).
   1. Chair cyclohexane (Section 4.5).
      a. The chair conformation of cyclohexane is strain-free.
      b. In a standard drawing of cyclohexane, the lower bond is in front, and the upper 
         bond is in back.
      c. The twist-boat conformation of cyclohexane has little angle strain but 
         experiences both steric strain and torsional strain.
   2. Axial and equatorial bonds in cyclohexane (Section 4.6).
      a. There are two kinds of positions on a cyclohexane ring.
         i. Six axial hydrogens are perpendicular to the plane of the ring.
         ii. Six equatorial hydrogens are roughly in the plane of the ring.
      b. Each carbon has one axial hydrogen and one equatorial hydrogen.
      c. Each side of the ring has alternating axial and equatorial hydrogens.
      d. All hydrogens on the same face of the ring are cis.
   3. Conformational mobility of cyclohexanes.
      a. Different chair conformations of cyclohexanes interconvert by a ring-flip.
      b. After a ring-flip, an axial bond becomes an equatorial bond, and vice versa.
      c. The energy barrier to interconversion is 45 kJ/mol, making interconversion 
         rapid at room temperature.
   4. Conformations of monosubstituted cyclohexanes (Section 4.7).
      a. Both conformations aren't equally stable at room temperature.
         i. In methylcyclohexane, 95% of molecules have the methyl group in the 
            equatorial position.
         b. The energy difference is due to 1,3-diaxial interactions.
            i. These interactions, between an axial group and a ring hydrogen two carbons 
               away, are due to steric strain.
            ii. They are the same interactions as occur in gauche butane.
      c. Axial methylcyclohexane has two gauche interactions that cause it to be 7.6 
         kJ/mol less stable than equatorial methylcyclohexane.
      d. All substituents are more stable in the equatorial position.
         i. The size of the strain depends on the nature and size of the group.
5. Conformations of disubstituted cyclohexanes (Section 4.8).
   a. In cis-1,2-dimethylcyclohexane, one methyl group is axial and one is equatorial in both chair conformations, which are of equal energy.
   b. In trans-1,2-dimethylcyclohexane, both methyl groups are either both axial or both equatorial.
      i. The conformation with both methyl groups axial is 15.2 kJ/mol less stable than the conformation with both groups equatorial due to 1,3 diaxial interactions.
      ii. The trans isomer exists almost exclusively in the diequatorial conformation.
   c. This type of conformational analysis can be carried out for most substituted cyclohexanes.

D. Conformations of polycyclic (fused-ring) molecules (Section 4.9).
   1. Decalin has two rings that can be either cis-fused or trans-fused.
      a. The two decalins are nonconvertible.
   2. Steroids have four fused rings.
   3. Bicyclic ring systems have rings that are connected by bridges.
      a. In norbornane, the six-membered ring is locked into a boat conformation.

Solutions to Problems

4.1 The steps for naming a cycloalkane are very similar to the steps used for naming an open-chain alkane.

Step 1: Name the parent cycloalkane. In (a), the parent is cyclohexane. If the compound has an alkyl substituent with more carbons than the ring size, the compound is named as a cycloalkyl-substituted alkane, as in (c).

Step 2: Identify the substituents. In (a), both substituents are methyl groups.

Step 3: Number the substituents so that the second substituent receives the lowest possible number. In (a), the substituents are in the 1- and 4- positions.

Step 4: Name the compound. If two different alkyl groups are present, cite them alphabetically. Halogen substituents follow the same rules as alkyl substituents.

(a) CH₃
    CH₃
    1,4-Dimethylcyclohexane
(b) CH₂CH₂CH₃
    CH₃
    1-Methyl-3-propylcyclopentane
(c) 
    3-Cyclobutylpentane
(d) 
    1-Bromo-4-ethylcyclodecane
(e) 
    1-Isopropyl-2-methylcyclohexane
(f) 
    4-Bromo-1-tert-butyl-2-methylcycloheptane
4.2 To draw a substituted cycloalkane, simply draw the ring and attach substituents in the specified positions. The structure in (b) is named as a cyclobutyl-substituted alkane because the alkyl chain has more carbons than the ring.

(a) 1,1-Dimethylcyclooctane  
(b) 3-Cyclobutylhexane

(c) 1,2-Dichlorocyclopentane  
(d) 1,3-Dibromo-5-methylcyclohexane

4.3

3-Ethyl-1,1-dimethylcyclopentane

4.4 Two substituents are cis if they both have either dashed or wedged bonds. The substituents are trans if one has a wedged bond and the other has a dashed bond.

(a) trans-1-Chloro-4-methylcyclohexane  
(b) cis-1-Ethyl-3-methylcycloheptane
4.5
(a) trans-1-Bromo-3-methylcyclohexane
(b) cis-1,2-Dimethylcyclobutane
(c) trans-1-tert-Butyl-2-ethylcyclohexane

4.6
Prostaglandin F$_{2\alpha}$

The two hydroxyl groups are cis because they both point behind the plane of the page (both dashed bonds). The carbon chains have a trans relationship (one is dashed and the other is wedged).

4.7
(a) cis-1,2-Dimethylcyclopentane
(b) cis-1-Bromo-3-methylcyclobutane

4.8
All hydrogen atoms on the same side of the cyclopropane ring are eclipsed by neighboring hydrogens. If we draw each hydrogen–hydrogen interaction, we count six eclipsing interactions, three on each side of the ring. Since each of these interactions costs 4.0 kJ/mol, all six cost 24.0 kJ/mol. 24 kJ/mol ÷115 kJ/mol x 100% = 21% of the total strain energy of cyclopropane is due to torsional strain.
The added energy cost of eclipsing interactions causes cis-1,2-dimethylcyclopropane to be of higher energy and to be less stable than the trans isomer.

If cyclopentane were planar, it would have ten hydrogen–hydrogen interactions with a total energy cost of 40 kJ/mol (10 x 4.0 kJ/mol). The measured total strain energy of 26 kJ/mol indicates that 14 kJ/mol of eclipsing strain in cyclopentane (35%) has been relieved by puckering.

The methyl groups are farther apart in the more stable conformation of cis-1,3-dimethylcyclobutane.
4.12 Use the technique in Section 4.5 to draw the cyclohexane ring. Figure 4.10 shows how to attach axial (a) and equatorial (e) bonds.

The conformation with –OH in the equatorial position is more stable. Note: The starred ring carbons lie in the plane of the paper.

4.13 In trans-1,4-disubstituted cyclohexanes, the methyl substituents are either both axial or both equatorial.

trans-1,4-Dimethylcyclohexane

4.14 In a ring-flip, an axial substituent becomes equatorial, and an equatorial substituent becomes axial.

4.15 Table 4.1 shows that an axial hydroxyl group causes $2 \times 2.1$ kJ/mol of steric strain. Thus, the energy difference between axial and equatorial cyclohexanol is 4.2 kJ/mol.
4.16 There is very little energy difference between an axial and an equatorial cyano group because the small linear cyano group takes up very little room and produces practically no 1,3-diaxial interactions.

\[
\text{Cyclohexanecarbonitrile}
\]

4.17 Table 4.1 shows that an axial bromine causes 2 \times 1.0 \text{ kJ/mol} of steric strain. Thus, the energy difference between axial and equatorial bromocyclohexane is 2.0 \text{ kJ/mol}. According to Figure 4.12, this energy difference corresponds approximately to a 75:25 ratio of more stable:less stable conformer. Thus, 75\% of bromocyclohexane molecules are in the equatorial conformation, and 25\% are in the axial conformation at any given moment.

4.18 Draw the two chair conformations of each molecule, and look for gauche and 1,3-diaxial interactions. Use Table 4.1 to estimate the values of the interactions. Calculate the total strain; the conformation with the smaller value for strain energy is more stable.

(a) \textit{trans}-1-Chloro-3-methylcyclohexane

\[
\begin{align*}
2 \ (H \leftrightarrow CH_3) &= 7.6 \text{ kJ/mol} \\
2 \ (H \leftrightarrow Cl) &= 2.0 \text{ kJ/mol}
\end{align*}
\]

The second conformation is more stable than the first.

(b) \textit{cis}-1-Ethyl-2-methylcyclohexane

\[
\begin{align*}
\text{one CH}_3 \leftrightarrow \text{CH}_2\text{CH}_3 \text{ gauche interaction} &= 3.8 \text{ kJ/mol} \\
2 \ (H-\text{CH}_2\text{CH}_3) &= 8.0 \text{ kJ/mol} \\
\text{Total} &= 11.8 \text{ kJ/mol}
\end{align*}
\]

\[
\begin{align*}
\text{one CH}_3 \leftrightarrow \text{CH}_2\text{CH}_3 \text{ gauche interaction} &= 3.8 \text{ kJ/mol} \\
2 \ (H-\text{CH}_3) &= 7.6 \text{ kJ/mol} \\
\text{Total} &= 11.4 \text{ kJ/mol}
\end{align*}
\]

The second conformation is slightly more stable than the first.
The second conformation is more stable than the first.

The second conformation is more stable than the first.

4.19 The three substituents have the orientations shown in the first structure. To decide if the conformation shown is the more stable conformation or the less stable conformation, perform a ring-flip on the illustrated conformation and do a calculation of the total strain in each structure as in the previous problem. Notice that each conformation has a Cl–CH$_3$ gauche interaction, but we don't need to know its energy cost because it is present in both conformations.

The illustrated conformation is the less stable chair form.
4.20

Trans-decalin is more stable than cis-decalin because of three 1,3-diaxial interactions present in the cis isomer. You can recognize these interactions if you think of the circled parts of cis-decalin as similar to axial methyl groups. The gauche interactions that occur with axial methyl groups also occur in cis-decalin.

4.21 Both ring fusions are trans because the bridgehead groups are on opposite faces of the fused ring system.

Visualizing Chemistry

4.22

(a) 

(cis)-1-Ethyl-3-methylcyclopentane

(b) 

1,1,4-Trimethylcyclohexane

4.23

trans-1-Chloro-3-methylcyclohexane

2 (H ↔ CH₃) = 7.6 kJ/mol
2 (H ↔ Cl) = 2.0 kJ/mol
The conformation shown (the left structure) is the less stable conformation.

4.24

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4.25 The green substituent is axial, and the red and blue substituents are equatorial.

cis relationship: blue–green
trans relationship: green–red, blue–red

4.26

The only difference between \( \alpha \)-glucose and \( \beta \)-glucose is in the orientation of the –OH group at carbon 1: the –OH group is axial in \( \alpha \)-glucose, and it is equatorial in \( \beta \)-glucose. You would expect \( \beta \)-glucose to be more stable because all of its substituents are in the equatorial position.

Additional Problems

Cycloalkane Isomers

4.27

The last two structures are cis-trans isomers.

4.28 Constitutional isomers differ in the way that atoms are connected.
4.29 Stereoisomers have different three-dimensional geometry.

\[\text{\textit{trans}-1,3-Dimethylcyclobutane} \quad \text{\textit{cis}-1,3-Dimethylcyclobutane}\]

4.30

(a) \[\text{\textit{cis}-1,3-Dibromocyclohexane} \quad \text{\textit{trans}-1,4-Dibromocyclohexane}\]

(b) \[\begin{align*}
\text{2,3-Dimethylhexane} & \quad \text{2,3,3-Trimethylpentane} \\
\end{align*}\]

(c) \[\begin{align*}
\text{identical} \\
\end{align*}\]

4.31 Stereoisomers:

\[\text{\textit{trans}-1,2-Dichlorocyclobutane} \quad \text{\textit{cis}-1,2-Dichlorocyclobutane}\]

Constitutional isomers of \textit{trans}-1,2-dichlorocyclobutane:

\[\text{1,1-Dichlorocyclobutane} \quad \text{\textit{cis}-1,3-Dichlorocyclobutane}\]

\textit{trans}-1,3-Dichlorocyclobutane is also a constitutional isomer.
4.32

cis relationship: red–green, blue–black
trans relationship: red–blue, green–blue
red–black, green–black

4.33

Two cis–trans isomers of 1,3,5-trimethylcyclohexane are possible. In one isomer (A), all methyl groups are cis; in B, one methyl group is trans to the other two.

Cycloalkane Conformation and Stability

4.34

4.35 Make a model of cis-1,2-dichlorocyclohexane. Notice that all cis substituents are on the same side of the ring and that two adjacent cis substituents have an axial–equatorial relationship. Now, perform a ring-flip on the cyclohexane.

After the ring-flip, the relationship of the two substituents is still axial–equatorial. No two adjacent cis substituents can be converted to being both axial or both equatorial by a ring-flip. Don’t forget that there are only two chair conformations of any given cyclohexane.
4.36 For a trans-1,2-disubstituted cyclohexane, two adjacent substituents must be either both axial or both equatorial.

A ring flip converts two adjacent axial substituents to equatorial substituents, and vice versa. As in Problem 4.35, no two adjacent trans substituents can have an axial-equatorial relationship.

4.37

A cis-1,3-disubstituted isomer exists almost exclusively in the diequatorial conformation, which has no 1,3-diaxial interactions. The trans isomer must have one group axial, leading to 1,3-diaxial interactions. Thus, the trans isomer is less stable than the cis isomer. When a molecule has two conformations available, the molecule exists mainly in the lower energy conformation.

4.38

The trans-1,4-isomer is more stable because both substituents can be equatorial.
Two types of interaction are present in cis-1,2-dimethylcyclobutane. One interaction occurs between the two methyl groups, which are almost eclipsed. The other is an across-the-ring interaction between methyl group at position 1 of the ring and a hydrogen at position 3. Because neither of these interactions are present in trans isomer, it is more stable than the cis isomer.

In trans-1,3-dimethylcyclobutane, an across-the-ring interaction occurs between the methyl group at position 3 of the ring and a hydrogen at position 1. Because no interactions are present in the cis isomer, it is more stable than the trans isomer.

4.40  To solve this problem: (1) Find the energy cost of a 1,3-diaxial interaction by using Table 4.1. (2) Convert this energy difference into a percent by using Figure 4.12.

(a)  $2 (H \leftrightarrow CH(CH_3)_2) = 9.2 \text{ kJ/mol}$

\begin{align*}
\% \text{ equatorial} &= 97 \\
\% \text{ axial} &= 3
\end{align*}

(b)  $2 (H \leftrightarrow F) = 1.0 \text{ kJ/mol}$

\begin{align*}
\% \text{ equatorial} &= 63 \\
\% \text{ axial} &= 37
\end{align*}

(c)  $2 (H \leftrightarrow CN) = 0.8 \text{ kJ/mol}$

\begin{align*}
\% \text{ equatorial} &= 60 \\
\% \text{ axial} &= 40
\end{align*}
4.41 Make sure you know the difference between axial–equatorial and cis–trans. Axial substituents are parallel to the axis of the ring; equatorial substituents lie around the equator of the ring. Cis substituents are on the same side of the ring; trans substituents are on opposite side of the ring.

(a) 1,3-trans

(b) 1,4-cis

(c) 1,3-cis

(d) 1,5-trans is the same as 1,3-trans

(e) 1,5-cis is the same as 1,3-cis

(f) 1,6-trans

1,6-trans is the same as 1,2-trans.
Cyclohexane Conformational Analysis

4.42

\[
\text{cis-1-Chloro-2-methylcyclohexane}
\]

Use Table 4.1 to find the values of 1,3-diaxial interactions. For the first conformation, the steric strain is \(2 \times 1.0 \text{ kJ/mol} = 2.0 \text{ kJ/mol}\). The steric strain in the second conformation is \(2 \times 3.8 \text{ kJ/mol}\), or 7.6 kJ/mol. The first conformation is more stable than the second conformation by 5.6 kJ/mol.

4.43

\[
\text{trans-1-Chloro-2-methylcyclohexane}
\]

Use Table 4.1 to find the values of 1,3-diaxial interactions. The first conformation is more stable than the second conformation by a maximum of 9.6 kJ/mol. (A gauche interaction between the two substituents in the diequatorial conformation reduces the value of the energy difference, but its value can't be determined with the given data.)

4.44

Galactose

In this conformation, all substituents, except for one hydroxyl group, are equatorial.
4.45 From the flat-ring drawing you can see that the methyl group and the –OH group have a cis relationship, and the isopropyl group has a trans relationship to both of these groups. Draw a chair cyclohexane ring and attach the groups with the correct relationship.

In this conformation, all substituents are equatorial. Now, perform a ring flip.

The second conformation is less stable because all substituents are axial.

4.46 The substituents on the ring have the following relationships:

<table>
<thead>
<tr>
<th>Menthol</th>
<th>Isomer A</th>
<th>Isomer B</th>
<th>Isomer C</th>
</tr>
</thead>
<tbody>
<tr>
<td>–CH(CH_3)_2, –CH_3</td>
<td>trans</td>
<td>trans</td>
<td>cis</td>
</tr>
<tr>
<td>–CH(CH_3)_2, –OH</td>
<td>trans</td>
<td>cis</td>
<td>trans</td>
</tr>
<tr>
<td>–CH_3, –OH</td>
<td>cis</td>
<td>trans</td>
<td>trans</td>
</tr>
</tbody>
</table>
4.47

The large energy difference between conformations is due to the severe 1,3 diaxial interaction between the two methyl groups.

4.48

Diaxial cis-1,3-dimethylcyclohexane contains three 1,3-diaxial interactions – two H ↔ CH₃ interactions of 3.8 kJ/mol each, and one CH₃ ↔ CH₃ interaction. If the diaxial conformation is 23 kJ/mol less stable than the diequatorial, 23 kJ/mol − 2(3.8 kJ/mol) ≈ 15 kJ/mol of this strain energy must be due to the CH₃ ↔ CH₃ interaction.

4.49

2 H ↔ CH₃ interactions = 7.6 kJ/mol  
2 H ↔ CH₃ interactions = 7.6 kJ/mol  
1 CH₃ ↔ CH₃ interaction = 15 kJ/mol  
≈ 23 kJ/mol

Conformation A is favored.

4.50

Conformation A of cis-1-chloro-3-methylcyclohexane has no 1,3-diaxial interactions and is the more stable conformation. Steric strain in B is due to one CH₃ ↔ H interaction (3.8 kJ/mol), one Cl ↔ H interaction (1.0 kJ/mol) and one CH₃ ↔ Cl interaction. Since the total-strain energy of B is 15.5 kJ/mol, 15.5 kJ/mol - 3.8 kJ/mol - 1.0 kJ/mol = 10.7 kJ/mol of strain is caused by a CH₃ ↔ Cl interaction.
General Problems

4.51 Note: In working with decalins, it is essential to use models. Many structural features of decalins that are obvious with models are not easily visualized with drawings.

trans-Decalin

cis-Decalin

No 1,3-diaxial interactions are present in trans-decalin.

At the ring junction of cis-decalin, one ring acts as an axial substituent of the other (see circled bonds). The circled part of ring B has two 1,3-diaxial interactions with ring A (indicated by arrows). Similarly, the circled part of ring A has two 1,3-diaxial interactions with ring B; one of these interactions is the same as an interaction of part of the B ring with ring A. These three 1,3-diaxial interactions have a total energy cost of $3 \times 3.8 \text{ kJ/mol} = 11.4 \text{ kJ/mol}$. Cis-decalin is therefore less stable than trans-decalin by 11.4 kJ/mol.

4.52 A ring-flip converts an axial substituent into an equatorial substituent and vice versa. At the ring junction of trans-decalin, each ring is a trans–trans diequatorial substituent of the other. If a ring-flip were to occur, the two rings would become axial substituents of each other. You can see with models that a diaxial ring junction is impossibly strained. Consequently, trans-decalin does not ring-flip.

The rings of cis-decalin are joined by an axial bond and an equatorial bond. After a ring-flip, the rings are still linked by an equatorial and an axial bond. No additional strain or interaction is introduced by a ring-flip of cis-decalin.
4.53 Build models to see the stability difference between the two \( [4.1.0] \) ring systems. In both cases, fusing a three-membered ring to a six-membered ring distorts the bond angles of both rings, causing angle strain. This strain is much more severe in the trans isomer than in the cis isomer.

\[
\text{cis-Bicyclo}[4.1.0]\text{heptane} \quad \text{trans-Bicyclo}[4.1.0]\text{heptane}
\]

4.54

\[
\text{Simvastatin (Zocor)} \quad \text{Pravastatin (Pravachol)}
\]

(a) The indicated bonds on simvastatin are trans.
(b) The \(-\text{H}\) bond and the \(-\text{OH}\) bond have a cis relationship. The third bond is trans to both of them.
(c) The three indicated bonds on atorvastatin are attached to \( sp^2 \)-hybridized carbons of a planar ring and lie in the same plane.

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In the flat-ring structure shown, all –OH groups have an alternating relationship except for the starred group (below). If all of the groups had a trans relationship, the most stable conformation would have all –OH groups in the equatorial position. We expect that the most stable conformation of this structure has one group in the axial position.

Draw both rings and add –OH groups having the indicated relationships. Perform a ring-flip on the structure you have drawn to arrive at the other conformation.

There are eight cis–trans stereoisomers of myo-inositol. The first isomer is the most stable because all hydroxyl groups can assume an equatorial conformation.
4.57

If you build a model of 1-norbornene, you will find that it is almost impossible to form the bridgehead double bond. $sp^2$-Hybridization at the double bond requires all carbons bonded to the starred carbons to lie in a common plane in order for the $p$ orbitals to overlap to form the $\pi$ bond. The bicyclic ring system forces these atoms out of plane, and the bridgehead double bond can’t form.

4.58 A steroid ring system is fused, and ring-flips don’t occur. Thus, substituents such as the methyl groups shown remain axial. Substituents on the same side of the ring system as the methyl groups are in alternating axial and equatorial positions. Thus, an "up" substituent at C3 (a) is equatorial.

Substituents on the bottom side of the ring system also alternate axial and equatorial positions. A substituent at C7 (b) is axial, and one at C11 (c) is equatorial.

4.59

4.60

The two trans-1,2-dimethylcyclopentanes are mirror images.
4.61 Draw the four possible isomers of 4-\textit{tert}-butylcyclohexane-1,3-diol. Make models of these isomers also. The bulky \textit{tert}-butyl group determines the stable conformation because of its strong preference for the equatorial position.

![Chemical structures of 4-\textit{tert}-butylcyclohexane-1,3-diol isomers]

Only when the two hydroxyl groups are cis diaxial (structure 1) can the acetal ring form. In any other conformation, the oxygen atoms are too far apart to be incorporated into a six-membered ring.

4.62

![Chemical structures of cyclohexane isomers showing cis and trans conformations]

All four conformations of the two isomers are illustrated. The second conformation of each pair has a high degree of steric strain, and thus each isomer adopts the first conformation. Since only the cis isomer has the hydroxyl group in the necessary axial position, it oxidizes faster than the trans isomer.
Chapter 5 – Stereochemistry at Tetrahedral Centers

Chapter Outline

I. Handedness (Sections 5.1–5.4).
   A. Enantiomers and tetrahedral carbon (Section 5.1).
      1. When four different groups are bonded to a carbon atom, two different
         arrangements are possible.
         a. These arrangements are mirror images.
         b. The two mirror-image molecules are enantiomers.
   B. The reason for handedness in molecules: chirality (Section 5.2).
      1. Molecules that are not superimposable on their mirror-images are chiral.
         a. A molecule is not chiral if it contains a plane of symmetry.
         b. A molecule with no plane of symmetry is chiral.
      2. A carbon bonded to four different groups is a chirality center.
      3. It is sometimes difficult to locate a chirality center in a complex molecule.
      4. The groups –CH₂–, –CH₃, C=O, C=C, and C≡C can’t be chirality centers.
   C. Optical activity (Section 5.3).
      1. Solutions of certain substances rotate the plane of plane-polarized light.
         a. These substances are said to be optically active.
      2. The angle of rotation can be measured with a polarimeter.
      3. The direction of rotation can also be measured.
         a. A compound whose solution rotates plane-polarized light to the right is termed
            dextrorotatory.
         b. A compound whose solution rotates plane-polarized light to the left is termed
            levorotatory.
      4. Specific rotation.
         a. The extent of rotation depends on concentration, path length and wavelength.
         b. Specific rotation is the observed rotation of a sample with concentration = 1
            g/mL, sample path length of 1 dm, and light of wavelength = 589 nm.
         c. Specific rotation is a physical constant characteristic of a given optically active
            compound.
   D. Pasteur’s discovery of enantiomerism (Section 5.4).
      1. Pasteur discovered two different types of crystals in a solution that he was
         evaporating.
      2. The crystals were mirror images.
      3. Solutions of each of the two types of crystals were optically active, and their
         specific rotations were equal in magnitude but opposite in sign.
      4. Pasteur postulated that some molecules are handed and thus discovered the
         phenomenon of enantiomerism.

II. Stereoisomers and configurations (Sections 5.5–5.8).
   A. Specification of configurations of stereoisomers (Section 5.5).
      1. Rules for assigning configurations at a chirality center:
         a. Assign priorities to each group bonded to the carbon by using
            Cahn–Ingold–Prelog rules.
            i. Rank each atom by atomic number.
               (a). An atom with a higher atomic number receives a higher priority than an
                   atom with a lower atomic number.
               ii. If a decision can’t be reached based on the first atom, look at the second or
                   third atom until a difference is found.
               iii. Multiple-bonded atoms are equivalent to the same number of single-bonded
                    atoms.
b. Orient the molecule so that the group of lowest priority is pointing to the rear.
c. Draw a curved arrow from group 1 to group 2 to group 3.
d. If the arrow rotates clockwise, the chirality center is $R$, and if the arrow rotates counterclockwise, the chirality center is $S$.

2. The sign of optical rotation is not related to $R,S$ designation.
3. X-ray experiments have proven $R,S$ conventions to be correct.

B. Diastereomers (Section 5.6).
1. A molecule with two chirality centers can have four possible stereoisomers.
   a. The stereoisomers group into two pairs of enantiomers.
   b. A stereoisomer from one pair is the diastereomer of a stereoisomer from the other pair.
2. Diastereomers are stereoisomers that are not mirror images.
3. Epimers are diastereomers whose configuration differs at only one chirality center.

C. Meso compounds (Section 5.7).
1. A meso compound occurs when a compound with two chirality centers possesses a plane of symmetry.
2. A meso compound is achiral despite having two chirality centers.
3. The physical properties of meso compounds, diastereomers and racemic mixtures differ from each other and from the properties of enantiomers.

D. Racemic mixtures and the resolution of enantiomers (Section 5.8).
1. A racemic mixture (racemate) is a 50:50 mixture of two enantiomers.
   a. Racemic mixtures show zero optical rotation.
2. Some racemic mixtures can be resolved into their component enantiomers.
   a. If a racemic mixture of a carboxylic acid reacts with a chiral amine, the product ammonium salts are diastereomers.
   b. The diastereomeric salts differ in chemical and physical properties and can be separated.
   c. The original enantiomers can be recovered by acidification.

III. A review of isomerism (Section 5.9).
A. Constitutional isomers differ in connections between atoms.
   1. Skeletal isomers have different carbon skeletons.
   2. Functional isomers contain different functional groups.
   3. Positional isomers have functional groups in different positions.
B. Stereoisomers have the same connections between atoms, but different geometry.
   1. Enantiomers have a mirror-image relationship.
   2. Diastereomers are non-mirror-image stereoisomers.
      a. Configurational diastereomers.
      b. Cis–trans isomers differ in the arrangement of substituents on a ring or a double bond.

IV. Chirality at atoms other than carbon (Section 5.10).
A. Other elements with tetrahedral atoms can be chirality centers.
B. Trivalent nitrogen can, theoretically, be chiral, but rapid inversion of the nitrogen lone pair interconverts the enantiomers.
C. Chiral phosphines and trivalent sulfur compounds can be isolated because their rate of inversion is slower.

V. Prochirality (Section 5.11).
A. A molecule is prochiral if it can be converted from achiral to chiral in a single chemical step.
B. Identifying prochirality.
1. For \( sp^2 \) carbon, draw the plane that includes the atoms bonded to the \( sp^2 \) carbon.
   a. Assign priorities to the groups bonded to the carbon.
   b. Draw an curved arrow from group 1 to group 2 to group 3.
   c. The face of the plane on which the curved arrow rotates clockwise is the Re face.
   d. The face on which the arrow rotates counterclockwise is the Si face.
2. An atom that is \( sp^3 \)-hybridized may have a prochirality center if, when one of its attached groups is replaced, it becomes a chirality center.
   a. For \(-\text{CH}_2\text{X}\), imagine a replacement of one hydrogen with deuterium.
   b. Rank the groups, including the deuterium.
   c. If the replacement leads to \( R \) chirality, the atom is pro-\( R \).
   d. If the replacement leads to \( S \) chirality, the atom is pro-\( S \).

C. Many biochemical reactions involve prochiral compounds.

VI. Chirality in nature and chiral environments (Section 5.12).
A. Different enantiomers of a chiral molecule have different properties in nature.
   1. (+)-Limonene has the odor of oranges, and (−)-limonene has the odor of lemons.
   2. Racemic fluoxetine is an antidepressant, but the \( S \) enantiomer is effective against migraine.
B. In nature, a molecule must fit into a chiral receptor, and only one enantiomer usually fits.

**Solutions to Problems**

5.1 Objects having a plane of symmetry are achiral.
   Chiral: screw, shoe.
   Achiral: soda can, screwdriver.

5.2 Use the following rules to locate centers that are not chirality centers, then examine the remaining centers to find a carbon with four different groups attached.

1. All \(-\text{CH}_3\) and \(-\text{CX}_3\) carbons are not chirality centers.

2. All \(-\text{CH}_2-\) and \(-\text{CX}_2-\) carbons are not chirality centers.

3. All \(-\overset{\equiv}{\text{C}}\) and \(-\overset{\equiv}{\text{C}}\) carbons are not chirality centers.
   By rule 3, all aromatic ring carbons are not chirality centers.

(a) \hspace{1cm} (b) \hspace{1cm} (c)

![Coniine](image1)

![Menthol](image2)

![Dextromethorphan](image3)

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5.3 Refer to Problem 5.2 if you need help.

\[
\begin{align*}
&\text{CO}_2\text{H} & &\text{CO}_2\text{H} \\
&\text{H}\text{H}_3\text{C} & &\text{H}_2\text{NCH}_3 \\
&\text{C} & &\text{C} \\
&\text{H}_2\text{N} & &\text{CH}_3 \\
&\text{NH}_2 & &\text{H} \\
&\text{H} & &\text{H}
\end{align*}
\]

Alanine

5.4

(a)

\[
\begin{align*}
&\text{HO} & &\text{H} \\
&\text{HO} & &\text{H} \\
&\text{H} & &\text{H} \\
&\text{H} & &\text{HO} \\
&\text{C} & &\text{C} \\
&\text{C} & &\text{C} \\
&\text{O} & &\text{O} \\
&\text{H} & &\text{H}
\end{align*}
\]

Threose

(b)

\[
\begin{align*}
&\text{F} & &\text{F} \\
&\text{F} & &\text{F} \\
&\text{F} & &\text{F} \\
&\text{Cl} & &\text{C} \\
&\text{H} & &\text{C} \\
&\text{C} & &\text{C} \\
&\text{O} & &\text{O} \\
&\text{H} & &\text{H}
\end{align*}
\]

Enflurane

5.5 By convention, a (–) rotation indicates rotation to the left, and thus cocaine is levorotatory.

5.6

Use the formula \([\alpha]_D = \frac{\alpha}{l \times c}\), where

- \([\alpha]_D\) = specific rotation
- \(\alpha\) = observed rotation
- \(l\) = path length of cell (in dm)
- \(c\) = concentration (in g/mL)

In this problem:

\[
\begin{align*}
\alpha &= 1.21° \\
l &= 5.00 \text{ cm} = 0.500 \text{ dm} \\
c &= 1.50 \text{ g/10.0 mL} = 0.150 \text{ g/mL} \\
[\alpha]_D &= \frac{1.21°}{0.500 \text{ dm} \times 0.150 \text{ g/mL}} = +16.1°
\end{align*}
\]

5.7 Review the sequence rules presented in Section 5.5. A summary:

**Rule 1:** An atom with a higher atomic number has priority over an atom with a lower atomic number.

**Rule 2:** If a decision can’t be reached by using Rule 1, look at the second, third, or fourth atom away from the double-bond carbon until a decision can be made.

**Rule 3:** Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.

<table>
<thead>
<tr>
<th>Higher</th>
<th>Lower</th>
<th>Rule</th>
<th>Higher</th>
<th>Lower</th>
<th>Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) –Br</td>
<td>–H</td>
<td>1</td>
<td>(b) –Br</td>
<td>–Cl</td>
<td>1</td>
</tr>
<tr>
<td>(c) –CH_2_CH_3</td>
<td>–CH_3</td>
<td>2</td>
<td>(d) –OH</td>
<td>–NH_2</td>
<td>1</td>
</tr>
<tr>
<td>(e) –CH_2_OH</td>
<td>–CH_3</td>
<td>2</td>
<td>(f) –CH=O</td>
<td>–CH_2_OH</td>
<td>3</td>
</tr>
</tbody>
</table>
5.8 Use the sequence rules in Section 5.5.

(a) By Rule 1, –H is of lowest priority, and –OH is of highest priority. By Rule 2, –CH₂CH₂OH is of higher priority than –CH₂CH₃.

\[
\begin{align*}
\text{Highest} & \quad \longrightarrow \quad \text{Lowest} \\
-\text{OH}, \quad -\text{CH₂CH₂OH}, \quad -\text{CH₂CH₃}, \quad -\text{H}
\end{align*}
\]

(b) By Rule 3, –CO₂H is considered as \( \text{C} - \text{OH} \). Because 3 oxygens are attached to a –CO₂H carbon and only one oxygen is attached to –CH₂OH, –CO₂H is of higher priority than –CH₂OH. –CO₂CH₃ is of higher priority than –CO₂H by Rule 2, and –OH is of highest priority by Rule 1.

\[
\begin{align*}
\text{Highest} & \quad \longrightarrow \quad \text{Lowest} \\
-\text{OH}, \quad -\text{CO₂CH₃}, \quad -\text{CO₂H}, \quad -\text{CH₂OH}
\end{align*}
\]

5.9 All stereochemistry problems are easier if you use models. Part (a) will be solved by two methods – with models and without models.

(a) With models: Build a model of (a). Orient the model so that group 4 is pointing to the rear. Note the direction of rotation of arrows that go from group 1 to group 2 to group 3. The arrows point counterclockwise, and the configuration is \( S \).

Without models: Imagine yourself looking at the molecule, with the group of lowest priority pointing to the back. Your viewpoint would be at the upper right of the molecule, and you would see group 1 on the left, group 3 on the right and group 2 at the bottom. The arrow of rotation travels counterclockwise, and the configuration is \( S \).
5.10 Step 1. For each chirality center, rank substituents by the Cahn–Ingold–Prelog system; give the number 4 to the lowest priority substituent. For part (a):

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Priority</th>
</tr>
</thead>
<tbody>
<tr>
<td>–SH</td>
<td>1</td>
</tr>
<tr>
<td>–CO₂H</td>
<td>2</td>
</tr>
<tr>
<td>–CH₃</td>
<td>3</td>
</tr>
<tr>
<td>–H</td>
<td>4</td>
</tr>
</tbody>
</table>

Step 2. As in the previous problem, orient yourself so that you are 180° from the lowest priority group (indicated by the arrow in the drawing). From that viewpoint, draw the molecule as it looks when you face it. Draw the arrow that travels from group 1 to group 2 to group 3, and note its direction of rotation. The molecule in (a) has S configuration.

(a)

(b)

(c)

In (b), the observer is behind the page, looking out and down toward the right. In (c), the observer is behind the page looking out and up to the left.

5.11

CH₃CH₂CH₂CH₂CH₃ (S)-2-Pentanol

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Priority</th>
</tr>
</thead>
<tbody>
<tr>
<td>–OH</td>
<td>1</td>
</tr>
<tr>
<td>–CH₂CH₂CH₃</td>
<td>2</td>
</tr>
<tr>
<td>–CH₃</td>
<td>3</td>
</tr>
<tr>
<td>–H</td>
<td>4</td>
</tr>
</tbody>
</table>
5.12 Fortunately, methionine is shown in the correct orientation.

\[
\begin{align*}
\text{CH}_3\text{SCH}_2\text{CH}_2\text{C}^2\text{H} & \quad (S)\text{-Methionine} \\
& \quad \text{NH}_2
\end{align*}
\]

5.13 For (a): (Note: the phosphate group is represented as P.)

\[
\begin{align*}
\text{CHO} & \quad \text{CHO} \\
\text{H} & \quad \text{H} \\
\text{CH}_2\text{OP} & \quad \text{CH}_2\text{OP}
\end{align*}
\]

(a) \(R, R\) \quad (b) \(S, R\) \quad (c) \(R, S\) \quad (d) \(S, S\)

a, d are enantiomers and are diastereomeric with b, c.
b, c are enantiomers and are diastereomeric with a, d.
Structure (a) is D-erythrose 4-phosphate, structure (d) is its enantiomer, and structures (b) and (c) are its diastereomers.

5.14

\[
\begin{align*}
\text{Morphine}
\end{align*}
\]

Morphine has five chirality centers and, in principle, can have \(2^5 = 32\) stereoisomers. Most of these stereoisomers are too strained to exist.

5.15

\[
\begin{align*}
\text{Isoleucine}
\end{align*}
\]
5.16 To decide if a structure represents a meso compound, try to locate a plane of symmetry that divides the molecule into two halves that are mirror images. Molecular models are always helpful.

(a) ![Plane of Symmetry](image)

(b) and (c) are not meso structures.

(d) ![Plane of Symmetry](image)

5.17 For a molecule to exist as a meso form, it must possess a plane of symmetry. 2,3-Butanediol can exist as a pair of enantiomers or as a meso compound, depending on the configurations at carbons 2 and 3.

(a) ![Not Meso](image)

(b) 2,3-Pentanediol has no symmetry plane and thus can't exist in a meso form.

(c) 2,4-Pentanediol can exist in a meso form.

2,4-Pentanediol can also exist as a pair of enantiomers (2R,4R) and (2S,4S) that are not meso compounds.
5.18 The molecule represents a meso compound. The symmetry plane passes through the carbon bearing the –OH group and between the two ring carbons that are bonded to methyl groups.

![Meso Compound Diagram](image)

5.19

\[
\begin{align*}
\text{Acetic acid} & + \text{(S)-2-Butanol} & \rightarrow & \text{sec-Butyl acetate} \\
\text{H}_3\text{C} & \text{C} & \text{CH}_2\text{CH}_3 & \text{OH} & \text{H}_3\text{C} & \text{C} & \text{CH}_2\text{CH}_3 & \text{OH} \\
\text{Acid catalyst} & & & & & & & & + \text{H}_2\text{O}
\end{align*}
\]

The product is the pure S-ester. No new chirality centers are formed during the reaction, and the configuration at the chirality center of (S)-2-butanol is unchanged.

5.20

\[
\begin{align*}
\text{R-CO}_2\text{H} & + \text{S-CO}_2\text{H} & \rightarrow & \text{An R,S salt} \\
\text{H}^+ & \text{C} & \text{CH}_3 & \text{S} & \text{C} & \text{CH}_3 & \text{H}_2\text{N} & \text{H} \\
\text{H}^+ & \text{C} & \text{CH}_3 & \text{S} & \text{C} & \text{CH}_3 & \text{H}_2\text{N} & \text{H} \\
& & & & & & & & + \text{S-CO}_2\text{H} \\
& & & & & & & & \text{An S,S salt}
\end{align*}
\]

The two product salts have the configurations (R,S) and (S,S) and are diastereomers.

5.21 (a)

\[
\begin{align*}
\text{Cl} & \text{C} & \text{CH}_3 & \text{CH}_2\text{CH}=\text{CHCH}_3 & \text{Cl} \\
\text{(S)-5-Chloro-2-hexene} & & & & \text{Chlorocyclohexane}
\end{align*}
\]

These two compounds are constitutional isomers (skeletal isomers).

(b) The two dibromopentane stereoisomers are diastereomers.
5.22 For each molecule, replace the left hydrogen with $^2\text{H}$. Give priorities to the groups and assign $R,S$ configuration to the chirality center. If the configuration is $R$, the replaced hydrogen is pro-$R$, and if the configuration is $S$, the replaced hydrogen is pro-$S$.

(a) (S)-Glyceraldehyde

(b) (S)-Phenylalanine

5.23 Draw the plane that includes the $sp^2$ carbon and its substituents, and rank the substituents. For the upper face, draw the arrow that proceeds from group 1 to group 2 to group 3. If the direction of rotation is clockwise, the face is the Re face; if rotation is counterclockwise, the face is the Si face.

(a) Re face (b) Re face

Hydroxyacetone Si face Crotlyl alcohol Si face

5.24 Use the strategy in the previous problem to identify the faces of the plane that contains the $sp^2$ carbon. Draw the product that results from reaction at the Re face, and assign configuration to the chirality center.

Re face

Pyruvate Si face (S)-Lactate

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Visualizing Chemistry

5.26 Structures (a), (b), and (d) are identical (R enantiomer), and (c) represents the S enantiomer.

5.27

(a)

(b)

(R)-Adrenaline

5.28 Locate the plane of symmetry that identifies the structure as a meso compound.

(a) (b) (c)
5.29

![Pseudoephedrine structure](image)

5.30

(a) ![C bond structure](image)
(b) ![C bond structure with S label](image)
(c) ![C bond structure with S label](image)

Additional Problems

Chirality and Optical Activity

5.31 Chiral: (d) golf club, (e) spiral staircase
Achiral: (a) basketball, (b) fork, (c) wine glass, (f) snowflake.

5.32

(a) ![2,4-Dimethylheptane structure](image) 2,4-Dimethylheptane has one chirality center.

(b) ![5-Ethyl-3,3-dimethylheptane structure](image) 5-Ethyl-3,3-dimethylheptane is achiral.

(c) ![cis-1,4-Dichlorocyclohexane structure](image) cis-1,4-Dichlorocyclohexane is achiral. Note the plane of symmetry that passes through the –Cl groups.
5.33
(a) 2-Chloropentane
(b) 2-Hexanol
(c) 3-Methyl-1-pentene
(d) 3-Methylheptane

5.34
(a) achiral
(b) chiral
(c) achiral
(d) achiral

5.35
(a) OH
(b) CH$_3$
(c) Br OH
(d) Br

5.36
Erythronolide B has ten chirality centers.
Assigning Configuration to Chirality Centers

5.37  Identical molecules: b (S enantiomer), c (R enantiomer), d (S enantiomer).
Pair of enantiomers: a

5.38  The specific rotation of (2R,3R)-dichloropentane is equal in magnitude and opposite in
sign to the specific rotation of (2S,3S)-dichloropentane because the compounds are
enantiomers. There is no predictable relationship between the specific rotations of the
(2R,3S) and (2R,3R) isomers because they are diastereomers.

5.39–5.40

The (2R,4S) stereoisomer is the enantiomer of the (2S,4R) stereoisomer.
The (2S,4S) and (2R,4R) stereoisomers are diastereomers of the (2S,4R) stereoisomer.

5.41
5.42

Highest → Lowest

(a) \(-\text{C(CH}_3\text{)}_3, \text{CH}=-\text{CH}, \text{CH}=(\text{CH}_3)_2, \text{CH}_2\text{CH}_3\)

(b) \(-\text{C}≡\text{CH}, \text{C}=(\text{CH}_3)_3, \text{CH}=-\text{CH}_2\)

(c) \(-\text{CO}_2\text{CH}_3, \text{COCH}_3, \text{CH}_2\text{OCH}_3, \text{CH}_2\text{CH}_3\)

(d) \(-\text{Br}, \text{CH}_2\text{Br}, \text{CN}, \text{CH}_2\text{CH}_2\text{Br}\)

5.43

(a) \(\text{HOCH}_2\text{CO}_2\text{H}\)

(b) \(\text{HOCH}_2\text{CO}_2\text{H}\)

(c) \(\text{HOCH}_2\text{CO}_2\text{H}\)

5.44

(a) \(\text{OH}\)

(b) \(\text{CH}_3\text{CH}_2\text{OH}\)

(c) \(\text{HOCH}_2\text{CO}_2\text{H}\)

5.45

(a) \(\text{Biotin}\)

(b) \(\text{Prostaglandin E}_1\)

5.46
5.47

(a) ![Chemical Structure A]

(b) ![Chemical Structure B]

5.48

Ascorbic acid

5.49

(a) ![Chemical Structure C]

(b) ![Chemical Structure D]

5.50

(+)-Xylose

Meso Compounds

5.51

(a) ![Chemical Structure E] symmetry plane

(b) ![Chemical Structure F] symmetry plane

(c) ![Chemical Structure G] symmetry plane

This compound is also a meso compound.
5.52

(a) \[
\begin{array}{c}
\text{H} \\
\text{H}_{3}\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{CH}_{2}\text{CH}_{2} \text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{H} \\
\text{H}_{3}\text{C} \\
\text{R} \\
\text{S} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

(c) plane of symmetry

5.53 Both of the diastereomers shown below are meso compounds with three chirality centers. Each is a meso compound because it has a symmetry plane, and in each structure the central carbon is bonded to four different groups (a group with \( R \) configuration, a group with \( S \) configuration, \(-\text{OH}\), and \(-\text{H}\)).

5.54 (a)–(c)

Ribose

Enantiomer of ribose

Ribose has three chirality centers, which give rise to eight \( (2^3) \) stereoisomers.

(d) Ribose has six diastereomers.
5.55 Ribitol is an optically inactive meso compound. Catalytic hydrogenation converts the aldehyde functional group into a hydroxyl group and makes the two halves of ribitol mirror images of each other.

\[
\begin{align*}
\text{Ribose} & \xrightarrow{\text{Pt catalyst}} \text{Ribitol} \\
\end{align*}
\]

**Prochirality**

5.56

(a) \(\text{pro-S}\) \(\text{pro-R}\)

(b) \(\text{pro-S}\) \(\text{pro-R}\)

(c) \(\text{pro-S}\) \(\text{pro-R}\)

5.57

(a) \(\text{Re face}\)

(b) \(\text{Si face}\)

5.58 Remember that each \(\text{sp}^2\) carbon has a \(\text{Re face}\) and a \(\text{Si face}\).
5.59 If you perform the “replacement test” to assign pro-R/pro-S prochirality, you will see that the right “arm” of citrate is pro-R and the product pictured on the right is formed. The pro-S arm is unchanged.

\[
\begin{align*}
\text{pro-S} & \quad \text{pro-R} \\
\text{citrate} & \quad \text{product}
\end{align*}
\]

5.60

\[
\text{pro-S} \quad \text{CH}_2\text{OH} \quad \text{ATP} \quad \text{ADP} \quad \text{pro-R} \quad \text{Glycerol} \quad \text{Glycerol phosphate}
\]

5.61

\[
\text{pro-R} \quad \text{H}_2\text{O} \quad \text{pro-S}
\]

(R)-3-Hydroxybutyryl ACP \quad trans-Crotonyl ACP

The reaction removes the pro-R hydrogen.

General Problems

5.62

\[
\begin{align*}
\text{cis} & \quad \text{meso} \\
\text{trans}
\end{align*}
\]

B and C are enantiomers and are optically active. Compound A is their diastereomer and is a meso compound, which is not optically active.

The two isomeric cyclobutane-1,3-dicarboxylic acids are achiral and are optically inactive.
Cystine has the \((S,S)\) configuration and is optically active.

(2S,3R)-2,3-Dibromopentane

\textit{meso}-3,5-Heptanediol

All chirality centers of Cephalexin have an \((R)\) configuration.
5.68 Mycomycin contains no chiral carbon atoms, yet is chiral. To see why, make a model of mycomycin. For simplicity, call –CH=CHCH=CHCH2CO2H “A” and –C≡C≡CH “B”. The carbon atoms of an allene have a linear relationship and that the \( \pi \) bonds formed are perpendicular to each other. Attach substituents at the \( sp^2 \) carbons.

\[
\begin{align*}
&\text{C} \quad \text{C} \quad \text{C} \\
&\text{B} \quad \text{C} \quad \text{C} \\
&\text{H}_b \quad \text{C} \quad \text{C} \\
&\text{A} \quad \text{C} \quad \text{C} \\
&\text{H}_a
\end{align*}
\]

Notice that the substituents A, H\(_{a}\), and all carbon atoms lie in a plane that is perpendicular to the plane that contains B, H\(_{b}\), and all carbon atoms.

\[
\begin{align*}
&\text{C} \quad \text{C} \\
&\text{B} \quad \text{C} \quad \text{C} \\
&\text{H}_b \\
&\text{A} \quad \text{C} \\
&\text{H}_a \\
&\text{C} \quad \text{C} \\
&\text{B} \quad \text{C} \quad \text{C} \\
&\text{H}_b \\
&\text{A} \quad \text{C} \\
&\text{H}_a
\end{align*}
\]

Now, make another model identical to the first, except for an exchange of A and H\(_{a}\). This new allene is not superimposable on the original allene. The two allenes are enantiomers and are chiral because they possess no plane of symmetry.

5.69 4-Methylcyclohexylideneacetic acid is chiral for the same reason that mycomycin (Problem 5.68) is chiral: It possesses no plane of symmetry and is not superimposable on its mirror image. As in the case of allenes, the two groups at one end of the molecule lie in a plane perpendicular to the plane that contains the two groups at the other end.

5.70 (a)

\[
\begin{align*}
&\text{CH}_3 \\
&(\text{S})-1\text{-Chloro-2-methylbutane} \\
&\text{H} \quad \text{C} \quad \text{C} \\
&\text{H}_2\text{Cl} \quad \text{CH}_2\text{CH}_3 \\
&\text{CS} \quad \text{Cl} \\
&\text{Cl}_2 \quad \text{Cl}_2
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 \\
&(\text{S})-1,4\text{-Dichloro-2-methylbutane} \\
&\text{H} \quad \text{C} \quad \text{C} \\
&\text{H}_2\text{Cl} \quad \text{CH}_2\text{CH}_3 \\
&\text{CS} \quad \text{Cl} \\
&\text{Cl}_2 \quad \text{Cl}_2
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 \\
&(\text{R})-1,2\text{-Dichloro-2-methylbutane} \\
&\text{H} \quad \text{C} \quad \text{C} \\
&\text{H}_2\text{Cl} \quad \text{CH}_2\text{CH}_3 \\
&\text{CS} \quad \text{Cl} \\
&\text{Cl}_2 \quad \text{Cl}_2
\end{align*}
\]

\[
\begin{align*}
&\text{CH}_3 \\
&(\text{S})-1,2\text{-Dichloro-2-methylbutane} \\
&\text{H} \quad \text{C} \quad \text{C} \\
&\text{H}_2\text{Cl} \quad \text{CH}_2\text{CH}_3 \\
&\text{CS} \quad \text{Cl} \\
&\text{Cl}_2 \quad \text{Cl}_2
\end{align*}
\]

Other products

1:1 mixture

(b) Chlorination at carbon 4 yields an optically active product because the chirality center at C2 is not affected. Chlorination at carbon 2 yields an optically inactive racemic product.
5.71

There are four stereoisomers of 2,4-dibromo-3-chloropentane. C and D are enantiomers and are optically active. A and B are optically inactive meso compounds and are diastereomers.

5.72

 cis-1,4-Dimethylcyclohexane  trans-1,4-Dimethylcyclohexane

(a) There is only one stereoisomer of each of the 1,4-dimethylcyclohexanes.
(b) Neither 1,4-dimethylcyclohexane is chiral.
(c) The two 1,4-dimethylcyclohexanes are diastereomers.

5.73

 cis-1,3-Dimethylcyclohexane  trans-1,3-Dimethylcyclohexane

(a) There is one stereoisomer of cis-1,3-dimethylcyclohexane, and there are two stereoisomers of trans-1,3-dimethylcyclohexane.
(b) cis-1,3-Dimethylcyclohexane is an achiral meso compound; trans-1,3-dimethylcyclohexane exists as a pair of chiral enantiomers.
(c) The two trans stereoisomers are enantiomers, and both are diastereomers of the cis stereoisomer.
The two *cis*-1,2-dimethylcyclohexane enantiomers rapidly interconvert by a ring flip, leading to an optically inactive 1:1 mixture.

The product is *(R)*-2-butanethiol.

The reaction proceeds by addition of acetylide anion to the carbonyl group and occurs with equal probability from either face of the planar ketone carbon.

(a) The product is an optically inactive racemic mixture.

(b) The two enantiomers are formed in a 50:50 ratio.
5.77

(a) Reaction of sodium acetylide with a chiral aldehyde yields chiral products; the product mixture is optically active.
(b) The two products are a mixture of the \((3R,4R)\) and \((3S,4R)\) diastereomers of 4-phenyl-1-pentyn-3-ol. The product ratio can't be predicted, but it is not 50:50.
Review Unit 2: Alkanes and Stereochemistry

Major Topics Covered (with Vocabulary):

Functional Groups.

Alkanes:
saturated aliphatic straight-chain alkane branched-chain alkane isomer constitutional isomer alkyl group primary, secondary, tertiary, quaternary carbon IUPAC system of nomenclature primary, secondary, tertiary hydrogen paraffin cycloalkane cis-trans isomer stereoisomer

Alkane Stereochemistry:
conformer sawhorse representation Newman projection staggered conformation eclipsed conformation torsional strain dihedral angle anti conformation gauche conformation steric strain angle strain heat of combustion chair conformation axial group equatorial group ring-flip 1,3-diaxial interaction conformational analysis boat conformation twist-boat conformation polycyclic molecules bicycloalkane

Handedness:
stereoisomer enantiomer chiral plane of symmetry achiral chirality center plane-polarized light optical activity levorotatory dextrorotatory specific rotation

Stereoisomers and configuration:
configuration Cahn–Ingold–Prelog rules absolute configuration diastereomer meso compound racemate resolution prochirality Re face Si face prochirality center pro-R pro-S

Types of Problems:

After studying these chapters, you should be able to:

– Identify functional groups, and draw molecules containing a given functional group.
– Draw all isomers of a given molecular formula.
– Name and draw alkanes and alkyl groups.
– Identify carbons and hydrogens as being primary, secondary or tertiary.
– Draw energy vs. angle of rotation graphs for single bond conformations.
– Draw Newman projections of bond conformations and predict their relative stability.

– Understand the geometry of, and predict the stability of, cycloalkanes having fewer than 6 carbons.
– Draw and name substituted cyclohexanes, indicating cis/trans geometry.
– Predict the stability of substituted cyclohexanes by estimating steric interactions.

– Calculate the specific rotation of an optically active compound.
– Locate chirality centers, assign priorities to substituents, and assign R,S designations to chirality centers.
– Given a stereoisomer, draw its enantiomer and/or diastereomers.
– Locate the symmetry plane of a meso compound.
– Assign Pro-R and Pro-S designations to prochiral groups.
– Identify the face of an $sp^2$-hybridized carbon as pro-R or pro-S.
Points to Remember:

* In identifying the functional groups in a compound, some groups have different designations that depend on the number and importance of other groups in the molecule. For example, a compound containing an \(-\text{OH}\) group and few other groups is probably named as an alcohol, but when several other groups are present, the \(-\text{OH}\) group is referred to as a hydroxyl group. There is a priority list of functional groups in the Appendix of the textbook, and this priority order will become more apparent as you progress through the text.

* It is surprising how many errors can be made in naming compounds as simple as alkanes. Why is this? Often the problem is a result of just not paying attention. It is very easy to undercount or overcount the \(-\text{CH}_2–\) groups in a chain and to misnumber substituents. Let's work through a problem, using the rules in Section 3.4.

\[
\text{CH}_3\text{CCH}_2\text{CHCH}_2\text{CH}_3
\]

Find the longest chain. In the above compound, the longest chain is a hexane (Try all possibilities; there are two different six-carbon chains in the compound.) Identify the substituents. The compound has two methyl groups and an ethyl group. It's a good idea to list these groups to keep track of them. Number the chain and the groups. Try both possible sets of numbers, and see which results in the lower combination of numbers. The compound might be named either as a 2,2,4-trisubstituted hexane or a 3,5,5-trisubstituted hexane, but the first name has a lower combination of numbers. Name the compound, remembering the prefix \textit{di}- and remembering to list substituents in alphabetical order. The correct name for the above compound is 4-ethyl-2,2-dimethylhexane.

The acronym FINN (from the first letters of each step listed above) may be helpful.

* When performing a ring-flip on a cyclohexane ring, keep track of the positions on the ring.

![Ring-flip](image)

* A helpful strategy for assigning \textit{R,S} designations: Using models, build two enantiomers by adding four groups to each of two tetrahedral carbons. Number the groups 1–4, to represent priorities of groups at a tetrahedral carbon, and assign a configuration to each carbon. Attach a label that indicates the configuration of each enantiomer. Keep these two enantiomers, and use them to check your answer every time that you need to assign \textit{R,S} configurations to a chiral atom.

* When assigning \textit{pro-R} or \textit{pro-S} designations to a hydrogen, mentally replace the hydrogen that points out of the plane of the page. The other hydrogen is then positioned for prochirality assignment without manipulating the molecule. If the designation is \textit{R}, the replaced hydrogen is \textit{pro-R}; if the designation is \textit{S}, the replaced hydrogen is \textit{pro-S}.
Self-test

Name A, and identify carbons as primary, secondary, tertiary or quaternary.
B is an amine with two alkyl substituents. Name these groups and identify alkyl hydrogens as primary, secondary or tertiary.

Identify all functional groups of C (metalaxyl).

Name D and indicate the cis/trans relationship of the substituents. Draw both possible chair conformations, and calculate the energy difference between them.

Assign R,S designations to the chiral carbons in E. Label the circled hydrogen as pro-R or pro-S. Indicate the chirality centers in F. How many stereoisomers of F are possible?
Multiple Choice

1. Which of the following functional groups doesn't contain a carbonyl group?
   (a) aldehyde   (b) ester   (c) ether   (d) ketone

2. Which of the following compounds contains primary, secondary, tertiary and quaternary carbons?
   (a) 2,2,4-Trimethylhexane   (b) Ethylcyclohexane   (c) 2-Methyl-4-ethylcyclohexane
   (d) 2,2-Dimethylcyclohexane

3. How many isomers of the formula C₄H₈Br₂ are there?
   (a) 4   (b) 6   (c) 8   (d) 9

4. The lowest energy conformation of 2-methylbutane occurs:
   (a) when all methyl groups are anti   (b) when all methyl groups are gauche
   (c) when two methyl groups are anti   (d) when two methyl groups are eclipsed

5. The strain in a cyclopentane ring is due to:
   (a) angle strain   (b) torsional strain   (c) steric stain   (d) angle strain and torsional strain

6. In which molecule do the substituents in the more stable conformation have a diequatorial relationship?
   (a) cis-1,2 disubstituted   (b) cis-1,3 disubstituted   (c) trans-1,3-disubstituted
   (d) cis-1,4 disubstituted

7. Which group is of lower priority than –CH=CH₂?
   (a) –CH(CH₃)₂   (b) –CH=C(CH₃)₂   (c) –C   (d) –C(CH₃)₃

8. A meso compound and a racemate are identical in all respects except:
   (a) molecular formula   (b) degree of rotation of plane-polarized light
   (c) connectivity of atoms   (d) physical properties

9. Which of the following projections represents an R enantiomer?
   (a)  
   (b)  
   (c)  
   (d)  

10. How many prochirality centers does 1-bromobutane have?
    (a) none   (b) 1   (c) 2   (d) 3