



Macular degeneration is a disease of the eye with symptoms that include loss of color vision and distortion, blurring, or complete loss of central vision. Peripheral vision is usually unaffected. People with this disease usually have trouble when it comes to reading or recognizing faces. There are a number of factors that increase the risk of getting macular degeneration, including advanced age, a history of smoking, and diabetes.

Stargardt's disease, an inherited form of macular degeneration that usually appears before age 30, results from damage to the retina caused by a malfunction in the recycling of an organic molecule essential to the visual process.

Photo source: Science VU/NIH/Visuals Unlimited.

4 AN

INTRODUCTION TO ORGANIC COMPOUNDS

Now that we have seen the basics of how atoms (Chapter 2) and compounds (Chapter 3) are put together, it is time to set the stage for the organic and biochemistry topics that we will encounter as we move through the text. This chapter will begin with an introduction to a range of diverse topics, all of which relate to how bonding patterns, the distribution of electrons, and the shape of a molecule influence the way that it interacts with others. In later sections of the chapter we will apply our knowledge of these interactions to understand the properties of a number of different families of **organic** compounds (*contain carbon atoms*). The shape that a molecule has and its interactions with others are important in determining its biological effects. Diseases ranging from Stargardt's disease (mentioned on the facing page) to mad cow disease (Health Link: Prion Diseases) are directly related to these properties.

objectives

After completing this chapter, you should be able to:

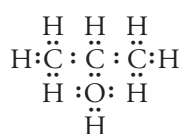
- 1 Draw molecules and polyatomic ions using electron dot and line-bond structures. Assign formal charges.
- 2 Describe how condensed structural formulas and skeletal structures differ from electron dot and line-bond structures.
- 3 Define electronegativity and explain its relationship to polar covalent bonds. Give a simple rule that can be used to predict whether or not a covalent bond is polar.
- 4 List the five basic shapes about an atom in a molecule and describe the rules used to predict shape. Explain how shape plays a role in determining overall polarity.
- 5 Describe the noncovalent interactions that attract one compound to another.
- 6 Describe the four families of hydrocarbons.
- 7 Explain the difference between constitutional isomers, conformations, and the stereoisomers known as geometric isomers. Give examples of two different families of hydrocarbons that can exist as geometric isomers.
- 8 Define the term functional group and describe the features that distinguish hydrocarbons, alcohols, carboxylic acids, and esters from one another.

4.1

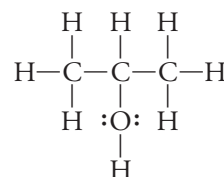
STRUCTURAL FORMULAS
AND FORMAL CHARGES

Before we can consider organic molecules, we must expand on the discussion of covalent bonds and molecules that was initiated in Chapter 3. Section 3.6 introduced molecules, the uncharged groups of nonmetal atoms that are connected to one another by covalent bonds, and showed that the structure of a given molecule can be represented by an electron dot structure (all valence electrons are shown using dots) or a line-bond structure (each pair of shared bonding electrons is represented by a line). In the structures of 2-propanol (rubbing alcohol) shown here, the carbon atoms and oxygen atom have formed the number of covalent bonds required to reach an octet—four bonds for carbon atoms and two bonds for oxygen atoms.

Electron dot structure



Line-bond structure

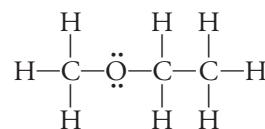
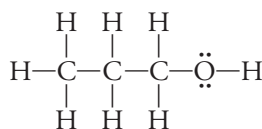
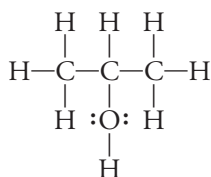


2-Propanol

Either of these **structural formulas** provides more information about the 2-propanol than does the molecular formula ($\text{C}_3\text{H}_8\text{O}$), because molecular formulas tell nothing about how atoms are attached to one another. Suppose, for example, that a toxicologist is reporting on the health problems associated with exposure to high levels of the compound $\text{C}_3\text{H}_8\text{O}$. Because this molecular formula does not tell us how the molecule is put together, it is not clear whether she is talking about 2-propanol or one of the other two molecules that have the formula $\text{C}_3\text{H}_8\text{O}$. Representing the molecule using a structural formula (Figure 4.1) clarifies the matter.

Given a molecular formula, how do we go about drawing a structural formula? For small molecules, knowing the number of covalent bonds that an atom is expected to form can be a good place to start. As we saw in Section 3.5, the number of covalent bonds that a nonmetal atom forms is generally the same as the number of electrons that it needs to gain in order to have an octet. An oxygen atom has six electrons, needs two more to gain an octet, and can form two covalent bonds. A nitrogen atom has five valence electrons, needs three more to gain an octet, and can form three covalent bonds. The expected bonding patterns for hydrogen and the period two nonmetals are:

- A carbon atom can form 4 covalent bonds.
- A nitrogen atom can form 3 covalent bonds.
- An oxygen atom can form 2 covalent bonds.
- A halogen atom can form 1 covalent bond.
- A hydrogen atom can form 1 covalent bond.



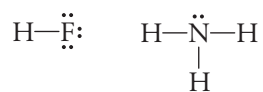
■ FIGURE | 4.1

Structural formulas

Structural formulas, like the line-bond formulas shown here for the three molecules with the formula $\text{C}_3\text{H}_8\text{O}$, indicate the relative position of each atom within a molecule.

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To draw the structural formula for HF, join H and F by a covalent bond to give each its required number of bonds. For NH_3 , N becomes the central atom by forming three covalent bonds, one to each H atom. Note that in the structures of HF and NH_3 , the F and N atoms each carry enough nonbonding electrons to have an octet. Figure 3.15 shows other structural formulas that can be drawn using this approach.



Not all structural formulas are this easy to come up with. Fortunately, for more challenging situations there is a systematic approach that can be used. This approach will be introduced by showing how NCl_3 is drawn.

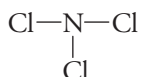
Drawing Line-Bond Structures

1. **Count the total number of valence electrons.** In a molecule, an atom's valence electrons end up either in covalent bonds or as nonbonding electrons. The structural formula of NCl_3 should show 26 electrons:

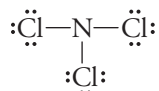
$$\begin{array}{rclclcl} 1 \text{ N atom} & + & 3 \text{ Cl atoms} & & & \\ 5 \text{ valence electrons} & + & 3 \times 7 \text{ valence electrons} & & & \\ 5 & + & 21 & = & 26 \text{ valence electrons} \end{array}$$

2. **Use single covalent bonds to connect the atoms to one another.** The one bit of guesswork here will be deciding which atom to attach to another. Although not always the case, central atoms often come first in the molecular formula. The structure of NCl_3 follows this pattern: N is the central atom. Note that although hydrogen is sometimes listed first in molecular formulas, it can never be a central atom. Hydrogen forms just one covalent bond.

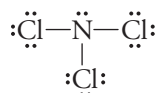
In NCl_3 , nitrogen is the central atom, so we will connect it to the chlorine atoms using single bonds.



3. **Beginning with the atoms attached to the central atom, add the remaining electrons in order to complete octets.** Six valence electrons have been used in the NCl_3 structure above: two for each of the three covalent bonds. Of the original 26 electrons, 20 must still be added. Drawing enough electrons to give each chlorine atom an octet gives



This structure is not complete, because only 24 electrons are shown (3 bonds and 9 pairs of nonbonding electrons). The two remaining electrons are added to the nitrogen atom.



4. **If the central atom does not have an octet, move pairs of nonbonding electrons from attached atoms to form multiple bonds with the central atom. Do so until the central atom has an octet.** The NCl_3 drawn in step 3 is completed and need not be modified. The nitrogen atom has an octet (3 bonds and 1 pair of nonbonding electrons), as do the chlorine atoms (1 bond and 3 pairs of nonbonding electrons each).

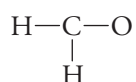
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Let us repeat this process for formaldehyde, which has the formula CH_2O . In this molecule, C is the central atom and is attached to each of the other three atoms.

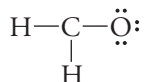
1. **Count the total number of valence electrons.** CH_2O has 12 valence electrons available.

$$\begin{array}{ccccccc} 1 \text{ C atom} & + & 2 \text{ H atoms} & + & 1 \text{ O atom} \\ 4 \text{ valence electrons} & + & 2 \times 1 \text{ valence electron} & + & 6 \text{ valence electrons} \\ 4 & + & 2 & + & 6 & = & 12 \text{ valence electrons} \end{array}$$

2. **Use single covalent bonds to connect the atoms to one another.** As the hint above explained, C is the central atom.

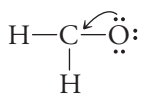


3. **Beginning with the atoms attached to the central atom, add the remaining electrons in order to complete octets.** The drawing above shows three single bonds, so 6 electrons are represented. That leaves 6 more to add. Hydrogen atoms form just one covalent bond and can accept no more electrons, so the remaining electrons must go to the oxygen atom.

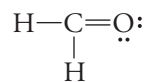


Additional nonbonding electrons are not added to the carbon atom because all of the 12 valence electrons have been used.

4. **If the central atom does not have an octet, move pairs of nonbonding electrons from attached atoms to form multiple bonds with the central atom. Do so until the central atom has an octet.** The carbon atom does not have an octet, so a pair of nonbonding electrons is moved from the oxygen atom and used to form a double bond with the carbon atom. This gives the carbon atom an octet and the drawing is complete.



Carbon has 6 valence electrons



Carbon has an octet

SAMPLE PROBLEM 4.1

Drawing line-bond structures

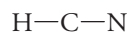
Draw the line-bond structure of hydrogen cyanide, HCN . In this molecule, carbon is the central atom.

Strategy

After completing step 3 of the procedure just described, you will find that the carbon atom does not have an octet. Move as many pairs of nonbonding electrons as needed to give carbon an octet.

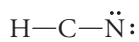
Solution

- The molecular formula of HCN indicates that 10 valence electrons are available, 1 from H, 4 from C, and 5 from N.
- Carbon is the central atom, so the initial structure is

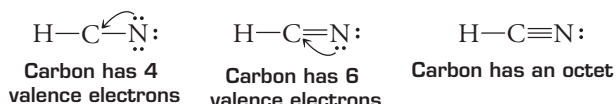


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3. Having two covalent bonds, the structure above uses only 4 of the available 10 valence electrons. The hydrogen atom cannot accept any more electrons, so the remaining 6 are added to nitrogen.



4. While the nitrogen atom has an octet, carbon does not. Nonbonding electrons from N are moved to form multiple bonds with C, until C has an octet.

**PRACTICE PROBLEM 4.1**

Draw the line-bond structure of carbon disulfide, CS_2 . In this molecule, C is the central atom.

In addition to describing the structure of molecules, structural formulas also provide details about the makeup of polyatomic ions. Nitrate ion (NO_3^-), for example, consists of a nitrogen atom covalently bonded to three oxygen atoms (Figure 4.2a). The charge on this ion is shown as a superscript to the right of the square brackets that surround the structural formula. As is always the case, the charge on the ion is due to an imbalance in the total number of protons and electrons in the structure.

To understand the behavior of molecules and polyatomic ions (including those present in cell membranes and those responsible for the cleansing action of soap), it is necessary to know *which atom or atoms carry a charge*. This charge, called **formal charge**, is determined by comparing the number of electrons that surround an atom in a compound to the number of valence electrons that it carries as a neutral atom. A formula to use when calculating formal charge is

$$\text{Formal charge} = \frac{\text{number of valence electrons for a neutral atom}}{\quad} - \frac{\text{number of electrons around the atom in the compound}}{\quad}$$

Using this formula, you assume that the atom “sees” its nonbonding electrons and the bonding electrons nearest to it (imagine that each covalent bond is split down the middle with each atom getting one electron).

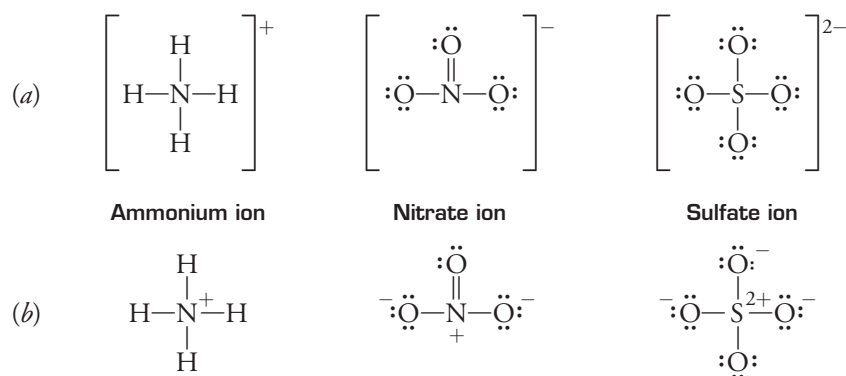


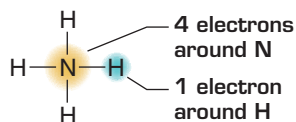
FIGURE 4.2

Polyatomic ions

Polyatomic ions are charged groups of nonmetal atoms that are connected by covalent bonds. (a) The net charge on the ion is shown as a superscript to the right. (b) The formal charge on each atom is shown.

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To see examples of how formal charge is calculated, let us consider two of the ions in Figure 4.2*a*. In an ammonium ion, the nitrogen atom sees four electrons (the four bonding electrons nearest it). Because a neutral nitrogen atom has five valence electrons, the formal charge on this nitrogen atom is 1+.



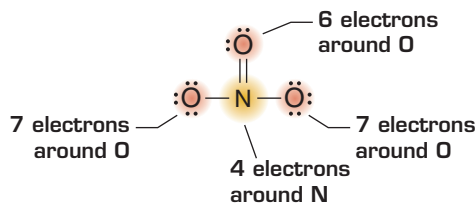
$$\begin{aligned}\text{Formal charge on N} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 5 - 4 = 1+\end{aligned}$$

In an ammonium ion, each hydrogen atom sees one electron. Because a neutral hydrogen atom has one valence electron, the formal charge on each hydrogen atom is 0.

$$\begin{aligned}\text{Formal charge on H} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 1 - 1 = 0\end{aligned}$$

The structure of the ammonium ion in Figure 4.2*b* shows the nitrogen atom carrying a formal charge of 1+.

In a nitrate ion, the nitrogen atom sees four electrons and has a formal charge of 1+.



$$\begin{aligned}\text{Formal charge on N} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 5 - 4 = 1+\end{aligned}$$

Two of the oxygen atoms see seven electrons and have a formal charge of 1−.

$$\begin{aligned}\text{Formal charge on O} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 6 - 7 = 1-\end{aligned}$$

The third oxygen atom sees six electrons and has a formal charge of 0.

$$\begin{aligned}\text{Formal charge on O} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 6 - 6 = 0\end{aligned}$$

■ Formal charges help keep track of the distribution of electrons in a compound.

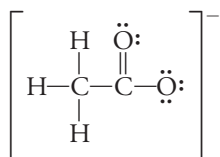
An interesting thing to note for nitrate ion is that, while the structure shown in Figure 4.2*a* indicates a net charge of 1− on the ion, the formal charges in Figure 4.2*b* indicate that this overall charge is due to two negative charges and one positive charge. The sum of the individual formal charges in a compound will always equal the overall charge on the compound. In sulfate ion (Figure 4.2*b*), the overall charge of 2− is the sum of the formal charges on the S and O atoms (2+, 1−, 1−, 1−, and 1−).

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SAMPLE PROBLEM 4.2

Assigning formal charges

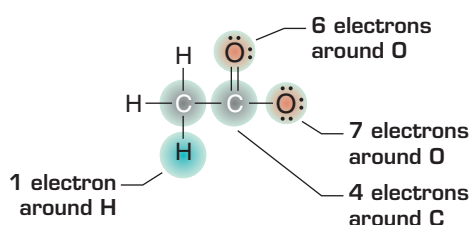
The line-bond structure of acetate ion (Table 3.2) is shown below. Assign formal charges to the atoms in this ion.



Strategy

For each atom, subtract the number of electrons that surround the atom from the number of valence electrons for the neutral atom.

Solution



Each carbon atom sees four electrons and has a formal charge of 0.

$$\begin{aligned} \text{Formal charge on C} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around the atom in the compound}}{\phantom{\text{for a neutral atom}}} \\ &= 4 - 4 = 0 \end{aligned}$$

Each hydrogen atom sees one electron and has a formal charge of 0.

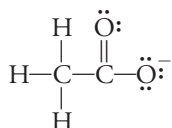
$$\begin{aligned} \text{Formal charge on H} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around the atom in the compound}}{\phantom{\text{for a neutral atom}}} \\ &= 1 - 1 = 0 \end{aligned}$$

The double-bonded oxygen atom sees six electrons and has a formal charge of 0.

$$\begin{aligned} \text{Formal charge on O} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around the atom in the compound}}{\phantom{\text{for a neutral atom}}} \\ &= 6 - 6 = 0 \end{aligned}$$

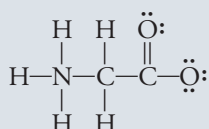
The remaining oxygen atom sees seven electrons and has a formal charge of 1−.

$$\begin{aligned} \text{Formal charge on O} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around the atom in the compound}}{\phantom{\text{for a neutral atom}}} \\ &= 6 - 7 = 1- \end{aligned}$$



PRACTICE PROBLEM 4.2

The line-bond structure of one form of glycine, an amino acid present in many proteins, is shown below. Assign formal charges to the atoms in this compound.



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We have just seen how to assign formal charges when given a structural formula. The structural formulas for polyatomic ions can be drawn using the same set of four guidelines that we used to draw line-bond structures. Let us use those guidelines to draw nitrite ion (NO_2^-).

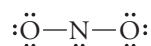
1. **Count the total number of valence electrons.** NO_2^- has 18 electrons available. In the case of polyatomic anions, one electron must be added for each negative charge. For polyatomic cations, one electron must be subtracted for each positive charge.

$$\begin{array}{rccccccc} 1 \text{ N atom} & + & 2 \text{ O atoms} & + & 1 \text{ negative charge} \\ 5 \text{ valence electrons} & + & 2 \times 6 \text{ valence electrons} & + & 1 \text{ electron} \\ 5 & + & 12 & + & 1 & = & 18 \text{ electrons} \end{array}$$

2. **Use single covalent bonds to connect the atoms to one another.** Nitrogen, which is listed first in the formula, is the central atom.



3. **Beginning with the atoms attached to the central atom, add the remaining electrons in order to complete octets.** In the drawing above, 4 of the 18 available electrons have been used. The remaining 14 will be added, beginning with the O atoms and then moving to the N atom.



4. **If the central atom does not have an octet, move pairs of nonbonding electrons from attached atoms to form multiple bonds with the central atom. Do so until the central atom has an octet.** The nitrogen atom does not have an octet, so a pair of nonbonding electrons are moved from one of the oxygen atoms (it does not matter which one). This gives the nitrogen atom an octet.



Formal charges must be added to complete the structure of NO_2^- . The formal charge on the nitrogen atom is 0,

$$\begin{aligned} \text{Formal charge on N} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 5 - 5 = 0 \end{aligned}$$

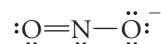
The formal charge on the oxygen atom on the left is 0.

$$\begin{aligned} \text{Formal charge on O} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 6 - 6 = 0 \end{aligned}$$

And the formal charge on oxygen atom on the right is 1-.

$$\begin{aligned} \text{Formal charge on O} &= \frac{\text{number of valence electrons}}{\text{for a neutral atom}} - \frac{\text{number of electrons around}}{\text{the atom in the compound}} \\ &= 6 - 7 = 1- \end{aligned}$$

The final, correct structure is



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SAMPLE PROBLEM 4.3

Drawing line-bond structures of polyatomic ions

Draw the line-bond structure of NO_2^+ , assigning formal charges.

Strategy

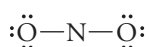
As in NO_2^- , nitrogen is the central atom in NO_2^+ . When counting available electrons in polyatomic cations, subtract one electron for each positive charge.

Solution

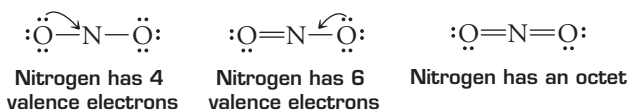
1. A nitrogen atom has 5 valence electrons and each oxygen atom has 6. This gives an initial total of 17 available electrons. Because of the positive charge on the ion, 1 electron is subtracted, giving a total of 16 available electrons for NO_2^+ .
2. Nitrogen is the central atom, so the initial structure is



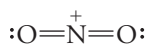
3. Having two covalent bonds, the structure above uses only 4 of the available 16 valence electrons. The remaining 12 are added to the oxygen atoms.



4. To give the nitrogen atom an octet, one pair of nonbonding electrons from each oxygen atom is used to make a multiple bond.



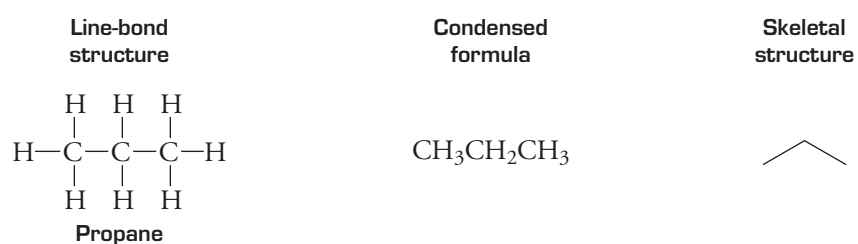
In this drawing the nitrogen atom has a formal charge of 1+ and the oxygen atoms each have a formal charge of zero. The final structure is



PRACTICE PROBLEM 4.3

Draw the line-bond structure of PO_3^{3-} .

Many compounds, especially those encountered in organic and biochemistry, are quite large, and drawing their electron dot or line-bond structural formulas can be a time-consuming task. For this reason, chemists have devised more abbreviated methods for representing structure. A **condensed structural formula** describes the attachment of atoms to one another, without showing all of the bonds. For example, a carbon atom with three attached hydrogen atoms can be written CH_3 and one with two attached hydrogen atoms can be written CH_2 . Several examples of condensed structural formulas are shown in Figure 4.3.



■ FIGURE 4.3

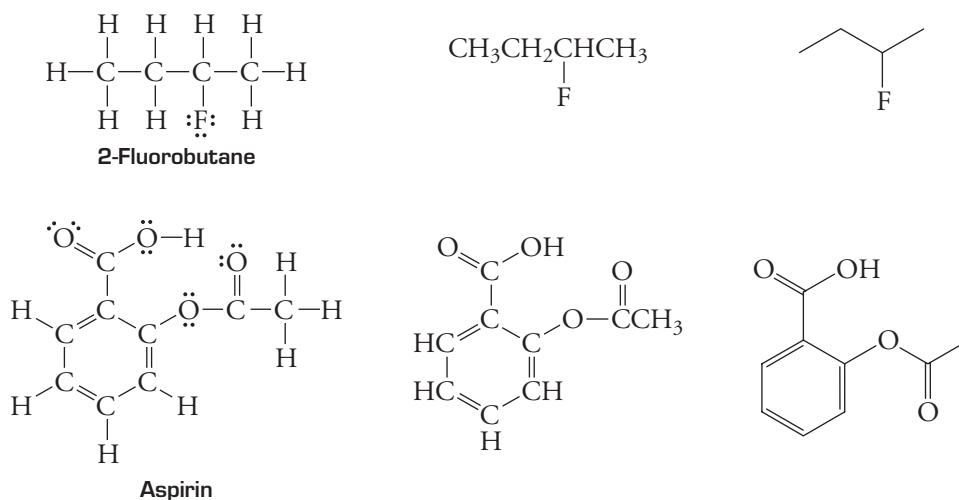
Condensed and skeletal structural formulas

Condensed formulas show the attachment of atoms without always showing covalent bonds and nonbonding electrons. In skeletal structures carbon atoms are not shown and hydrogen atoms appear only when attached to atoms other than carbon.
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■ FIGURE 4.3

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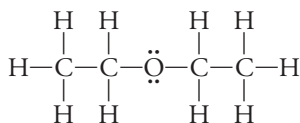


In **skeletal structures** (Figure 4.3), covalent bonds are represented by lines, carbon atoms are not shown, and hydrogen atoms are drawn only when attached to atoms other than carbon. To read a skeletal structure, you assume that a carbon atom appears where lines (bonds) meet and at the end of each line. To simplify matters, nonbonding electrons (Section 3.5) are sometimes omitted from skeletal and other structural formulas.

SAMPLE PROBLEM 4.4

Drawing condensed and skeletal structures

Draw condensed and skeletal structures of diethyl ether, a compound once used as a general anesthetic.



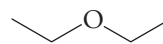
Strategy

To write the condensed formula, begin by thinking of the molecule as a chain of five atoms ($\text{C}-\text{C}-\text{O}-\text{C}-\text{C}$) and then add in the atoms attached to these five (CH_3 , etc.). The skeletal structure of diethyl ether is drawn by leaving out all of the carbon and hydrogen atoms, showing only the oxygen atom and the $\text{C}-\text{C}$ and $\text{C}-\text{O}$ bonds.

Solution



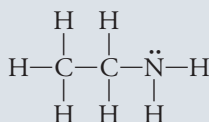
Condensed structure



Skeletal structure

PRACTICE PROBLEM 4.4

Research suggests that drinking green tea may help boost the immune system. Ethylamine (below), produced when one of the compounds in green tea is broken down in the liver, may be responsible for this immune response. Draw condensed and skeletal structures for the molecule.



4.2

POLAR COVALENT BONDS,
SHAPE, AND POLARITY

We have described a covalent bond as consisting of a shared pair of valence electrons. This is not the complete story, however, because the electrons in a covalent bond are not always shared equally between the two atoms. An unequal sharing of electrons is attributed to differences in **electronegativity**, *the ability of an atom to attract bonding electrons*. As shown in Figure 4.4, electronegativity displays a periodic trend—moving to the right across a period or up a group, electronegativity generally increases, with fluorine atoms being the most electronegative.

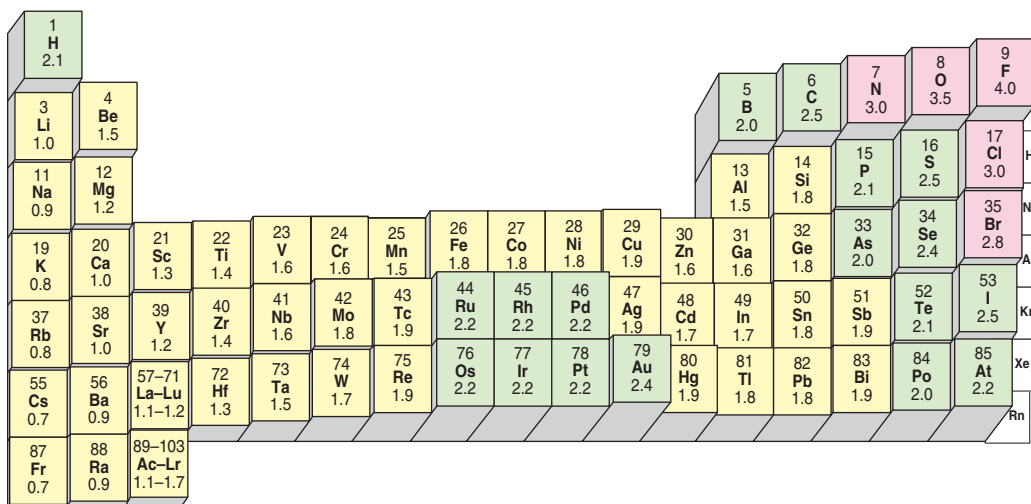


FIGURE | 4.4

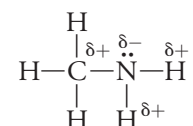
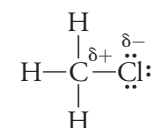
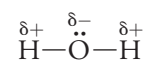
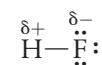
Electronegativity

Electronegativity reflects the ability of an atom to attract bonding electrons. Fluorine (F) is the most electronegative atom, and cesium (Cs) and francium (Fr) are the least electronegative. Inert gases do not attract bonding electrons and are not assigned an electronegativity value.

When the electrons in covalent bonds are shared by atoms with different electronegativities, a **polar covalent bond** results. In a polar covalent bond, *the unequal sharing of electrons gives the bond a partially positive end and a partially negative end (pole)*. Fluorine is much more electronegative than hydrogen, so when a fluorine atom and a hydrogen atom combine to form a covalent bond, the fluorine atom pulls the shared pair of bonding electrons toward itself. As a result, the fluorine atom carries a partial negative charge, represented by δ^- (delta minus), the hydrogen atom carries a partial positive charge (δ^+), and the bond is polar (Figure 4.5).

Any covalent bond that forms between atoms of different electronegativity is polar covalent to some extent, although some levels of polarity are so small that the bonds behave as if they were nonpolar (not polar). For the compounds that we are most likely to encounter in organic and biochemistry, the important polar covalent bonds are those in which *either hydrogen or carbon atoms are covalently attached to nitrogen, oxygen, fluorine, or chlorine atoms*.

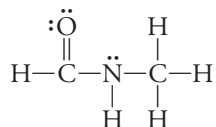
- Bonds between carbon or hydrogen atoms and nitrogen, oxygen, fluorine, or chlorine atoms are polar covalent.



SAMPLE PROBLEM 4.5

Identifying polar covalent bonds

The compound below has been used to kill any insect larvae present in cereal and dried fruit. Label the polar covalent bonds, using the symbols δ^+ and δ^- .

**Strategy**

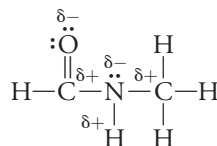
We have defined polar covalent bonds as those between H or C atoms and N, O, F, or Cl atoms. In a polar covalent bond, the δ^+ belongs with the less electronegative atom (H or C) and the δ^- with the more electronegative one (N, O, F, or Cl).

FIGURE | 4.5

Polar covalent bonds

Electrons are shared unequally in polar covalent bonds, which sets up partial positive (δ^+) and partial negative (δ^-) charges.

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Solution**PRACTICE PROBLEM 4.5**

Label the polar covalent bonds in aspirin (see Figure 4.3), using the symbols $\delta+$ and $\delta-$.

The range of bond types that we have seen in this and the previous chapter can be explained in terms of the electronegativity differences between the atoms involved (Table 4.1). Combining nonmetal atoms of identical electronegativity produces covalent bonds in which electrons are shared equally. When the electronegativity difference between the two atoms involved in a covalent bond is small (C and H, etc.), the bond is only slightly polar and behaves as if it were nonpolar. A greater difference in electronegativity (H and F, C and O, etc.) produces a polar covalent bond, and an even greater difference (Li and F, Na and Cl, etc.) results in the transfer of electrons from the less electronegative atom (the metal) to the more electronegative atom (the nonmetal), producing ions and an ionic bond.

TABLE 4.1 BOND TYPES

Bond	Ionic	Polar Covalent	Covalent
Characteristics	Attraction of opposite charges	Unequal sharing of an electron pair	Equal sharing of an electron pair
Example	$\text{Na}^+ \quad \text{Cl}^-$	$\delta^+ \text{C} - \text{O} \delta^-$	$\text{C} - \text{C}$
Electronegativity difference	Very large	Large	None

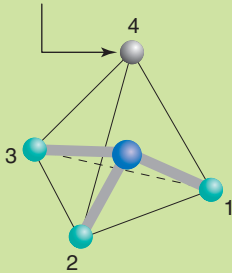
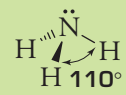
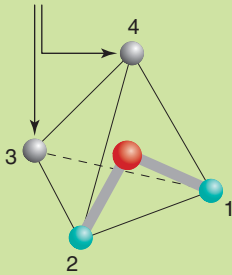
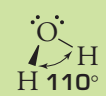
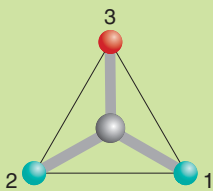
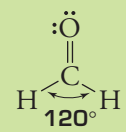
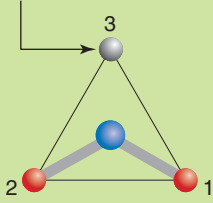
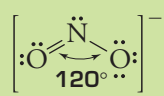

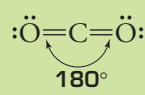
Electron dot, line-bond, condensed, and skeletal structures are designed to show how the atoms in a compound are attached to one another, but are not intended to necessarily represent its actual shape. Shape can be predicted, however, based on these structural formulas.

Consider the way that four groups of electrons arrange themselves around an atom. The carbon atom in methane (Table 4.2) has four single bonds, one to each of the four hydrogen atoms. The best way for these four groups of electrons to be as far apart from one another as

TABLE 4.2 COMMON MOLECULAR SHAPES

Number of Groups of Electrons ^a	Shape ^b (Bond Angles)	Example	Line-Bond Structure	Three-dimensional View ^c
4	Tetrahedral (110°)			
 A tetrahedron		Methane		 H 110°

4.2 POLAR COVALENT BONDS, SHAPE, AND POLARITY 105

Number of Groups of Electrons ^a	Shape ^b (Bond Angles)	Example	Line-Bond Structure	Three-dimensional View ^c
	Pyramidal (110°) (nonbonding electron pair) 	Ammonia	$\text{H}-\ddot{\text{N}}-\text{N}$ $\quad \quad \quad \text{H}$	
	Bent (110°) (nonbonding electron pairs) 	Water	$\text{H}-\ddot{\text{O}}-\text{H}$	
3	Trigonal planar (120°) 	Formaldehyde	$\text{H}-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{H}$	
	Bent (120°) (nonbonding electron pair) 	Nitrite ion	$[\ddot{\text{O}}=\ddot{\text{N}}-\ddot{\text{O}}:]^{-}$	
2	Linear (180°) 	Carbon dioxide	$:\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$	

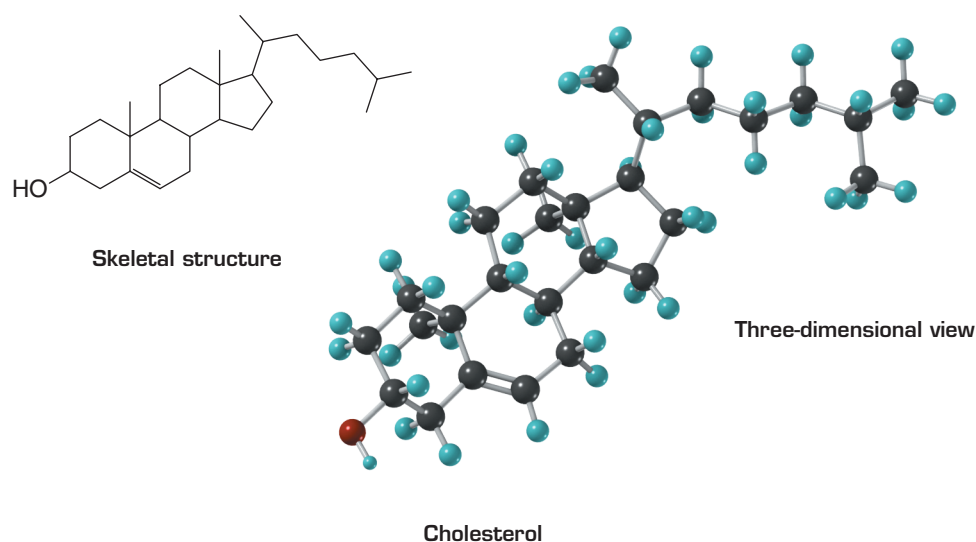
^aThe number of groups of electrons around an atom is the sum of the attached atoms (the single, double, or triple bond to an atom counts as one group of electrons) and attached pairs of nonbonding electrons.

^bMolecular shape is based on the relative placement of atoms. Nonbonding electron pairs are ignored.

^cWedge and dashed line notation can be used to show three-dimensional shapes. A solid wedge points out of the plane of the paper and a dashed wedge points in to the paper.

■ **FIGURE 4.6****Complex shapes**

Large molecules, like cholesterol, can assume complex shapes.



possible (electrons all have the same $1-$ charge and similar charges repel) is for them to point to the four corners of a tetrahedron. This results in a **tetrahedral** shape, in which the hydrogen atoms of methane are placed at each of the four corners of the same tetrahedron.

In ammonia, the nitrogen atom also has four groups of electrons surrounding it—three single bonds and one pair of nonbonding electrons. As with methane, the four groups of electrons arrange themselves to point to the four corners of a tetrahedron. With the three hydrogen atoms of ammonia sitting at three corners of the tetrahedron, the molecule has a **pyramidal** shape. Using a similar argument, the oxygen atom in water has four groups of electrons (two single bonds and two nonbonding pairs) and the molecule has a **bent** shape.

When three groups of electrons surround an atom, the two common shapes observed are **trigonal planar** and bent. The carbon atom in formaldehyde has three groups of electrons (two single bonds and one double bond) and is trigonal planar. The nitrogen atom in nitrite ion has three groups of electrons (one single bond, one double bond, and one pair of nonbonding electrons) and is bent. Two groups of electrons assume a **linear** shape, as seen for carbon dioxide. When many atoms are present in a molecule it can assume a very complex shape (Figure 4.6).

Polarity

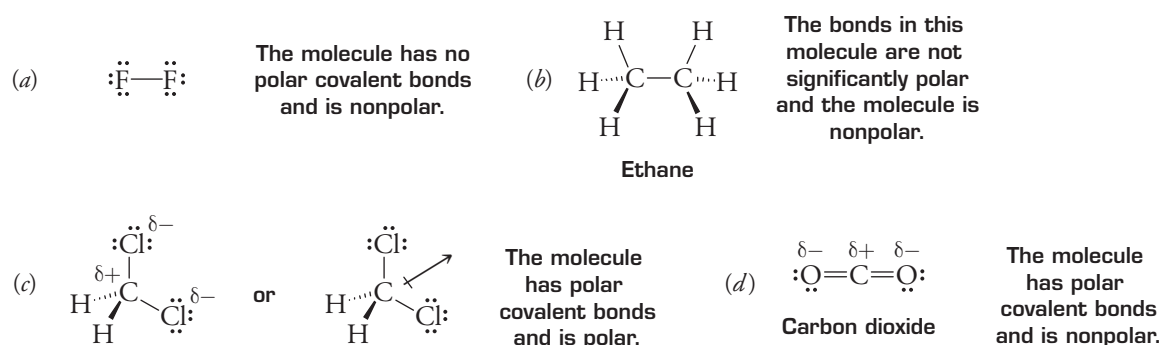
Now that we have seen how to identify polar covalent bonds and to determine the shape about an atom, we can see how these two characteristics determine if a molecule, as a whole, is polar. In a **polar** molecule, *one side has a partial positive charge and the other has a partial negative charge*. Knowing whether or not a molecule is polar helps us to understand how it interacts with other compounds, as we will see in Section 4.3.

If a molecule has no polar covalent bonds, it is nonpolar. The molecule F_2 , for example, is nonpolar because it contains only one covalent bond—a nonpolar one (Figure 4.7a). Although the carbon and hydrogen atoms in ethane (CH_3CH_3) have a slightly different electronegativity, the C—H bonds behave as if they are nonpolar. For this reason ethane molecules are also nonpolar (Figure 4.7b).

For a molecule to be polar, it must contain one or more polar covalent bonds. In methylene chloride (CH_2Cl_2) each of the C—Cl bonds is polar covalent. The molecule has a tetrahedral shape, so the partial negative charges are focused on one side of the molecule and the partial positive charge on the other; thus the molecule is polar (Figure 4.7c). For polar molecules, an alternative to showing the partial charges ($\delta+$ and $\delta-$) for each individual polar covalent bond is to use an arrow that represents the overall contribution of each. This arrow points toward the partially negative end of the molecule. The other end of the arrow, which looks like a plus sign, is directed toward the partially positive end.

- In a polar molecule, one side is partially positive and the other is partially negative.

4.2 POLAR COVALENT BONDS, SHAPE, AND POLARITY 107



■ FIGURE 4.7

Polarity

Molecules that contain only nonpolar bonds are nonpolar. Depending on their shape, molecules that contain one or more polar covalent bonds may be polar or nonpolar.

Not all molecules with polar covalent bonds are polar, however. Carbon dioxide (CO_2) contains two polar covalent $\text{C}=\text{O}$ bonds but is nonpolar because the linear shape of the CO_2 molecule causes the two polar covalent bonds to oppose and cancel one another (Figure 4.7*d*). Although each end of the molecule has a partial negative charge, one end is no more negative than the other. This shows why it is important to consider both the polarity of covalent bonds and the molecular shape when predicting the overall polarity of a molecule.

SAMPLE PROBLEM 4.6**Identifying polar molecules**

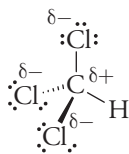
Chloroform (CHCl_3) was once used as a general anesthetic. Its use for this purpose has been discontinued due to toxicity concerns. Is a chloroform molecule polar? (Hint: Carbon is the central atom.)

Strategy

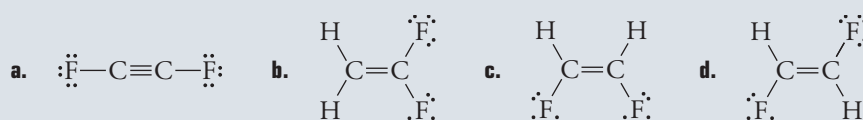
To solve this problem you must first look for polar covalent bonds—for a molecule to be polar it must have at least one polar covalent bond. Then determine its shape—for a molecule to be polar, the shape must not cancel the contributions of the polar covalent bonds.

Solution

Yes. The molecule has a tetrahedral shape, and the three polar covalent bonds are arranged such that the partial positive and negative charges are on opposite sides of the molecule.

**PRACTICE PROBLEM 4.6**

Which of the following molecules are polar? Each is drawn showing its actual three-dimensional shape.



4.3 NONCOVALENT INTERACTIONS

Up to this point in the chapter we have seen that atoms involved in polar covalent bonds carry a partial charge and that atoms can be assigned formal charges. We have also seen that, while the presence of polar covalent bonds is a requirement for a molecule to be polar, not all molecules that contain polar covalent bonds are polar; the shape of the molecule is a deciding factor. In this section we will see how all of these properties help determine the forces that attract molecules or ions to one another, which allows us to understand their properties (why some vitamins are water soluble and others are not, why some drugs remain in the body for months, etc.).

When neighboring molecules or ions (or remote parts of the same molecule or ion) interact with one another, they do so through **noncovalent interactions**—*interactions that do not involve the sharing of valence electrons*. Noncovalent interactions can be divided into two broad categories, those due to the attraction of permanent charges (hydrogen bonds, salt bridges, dipole–dipole interactions, ion–dipole interactions, and coordinate-covalent bonds) and those due to the attraction of temporary partial charges (London forces).

Noncovalent Interactions Due to Permanent Charges

- In a hydrogen bond, an H atom attached to N, O, or F is attracted to a different N, O, or F.

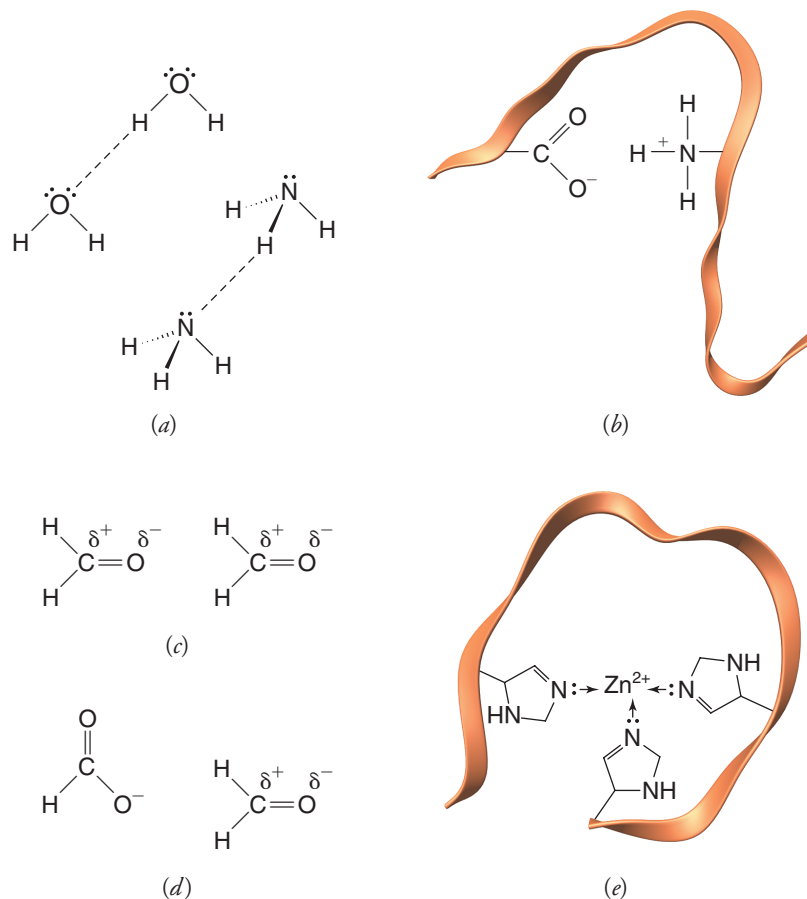
A **hydrogen bond** is the interaction of a nitrogen, oxygen, or fluorine atom with a hydrogen atom that is covalently bonded to a different nitrogen, oxygen, or fluorine atom (Figure 4.8a).

When a hydrogen atom is covalently bonded to a highly electronegative atom (N, O, or F), a polar covalent bond exists and the hydrogen atom carries a partial positive charge (Section 4.2). A hydrogen bond is the interaction of this partially charged hydrogen atom with a pair of electrons on a different highly electronegative atom (N, O, or F). While

■ FIGURE | 4.8

Noncovalent interactions and permanent charges

(a) Hydrogen bonds (dashed lines) form when a hydrogen atom, covalently bonded to an N, O, or F atom, is attracted to a different N, O, or F atom. (b) Salt bridges (ionic bonds) help proteins to maintain their correct three-dimensional shape. (c) Dipole–dipole forces, which are due to the attraction of opposite partial charges, hold neighboring polar groups to one another. (d) Ion–dipole interactions occur when an ion is attracted to the partially (and oppositely) charged end of a polar group. (e) The activity of many enzymes requires that a trace element be attached to the enzyme molecule. Here, Zn^{2+} is held in place by coordinate-covalent bonds (represented by arrows).



hydrogen bonds vary in strength, the average hydrogen bond is about ten times weaker than a typical covalent bond. As we will see in later chapters, hydrogen bonding makes an important contribution to the structure and function of proteins, nucleic acids, and other biologically important compounds.

A **salt bridge** is another name for an ionic bond. The term is used by biochemists to describe ionic bonds that form between charged groups in protein molecules (Figure 4.8*b*).

Dipole–dipole forces are the attraction of neighboring polar groups for one another. When polar compounds interact they do so by orienting themselves with the partially negative end of one pointing to the partially positive end of the other (Figure 4.8*c*).

Ion–dipole interactions occur between ions and atoms with a partial charge, as shown in Figure 4.8*d*. In a related interaction called a **coordinate-covalent bond**, the nonbonding electrons of a nonmetal atom (N, S, etc.) associate with metal cations (Fe^{3+} , Zn^{2+} , etc.). Many enzymes function properly only when a specific ion is held in place by a coordinate-covalent bond (Figure 4.8*e*).

Noncovalent Interactions Due to Temporary Partial Charges

Individual atoms, nonpolar molecules, or nonpolar parts of molecules or ions are attracted to one another by **London forces**. Named after the German physicist Fritz London, this force is the result of the continuous motion of electrons. Electron movement within a substance creates a temporary dipole, which tends to produce temporary dipoles on its neighbors as electrons in the neighbor become attracted to or repelled by the temporary charges. As the temporary dipole shifts, so do the dipoles on neighbors (Figure 4.9*a*), so London forces are a fleeting attraction between temporary dipoles.

The strength of London forces depends on the surface area of the substance involved. Greater surface area leads to stronger London force attraction (Figure 4.9*b*).

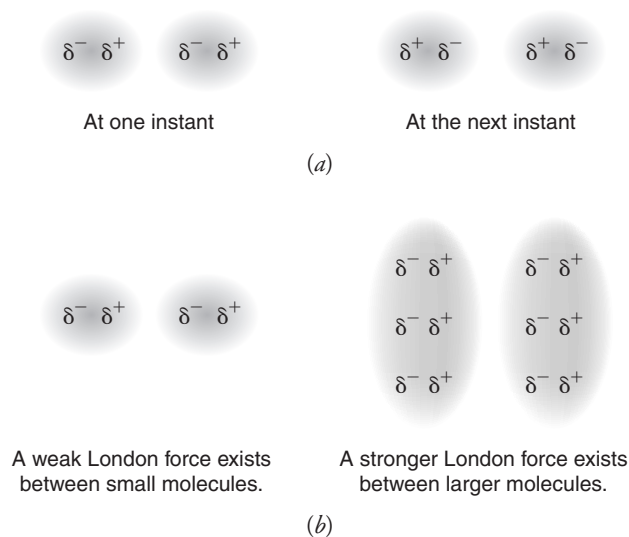


FIGURE 4.9

Noncovalent interactions and temporary charges

London forces are attractive forces that result from temporary dipoles. (a) The movement of electrons within an atom, nonpolar molecule, or nonpolar parts of a compound creates a momentary dipole, which attracts or repels electrons in a neighbor to create another temporary dipole and a fleeting attraction between the oppositely charged ends of each. At the next instant, the electrons may have shifted to create an entirely new set of dipoles. (b) London forces depend on surface area. Small, spherical molecules have a minimal area of surface contact, so they are attracted to one another by relatively weak London forces. Large, nonspherical molecules have greater surface contact, and therefore, a stronger London force attraction for one another.

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SAMPLE PROBLEM 4.7

Noncovalent interactions

Which noncovalent interactions can take place between the molecule shown below and another identical to it?



Strategy

Possible answers include: hydrogen bonding, salt bridges, dipole–dipole forces, ion–dipole interactions, coordinate–covalent bonds, and London forces. Refer to Figures 4.8 and 4.9 for help deciding which noncovalent interactions can occur and which cannot.

Solution

The answers are dipole–dipole forces (the C=O bond is polar) and London forces. Hydrogen bonding is not possible because the molecule does not have a hydrogen atom covalently bonded to an N, O, or F atom. Salt bridges, ion–dipole interactions, and coordinate–covalent bonds do not occur because no ion is present.

PRACTICE PROBLEM 4.7

The molecule in Sample Problem 4.7 cannot form hydrogen bonds with another identical to it. Can the molecule hydrogen bond with a water molecule? Explain.

4.4 ALKANES

- Alkanes are hydrocarbons that contain only single bonds.
- Hydrocarbons contain only carbon and hydrogen atoms.

For the remainder of this chapter, we will turn our attention to organic compounds. As part of our discussion, we will revisit the topics presented above: structural formulas, polar covalent bonds, shape, polarity, and noncovalent interactions.

The first family of organic compounds that we will consider is the **alkanes**. The members of this family are molecules that consist only of carbon and hydrogen atoms and contain only single bonds. Examples include methane (CH_4), ethane (CH_3CH_3), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) (Figure 4.10). The alkanes in this figure are *normal* alkanes, which means that *their carbon chains are unbranched* (are joined in one continuous line).

Alkanes belong to a larger grouping of organic compounds called **hydrocarbons**. While, as the name implies, all hydrocarbons contain only carbon and hydrogen atoms, they differ in the types of covalent bonds that they contain (Table 4.3). Later in this chapter the three other families of hydrocarbons—alkenes, alkynes, and aromatic compounds—will be introduced.

Each carbon atom in an alkane molecule has four covalent bonds that are arranged in a tetrahedral shape about the atom. The molecules in Figure 4.10 are represented using wedge and dashed line notation (see the footnote to Table 4.2 for an explanation).

Alkanes contain only nonpolar covalent bonds, are nonpolar molecules, and are attracted to one another by London forces. Table 4.4 shows that the more carbon atoms in a *normal* alkane, the higher its boiling point. The reason for this is that the longer the alkane, the greater its surface area and the stronger the London force that holds it to other molecules. Boiling points increase with strengthened intermolecular forces, because this

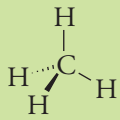
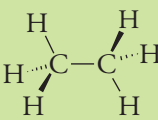
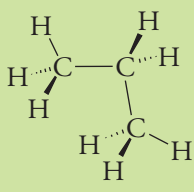
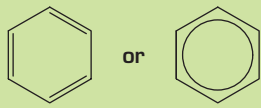

Name	Condensed structural formula	Three-dimensional structure
Methane	CH ₄	
Ethane	CH ₃ CH ₃	
Propane	CH ₃ CH ₂ CH ₃	

FIGURE | 4.10

Alkanes

Methane, ethane, and propane are alkanes. A condensed structural formula and three-dimensional view of each are shown.

TABLE | 4.3 THE HYDROCARBONS


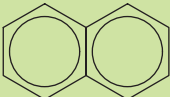
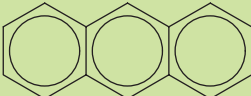
Family	Key Feature	Class	Example	Name
Alkanes	Atoms joined by single bonds only	Saturated	CH ₃ CH ₂ CH ₃	Propane
Alkenes	At least one carbon–carbon double bond	Unsaturated	CH ₂ =CHCH ₃	Propene
Alkynes	At least one carbon–carbon triple bond	Unsaturated	HC≡CCH ₃	Propyne
Aromatic compounds	Contains a ring of alternating single and double bonds	Unsaturated	 or 	Benzene

physical change involves pulling molecules in the liquid phase apart from one another and moving them into the gas phase. An increase in London forces is also associated with a rise in melting point, because more energy (a higher temperature) is required to loosen the attraction between molecules in the solid phase. (More details about the transitions between solid, liquid, and gas phases will be presented in Chapter 5.)

The boiling points of the first four *normal* alkanes, methane through butane, are lower than room temperature (about 25°C), so at this temperature each exists as a gas. Larger *normal* alkanes, pentane through heptadecane (17 carbon atoms), are liquids at room temperature, while those larger than heptadecane are solids.

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■ TABLE | 4.4 STRUCTURE, NAME, AND PROPERTIES OF SELECTED HYDROCARBONS

Structural Formula	IUPAC Name	Common Name	Boiling Point (°C)
Alkanes			
CH ₄	Methane		−164
CH ₃ CH ₃	Ethane		−89
CH ₃ CH ₂ CH ₃	Propane		−42
CH ₃ CH ₂ CH ₂ CH ₃	Butane		0
CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	Pentane		36
Alkenes			
CH ₂ =CH ₂	Ethene	Ethylene	−102
CH ₂ =CHCH ₃	Propene	Propylene	−98
CH ₂ =CHCH ₂ CH ₃	1-Butene		−6.5
CH ₂ =CHCH ₂ CH ₂ CH ₃	1-Pentene		30
Alkynes			
HC≡CH	Ethyne	Acetylene	−75
HC≡CCH ₃	Propyne		−23
HC≡CCH ₂ CH ₃	1-Butyne		9
HC≡CCH ₂ CH ₂ CH ₃	1-Pentyne		40
Aromatic compounds			
	Benzene		80
	Naphthalene		218
	Anthracene		340

In Chapter 3 we saw that binary molecules are named by listing the number of each element that is present in the formula (CO₂ is carbon dioxide, N₂O₅ is dinitrogen pentoxide, and so on). Alkanes cannot be named this way because, in most cases, a particular molecular formula refers to more than one molecular structure. (Section 4.5 will expand on this idea.) For this reason, the names of alkanes and other organic molecules are based on structure, rather than on molecular formula.

IUPAC rules, devised by the International Union of Pure and Applied Chemistry, are a widely used method of naming organic compounds. Using the IUPAC rules to name an alkane involves identifying the **parent chain** (*the longest continuous chain of carbon atoms in the molecule*) and **substituents** (*atoms or groups of atoms attached to the parent chain*). In alkanes the substituents, called **alkyl groups**, are constructed solely of carbon and hydrogen atoms. The paragraphs that follow will briefly introduce the use of the IUPAC rules for naming alkanes.

IUPAC Rules for Naming Alkanes

- 1. Name the parent chain.** The parent chain is named by combining a numbering prefix (Table 4.5), which specifies the number of carbon atoms in the parent, with “ane,” which identifies the molecule as an alkane. In Table 4.4, for example, propane gets its name from the fact that its parent chain has three carbon atoms (“prop”) and is an alkane (“ane”). Similarly, the parent chain of butane has four carbon atoms and that of pentane has five.
- 2. Name any alkyl groups attached to the parent chain.** Table 4.6 gives the names and structural formulas for the most commonly encountered alkyl groups, some branched and others unbranched. Note that the same numbering prefixes used to name parent chains are used to indicate the total number of carbon atoms in an alkyl group. The simplest alkyl groups are the methyl group, which has one carbon atom, and the ethyl group, which has two. A three-carbon substituent can be attached by an end carbon atom (propyl group) or by the middle carbon atom (isopropyl group). It may help to think of the “iso” prefix as referring to an alkyl group that branches into two methyl ($-\text{CH}_3$) groups. The alkyl groups with four carbon atoms are butyl, isobutyl, *sec*-butyl, and *tert*-butyl. A butyl group consists of an unbranched chain of four carbon atoms and an isobutyl group is a chain that branches into two methyl groups. A *sec*-butyl group has a chain of carbon atoms that branches into a methyl group and an ethyl group ($-\text{CH}_2\text{CH}_3$). In a *tert*-butyl group, the carbon atom attached directly to the parent chain branches into three methyl groups.
- 3. Determine the point of attachment of alkyl groups to the parent chain.** The parent chain is numbered from the end nearer the first alkyl group. The molecule in Figure 4.11a is numbered from the right end of the parent, the end nearer the alkyl group, which places the methyl group on carbon 3. Numbering from the left would place the methyl group on carbon 4.

TABLE 4.5
THE FIRST TEN
NUMBERING
PREFIXES FOR
IUPAC NAMING

Number of Carbon Atoms	Prefix
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec

TABLE 4.6 FORMULAS AND NAMES OF ALKYL GROUPS

Formula ^a	Name
$-\text{CH}_3$	Methyl
$-\text{CH}_2\text{CH}_3$	Ethyl
$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl
$\begin{array}{c} -\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array}$	Isopropyl
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl
$\begin{array}{c} -\text{CH}_2\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array}$	Isobutyl
$\begin{array}{c} -\text{CHCH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	<i>sec</i> -Butyl or <i>s</i> -butyl
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl or <i>t</i> -butyl

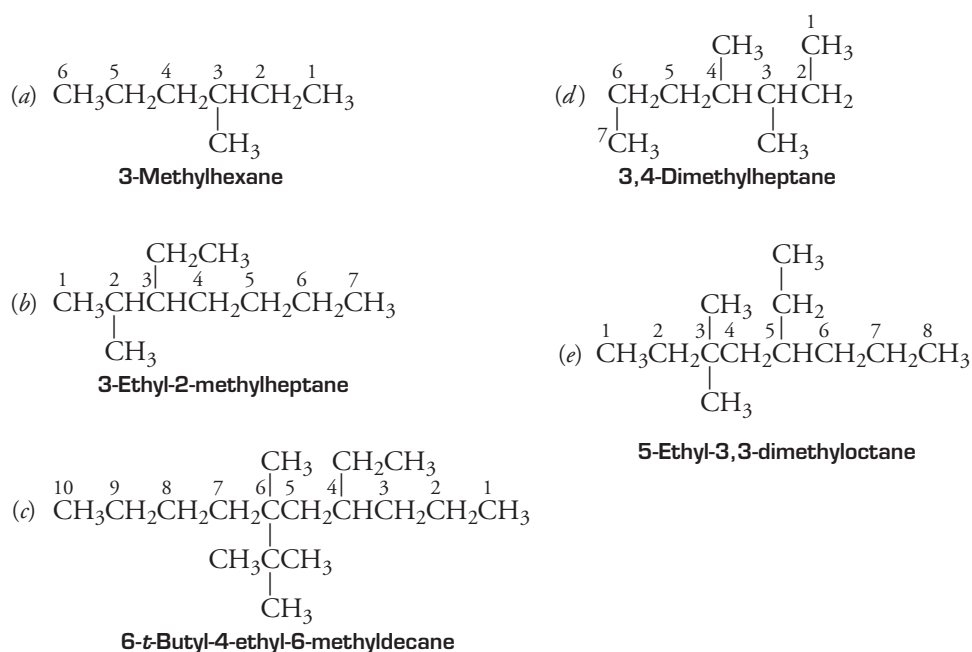
^aThe bond drawn to the left of each formula is the point of attachment to the parent chain.

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■ FIGURE 4.11

IUPAC names of alkanes

(a) The parent chain is numbered from the end nearer the first substituent. (b and c) Substituents are listed in alphabetical order (ignoring italicized letters), along with a number indicating their position of attachment to the parent chain. (d) If a substituent appears more than once, labels such as di, tri, and tetra are added to the substituent name. (e) The labels di, tri, and tetra are not used in alphabetizing.

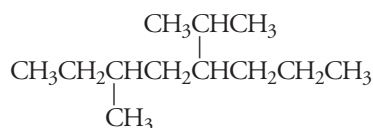


4. **Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain. The labels di, tri, tetra, etc., are added if two or more identical substituents are present.** The molecule in Figure 4.11a is named 3-methylhexane. Ethyl takes priority over methyl, so the molecule in Figure 4.11b is called 3-ethyl-2-methylheptane, not 2-methyl-3-ethylheptane. When alphabetizing substituents, italicized letters are not considered—*t*-butyl is listed before ethyl and methyl (Figure 4.11c). The molecule in Figure 4.11d, which has methyl groups on carbons 3 and 4, is called 3,4-dimethylheptane, not 3-methyl-4-methylheptane. A separate number must be used each time that a substituent appears, so the molecule in Figure 4.11e is called 5-ethyl-3,3-dimethyloctane. The prefixes di, tri, tetra, etc., are ignored when alphabetizing the names of substituents.

As seen in the names just given, the IUPAC rules call for separating numbers from numbers by using a comma, and numbers from letters by using a hyphen.

SAMPLE PROBLEM 4.8**Using the IUPAC rules**

Give the correct IUPAC name for the molecule.

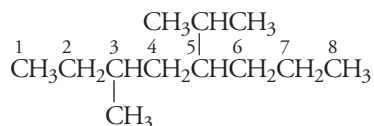
**Strategy**

The best way to approach the naming of this molecule is to apply the IUPAC rules step by step, as described above. Find and name the parent chain and then assign a name and position to each substituent.

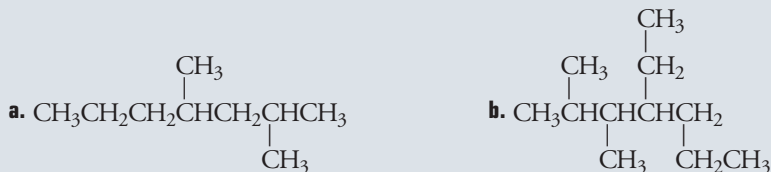
Solution

5-isopropyl-3-methyloctane

The first step in determining the IUPAC name involves finding the parent chain. Here, the parent has eight carbon atoms, which makes it “octane.” One methyl group and one isopropyl group are attached to the parent, which is numbered from the left side, nearer the first alkyl group. In the name 5-isopropyl-3-methyloctane, the alkyl groups are arranged alphabetically (isopropyl before methyl).

**PRACTICE PROBLEM 4.8**

Give the correct IUPAC name for each molecule.

**4.5 CONSTITUTIONAL ISOMERS**

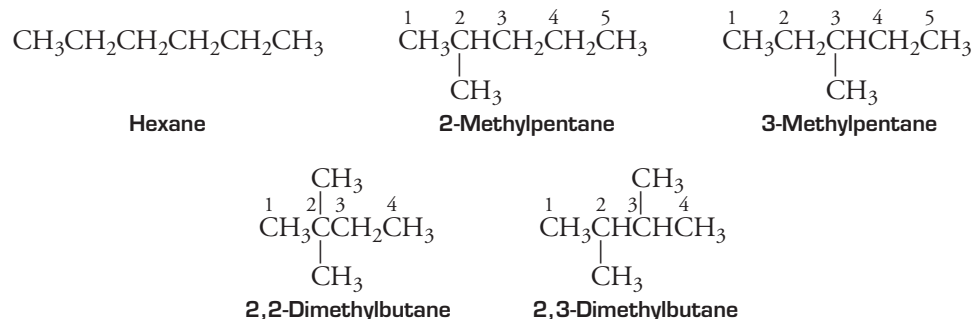
As has already been mentioned in this chapter, different molecules can share the same molecular formula. This is the case for butane and 2-methylpropane, each of which has the molecular formula C_4H_{10} .



Molecules, like the two shown above, that have the *same molecular formula but different atomic connections*, are called **constitutional isomers**.

As the number of atoms in a molecular formula increases, so does the number of possible constitutional isomers. The molecular formula C_6H_{14} , for example, gives rise to five constitutional isomers: hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane (Figure 4.12). The number of constitutional isomers grows

■ Constitutional isomers are molecules that have the same molecular formula, but whose atoms are connected differently.

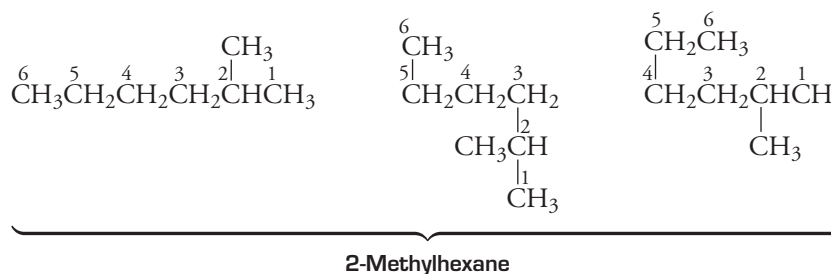
**FIGURE 4.12**

Constitutional isomers of C_6H_{14}
The five molecules shown are the constitutional isomers with the molecular formula C_6H_{14} . Constitutional isomers always have different names from one another.

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rapidly with an increase in alkane size. C_8H_{18} has 18 constitutional isomers, $C_{15}H_{32}$ has 4,347 isomers, and $C_{30}H_{62}$ has 4,111,846,763.

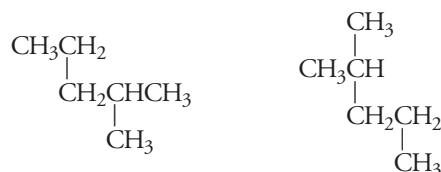
In some cases, as is true for the formulas in Figure 4.12, identifying constitutional isomers is a simple process. Their structures look different enough that there is no question that they are constitutional isomers. At other times, making this identification can be more difficult. For example, although the molecules below might, at first, appear to be different, all structures represent the same molecule, 2-methylhexane. It is important to remember that line-bond structures do not show the true shape of a molecule, just the bonding arrangements.



One sure way to decide whether two molecules are identical or are constitutional isomers is to name them. Identical molecules have the same IUPAC name and constitutional isomers have different IUPAC names.

SAMPLE PROBLEM 4.9**Identifying constitutional isomers**

Are the two alkanes constitutional isomers or are they identical?

**Strategy**

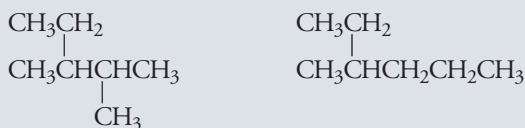
Constitutional isomers have the same molecular formula but different structures (and names).

Solution

Identical molecules. They both have the same formula (C_6H_{14}) and the same name (2-methylpentane).

PRACTICE PROBLEM 4.9

Are the two alkanes constitutional isomers or are they identical?



While on the subject of alkane constitutional isomers, it is worth discussing how we obtain and use some alkanes. The natural gas used to heat homes is mostly methane, mixed with smaller amounts of ethane, propane, and butane. Propane, by itself, is used as a fuel for camp stoves and barbecues and butane is used in disposable lighters.

Petroleum (crude oil), a mixture of hydrocarbons and lesser amounts of organic molecules that contain oxygen, nitrogen, and sulfur, is the source of most of the other alkanes that we use. Gasoline is a mixture of alkanes, having between 5 and 12 carbon atoms, other hydrocarbons, and additional compounds that are added to improve the performance of automobile engines. Gasoline contains a greater number of different alkanes than you might expect. There being three alkane constitutional isomers with the formula C_5H_{12} , five isomers with the formula C_6H_{14} , and many more with the formulas C_7H_{16} through $C_{12}H_{26}$, hundreds of different alkanes can be found in gasoline. Other important mixtures of alkanes include diesel fuel (contains alkanes with between 12 and 18 carbon atoms), motor oil (alkanes with more than 15 carbon atoms), and asphalt (alkanes with more than 35 carbon atoms).

4.6 CONFORMATIONS

When dealing with organic or biomolecules, it is often not enough to know only which constitutional isomer is present. Sometimes we must also know something about which of a number of possible three-dimensional shapes a molecule is found in. Among other things, the three-dimensional shape that a molecule has can affect the transport of certain compounds across cell membranes, the ability of the light-absorbing pigment present in the retina to absorb light, and the proper functioning of proteins (Health Link: Prion Diseases).

Rotation about single bonds allows most molecules to assume a number of different three-dimensional shapes. *The shapes that a molecule can take because of bond rotations* are called **conformations**. The different conformations of a molecule

- have the same molecular formula
- have the same atomic connections
- have different three-dimensional shapes
- are interchanged by the rotation of single bonds

Switching from one conformation to another always involves single bond rotation, never bond breaking. In the case of butane, pictured in Figure 4.13, three of the many possible conformations resulting from rotations about the bond between carbons 2 and 3 are shown. Of these three, the one shown in Figure 4.13c is the most stable (most favored) because it minimizes crowding by placing all of the atoms and bonds as far apart as possible.

Conformations are interchanged by rotation around single bonds.

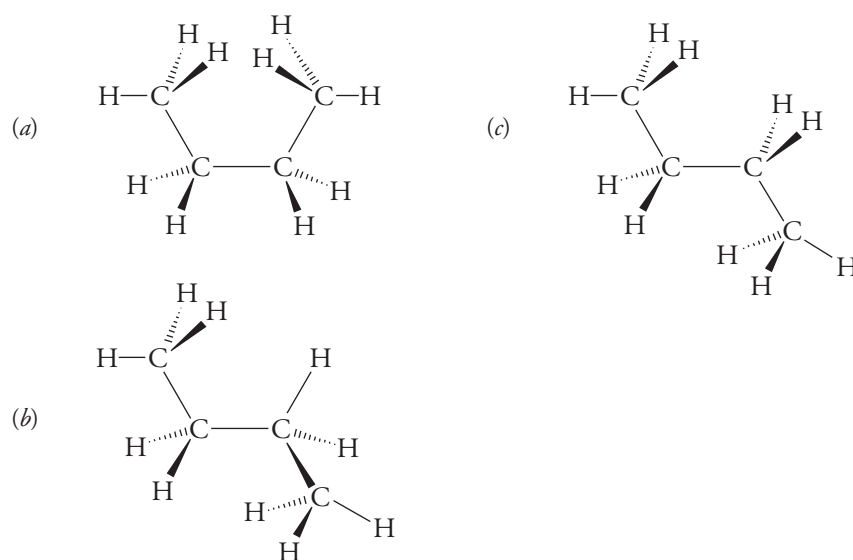


FIGURE 4.13

Conformations of butane
Rotation about the bond between carbons 2 and 3 in butane gives rise to different conformations (three-dimensional shapes) for the molecule.

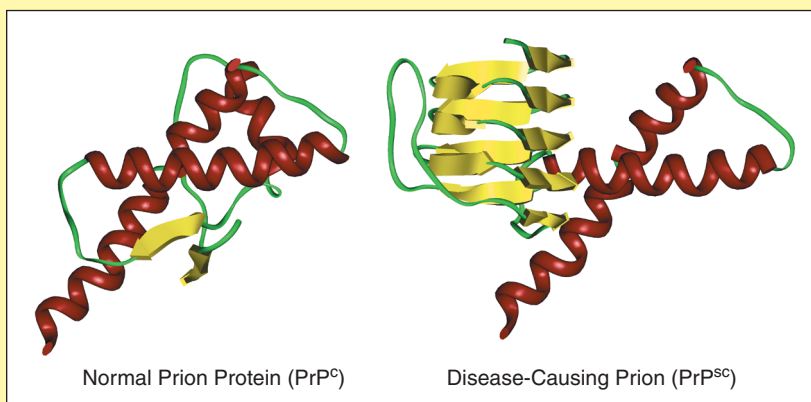
HEALTH

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Prion Diseases

The conformation, or shape, that a molecule takes can greatly influence its biological action. This point is well illustrated by a particular class of proteins, called prions, that have been identified as the cause of mad cow disease (in cattle), scrapie (in sheep), chronic wasting disease (in deer and elk), and new variant Creutzfeldt-Jakob disease, or vCJD (in humans).

Proteins are very large molecules formed from amino acid building blocks. Each protein has a favored conformation—



■ FIGURE 4.14

Prions

(a) The prion protein (PrP^{C}) in its normal conformation. (b) The prion in its incorrectly folded (PrP^{Sc}) form.

Source: Fred E. Cohen, M.D., D. Phil and Cedric Govaerts, Ph.D., Department of Cellular & Molecular Pharmacology, University of California San Francisco (UCSF).

some with the protein chain twisted into spirals and bends and some with the chain zigzagged back and forth in a compact form. Prions, short for *proteinaceous infection* particles, are a type of protein found in the membranes of nerve cells. The prion diseases mentioned above are caused when the normal prion conformation (PrP^{C}) is twisted into an abnormal shape (PrP^{Sc}) (Figure 4.14). When PrP^{Sc} comes into contact with PrP^{C} , the PrP^{C} proteins change conformation and become PrP^{Sc} . As PrP^{Sc} accumulates in affected animals or humans, sponge-like holes form in the brain, causing dizziness, seizures, and death.

Prion diseases can be transferred from one species to another. Cattle are known to get mad cow disease when fed parts of scrapie-infected sheep, and vCJD in humans has been linked to eating mad cow-infected beef.

4.7

CYCLOALKANES

In some alkanes, called **cycloalkanes**, *carbon atoms are joined into rings* (Figure 4.15). Like their noncyclic counterparts, cycloalkanes are nonpolar molecules that are attracted to one another by London forces. To simplify matters, cycloalkanes are usually drawn using skeletal structures, although side views can be useful when considering the orientation of substituents attached to a ring.

When naming cycloalkanes, the ring is usually designated as the parent, which is named by combining “cyclo” with the appropriate numbering prefix (Table 4.5) and “ane.” When only one alkyl group is attached to a cycloalkane parent, the carbon atom that holds that group is carbon 1 (Figure 4.16a), but the number is not included in the name. When a ring holds more than one alkyl group, the ring is numbered from the position and in the direction that gives the lowest numbers. Figure 4.16b shows how this works for the three dimethylcyclopentane constitutional isomers.

Geometric Isomers

The limited rotation of the carbon–carbon single bonds in cycloalkanes has an interesting side effect in that it allows for the existence of **stereoisomers**, molecules that

- have the same molecular formula
- have the same atomic connections
- have different three-dimensional shapes
- are interchanged only by breaking bonds

Name	Line-bond structure	Skeletal structure	Side-view
Cyclopropane			
Cyclobutane			
Cyclopentane			
Cyclohexane			

■ FIGURE 4.15

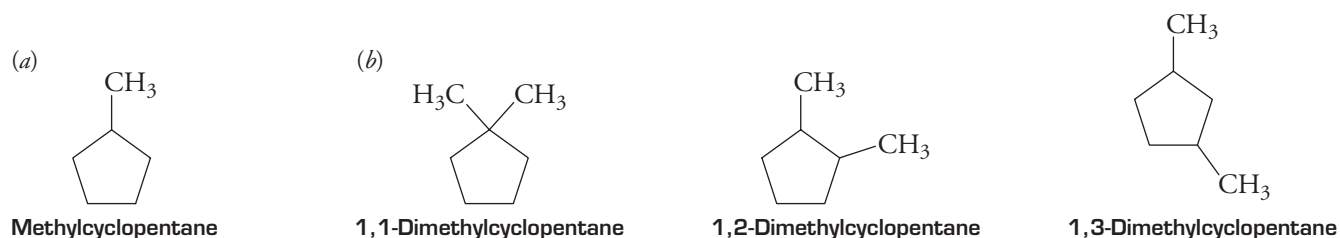
Cycloalkanes

Cycloalkanes are alkanes whose carbon atoms are joined in a ring.

Except for the last item in the list (*are interchanged only by breaking bonds*), the description above is identical to that given for conformations (Section 4.6). When stereoisomers exist because of restricted bond rotation, the stereoisomers are called **geometric isomers**.

To explore this concept, let us compare the three-dimensional structure of a noncyclic alkane with that of a cycloalkane. Figure 4.17*a* shows two conformations of butane, interchanged by rotation about the carbon–carbon single bond between carbons 2 and 3. The two 1,2-dimethylcyclohexane molecules in Figure 4.17*b* are stereoisomers. Rotation of the ring carbon–carbon bonds is limited, so the molecule that has methyl groups on the same face of the ring can never be rotated enough to look like the molecule with the methyl groups on opposite faces. Transforming one of these molecules into the other requires the breaking of covalent bonds, which makes them geometric isomers.

■ Stereoisomers are interchanged only by breaking bonds.



■ FIGURE 4.16

IUPAC names of cycloalkanes

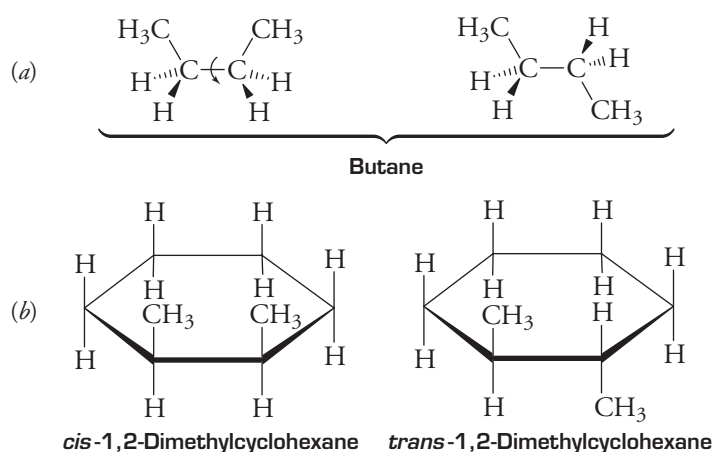
(a) With one substituent present, the parent ring is numbered starting at the substituent. The position number is omitted from the name, however. (b) When more than one substituent is present, the parent ring is numbered from the position and in the direction that gives the lowest numbers.

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■ FIGURE 4.17

Geometric isomers

(a) Two conformations of butane are interchanged by single bond rotation. (b) Two geometric isomers of 1,2-dimethylcyclohexane are interchanged only by bond breaking. In *cis*-1,2-dimethylcyclohexane the methyl groups are on the same face of the ring. In *trans*-1,2-dimethylcyclohexane they are on opposite sides.



Geometric isomers come in pairs—one is *cis* and one is *trans*. For cycloalkanes, a *cis* geometric isomer has the two alkyl groups on the *same face* of the ring and a *trans* isomer has them on *opposite faces*.

SAMPLE PROBLEM 4.10**Identifying isomers**

Identify each pair as being geometric isomers, constitutional isomers, or identical molecules.

- cis*-1,4-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane
- cis*-1,4-dimethylcyclohexane and *trans*-1,4-dimethylcyclohexane

Strategy

To solve this problem it will help you to remember that geometric isomers (stereoisomers) have the same molecular formula and atomic connections, while constitutional isomers have the same molecular formula and different atomic connections.

Solution

- Constitutional isomers. While *cis* and *trans* molecules are geometric isomers, these two molecules are not geometric isomers of the same molecule. They are constitutional isomers because they have different atomic connections (1,4-dimethyl versus 1,2-dimethyl).
- Geometric isomers. These two molecules have the same atomic connections (both are 1,4-dimethyl), so they are not constitutional isomers. They are geometric isomers of 1,4-dimethylcyclohexane.

PRACTICE PROBLEM 4.10

Draw and name the geometric isomers of 1-ethyl-2-methylcyclohexane.

4.8

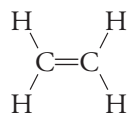
ALKENES, ALKYNES, AND AROMATIC COMPOUNDS

- Unsaturated molecules contain double or triple bonds.

Alkanes and cycloalkanes are **saturated** hydrocarbons, which is another way of saying that *they contain only single bonded carbon atoms*. The three other families of hydrocarbons (Table 4.3) are **unsaturated**, which means that *they contain double or triple bonds*. This use of the terms saturated and unsaturated is related to a reaction involving hydrogen gas (H_2) that will be introduced in Section 6.3.

4.8 ALKENES, ALKYNES, AND AROMATIC COMPOUNDS 121

Alkenes contain at least one carbon–carbon double bond. In ethylene, the smallest alkene, the carbon atoms carry three groups of electrons—one double bond and two single bonds. This results in a trigonal planar shape around each carbon atom (Table 4.2). **Alkynes** contain at least one carbon–carbon triple bond and the smallest member of this family is acetylene. Each carbon atom in acetylene has two groups of electrons arranged in a linear shape.



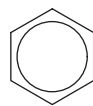
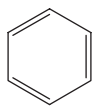
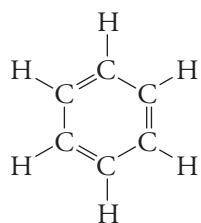
Ethylene



Acetylene

Some alkenes and alkynes can be obtained from petroleum, but many are produced by living things. The alkene called muscalure is a sex-attractant pheromone (chemical messenger) produced by houseflies (Figure 4.18).

The third family of unsaturated hydrocarbons is **aromatic hydrocarbons**. A well-known member of this family, benzene, is a ring of six carbon atoms that can be drawn with each carbon atom having one single and one double bond to neighboring carbon atoms, and one bond to a hydrogen atom.



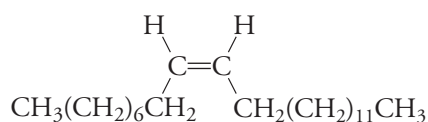
Benzene

Although the double bonds give benzene the appearance of being an alkene, it and other aromatic compounds do not behave as alkenes. To de-emphasize their alkene-like appearance, aromatic compounds are often drawn with a circle replacing the double bonds.

Like alkanes, the unsaturated hydrocarbons (alkenes, alkynes, and aromatic compounds) have only nonpolar covalent bonds and are nonpolar molecules. London forces hold members of these hydrocarbon families to one another, and increasing size leads to stronger London force attractions between molecules and higher melting and boiling points (Table 4.4).

Naming

When using the IUPAC rules to name alkenes or alkynes, the parent is the longest chain of carbon atoms that has the carbon–carbon double or triple bond. Numbering of the parent begins at the end nearer the double or triple bond, and the position of the bond is indicated using the lower number assigned to the multiply bonded carbon atoms. As for naming alkanes, the ending on the name indicates the organic family—IUPAC names of alkenes end with “ene” and those of alkynes end with “yne.” Once the parent chain has been determined, alkyl groups are identified by name, position, and number of appearances (Figure 4.19a). Sometimes organic compounds are known by **common names**, names that are not assigned according to the IUPAC rules. Ethylene (for ethene), propylene (for propene), and acetylene (for ethyne) are examples.



Muscalure

FIGURE 4.18

Muscalure

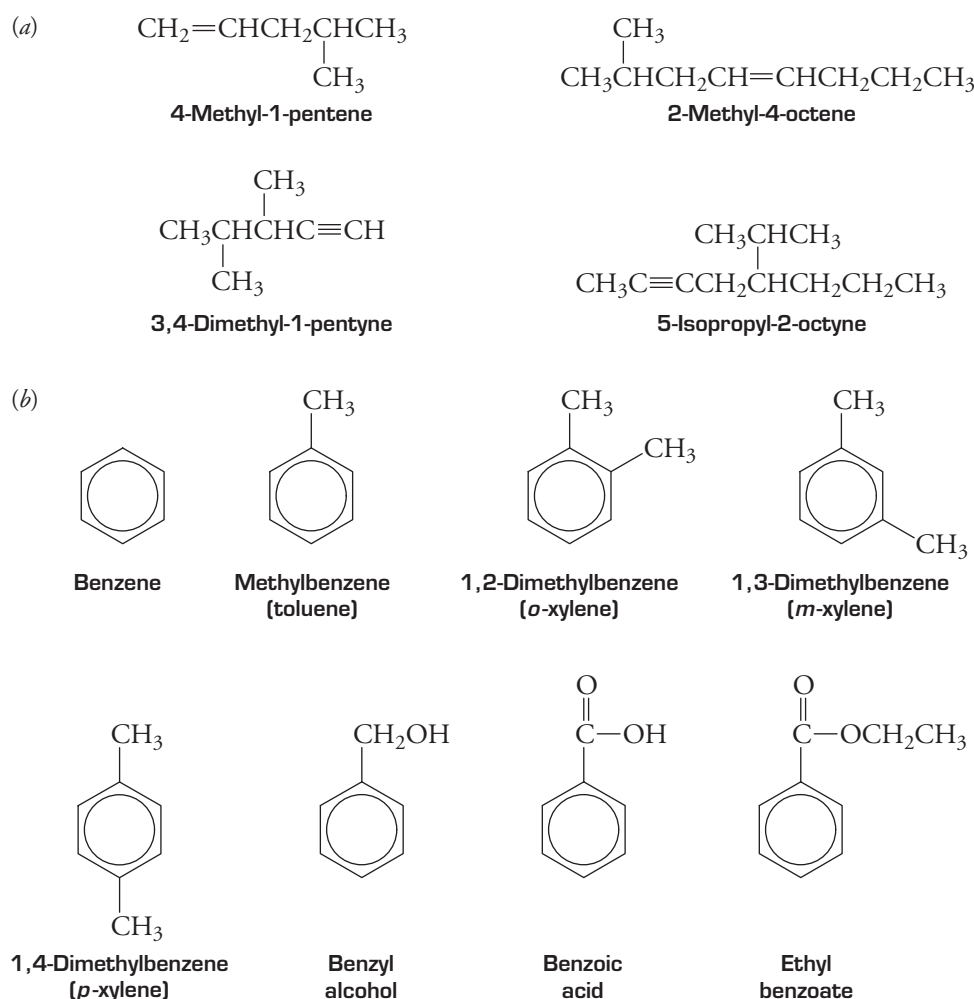
This alkene, produced by the female housefly, is a pheromone (a chemical messenger) that is used to attract a mate. In this condensed structure, $(\text{CH}_2)_6$ indicates six repeats of CH_2 and $(\text{CH}_2)_{11}$ indicates eleven repeats.

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■ FIGURE 4.19

Naming unsaturated hydrocarbons

(a) **Alkenes and alkynes.** When assigning IUPAC names, parent chains, which must contain the carbon-carbon double or triple bond, are numbered from the end nearer these groups. For alkenes and alkynes containing two or three carbon atoms, the position of the double or triple bond is not specified. Alkene names end in “ene” and alkyne names end in “yne.” (b) **Aromatic compounds.** Methylbenzene is also known as toluene. In common names, a 1,2 arrangement of substituents on a benzene ring is an *ortho* arrangement and dimethylbenzenes are called xylene, so 1,2-dimethylbenzene is *ortho*-xylene or *o*-xylene. Benzyl alcohol, benzoic acid, and ethyl benzoate are aromatic compounds that are not pure hydrocarbons.



- When only two substituents are attached to benzene, they will be *ortho*, *meta*, or *para* to one another.

“Benzene” is an accepted IUPAC name, so benzene-related compounds are named using benzene as the parent ring. When only one substituent is attached, its position is not specified in the name, as is the case for methylbenzene (Figure 4.19b). In the presence of more than one substituent, the ring is numbered from the position and in the direction to give the lowest substituent numbers possible. Methylbenzene and 1,2-dimethylbenzene are also known, respectively, by the common names toluene and *ortho*-xylene. For common names of benzene-based compounds that have only two substituents attached to the ring, *ortho* or *o* refers to a 1,2 arrangement, *meta* or *m* to a 1,3 arrangement, and *para* or *p* to a 1,4 arrangement.

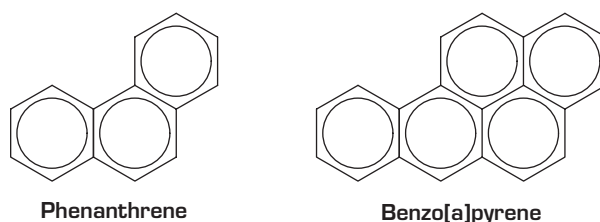
An aromatic ring may be part of a larger molecule, so not all aromatic compounds are pure hydrocarbons. This includes benzyl alcohol, benzoic acid, and ethyl benzoate, examples from three of the organic families that we will encounter in the section that follows.

Some aromatic compounds, called **polycyclic aromatic hydrocarbons (PAHs)**, contain benzene rings that are fused to one another (they share atoms and bonds). Naphthalene and anthracene (Table 4.4), and phenanthrene (Figure 4.20), all of which can be obtained from coal, are simple examples. Benzo[a]pyrene, a large PAH formed during the burning of tobacco, coal, gasoline, and many other substances, is known to cause cancer.

■ FIGURE 4.20

Polycyclic aromatic hydrocarbons

Phenanthrene, benzo[a]pyrene, and other PAHs contain fused benzene rings.



Geometric Isomers

Unlike single bonds, which rotate freely (except when they are in rings; see Section 4.7), double bonds cannot rotate. With this restricted bond rotation comes the possibility of some alkenes existing as *cis* and *trans* stereoisomers. In Figure 4.21*a*, the two geometric isomers of 2-butene are shown. In the *cis* isomer, the two methyl groups (—CH_3) are on the same side of a line connecting the two double-bonded carbon atoms, and in the *trans* isomer these groups are on opposite sides of that line.

Not all alkenes are found as *cis* and *trans* isomers. For geometric isomers to exist, neither carbon atom of the double bond may carry two identical attached atoms or groups of atoms. The alkene in Figure 4.21*b*, 2-methyl-2-butene, has two identical groups (—CH_3) attached to the carbon atom to the left side of the double bond. If the molecule drawn on the right is flipped top to bottom, it is identical to the one on the left and *cis* and *trans* isomers do not exist. In Figure 4.21*c* each of the carbons in the double bond has two different atoms or groups of atoms attached to it. If flipped, the 2-pentene on the right cannot be superimposed on the molecule to the left—this alkene has *cis* and *trans* isomers.

Alkynes, having a linear shape across the carbon–carbon triple bond, do not exist as *cis* and *trans* isomers.

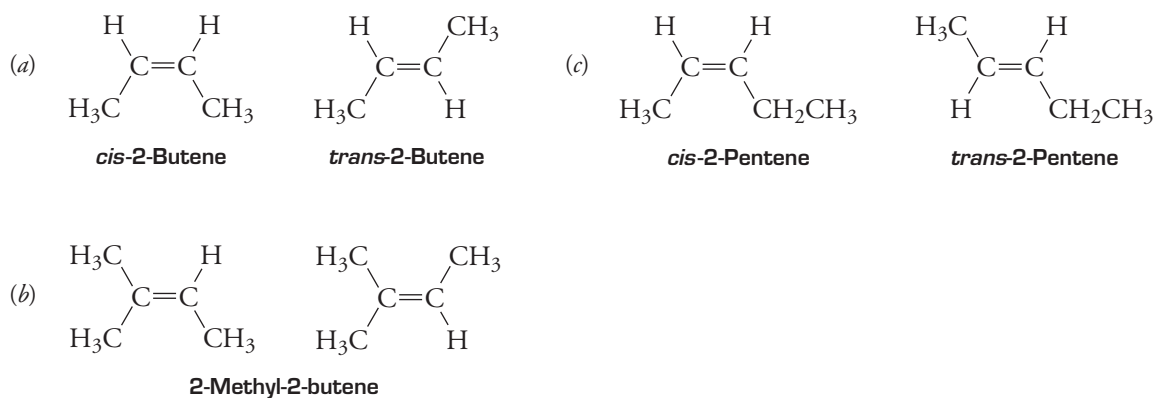


FIGURE 4.21

Geometric isomers of alkenes

(a) In the *cis* isomer the —CH_3 groups are on the same side of a line that connects the two double-bonded carbon atoms, and in the *trans* isomer they are on opposite sides. (b) 2-Methyl-2-butene has no *cis* or *trans* isomers, because the double-bonded carbon atom on the left is attached to identical groups of atoms (—CH_3 groups). When flipped top to bottom, the molecule on the right is the same as the one on the left. (c) In the *cis* isomer of 2-pentene, the alkyl groups are on the same side of the double bond.

SAMPLE PROBLEM 4.11

Identifying geometric isomers

Which geometric isomer of muscalure is shown in Figure 4.18?

Strategy

To distinguish the *cis* from the *trans* isomer, compare the relative positions of the carbon atoms attached to the carbon–carbon double bond.

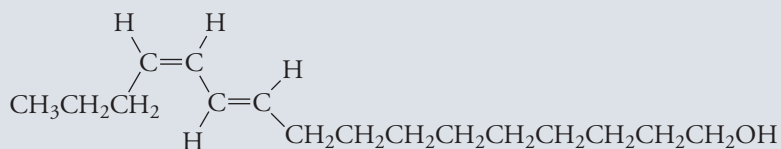
Solution

The *cis* isomer. Both ends of the carbon chain are on the same side of a line that connects the double-bonded carbon atoms.

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PRACTICE PROBLEM 4.11

Designate each of the carbon–carbon double bonds in bombykol, a moth pheromone, as *cis* or *trans*.



Bombykol

HEALTH

ink

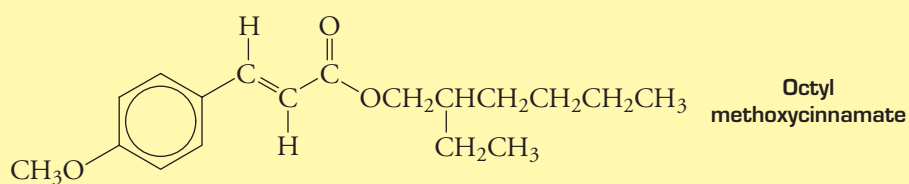
Sunscreens

In addition to the visible light that is present in sunlight, a higher energy form of electromagnetic radiation called ultraviolet (UV) is also found. It is this UV radiation that makes spending too much time in the sun hazardous to your health.

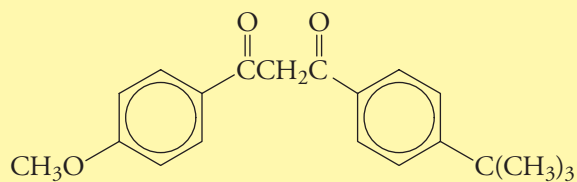


UV radiation is divided into three categories (arranged in order of increasing energy) UV-A, UV-B, and UV-C. Although all forms of UV radiation can be harmful, UV-C is the most damaging. We do not usually worry about exposure to UV-C from sunlight, however, because most is screened out by atmospheric ozone. The UV-A and UV-B in sunlight are not blocked by the atmosphere and it is exposure to UV-B that causes sunburns. This form of radiation has also been identified as one of the causes of skin cancer. While UV-A was once thought to be relatively harmless, there is now strong evidence that links wrinkles, other skin damage, and skin cancer to UV-A exposure.

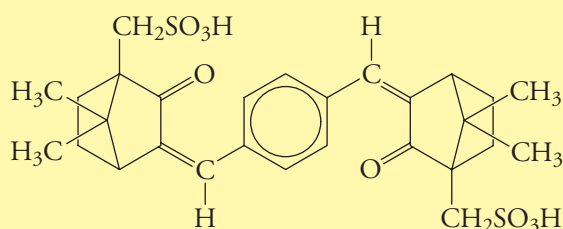
To some extent, your skin can protect itself from UV radiation. When sunlight hits the skin, a particular type of cells produce melanin, a black pigment that absorbs UV radiation. A suntan is the result of melanin production. Sunscreens can also provide some degree of protection from the sun. These contain aromatic compounds that block UV-A and UV-B light (Figure 4.22). Not all aromatic compounds are suitable for use as sunscreens—many do not absorb UV, and many are toxic.

Octyl
methoxycinnamate

The SPF (sun protection factor) listed on the label of a sunscreen indicates how effective it is at blocking UV radiation. An SPF of 25 means that it takes 25 times longer to get sunburned with the sunscreen applied than without.



Avobenzone



Ecamsule

■ FIGURE 4.22

UV-B and UV-A absorbing compounds in sunscreens

Octyl methoxycinnamate is the UV-B blocker most commonly used in sunscreens. Avobenzone and Ecamsule are UV-A blockers. Ecamsule, which was recently approved for use in the United States, has been a sunscreen ingredient in Canada and Europe since 1993.

4.9

ALCOHOLS, CARBOXYLIC ACIDS, AND ESTERS

In addition to the saturated and unsaturated hydrocarbons introduced in this chapter, there are a large number of other important families of organic molecules. In this section three of these families will be briefly considered: alcohols, carboxylic acids, and esters (Table 4.7).

TABLE 4.7 STRUCTURE, NAME, AND BOILING POINT OF SELECTED ALCOHOLS, CARBOXYLIC ACIDS, AND ESTERS

Formula	IUPAC Name ^a	Boiling Point (°C)
Alcohols		
CH ₃ OH	Methanol	65.0
CH ₃ CH ₂ OH	Ethanol	78.5
CH ₃ CH ₂ CH ₂ OH	1-Propanol	97.4
CH ₃ CH ₂ CH ₂ CH ₂ OH	1-Butanol	117.3
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	1-Pentanol	138
Carboxylic acids		
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{OH} \end{array}$	Methanoic acid	100
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OH} \end{array}$	Ethanoic acid	118
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C}-\text{OH} \end{array}$	Propanoic acid	141
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{C}-\text{OH} \end{array}$	Butanoic acid	164
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}-\text{OH} \end{array}$	Pentanoic acid	187
Esters		
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{OCH}_2\text{CH}_3 \end{array}$	Ethyl methanoate	53
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{OCH}_2\text{CH}_3 \end{array}$	Ethyl ethanoate	77
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C}-\text{OCH}_2\text{CH}_3 \end{array}$	Ethyl propanoate	99
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{C}-\text{OCH}_2\text{CH}_3 \end{array}$	Ethyl butanoate	120

^aNames are given here for reference purposes. The IUPAC rules for naming alcohols, carboxylic acids, and esters will be presented in later chapters.

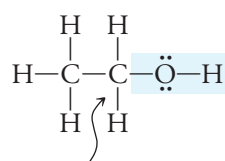
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- Functional groups determine to which family an organic molecule belongs.

These particular families have been selected for two reasons. First, they provide examples of compounds that interact by noncovalent interactions (Section 4.3) other than the London forces that come into play for hydrocarbons. Second, having some knowledge of the members of these classes of compounds will help us understand material presented in some of the chapters soon to follow.

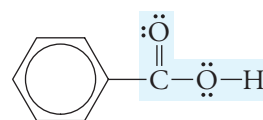
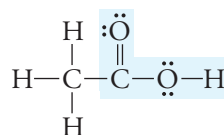
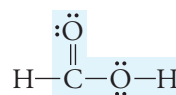
What distinguishes alcohols, carboxylic acids, and esters from the hydrocarbons is that their **functional groups** contain atoms other than carbon and hydrogen. A functional group is *an atom, group of atoms, or bond that gives a molecule a particular set of chemical properties*, and each organic family of organic compounds is defined by the functional group that its members contain. We have already encountered three functional groups in this chapter, the carbon–carbon double bond of alkenes, the carbon–carbon triple bond of alkynes, and the ring with alternating double and single bonds of aromatic compounds.

All **alcohols** contain a **hydroxyl** (—OH) functional group that is attached to an **alkane-type carbon atom**. An alkane-type carbon atom is singly bonded to carbon or hydrogen atoms.



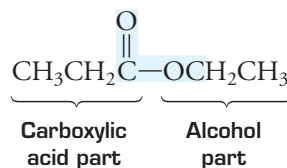
An alkane-type carbon atom

Carboxylic acids contain a **carboxyl** functional group, which is the combination of a hydroxyl (—OH) group and a **carbonyl** (C=O) group. In carboxylic acids, the carbon atom of the carboxyl group is attached to a hydrogen atom, an alkane-type carbon atom, or an aromatic ring.



Although **carboxylic acids** contain an —OH group, they are not considered alcohols. The chemistry of carboxyl —OH groups and alcohol —OH groups is very different.

Esters contain a C—O—C linkage in which one of the carbon atoms belongs to a carbonyl group. Esters can be formed by reacting carboxylic acids with alcohols, and part of each original molecule can be seen in the ester structure.



Physical Properties

While the functional groups present in alcohols, carboxylic acids, and esters all contain one or more oxygen atoms, there are some differences in the intermolecular forces that each can experience. The hydroxyl group in alcohols, for example, contains an oxygen–hydrogen covalent bond, which allows alcohols to participate in hydrogen bonding (Figure 4.23*a*).

While the primary force that holds one alcohol molecule to another is a hydrogen bond, this is not the only intermolecular force that operates. Note in Table 4.7 that the longer the carbon chain for an alcohol, the higher its boiling point. Since all alcohols form hydrogen bonds with one another, the increase in boiling points is attributed to a greater contribution by London forces between the hydrocarbon parts of the alcohols, the larger they become.

Carboxylic acids contain a hydrogen–oxygen covalent bond and, like alcohols, they can form hydrogen bonds with one another. With the presence of an oxygen atom in the C=O group, each carboxylic acid molecule can be involved in two hydrogen bonds with another carboxylic acid, one involving the H of the —OH group and the other involving the O of the C=O (Figure 4.23*b*). As with alcohols, an increase in the number of carbon atoms in a carboxylic acid leads to stronger London force attractions and a higher boiling point (Table 4.7).

Esters are unable to form hydrogen bonds because they have no covalent bond between a hydrogen atom and an oxygen atom. Therefore, the forces that hold one ester to another are dipole–dipole interactions and London forces (Figure 4.23*c*). The more carbon atoms in an ester molecule, the greater the contribution of London forces and the higher its boiling point.

The effect that intermolecular forces have on boiling points is clearly demonstrated by comparing molecules of similar molecular weight. Molecules listed in Tables 4.4 and 4.7 with molecular weights ranging between 72 and 74 amu (pentane, ethyl methanoate, 1-butanol, and propanoic acid) have very different boiling points. Pentane has the lowest boiling point because its molecules are held to one another by the relatively weak London forces. The next highest boiling point is that of ethyl methanoate (the naming of alcohols, carboxylic acids, and esters will be covered in later chapters). These ester molecules are attracted to one another by the relatively stronger dipole–dipole forces. The molecules able to form hydrogen bonds—1-butanol and propanoic acid—have even higher boiling points.

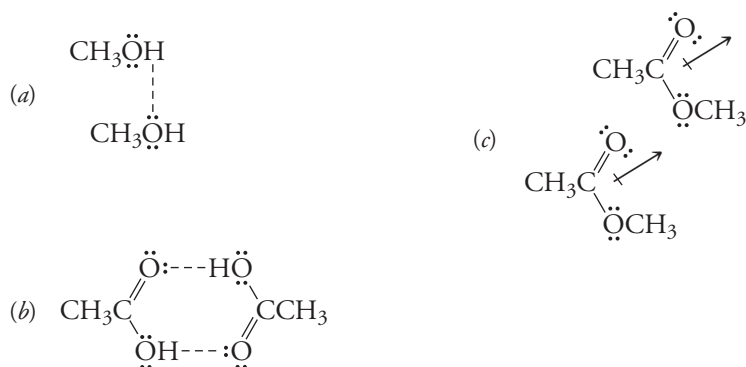


FIGURE 4.23

Noncovalent forces of alcohols, carboxylic acids, and esters

(*a*) Alcohol molecules interact primarily through hydrogen bonds. (*b*) Carboxylic acid molecules can form two hydrogen bonds with other carboxylic acids. (*c*) Ester molecules can interact via dipole–dipole attractions.

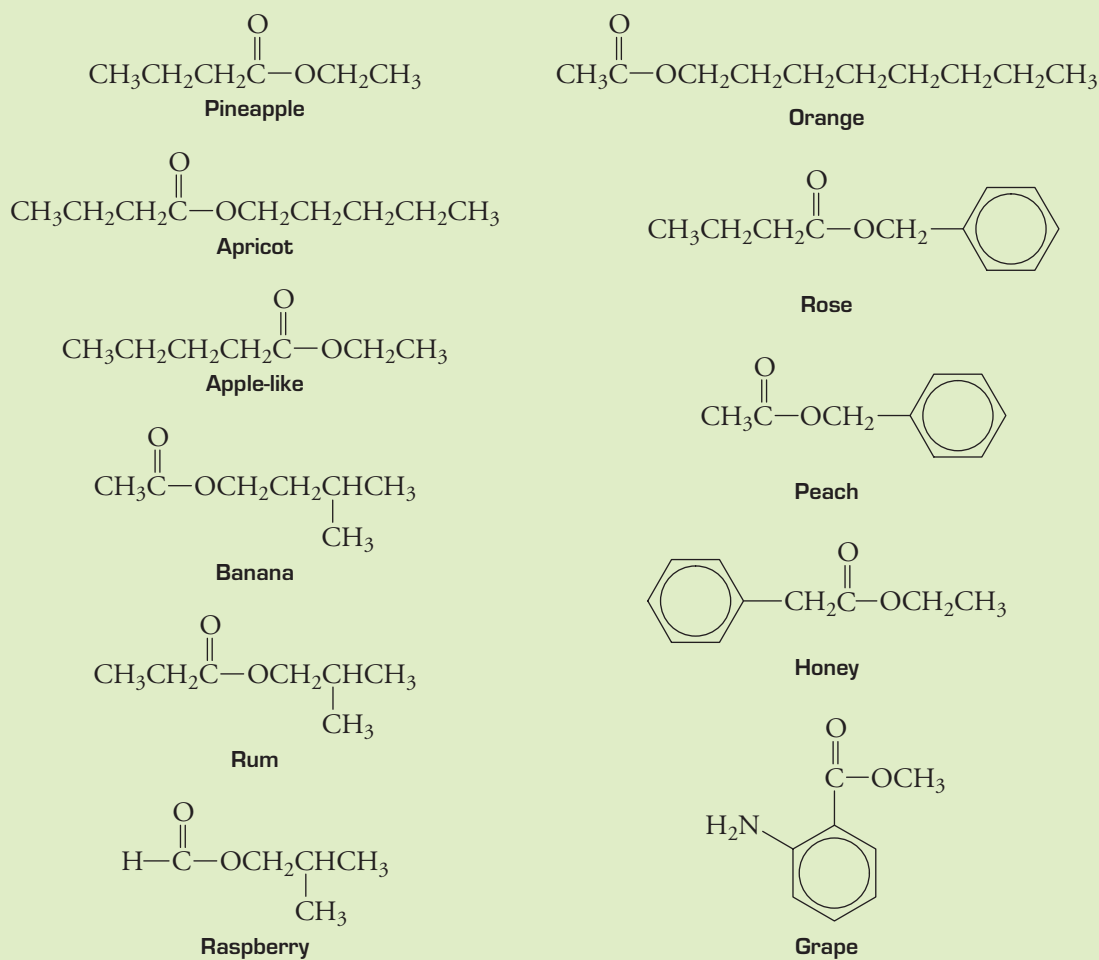
L BIOCHEMISTRY n k

Odor and Flavor

The senses of smell and taste depend on specific receptors located in the nose and in the mouth, respectively. We detect an odor or flavor when a compound attaches to these receptors and triggers nerve responses. How the compound interacts with a given receptor determines the particular odor or flavor that it has. In 2004, the Nobel Prize in Physiology or Medicine was awarded to two researchers who study the biochemistry of the sense of smell.

The odor and flavor of fruits is often due to a mixture of esters. The structure of a particular ester determines how it fits a given receptor, so esters containing a different number of carbon atoms are associated with different odors and flavors. For example, the “pineapple” and “apricot” esters differ by three CH_2 groups (Figure 4.24).

Constitutional isomers can also have different odors and flavors, as is the case for the “apple-like” and “banana” esters, each of which has the molecular formula $\text{C}_7\text{H}_{14}\text{O}_2$.



■ **FIGURE 4.24**

Esters

Many esters have pleasing odors and flavors.

The light-absorbing molecule present in the rods and cones of the retina is called rhodopsin. It is formed by the combination of a particular protein with an unsaturated molecule called 11-*cis*-retinal (derived from vitamin A; see Problem 4.74). When light enters the eye and hits rhodopsin, the 11-*cis*-retinal part of rhodopsin is converted to all-*trans*-retinal (another vitamin A

derivative) and the change in rhodopsin's shape triggers a nerve response that tells the brain that light has reached the eye.

After this *cis* to *trans* change, rhodopsin is broken apart and all-*trans*-retinal is transported to a layer of cells behind the retina, where it is recycled back to 11-*cis*-retinal. In people with Stargardt's disease, the recycling reactions do not take place properly. When retinal remains in the *trans* isomer shape, it reacts with a cell membrane component called phosphatidyl ethanolamine (Section 8.4) to produce a molecule linked to the degeneration of vision associated with the disease.



summary of objectives

1 Draw molecules and polyatomic ions using electron dot and line-bond structures. Assign formal charges.

Drawing the structure of a molecule or polyatomic ion involves counting the number of available valence electrons, joining the atoms by covalent bonds, and then adding the remaining electrons in a way that gives each atom an octet. Formal charge is determined by subtracting the number of electrons around a given atom in a molecule or ion from the number of valence electrons for the neutral, individual atom.

2 Describe how condensed structural formulas and skeletal structures differ from electron dot and line-bond structures.

In an electron dot structure, all valence electrons (nonbonding electrons, as well as those in bonds) are represented by dots. In the line-bond method, each pair of shared bonding electrons is represented by a line. A **condensed structural formula** describes the attachment of atoms to one another, without showing all of the bonds. A carbon atom with three attached hydrogen atoms is written CH₃ and one with two attached hydrogen atoms is written CH₂. In a **skeletal structure**, covalent bonds are represented by lines, carbon atoms are not shown, and hydrogen atoms are drawn only when attached to atoms other than carbon. To simplify matters, nonbonding electrons are sometimes omitted from structural formulas.

3 Define electronegativity and explain its relationship to polar covalent bonds. Give a simple rule that can be used to predict whether or not a covalent bond is polar.

Electronegativity is the ability of an atom to attract electrons in covalent bonds. When the two atoms in a covalent bond have different electronegativities, the bonding

electrons are pulled nearer the atom with the higher electronegativity (stronger attraction). This puts partial charges on the atoms involved ($\delta+$ and $\delta-$) and a polar covalent bond exists. A bond will be polar covalent if it consists of a hydrogen or carbon atom covalently attached to a nitrogen, oxygen, fluorine, or chlorine atom.

4 List the five basic shapes about an atom in a molecule and describe the rules used to predict shape. Explain how shape plays a role in determining overall polarity.

The basic shapes are **tetrahedral**, **pyramidal**, **trigonal planar**, **bent**, and **linear**. The shape about a particular atom depends on how many groups of electrons it holds (a group of electrons is either a pair of nonbonding electrons or a single, double, or triple covalent bond) and on how many of those groups are nonbonding pairs. An atom attached to four groups of electrons will be surrounded by a tetrahedral shape if it has no nonbonding pairs, a pyramidal shape if it has just one nonbonding pair, and a bent shape if it has two nonbonding pairs. An atom attached to three groups of electrons will be trigonal planar if it has no nonbonding pairs and bent if it has one nonbonding pair. An atom attached to just two groups of electrons is linear.

Molecules, as a whole, are **polar** when polar covalent bonds and the shapes around atoms combine to give one side of the molecule a partial negative charge and the other side a partial positive charge.

5 Describe the noncovalent interactions that attract one compound to another.

Compounds (or remote parts of the same compound) are attracted to one another through **noncovalent interactions**. A **hydrogen bond** is the attraction of a nitrogen, oxygen, or fluorine atom to a hydrogen atom covalently bonded to a different nitrogen, oxygen, or fluorine atom. **Salt bridge** is the term used by biochemists to describe an ionic bond. A **dipole–dipole interaction** is the attraction between opposite partial charges in polar groups and an **ion–dipole interaction** is the attraction of an ion for a polar group. A **coordinate-covalent interaction** involves the attraction between a cation and the nonbonding electrons of a nonmetal ion, and **London forces** arise from temporary dipoles.

6 Describe the four families of hydrocarbons.

Hydrocarbons contain only carbon and hydrogen atoms. Hydrocarbons that contain only single covalent bonds are called **alkanes**. **Alkenes** and **alkynes** are hydrocarbons that, respectively, have at least one carbon–carbon double bond and at least one carbon–carbon triple bond. **Aromatic compounds** consist of rings of carbon atoms joined by alternating double and single bonds.

7 Explain the difference between constitutional isomers, conformations, and the stereoisomers known as geometric isomers. Give examples of two different families of hydrocarbons that can exist as geometric isomers.

Constitutional isomers are molecules that have the same molecular formula, but different atomic connections. **Conformations** are the different three-dimensional shapes that a molecule can assume through rotation of single bonds. **Stereoisomers** are molecules that have the same molecular formula and the same atomic connections, but different three-dimensional shapes that can be interchanged only by bond breaking. Stereoisomers that result due to limited rotation about covalent bonds are called **geometric isomers**. The limited rotation of single bonds in the ring structure of **cycloalkanes** can produce *cis* (the substituents are on the same face of the ring) and *trans* (substituents are on opposite faces of the ring) geometric isomers. Because double bonds do not rotate, **alkenes** can also exist as *cis* and *trans* isomers—in *cis* alkenes the groups being compared are on the same side of a line connecting the two double-bonded carbon atoms, and in *trans* isomers they are on opposite sides.

8 Define the term “functional group” and describe the features that distinguish hydrocarbons, alcohols, carboxylic acids, and esters from one another.

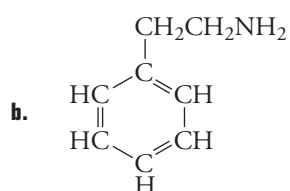
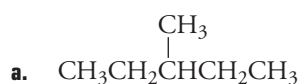
Functional groups are atoms, groups of atoms, or bonds that give a molecule a particular set of chemical properties. The functional groups represented in hydrocarbons are the carbon–carbon double bond (in alkenes), the carbon–carbon triple bond (in alkynes), and alternating double and single bonds in a ring (in aromatic compounds). **Alcohols** contain the hydroxyl (—OH) functional group attached to an alkane-like carbon atom. **Carboxylic acids** contain the hydroxyl group attached to a carbonyl (C=O) group, and **esters** contain a C—O—C linkage, with one of the carbon atoms belonging to a carbonyl group.

END OF CHAPTER PROBLEMS

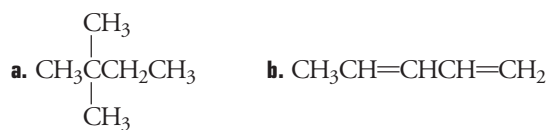
Answers to problems whose numbers are printed in color are given in Appendix D. More challenging questions are marked with an asterisk. Problems within colored rules are paired. **ILW** = Interactive Learning Ware solution is available at www.wiley.com/college/raymond.

4.1 STRUCTURAL FORMULAS AND FORMAL CHARGES

4.1 Draw the line-bond structure of each molecule.



4.2 Draw the line-bond structure of each molecule.



4.3 What is the shape around the nitrogen and sulfur atoms in the ions shown in Figure 4.2?

4.4 What is the shape around each of the carbon atoms in aspirin (Figure 4.3)?

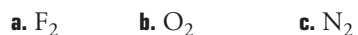
4.5 Draw each molecule.



4.6 Draw each molecule.

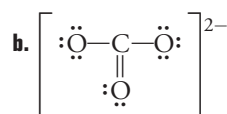


4.7 Draw each diatomic element.

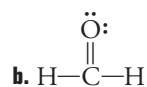
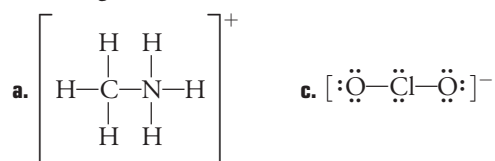


***4.8** Draw two different molecules that have the formula $\text{C}_2\text{H}_6\text{O}$.

4.9 What is the formal charge on each atom in the following molecules or ions?



4.10 What is the formal charge on each atom in the following molecules or ions?



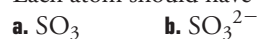
4.11 Draw each polyatomic ion and assign formal charges. Each atom, except for hydrogen, should have an octet of valence electrons.



4.12 Draw each polyatomic ion and assign formal charges. Each atom, except for hydrogen, should have an octet of valence electrons.



4.13 Draw each of the following and assign formal charges. Each atom should have an octet of valence electrons.



4.14 Draw each molecule and assign formal charges. Each atom should have an octet of valence electrons.



- 4.36** Which has the higher boiling point, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$? Explain.
- 4.37** Arrange the molecules in order, from highest boiling point to lowest boiling point: decane, propane, butane.
- 4.38** Arrange the molecules in order, from highest boiling point to lowest boiling point: pentane, octane, methane.

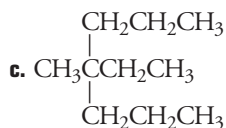
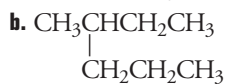
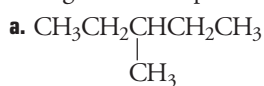
4.39 Draw a line-bond structure of each alkane.

- a. $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_3$
 b. $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

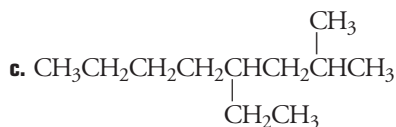
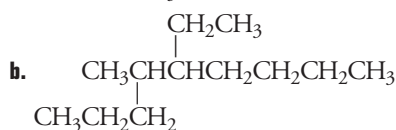
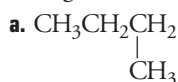
4.40 Draw a line-bond structure of each alkane.

- a. $\text{CH}_3\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_3$
 b. $\text{CH}_3\text{C}(\text{CH}_2\text{CH}_3)_2\text{CH}(\text{CH}_3)\text{CH}_3$

4.41 Find and name the parent chain for each molecule, then give the complete IUPAC name for each.



4.42 Find and name the parent chain for each molecule, then give the complete IUPAC name for each.

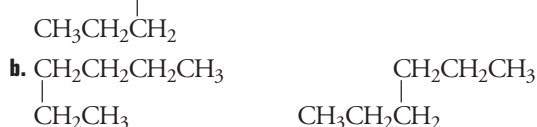


4.5 CONSTITUTIONAL ISOMERS

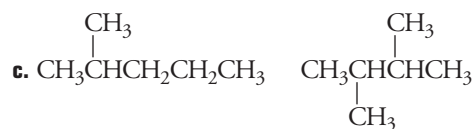
***4.43** Draw and name six of the constitutional isomers with the formula C_7H_{16} .

***4.44** Draw and name six of the constitutional isomers with the formula C_8H_{18} .

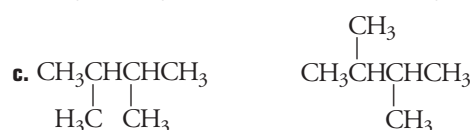
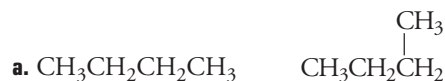
4.45 Which pairs of molecules are constitutional isomers? Which are identical?



END OF CHAPTER PROBLEMS 133



4.46 Which pairs of molecules are constitutional isomers? Which are identical?



4.47 Which are constitutional isomers?

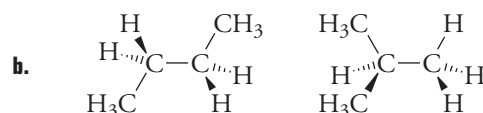
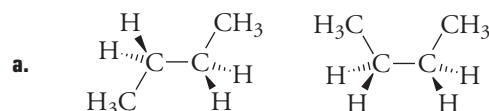
- a. pentane and 2-methylpentane
 b. 2-methylpentane and 3-methylpentane
 c. 2,2-dimethylpropane and pentane
 d. 2,2-dimethylpropane and cyclopentane

4.48 Which are constitutional isomers?

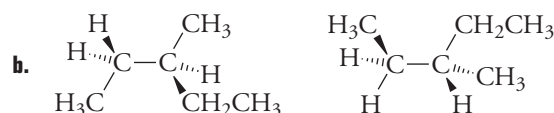
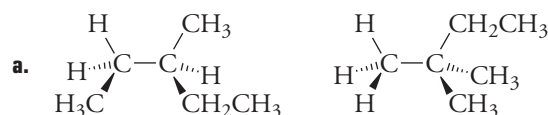
- a. hexane and 3-methylpentane
 b. hexane and 2,3-dimethylpentane
 c. hexane and 2,3-dimethylbutane
 d. hexane and cyclohexane

4.6 CONFORMATIONS

***4.49** Which pairs of molecules are constitutional isomers? Which are different conformations of the same molecule?



***4.50** Which pairs of molecules are constitutional isomers? Which are different conformations of the same molecule?



4.51 a. How are constitutional isomers and conformations similar?

b. How are constitutional isomers and conformations different?

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4.52 True or false?

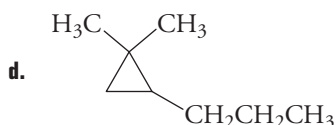
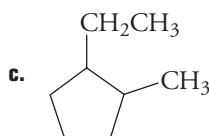
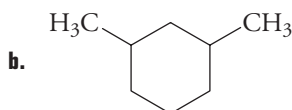
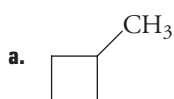
- Constitutional isomers have the same IUPAC name.
- The different conformations of an alkane have the same IUPAC name.

4.7 CYCLOALKANES

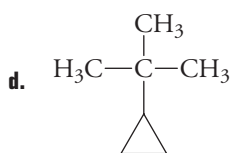
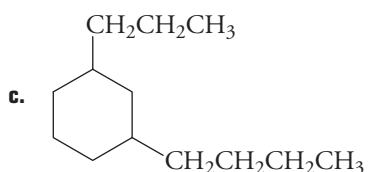
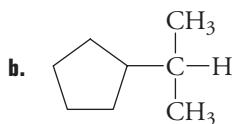
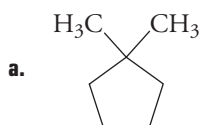
4.53 Draw and name the three ethylmethylcyclobutane constitutional isomers.

4.54 Draw and name three ethyldimethylcyclohexane constitutional isomers.

4.55 Give the correct IUPAC name for each molecule.



4.56 Give the correct IUPAC name for each molecule.

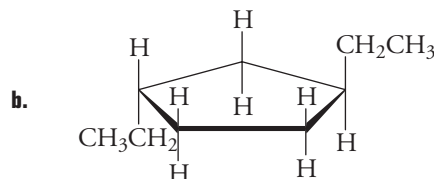
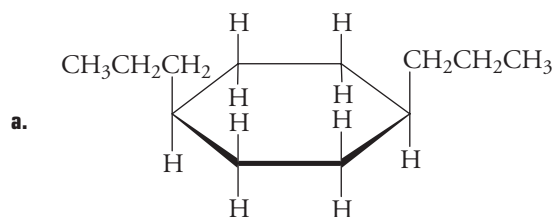
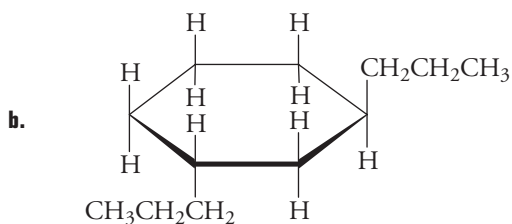
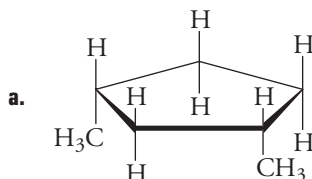
4.57 Which molecule(s) in Problem 4.55 can exist as *cis* and *trans* isomers?4.58 Which molecule(s) in Problem 4.56 can exist as *cis* and *trans* isomers?

4.59 Draw a side view of each cycloalkane. (See Figure 4.15 for examples.)

- trans*-1,2-dimethylcyclohexane
- trans*-1-ethyl-2-methylcyclohexane
- cis*-1,3-diethylcyclopentane

4.60 Draw a side view of each cycloalkane. (See Figure 4.15 for examples.)

- cis*-1,2-dimethylcyclopentane
- trans*-1,2-dimethylcyclopentane
- cis*-1-ethyl-2-isopropylcyclohexane

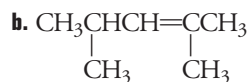
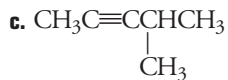
4.61 Give the complete IUPAC name (including the use of the term *cis* or *trans*) for each molecule.4.62 Give the complete IUPAC name (including the use of the term *cis* or *trans*) for each molecule.

4.8 ALKENES, ALKYNES, AND AROMATIC COMPOUNDS

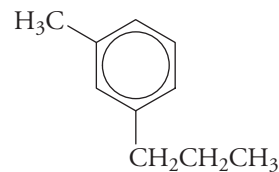
4.63 Draw propene, showing the proper three-dimensional shape about each atom.

4.64 Draw propyne showing the proper three-dimensional shape about each atom.

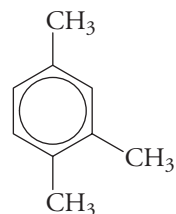
4.71 Name each molecule.



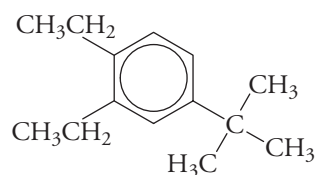
a.



b.



C.



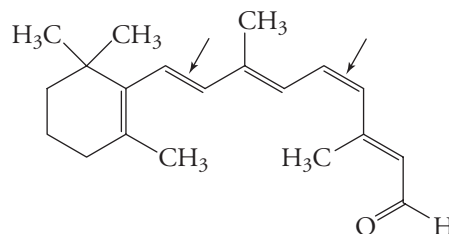
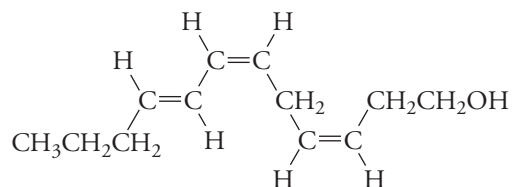
4.72 Draw each molecule.

- 1,3-dipropylbenzene
- p*-diethylbenzene
- 4-isobutyl-1,2-dimethylbenzene

4.73 Draw each molecule

- a.** 1,2-dipropylbenzene
b. *m*-diisopropylbenzene
c. 1,2,4-trimethylbenzene

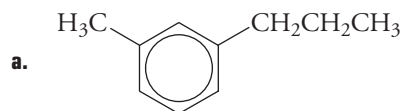
***4.74** Label the indicated carbon–carbon double bonds as *cis* or *trans*.



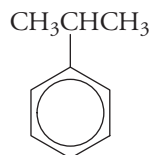
11-*cis*-Retinal
(a derivative of vitamin A)

4.75 Is the double bond in octyl methoxycinnamate (Figure 4.22) *cis*, *trans*, or neither?

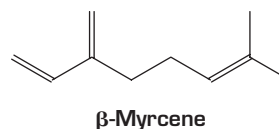
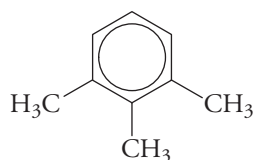
4.76 Does β -myrcene, a compound present in lemon grass, bay, and hops, contain any *cis* or *trans* double bonds?



b.



C.



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4.9 ALCOHOLS, CARBOXYLIC ACIDS, AND ESTERS

4.77 List the primary noncovalent attraction between each pair of molecules.

a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

b. CH_3COOH and CH_3COOH

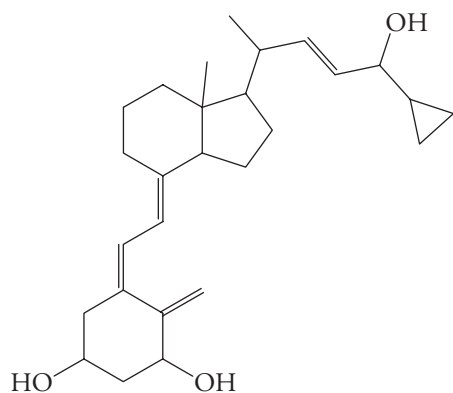
c. $\text{H}-\text{C}(=\text{O})-\text{OCH}_3$ and $\text{H}-\text{C}(=\text{O})-\text{OCH}_3$

4.78 This molecule is an elephant sex pheromone.



- Which functional groups are present in this molecule?
- Which geometric isomer is present?
- Is the molecule saturated or unsaturated?

4.79 Dovonex is a prescription drug used to treat psoriasis.



Dovonex

- Which functional groups are present in this molecule?
- Indicate which geometric isomer is present for the alkene group at the top of the structure.
- Are any fused rings present in this molecule?
- Three different types of cycloalkane rings are present. Identify them.
- Is this molecule saturated or unsaturated?

HEALTHLink Prion Diseases

4.80 Are covalent bonds broken when PrP^c is converted into PrP^{sc} ? Explain.

4.81 Suggest a way to reduce the spread of mad cow disease between cattle.

HEALTHLink Sunscreens

4.82 What properties are important for molecules used as sunscreens?

4.83 When applied to the skin of mice, Forskolin, a compound present in an Asian plant, was shown to increase the production of melanin. Which, do you suppose, were the results of this scientific study?

- The mice tanned more quickly.
- The mice did not sunburn as easily.
- The mice were less susceptible to skin cancer.



4.84 a. "Tanning and Health" presented the results of a study in which mice were exposed to UV radiation. Based on this study, which leads to more skin cancer, a single dose of UV that causes sunburn or small doses of UV over several weeks?
b. While this video-clip describes hazards associated with exposure to UV radiation, it also presents an alternative view which contends that UV exposure is a good thing. How might UV exposure be beneficial to your health?

BIOCHEMISTRYLink Odor and Flavor

***4.85** Although esters are generally known to have pleasant odors, many large esters have no odor. Explain.

4.86 Would you expect esters that are constitutional isomers of one another to have the same odor? Explain.

THINKING IT THROUGH

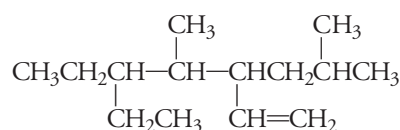
4.87 The term "organic" can have different meanings. What are two different ways to interpret a sign at the grocery store that reads "organic foods"?

4.88 If you were given the assignment to come up with a few likely candidates for new esters that might have the odor and flavor of grapes, where would you begin? (Refer to Figure 4.24.)

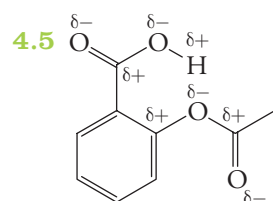
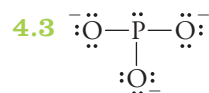
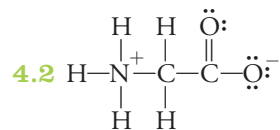
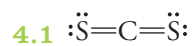
INTERACTIVE LEARNING PROBLEMS



4.89 What is the IUPAC name for:



SOLUTIONS TO PRACTICE PROBLEMS

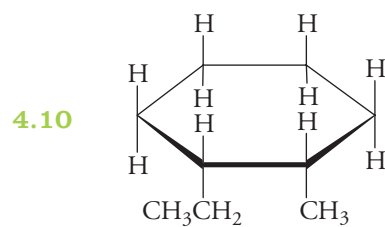


4.6 **b.** and **c.**

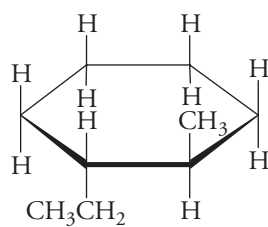
4.7 Yes. The O atom can form a hydrogen bond with an H atom in a water molecule.

4.8 **a.** 2,4-dimethylheptane; **b.** 4-ethyl-2,3-dimethylheptane

4.9 Constitutional isomers.



cis-1-ethyl-2-methylcyclohexane



trans-1-ethyl-2-methylcyclohexane

