1

A Review of General Chemistry

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

DID YOU EVER **WONDER...**
what causes lightning?

Believe it or not, the answer to this question is still the subject of debate (that's right… scientists have not yet figured out everything, contrary to popular belief). There are various theories that attempt to explain what causes the buildup of electric charge in clouds. One thing is clear, though—lightning involves a flow of electrons. By studying the nature of electrons and how electrons flow, it is possible to control where lightning will strike. A tall building can be protected by installing a lightning rod (a tall metal column at the top of the building) that attracts any nearby lightning bolt, thereby preventing a direct strike on the building itself. The lightning rod on the top of the Empire State Building is struck over a hundred times each year.

Just as scientists have discovered how to direct electrons in a bolt of lightning, chemists have also discovered how to direct electrons in chemical reactions. We will soon see that although organic chemistry is defined as the study of compounds containing carbon atoms, its true essence is actually the study of electrons, not atoms. Rather than thinking of reactions in terms of the motion of atoms, we must

continued >

recognize that *reactions occur as a result of the motion of electrons*. For example, in the following reaction the curved arrows represent the motion, or flow, of electrons as one bond breaks and a new bond forms. This flow of electrons causes the chemical change shown:

Throughout this course, we will learn how, when, and why electrons flow during reactions. We will learn about the barriers that prevent electrons from flowing, and we will learn how to overcome those barriers. In short, we will study the behavioral patterns of electrons, enabling us to predict, and even control, the outcomes of chemical reactions.

This chapter reviews some relevant concepts from your general chemistry course that should be familiar to you. Specifically, we will focus on the central role of electrons in forming bonds and influencing molecular properties.

1.1 Introduction to Organic Chemistry

In the early nineteenth century, scientists classified all known compounds into two categories: *Organic compounds* were derived from living organisms (plants and animals), while *inorganic compounds* were derived from nonliving sources (minerals and gases). This distinction was fueled by the observation that organic compounds seemed to possess different properties than inorganic compounds. Organic compounds were often difficult to isolate and purify, and upon heating, they decomposed more readily than inorganic compounds. To explain these curious observations, many scientists subscribed to a belief that compounds obtained from living sources possessed a special "vital force" that inorganic compounds lacked. This notion, called vitalism, stipulated that it should be impossible to convert inorganic compounds into organic compounds without the introduction of an outside vital force. Vitalism was challenged in 1828 when German chemist Friedrich Wöhler demonstrated the conversion of ammonium cyanate (a known inorganic salt) into urea, a known organic compound found in urine:

Ammonium cyanate (Inorganic) **Urea** (Organic)

Over the decades that followed, other examples were found, and the concept of vitalism was gradually rejected. The downfall of vitalism shattered the original distinction between organic and inorganic compounds, and a new definition emerged. Specifically, **organic** compounds became defined as those compounds containing carbon atoms, while **inorganic** compounds generally were defined as those compounds lacking carbon atoms. There are a few exceptions to this general definition. For example, ammonium cyanate (seen on this page) is still classified as inorganic, despite the presence of a carbon atom. Some other carbon-containing compounds that are considered to be inorganic are carbon dioxide (CO_2), sodium carbonate (Na_2CO_3), and potassium cyanide (KCN).

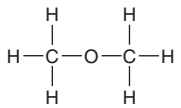
Organic chemistry occupies a central role in the world around us, as we are surrounded by organic compounds. The food that we eat and the clothes that we wear are comprised of organic compounds. Our ability to smell odors or see colors results from the behavior of organic compounds. Pharmaceuticals, bug sprays, paints, adhesives, and plastics are all made from organic compounds. In fact, our bodies are constructed mostly from organic compounds (DNA, RNA, proteins, etc.), and the responses of our bodies to pharmaceuticals are the results of reactions guided by the principles of organic chemistry. A deep understanding of those principles enables the design of new drugs that fight disease and improve the overall quality of life and longevity. Accordingly, it is not surprising that organic chemistry is required knowledge for anyone entering the health professions.

Organic Food vs. Organic Chemistry

You have undoubtedly encountered the term "organic" before taking this course. Food that is labeled "organic" is grown and processed according to defined standards. For example, organic *foods* contain only natural additives, and organic *farming* restricts the use of certain pesticides and fertilizers. Now that you have learned the definition of organic *chemistry*, you can see that the word "organic" depends heavily on context. Afterall, many pesticides are in fact organic compounds! With this newly acquired lens, you will find that organic compounds, products, and materials can be found in every part of our lives. Many organic materials are made by nature, and others are synthetic (made by humans), but they are all part of the story of organic chemistry. Perhaps you can identify some examples of organic chemistry in the photos below? You certainly have an exciting journey ahead, as we explore this fascinating world together. In the meantime, visit the Student Solutions Manual to learn more about what can be found in these photos.

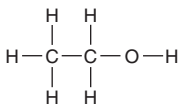
1.2 Constitutional Isomerism

As we explore organic compounds in the following chapters, an extraordinary variety of chemical and physical properties will be revealed. What makes every organic compound unique is not only the number and types of atoms from which it is composed (its **molecular formula**), but the way in which the atoms are connected. As an example, consider the following two compounds:



Dimethyl ether

- ✓ Boiling point = −23°C
- ✓ Gas at room temp.
- ✓ Found in a can of spray paint

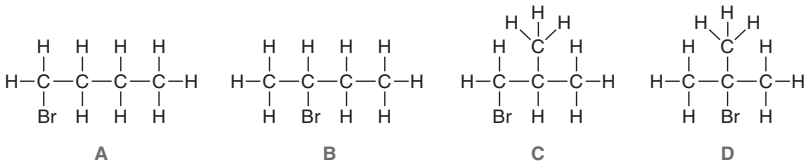


Ethanol

- ✓ Boiling point = 78.4°C
- ✓ Liquid at room temp.
- ✓ Found in a bottle of wine

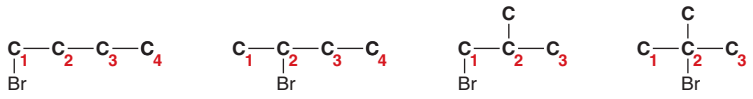
These compounds have the same molecular formula (C_2H_6O), yet they differ from each other in the way the atoms are connected—that is, they differ in their constitution. As a result, they are called constitutional isomers. **Constitutional isomers** have different physical properties and different names. The first compound is a colorless gas used as an aerosol spray propellant, while the second compound is a clear liquid, commonly referred to as "alcohol," found in alcoholic beverages.

Let's look more closely at what it means to be a constitutional isomer. There are four constitutional isomers with the formula C_4H_9Br, as shown below (labeled **A-D**):



A **B** **C** **D**

We can see that each compound indeed has four carbon atoms, one bromine atom, and nine hydrogen atoms. Constitutional isomers have the same molecular formula, but the atoms are assembled in different ways to make them different compounds. How can we confirm that the atoms are connected differently in each structure **A-D**? When all the bonds are drawn out, there is a lot of information to process. To see the connectivity of the atoms more clearly, we can mentally simplify the structures by ignoring the hydrogen atoms, and then we can number the carbon atoms in the longest carbon chain (C1, C2, etc.):



A **B** **C** **D**

Keep in mind that when drawing organic compounds, it is not acceptable to draw carbon atoms (C) without also drawing the attached hydrogen atoms (H). However, these skeletal drawings can be helpful tools for solving problems, even though they are not complete representations of compounds **A**-**D**. Indeed, examination of these skeletons reveals that each compound is unique. Isomers **A** and **B** both have a four-carbon chain, but the bromine atom is connected at different positions on the chain (C1 for compound **A** and C2 for compound **B**). Isomers **C** and **D** have the same, branched carbon backbone (a three-carbon chain, with a fourth carbon attached at the middle position), but they differ in the placement of the bromine atom. There are many acceptable ways to draw a given compound, so it's important to be able to recognize when identical structures are drawn.

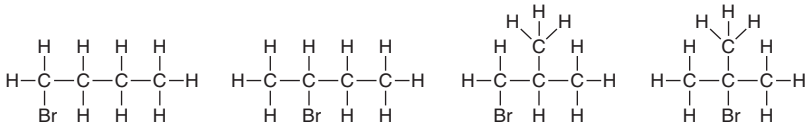
Let's further develop our ability to evaluate drawings with the following module called a SkillBuilder. You will see several SkillBuilders throughout every chapter, and they deserve special attention. Working on SkillBuilders as you encounter them will be critical to your success, as it enables you to be actively engaged in the material. Organic chemistry is not a spectator sport, so let's roll up our sleeves and get to work!

SKILLBUILDER

1.1 IDENTIFYING CONSTITUTIONAL ISOMERS

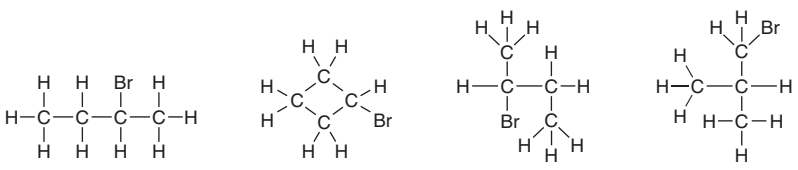
LEARN the skill

Shown below are the four constitutional isomers with the molecular formula C_4H_9Br:



A **B** **C** **D**

Consider the following drawings. Evaluate each drawing and determine whether or not it represents one of the constitutional isomers given above.

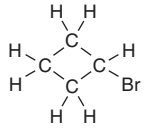


1 **2** **3** **4**

SOLUTION

STEP 1
Check the molecular formula

Let's begin by checking to see if each structure matches the given molecular formula (C_4H_9Br). Counting the atoms is a straightforward exercise, and we can see that compounds **1**, **3** and **4** all have four carbon atoms, one bromine atom, and nine hydrogen atoms. Structure **2**, however, has only seven hydrogen atoms, so it is not one of the given isomers **A-D**.

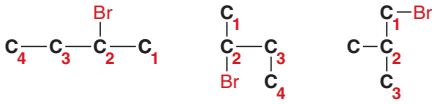


2

C_4H_7Br
✗ not a constitutional isomer
✗ does not match any structure **A-D**

STEP 2
Determine the connectivity of the atoms.

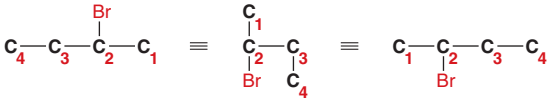
Next, the connectivity of the atoms must be determined. To simplify the drawings mentally, disregard the hydrogen atoms and then assign a number to each carbon atom in the longest carbon chain (C1, C2, etc.). To facilitate the comparison to structures **A-D**, we consistently number the carbon chain from the end closest to the bromine atom.



1 3 4

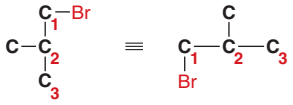
STEP 3
Compare the drawings to determine their relationship.

Finally, compare each structure to the given isomers to find its match. Drawings **1** and **3** both have a four-carbon chain with the bromine atom connected at C2, so these two drawings represent the same compound (isomer **B**).



1 3 B

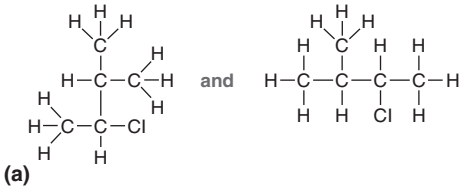
On the other hand, drawing **4** has a branched, three-carbon chain, with the bromine atom on C1. This drawing matches the structure of isomer **C**.



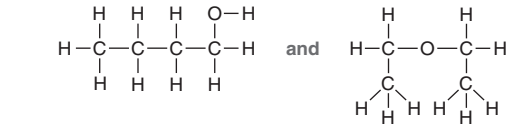
4 C

PRACTICE the skill

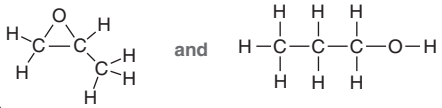
1.1 In each of the following cases, determine whether the two structures shown represent the same compound, constitutional isomers, or unrelated compounds.



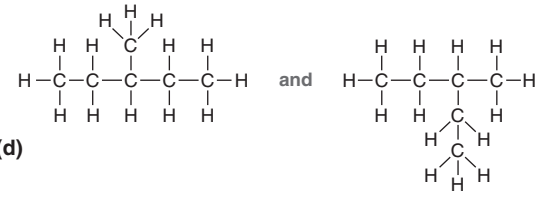
(a)



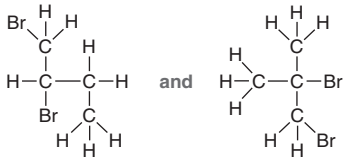
(b)



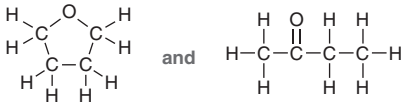
(c)



(d)



(e)



(f)

APPLY the skill

A gas called a *refrigerant* is what enables an air conditioning system to cool the air in your car. CFCs are no longer used as refrigerants, thanks to the Montreal Protocol, a 1987 international treaty aimed at protecting the ozone layer.

1.2 Chlorofluorocarbons (CFCs) are gases that were once widely used as refrigerants and propellants. When it was discovered that these molecules contributed to the depletion of the ozone layer, their use was banned, but CFCs continue to be detected as contaminants in the environment.[1] There are two CFCs with the molecular formula $C_2Cl_3F_3$ that are constitutional isomers. Draw these two isomers. (**Hint:** carbon atoms typically form four bonds, so the two carbon atoms should be drawn at the center of the compound). How would you explain to another student that the two structures are different?

need more **PRACTICE?** **Try Problems 1.42 and 1.64**

1.3 Electrons, Bonds, and Lewis Structures

What Are Bonds?

As mentioned, atoms are connected to each other by bonds. That is, bonds are the "glue" that hold atoms together. But what is this mysterious glue and how does it work? As suggested in the chapter introduction, we must focus our attention on electrons.

In 1916, Gilbert Lewis (University of California, Berkeley) defined a **covalent bond** as the result of *two atoms sharing a pair of electrons*. As a simple example, consider the formation of a bond between two hydrogen atoms:

Each hydrogen atom has one electron. When these electrons are shared to form a bond, there is a decrease in energy, indicated by the negative value of ΔH. The energy diagram in Figure 1.1 plots the energy of the two hydrogen atoms as a function of the distance between them. Focus on the right side of the diagram, which represents the hydrogen atoms separated by a large distance. Moving toward the left on the diagram, the hydrogen atoms approach each other, and there are several forces that must be taken into account: (1) the force of repulsion between the two negatively charged electrons, (2) the force of repulsion between the two positively charged nuclei, and (3) the forces of attraction between the positively charged nuclei and the negatively charged electrons. As the hydrogen atoms get closer to each other, all of these forces get stronger. Under these circumstances, the electrons are capable of moving in such a way so as to minimize the repulsive forces between them while maximizing their attractive forces with the nuclei. This provides for a net force of attraction, which lowers the energy of the system. As the hydrogen atoms move still closer together, the energy continues to be lowered until the nuclei achieve a separation (internuclear distance) of 0.74 angstroms (Å). At that point, the force of repulsion between the nuclei begins to overwhelm the forces of attraction, causing the energy of the system to increase if the atoms are brought any closer together. The lowest point on the curve represents the lowest energy (most stable) state. This state determines both the bond length (0.74 Å) and the bond strength (436 kJ/mol).

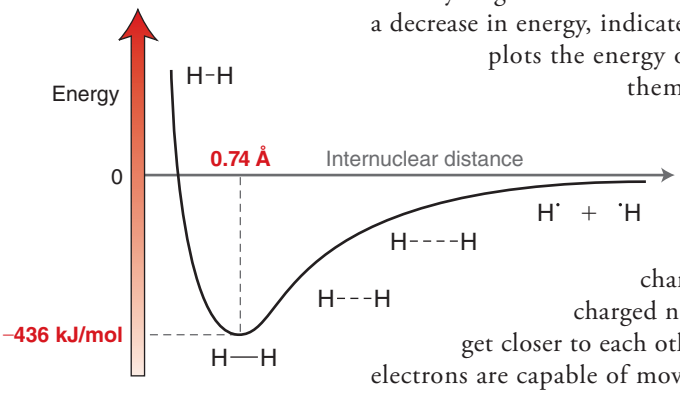


FIGURE 1.1
An energy diagram showing the energy as a function of the internuclear distance between two hydrogen atoms.

BY THE WAY
1 Å = 10^{-10} meters.

Drawing the Lewis Structure of an Atom

Armed with the idea that a bond represents a pair of shared electrons, Lewis then devised a method for drawing structures. In his drawings, called **Lewis structures**, the electrons take center stage. We

will begin by drawing individual atoms, and then we will draw Lewis structures for small molecules. First, we must review a few simple features of atomic structure:

- The nucleus of an atom is comprised of protons and neutrons. Each proton has a charge of +1, and each neutron is electrically neutral.
- For a neutral atom, the number of protons is balanced by an equal number of electrons, which have a charge of −1 and exist in shells. The first shell, which is closest to the nucleus, can contain two electrons, and the second shell can contain up to eight electrons.
- The electrons in the outermost shell of an atom are called the **valence electrons**. The number of valence electrons in an atom is identified by its group number in the periodic table (Figure 1.2). So, for example, carbon (C) has four valence electrons because it is in group 4A of the periodic table.

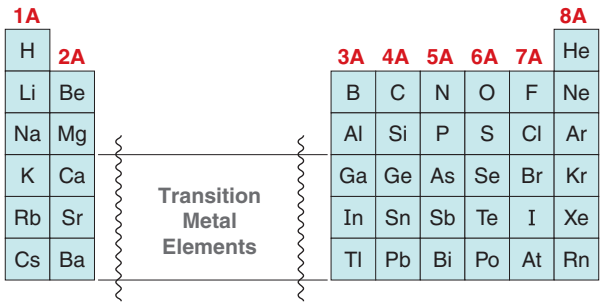
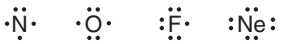


FIGURE 1.2
A periodic table showing group numbers.

The Lewis structure of an individual atom indicates the number of valence electrons, which are placed as dots around the periodic symbol of the atom (C for carbon, O for oxygen, etc.). For atoms with four or fewer valence electrons, each valence electron is drawn by itself (unpaired), as seen in the following cases:

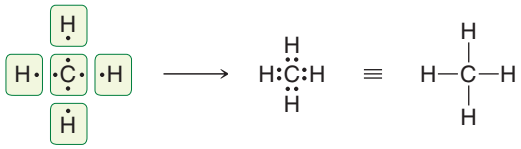
For atoms with more than four valence electrons, the first four valence electrons are drawn unpaired (as seen in the case of carbon above), and then each of the remaining valence electrons is paired up with an electron already drawn:



Drawing the Lewis Structure of a Small Molecule

Lewis structures are constructed based on the observation that atoms tend to bond in such a way so as to achieve a stable electron configuration with a full valence shell, just like that of a noble gas (group 8A in Figure 1.2). For example, hydrogen will form one bond to achieve the electron configuration of helium (two valence electrons), while second-row elements (C, N, O, and F) will form the necessary number of bonds so as to achieve the electron configuration of neon (eight valence electrons). This observation is called the **octet rule**.

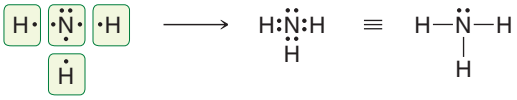
The octet rule explains why carbon typically forms four bonds and is therefore said to be **tetravalent**. As shown below, carbon can achieve an octet of electrons by using each of its four valence electrons to form a bond with a hydrogen atom, thus producing a CH_4 molecule.



Here, the dots are shown to illustrate the eight electrons around the carbon atom (a full octet has been achieved), but in a Lewis structure, covalent bonds are drawn as lines. Each line connecting two atoms represents two electrons being shared as a bond.

The octet rule also explains why nitrogen is **trivalent** (typically forms three bonds). Specifically, it has five valence electrons and therefore requires three bonds to achieve an octet of electrons.

Shown here is the Lewis structure for ammonia, NH_3. Notice that the nitrogen atom in ammonia contains one pair of unshared, or nonbonding, electrons, called a **lone pair**.



Applying the octet rule to other commonly encountered elements, we observe that oxygen typically forms two bonds, making it **divalent**, and has two lone pairs of electrons (Figure 1.3). Hydrogen and the halogens (group 7A on the periodic table) all form one bond, making them **monovalent**. In addition to having one bond, a typical halogen atom also bears three lone pairs, thus completing its octet (two shared electrons + six nonbonded electrons = eight total electrons).

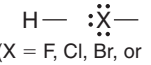
Tetravalent	*Trivalent*	*Divalent*	*Monovalent*
			 (X = F, Cl, Br, or I)
Carbon generally forms ***four*** bonds.	Nitrogen generally forms ***three*** bonds.	Oxygen generally forms ***two*** bonds.	Hydrogen and halogens generally form ***one*** bond.

FIGURE 1.3
Typical bonding patterns of some common elements encountered in organic chemistry.

At first, it may seem like there is a lot to memorize, but the periodic table can help you predict these expected bonding patterns. Group 4A elements (such as carbon) have four valence electrons and need four more to achieve an octet, so they make four bonds (4 + 4 = 8). Group 5A elements (*e.g.*, nitrogen) have five electrons, so they will form three bonds (5 + 3 = 8). You might note that a pattern is emerging. A group 6A element (*e.g.*, oxygen) forms two bonds (6 + 2 = 8), and an element from group 7A (*e.g.*, chlorine) forms one bond (7 + 1 = 8).

In Chapter 2, we will see applications of the octet rule in more detail. For now, let's practice drawing Lewis structures.

SKILLBUILDER

1.2 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

LEARN the skill

Draw the Lewis structure of CH_3CHO.

SOLUTION

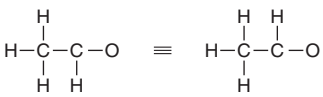
There are five discrete steps when drawing a Lewis structure. First, connect the atoms that form more than one bond. Hydrogen atoms only form one bond each, so we will save those for last. In this case, the order in which the atoms are connected is implied by the given condensed formula:

STEP 1
Connect atoms that form more than one bond.

CH_3CHO indicates this connectivity: C—C—O

Then, connect all the hydrogen atoms. We place the hydrogen atoms on the carbon atoms as indicated in the condensed formula. Note that the hydrogen atoms can be positioned in any direction, as long as three hydrogen atoms are attached to the end carbon atom and one is attached to the middle carbon atom:

STEP 2
Connect the hydrogen atoms.

CH_3CHO indicates this connectivity: 

STEP 3
Determine the total number of valence electrons.

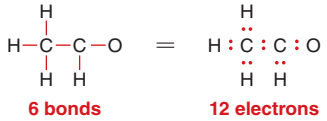
A complete Lewis structure shows all the valence electrons in the compound, so the next step is to calculate the number of electrons that will be included in the final structure. To determine the total number, we simply add up the valence electrons contributed by each atom. There are two carbon atoms, and each brings four valence electrons (because carbon is in group 4A). Likewise, the oxygen atom contributes six electrons and each of the five

hydrogen atoms brings one electron, for a total of 18 valence electrons.

C × 2	4 electrons × 2 carbon atoms	=	8 electrons from the carbon atoms
O	6 electrons × 1 oxygen atom	=	6 electrons from the oxygen atom
H × 4	1 electron × 4 hydrogen atoms	=	4 electrons from the hydrogen atoms
			8 + 6 + 4 = 18 total valence electrons

STEP 4
Determine how many electrons have already been drawn.

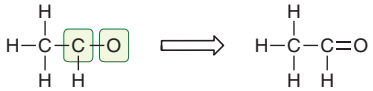
Next, we determine how many of the total valence electrons have already been placed on the structure. If you don't remember drawing electrons up to this point, recall that we used *electrons* to connect the atoms in the first two steps! Each line represents a covalent bond and two shared electrons. In the process of connecting all the atoms, we drew six bonds, which required 12 electrons:



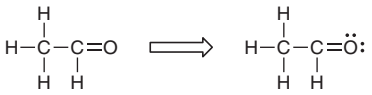
STEP 5
Add remaining electrons so that each atom achieves an octet.

Finally, we complete the structure by adding the remaining electrons. In this case, we have already used 12, so we need to add six electrons to reach the required 18 electrons calculated in Step 3. But how do we know where to place them? We look for atoms that are missing an octet, and we place the electrons on those atoms as a lone pair or as an additional bond (to convert a single bond into a double bond or a triple bond).

Recall that hydrogen atoms achieve the stable, noble gas configuration of helium with only two electrons (rather than eight), so every attached hydrogen atom is perfectly satisfied with its one bond. The end carbon atom is also satisfied, because four bonds give it an octet of electrons. However, the middle carbon and the oxygen atom are both missing octets. We know that carbon is tetravalent, so we can use two electrons to make a C═O double bond, thus adding a fourth bond to the middle carbon atom. This gives an octet to the carbon atom:



We have now used 14 electrons to build our Lewis structure, and we have four more electrons that must be added. The last four electrons are drawn on the oxygen atom (as two lone pairs) to complete its octet and to complete the Lewis structure:



PRACTICE the skill

1.3 Draw a Lewis structure for each of the following compounds:

(a) CH_3OH **(b)** CH_2CHBr **(c)** C_2H_6 **(d)** $CH_3CH_2NH_2$ **(e)** CH_3CCH

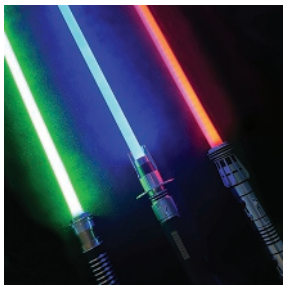
APPLY the skill

1.4 Borane (BH_3) is very unstable and quite reactive. Draw a Lewis structure of borane and explain the source of the instability.

1.5 Smoking tobacco with a water pipe, or hookah, is often perceived as being less dangerous than smoking cigarettes, but hookah smoke has been found to contain the same variety of toxins and carcinogens (cancer-causing compounds) as cigarette smoke.[2] Draw a Lewis structure for each of the following dangerous compounds found in tobacco smoke:

(a) HCN (hydrogen cyanide) **(b)** $CH_2CHCHCH_2$ (1,3-butadiene)

When a hookah is used to smoke flavored tobacco, the smoke passes through a water-filled chamber before being inhaled.



Lightsabers are used in a galaxy far, far away, but on earth we use lasers to cut through various materials.

1.6 Since 1977, Star Wars fans have been obsessed with the lightsaber, an all-powerful sword used by the Jedi. You might think that using light energy as a cutting tool is relegated to science fiction, but pulsed lasers are used routinely in the medical profession for the removal or destruction of tissue.[3] This process, known as laser ablation, uses light as a very sharp and extremely precise scalpel that simultaneously cauterizes the wound. Pulsed lasers are used regularly by ophthalmologists (*e.g.*, LASIK eye surgery), and dermatologists use carbon dioxide (CO_2) lasers for skin resurfacing and rejuvenation procedures. Draw a Lewis structure for carbon dioxide. *Note: if the connectivity of the atoms is not indicated, select the least electronegative element (carbon in this case) to be the central atom.*

need more **PRACTICE?** **Try Problem 1.35 and 1.51**

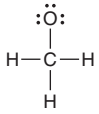
1.4 Identifying Formal Charges

A **formal charge** is associated with any atom that does not exhibit the appropriate number of valence electrons. When such an atom is present in a Lewis structure, the formal charge must be drawn. Identifying a formal charge requires two discrete tasks:

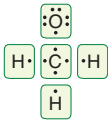
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

The first task can be accomplished by inspecting the periodic table. As mentioned earlier, the group number indicates the appropriate number of valence electrons for each atom. For example, carbon is in group 4A and therefore has four valence electrons. Oxygen is in group 6A and has six valence electrons.

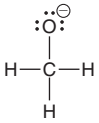
After drawing a Lewis structure, the next task is to determine if any of the atoms exhibit an unexpected number of electrons. For example, consider the structure shown on the right.



Each line represents two shared electrons (a bond). For our purposes, we must split each bond apart equally, and then count the number of electrons that are attributed to each atom. If the number of electrons "owned" by the atom in the Lewis structure is equal to the number of valence electrons "expected" by the atom, then the atom is uncharged. If the electron count does not match the valence, then the atom bears a formal charge.



After mentally splitting the bonds, each hydrogen atom exhibits one electron, as expected. The carbon atom also has the appropriate number of electrons attributed to it (four), but the oxygen atom does not. The oxygen atom in this structure exhibits seven electrons, but it should only have six. In this case, the oxygen atom has one extra electron, and it must therefore bear a negative formal charge, which is indicated as shown on the right.



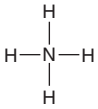
The most common formal charge we will encounter in organic compounds is either +1 or −1. A charge of +2 or −2 on a given atom would be highly unstable and, therefore, highly unlikely.

SKILLBUILDER

1.3 CALCULATING FORMAL CHARGE

LEARN the skill

Consider the nitrogen atom in the structure below and determine if it has a formal charge:



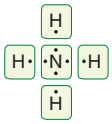
SOLUTION

STEP 1
Determine the appropriate number of electrons.

Recall that we are focusing on *valence* electrons for these calculations. We begin by determining the appropriate number of electrons that should be attributed to a nitrogen atom. Nitrogen is in group 5A of the periodic table, and it should therefore have five electrons.

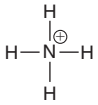
STEP 2
Determine the actual number of electrons in this case.

Next, we count how many electrons are exhibited by the nitrogen atom in this particular example. Every bond is cut in half for this calculation, with one electron being being attributed to each atom. In this case, the nitrogen atom exhibits four electrons (one from each bond).



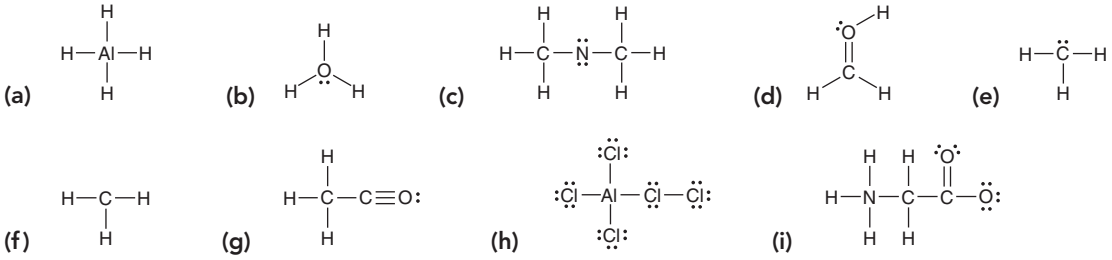
STEP 3
If the numbers from Steps 1 and 2 do not match, assign a formal charge.

Finally, we compare the electron count from Step 2 to the atom's valence (Step 1). We assign a negative formal charge if there is an extra electron, and a positive formal charge if the atom is missing an electron. In this case, compared to its expected five valence electrons, the nitrogen atom is missing one electron, so it must bear a positive charge, which is shown like this:



PRACTICE the skill

1.7 Identify any formal charges in the structures below:

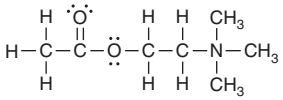


1.8 Draw a complete Lewis structure for each of the following ions; in each case, indicate which atom possesses the formal charge:

(a) BH_4^- **(b)** NH_2^- **(c)** $C_2H_5^+$

APPLY the skill

1.9 If you are having trouble paying attention during a long lecture, your levels of acetylcholine (a neurotransmitter) may be to blame.[4] Identify any formal charges in acetylcholine.



Acetylcholine

Green Chemistry

One goal of "green chemistry" is to reduce or eliminate the generation of hazardous substances.

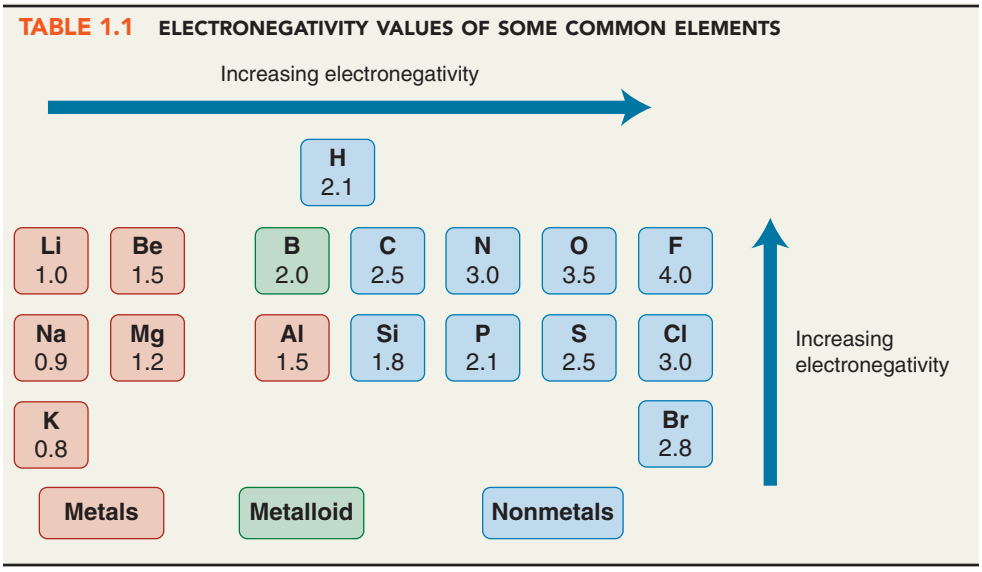
1.10 Elemental phosphorus exists in two major forms, or allotropes, known as white phosphorus and red phosphorus. Although it is toxic and flammable, white phosphorus is the more reactive allotrope, so that is what chemists often use to synthesize phosphorus-containing compounds. Thanks to researchers at Florida State University, a safer and greener process was developed for making phosphorus compounds by passing potassium ethoxide (CH_3CH_2OK) through a column packed with the relatively inert red phosphorus.[5] Draw a complete structure for potassium ethoxide, which exhibits both ionic and covalent bonding.

need more **PRACTICE?** **Try Problems 1.66 and 1.81a**

1.5 Electronegativity and Polar Bonds

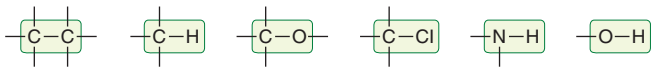
Chemists classify bonds into two categories: covalent and ionic. These categories emerge from the electronegativity values of the atoms involved. **Electronegativity** is a measure of the ability of an atom to attract electrons. Table 1.1 gives electronegativity values for elements commonly encountered in organic chemistry. Fluorine is the most electronegative atom, and the periodic table reveals a trend of increasing electronegativity for elements closer to F (moving from left to right in a given row, and from bottom to top in a column).

TABLE 1.1 ELECTRONEGATIVITY VALUES OF SOME COMMON ELEMENTS



When two atoms form a bond, one critical consideration allows us to classify the bond: What is the difference in the electronegativity values of the two atoms? Rather than referring to precise electronegativity values, we can use the periodic table to make general predictions. The elements on the far left in the periodic table are classified as metals, and they do not exhibit a strong attraction to electrons. Accordingly, you can see that the elements labeled as metals in Table 1.1 have relatively low electronegativity values. On the other hand, nonmetals (found toward the upper-right portion of the table) have relatively high electronegativity values. Note that hydrogen is classified as a nonmetal, with an electronegativity value that is very similar to carbon. Life would be simple if we could consider everything as falling into one of these two categories, but reality is more complex. The nonbinary behavior of elements along the border of these two extremes is demonstrated by boron, which is described as a metalloid.

When *two nonmetals* are bonded together, they *share* two electrons to form a **covalent bond** (drawn as a line connecting the two atoms). Examples include C—C, C—H, C—O, C—Cl, N—H, and O—H:



If the two atoms have similar electronegativity values, the electrons in the bond are shared equally (or nearly equally), resulting in a **nonpolar covalent bond**. Examples of commonly encountered nonpolar bonds include C—C and C—H.

nonpolar covalent bonds: C—C C—H

If the difference in electronegativity between the two bonded atoms is between 0.5 and 1.7, the electrons are not shared equally, resulting in a **polar covalent bond**. For example, consider a bond between carbon and oxygen (C—O). Oxygen is significantly more electronegative (3.5) than carbon (2.5), and therefore oxygen will more strongly attract the electrons of the bond. The withdrawal of electrons toward oxygen can be indicated with a dipole arrow like this:

a **polar** covalent bond: 

Notice that the dipole arrow points in the direction to which the electrons are drawn. The large difference in electronegativity causes the formation of a dipole, which is comprised of a partial positive charge and a partial negative charge. The Greek symbol delta (δ) is used to symbolize the partial charges, with δ+ "delta plus" to denote an electron-deficient atom and δ− "delta minus" to indicate an electron-rich atom. The partial charges that result from polar bonds will be very important in upcoming chapters.

Covalent bonds are observed when two nonmetals are involved, because the difference in electronegativity between such elements is relatively small (below 1.7). On the other hand, when a nonmetal forms a bond with a metal (group 1A or 2A elements), the difference in their electronegativity values is too great to share electrons. In those cases, an **ionic bond** is generally observed (drawn as a separate cation and anion). Ionic bonds are observed in salts such as NaCl, KOH and LiBr:

In sodium chloride (NaCl), both electrons of the bond are possessed solely by the chlorine atom, rendering the chlorine negatively charged (a chloride ion) and the sodium positively charged. Note that no line is drawn between the two atoms—an ionic bond is the result of the force of attraction between the two oppositely charged ions.

The cutoff number of 1.7 should be thought of as a rough guideline. Rather than viewing it as absolute, we must view the various types of bonds as belonging to a spectrum without clear cutoffs (Figure 1.4).

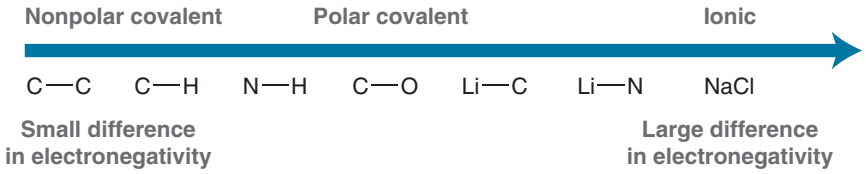
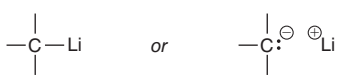


FIGURE 1.4
The nature of various bonds commonly encountered in organic chemistry.

This spectrum has two extremes: nonpolar covalent bonds on one end and ionic bonds on the other. Between these two extremes are the polar covalent bonds. Some bonds fit clearly into one category, such as C—H bonds (nonpolar covalent), C—O bonds (polar covalent), or NaCl bonds (ionic). However, there are many cases that are not so clear-cut. For example, a C—Li bond has a difference in electronegativity of 1.5, and this bond is often drawn either as polar covalent or as ionic. Both drawings are acceptable:

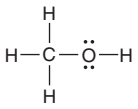


SKILLBUILDER

1.4 LOCATING PARTIAL CHARGES

LEARN the skill

Consider the structure of methanol. Identify all polar covalent bonds and show any partial charges



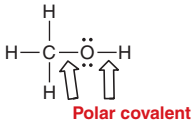
Methanol

SOLUTION

First identify all polar covalent bonds. The C—H bonds are considered to be nonpolar covalent because the electronegativity values for C and H are fairly close. It is true that carbon is more electronegative than hydrogen, but we will generally consider this difference to be negligible for C—H bonds.

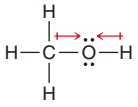
The C—O bond and the O—H bond are both polar covalent bonds:

STEP 1 Identify all polar covalent bonds.



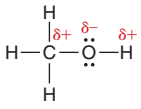
Now determine the direction of the dipoles. Oxygen is more electronegative than C or H, so the dipole arrows are shown pointing in the direction that the electrons are being pulled toward the oxygen atom like this:

STEP 2 Determine the direction of each dipole.



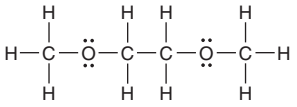
These dipoles dictate the locations of the partial charges. There is a partial negative charge (δ–) on the oxygen atom, and there are partial positive charges (δ+) on the carbon and hydrogen atoms attached to the oxygen atom.

STEP 3 Indicate the location of partial charges.

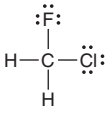


PRACTICE the skill

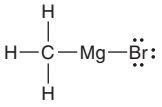
1.11 For each of the following compounds, identify any polar covalent bonds by drawing δ+ and δ− symbols in the appropriate locations:



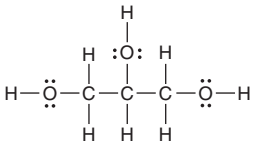
(a)



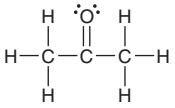
(b)



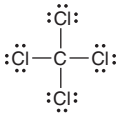
(c)



(d)



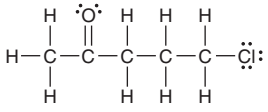
(e)



(f)

APPLY the skill

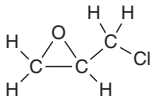
1.12 The δ+ regions in a compound are the electron-deficient regions most likely to be attacked by an anion, such as hydroxide (HO^-). In the compound shown, identify the two carbon atoms that are most likely to be attacked by a hydroxide ion.



Green Chemistry

One principle of *green chemistry* is the use of renewable starting materials (also known as feedstocks).

1.13 Plastics and synthetic fibers are examples of *polymers*, which are very large molecules made by joining repeating subunits of carbon-containing molecules (explored in more detail in Chapter 27). Although most synthetic polymers are prepared from fossil fuel sources, many researchers are exploring ways to make polymers from renewable sources instead. One example is the synthesis of an epoxy resin polymer using a by-product from cashew nut processing, another compound isolated from corn cobs, and epichlorohydrin, shown here.[6] Identify any polar covalent bonds in epichlorohydrin by drawing δ+ and δ− symbols in the appropriate locations.



Epichlorohydrin

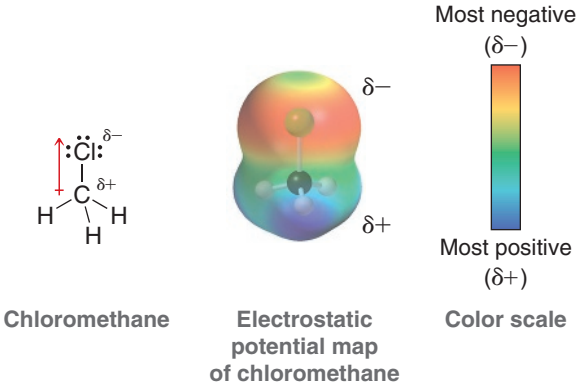
need more **PRACTICE?** **Try Problems 1.33, 1.34, 1.43, 1.54**

Electrostatic Potential Maps

BY THE WAY

Electrostatic potential maps are generated by performing a series of calculations. Specifically, an imaginary point positive charge is positioned at various locations, and for each location, we calculate the potential energy associated with the attraction between the point positive charge and the surrounding electrons. A large attraction indicates a position of δ−, while a small attraction indicates a position of δ+. The results are then illustrated using colors, as shown for chloromethane.

Partial charges can be visualized with three-dimensional, rainbow-like images called **electrostatic potential maps**. As an example, consider the following electrostatic potential map of chloromethane:

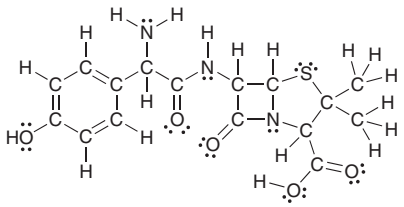


In the image, a color scale is used to represent areas of δ− and δ+. As indicated, red represents a region that is electron-rich, δ−, while blue represents a region that is electron-deficient, δ+. In reality, electrostatic potential maps are rarely used by practicing organic chemists when they communicate with each other; however, these illustrations can often be helpful to students who are learning organic chemistry.

A comparison of any two electrostatic potential maps is only valid if both maps were prepared using the same color scale. Throughout this book, care has been taken to use the same color scale whenever two maps are directly compared to each other. However, it will not be useful to compare two maps from different pages of this book (or any other book), as the exact color scales are likely to be different.

1.6 Reading Bond-Line Structures

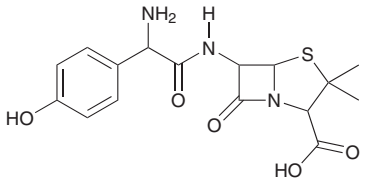
It is not practical to draw Lewis structures for all compounds, especially large ones. As an example, consider the structure of amoxicillin, one of the most commonly used antibiotics in the penicillin family:



Amoxicillin

Previously fatal infections have been rendered harmless by antibiotics such as the one above. Amoxicillin is not a large compound, yet drawing this compound is time consuming. To deal with this problem, organic chemists have developed an efficient drawing style that can be used to draw

molecules very quickly. **Bond-line structures** not only simplify the drawing process but also are easier to read. The following is a bond-line structure of amoxicillin.



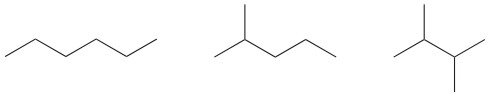
Most of the atoms are not drawn, but with practice, these drawings will become very user-friendly. Throughout the rest of this textbook, most compounds will be drawn in bond-line format, and therefore, it is absolutely critical that you are able to read these types of drawings. This section is designed to develop the skills necessary to read and interpret bond-line drawings.

BY THE WAY

You may find it worthwhile to purchase or borrow a molecular model set. There are several different kinds of molecular model sets on the market, and most of them are comprised of plastic pieces that can be connected to generate models of small molecules. Any one of these model sets will help you to visualize the relationship between molecular structures and the drawings used to represent them.

How to Read Bond-Line Structures

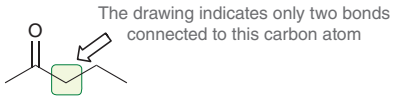
Bond-line structures are drawn in a zigzag format (), where each corner or endpoint represents a carbon atom. For example, each of the following compounds has six carbon atoms (count them!):



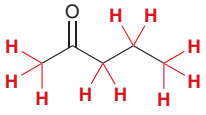
Double bonds are shown with two lines, and triple bonds are shown with three lines. Each of the following compounds has four carbon atoms:

Notice that triple bonds are drawn in a linear fashion rather than in a zigzag format because triple bonds have linear geometry (as we will see in Section 1.10). The two carbon atoms of a triple bond and the two carbon atoms connected to them are drawn in a straight line. All other bonds are drawn in a zigzag format; for example, the following compound has eight carbon atoms:

Hydrogen atoms bonded to carbon are also not shown in bond-line structures, because it is assumed that each carbon atom will possess enough hydrogen atoms so as to achieve a total of four bonds (an octet of electrons). For example, the following highlighted carbon atom appears to have only two bonds:



Therefore, we can infer that there must be two more bonds to hydrogen atoms that have not been drawn (to give a total of four bonds). In this way, all hydrogen atoms are inferred by the drawing:



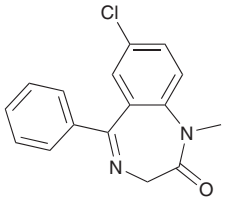
With a bit of practice, it will no longer be necessary to count bonds. Familiarity with bond-line structures will allow you to "see" all of the hydrogen atoms even though they are not drawn. This level of familiarity is absolutely essential, so let's get some practice.

SKILLBUILDER

1.5 READING BOND-LINE STRUCTURES

LEARN the skill

Consider the structure of diazepam, first marketed by the Hoffmann-La Roche Company under the trade name Valium. Diazepam is a sedative and muscle relaxant used in the treatment of anxiety, insomnia, and seizures. Identify the number of carbon atoms in diazepam, then fill in all the missing hydrogen atoms that can be inferred from the drawing.

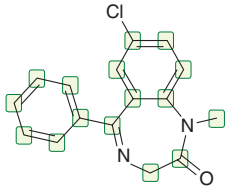


diazepam (Valium)

SOLUTION

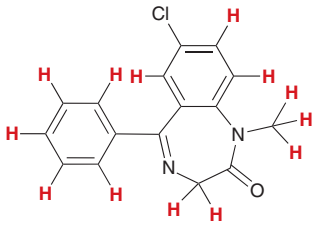
STEP 1
Count the carbon atoms, which are represented by corners or endpoints.

Remember that each corner and each endpoint represents a carbon atom. This compound therefore has 16 carbon atoms, highlighted here.



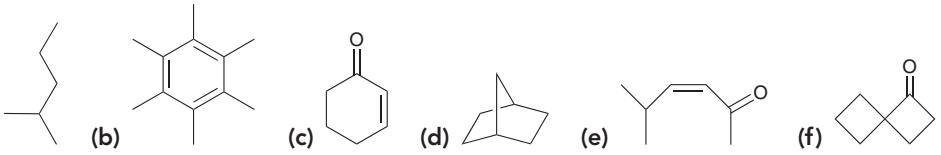
STEP 2
Count the hydrogen atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds.

Each carbon atom should have four bonds. We therefore draw enough hydrogen atoms in order to give each carbon atom a total of four bonds. Any carbon atoms that already have four bonds will not have any hydrogen atoms:



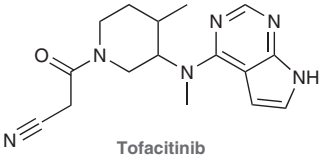
PRACTICE the skill

1.14 For each of the following molecules, determine the number of carbon atoms present and then determine the number of hydrogen atoms connected to each carbon atom:

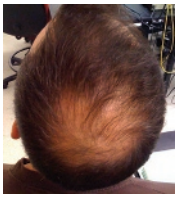


APPLY the skill

1.15 Initially approved to treat psoriasis (a skin disorder) and rheumatoid arthritis, the drug tofacitinib has also been found to promote hair growth and restore hair loss.[7] Identify the number of carbon atoms in tofacitinib, and then fill in all of the missing hydrogen atoms that are inferred by the drawing.



Tofacitinib



Certain types of baldness can be treated with topical creams that promote hair growth.

need more **PRACTICE?** **Try Problems 1.46, 1.47, 1.71**

1.7 Atomic Orbitals

Quantum Mechanics

By the 1920s, vitalism had been discarded. Chemists had developed the structural theory of matter, which proposed that substances are defined by a specific arrangement of atoms. The electron had been discovered and identified as the source of bonding, and Lewis structures were used to keep track of shared and unshared electrons. But the understanding of electrons was about to change dramatically.

In 1924, French physicist Louis de Broglie suggested that electrons, heretofore considered as particles, also exhibited wavelike properties. Based on this assertion, a new theory of matter was born. In 1926, Erwin Schrödinger, Werner Heisenberg, and Paul Dirac independently proposed a mathematical description of the electron that incorporated its wavelike properties. This new theory, called *wave mechanics*, or **quantum mechanics**, radically changed the way we viewed the nature of matter and laid the foundation for our current understanding of electrons and bonds.

Quantum mechanics is deeply rooted in mathematics and represents an entire subject by itself. The mathematics involved is beyond the scope of our course, and we will not discuss it here. However, in order to understand the nature of electrons, it is critical to understand a few simple highlights from quantum mechanics:

- An equation is constructed to describe the total energy of a hydrogen atom (i.e., one proton plus one electron). This equation, called the **wave equation**, takes into account the wavelike behavior of an electron that is in the electric field of a proton.
- The wave equation is then solved to give a series of solutions called **wavefunctions**. The Greek symbol psi (ψ) is used to denote each wavefunction (ψ_1, ψ_2, ψ_3, etc.). Each of these wavefunctions corresponds to an allowed energy level for the electron. This result is incredibly important because it suggests that an electron, when contained in an atom, can only exist at discrete energy levels (ψ_1, ψ_2, ψ_3, etc.). In other words, the energy of the electron is *quantized*.
- Each wavefunction is a function of spatial location. It provides information that allows us to assign a numerical value for each location in three-dimensional space relative to the nucleus. The square of that value (ψ^2 for any particular location) has a special meaning. It indicates the probability of finding the electron in that location. Therefore, a three-dimensional plot of ψ^2 will generate an image of an atomic orbital (Figure 1.5).

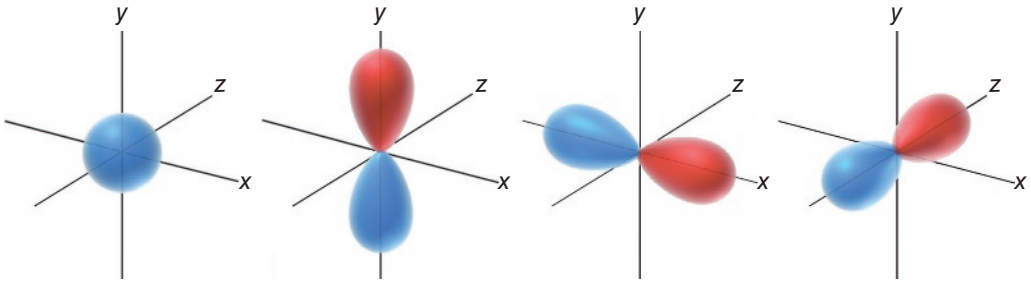


FIGURE 1.5
Illustrations of an *s* orbital and three *p* orbitals.

Electron Density and Atomic Orbitals

An *orbital* is a region of space that can be occupied by an electron. But care must be taken when trying to visualize this. There is a statement from earlier in this section that must be clarified because it is potentially misleading: "ψ^2 *represents the probability of finding an electron in a particular location.*" This statement seems to treat an electron as if it were a particle flying around within a specific region of space. But remember that an electron is not purely a particle—it has wavelike properties as well. Therefore, we must construct a mental image that captures both of these properties. That is not easy to do, but the following analogy might help. We will treat an occupied orbital as if it is a cloud—similar to a cloud in the sky. No analogy is perfect, and there are certainly features of clouds that are very different from orbitals. However, focusing on some of these differences between electron

clouds (occupied orbitals) and real clouds makes it possible to construct a better mental model of an electron in an orbital:

- Clouds in the sky can come in any shape or size. However, electron clouds have specific shapes and sizes (as defined by the orbitals).
- A cloud in the sky is comprised of billions of individual water molecules. An electron cloud is not comprised of billions of particles. We must think of an electron cloud as a single entity, even though it can be thicker in some places and thinner in other places. This concept is critical and will be used extensively throughout the course in explaining reactions.
- A cloud in the sky has edges, and it is possible to define a region of space that contains 100% of the cloud. In contrast, an electron cloud does not have defined edges. We frequently use the term **electron density**, which is associated with the probability of finding an electron in a particular region of space. The "shape" of an orbital refers to a region of space that contains 90–95% of the electron density. Beyond this region, the remaining 5–10% of the electron density tapers off but never ends. In fact, if we want to consider the region of space that contains 100% of the electron density, we must consider the entire universe.

In summary, we must think of an orbital as a region of space that can be occupied by electron density. An occupied orbital must be treated as a *cloud of electron density*. This region of space is called an **atomic orbital** (AO), because it is a region of space defined with respect to the nucleus of a single atom. Examples of atomic orbitals are the *s*, *p*, *d*, and *f* orbitals that were discussed in your general chemistry textbook.

Phases of Atomic Orbitals

Our discussion of electrons and orbitals has been based on the premise that electrons have wavelike properties. As a result, it will be necessary to explore some of the characteristics of simple waves in order to understand some of the characteristics of orbitals.

Consider a wave that moves across the surface of a lake (Figure 1.6). The wavefunction (ψ) mathematically describes the wave, and the value of the wavefunction is dependent on location. Locations above the average level of the lake have a positive value for ψ (indicated in red), and locations below the average level of the lake have a negative value for ψ (indicated in blue). Locations where the value of ψ is zero are called **nodes**.

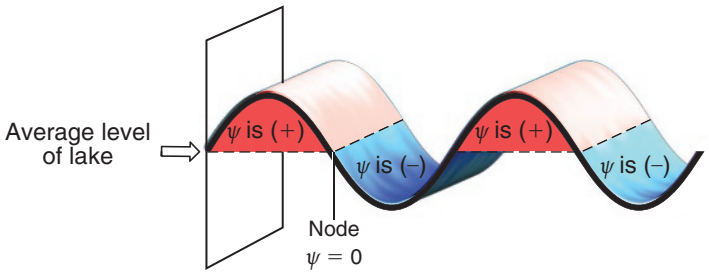


FIGURE 1.6
Phases of a wave moving across the surface of a lake.

Similarly, orbitals can have regions where the value of ψ is positive, negative, or zero. For example, consider a *p* orbital (Figure 1.7). Notice that the *p* orbital has two lobes: the top lobe is a region of space where the values of ψ are positive, while the bottom lobe is a region where the values of ψ are negative. Between the two lobes is a location where $\psi = 0$. This location represents a node.

Be careful not to confuse the sign of ψ (+ or −) with electrical charge. A positive value for ψ does not imply a positive charge. The value of ψ (+ or −) is a mathematical convention that refers to the *phase* of the wave (just like in the lake). Although ψ can have positive or negative values, nevertheless ψ^2 (which describes the electron density as a function of location) will always be a positive number. At a node, where $\psi = 0$, the electron density (ψ^2) will also be zero. This means that there is no electron density located at a node.

From this point forward, we will draw the lobes of an orbital with colors (red and blue) to indicate the phase of ψ for each region of space.

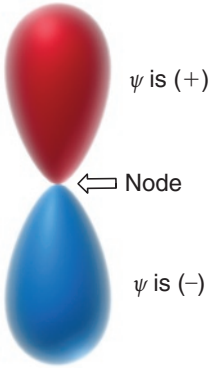


FIGURE 1.7
The phases of a *p* orbital.

Filling Atomic Orbitals with Electrons

The energy of an electron depends on the type of orbital that it occupies. Most of the organic compounds that we will encounter will be composed of first- and second-row elements (H, C, N, and O). These elements utilize the 1*s* orbital, the 2*s* orbital, and the three 2*p* orbitals. Our discussions will therefore focus primarily on these orbitals (Figure 1.8). Electrons are lowest in energy when they occupy a 1*s* orbital, because the 1*s* orbital is closest to the nucleus and it has no nodes (the more nodes that an orbital has, the greater its energy). The 2*s* orbital has one node and is farther away from the nucleus; it is therefore higher in energy than the 1*s* orbital. After the 2*s* orbital, there are three 2*p* orbitals that are all equivalent in energy to one another. Orbitals with the same energy level are described as **degenerate**.

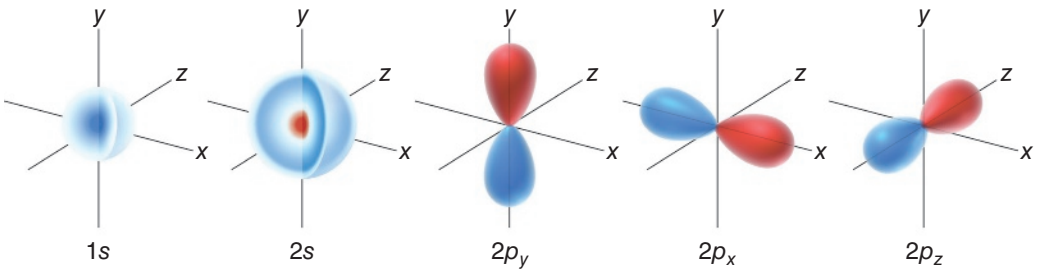


FIGURE 1.8
Illustrations of *s* orbitals and three *p* orbitals.

As we move across the periodic table, starting with hydrogen, each element has one more electron than the element before it (Figure 1.9). The order in which the orbitals are filled by electrons is determined by just three simple principles:

1. The **Aufbau principle.** The lowest energy orbital is filled first.
2. The **Pauli exclusion principle.** Each orbital can accommodate a maximum of two electrons that have opposite spin. To understand what "spin" means, we can imagine an electron spinning in space (although this is an oversimplified explanation of the term "spin"). For reasons that are beyond the scope of this course, electrons only have two possible spin states (designated by ↓ or ↑). In order for the orbital to accommodate two electrons, the electrons must have opposite spin states.
3. **Hund's rule.** When dealing with degenerate orbitals, such as *p* orbitals, one electron is placed in each degenerate orbital first, before electrons are paired up.

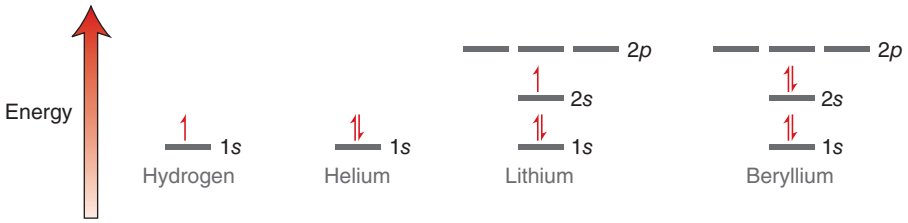


FIGURE 1.9
Energy diagrams showing the electron configurations for H, He, Li, and Be.

The application of the first two principles can be seen in the electron configurations shown in Figure 1.9 (H, He, Li, and Be). The application of the third principle can be seen in the electron configurations for the remaining second-row elements (Figure 1.10).

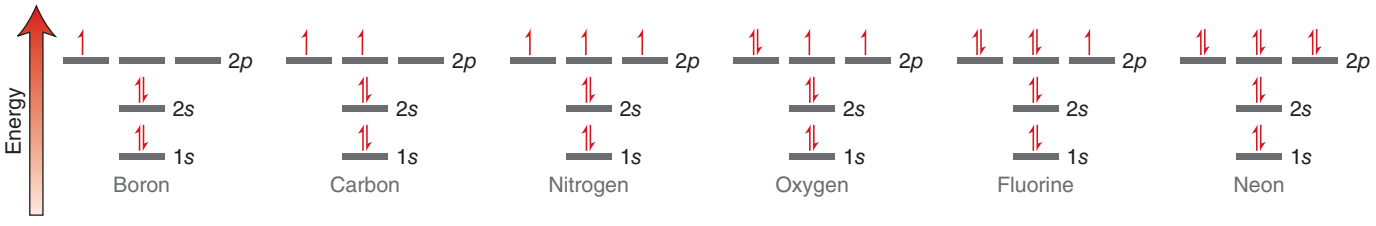


FIGURE 1.10
Energy diagrams showing the electron configurations for B, C, N, O, F, and Ne.

The electron configuration for each element can be summarized using a standard notation. For example, consider nitrogen: two electrons occupy the 1*s* orbital, two electrons occupy the 2*s* orbital, and three electrons occupy the 2*p* orbitals. The electron configuration for N is given as $1s^2 2s^2 3p^3$. Similarly, the electron configuration for oxygen is $1s^2 2s^2 3p^4$.

1.8 Valence Bond Theory

With the understanding that electrons occupy regions of space called orbitals, we can now turn our attention to a deeper understanding of covalent bonds. Specifically, a covalent bond is formed from the overlap of atomic orbitals. There are two commonly used theories for describing the nature of atomic orbital overlap: valence bond theory and molecular orbital (MO) theory. The valence bond approach is more simplistic in its treatment of bonds, and therefore we will begin our discussion with valence bond theory.

If we are going to treat electrons as waves, then we must quickly review what happens when two waves interact with each other. Two waves that approach each other can interfere in one of two possible ways—constructively or destructively. Similarly, when atomic orbitals overlap, they can interfere either constructively (Figure 1.11) or destructively (Figure 1.12).

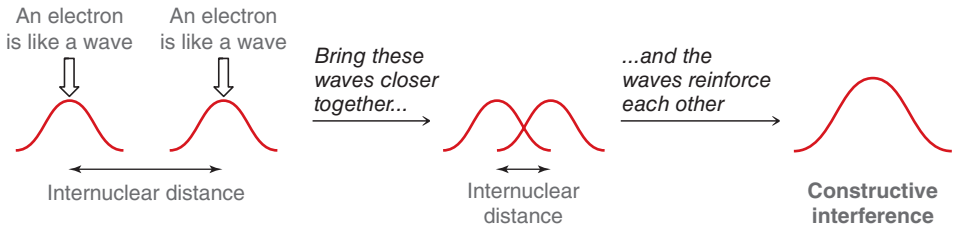


FIGURE 1.11
Constructive interference resulting from the interaction of two electrons.

Constructive interference produces a wave with larger amplitude. In contrast, destructive interference results in waves canceling each other, which produces a node (Figure 1.12).

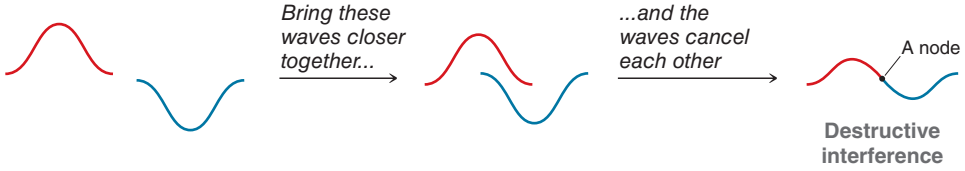


FIGURE 1.12
Destructive interference resulting from the interaction of two electrons.

According to **valence bond theory**, a bond is simply the sharing of electron density between two atoms as a result of the constructive interference of their atomic orbitals. Consider, for example, the bond that is formed between the two hydrogen atoms in molecular hydrogen (H_2). This bond is formed from the overlap of the 1*s* orbitals of each hydrogen atom (Figure 1.13).

The electron density of this bond is primarily located on the bond axis (the line that can be drawn between the two hydrogen atoms). This type of bond is called a **sigma (σ) bond** and is characterized by circular symmetry with respect to the bond axis. To visualize what this means, imagine a plane that is drawn perpendicular to the bond axis. This plane will carve out a circle (Figure 1.14). This is the defining feature of σ bonds and will be true of all purely single bonds. Therefore, *all single bonds are σ bonds*.

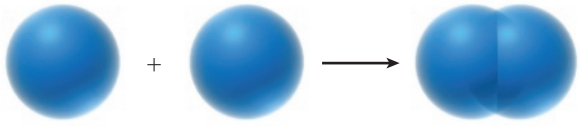


FIGURE 1.13
The overlap of the 1*s* atomic orbitals of two hydrogen atoms, forming molecular hydrogen (H_2).

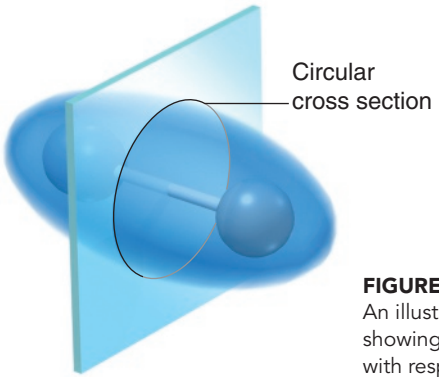


FIGURE 1.14
An illustration of a sigma bond, showing the circular symmetry with respect to the bond axis.

1.9 Molecular Orbital Theory

In most situations, valence bond theory will be sufficient for our purposes. However, there will be cases in the upcoming chapters where valence bond theory will be inadequate to describe the observations. In such cases, we will utilize molecular orbital theory, a more sophisticated approach to viewing the nature of bonds.

Molecular orbital (MO) theory uses a mathematical method called the *linear combination of atomic orbitals (LCAO)*. According to this theory, atomic orbitals are mathematically combined to produce new orbitals, called **molecular orbitals**.

It is important to understand the distinction between atomic orbitals and molecular orbitals. Both types of orbitals are used to accommodate electrons, but an atomic orbital is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule. That is, the molecule is considered to be a single entity held together by many electron clouds, some of which can actually span the entire length of the molecule. These molecular orbitals are filled with electrons in a particular order in much the same way that atomic orbitals are filled. Specifically, electrons first occupy the lowest energy orbitals, with a maximum of two electrons per orbital. In order to visualize what it means for an orbital to be associated with an entire molecule, we will explore two molecules: molecular hydrogen (H_2) and bromomethane (CH_3Br).

Consider the bond formed between the two hydrogen atoms in molecular hydrogen. This bond is the result of the overlap of two atomic orbitals (*s* orbitals), each of which is occupied by one electron. According to MO theory, when two atomic orbitals overlap, they cease to exist. Instead, they are replaced by two molecular orbitals, each of which is associated with the entire molecule (Figure 1.15).

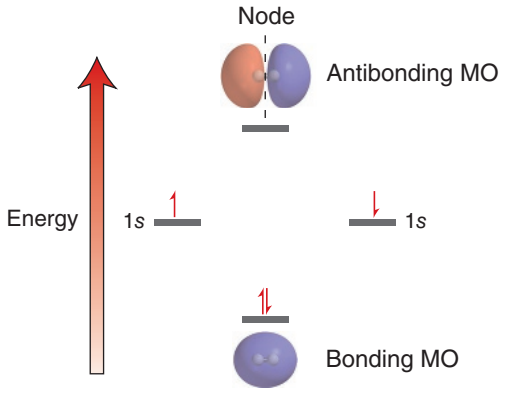


FIGURE 1.15
An energy diagram showing the relative energy levels of bonding and antibonding molecular orbitals.

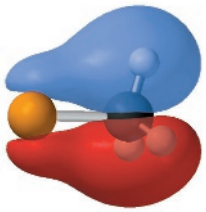


FIGURE 1.16
One of the many low-energy molecular orbitals of CH_3Br. Red and blue regions indicate the different phases, as described in Section 1.7. Notice that this molecular orbital is associated with the entire molecule, rather than being associated with two specific atoms.

In the energy diagram shown in Figure 1.15, the individual atomic orbitals are represented on the right and left, with each atomic orbital having one electron. These atomic orbitals are combined mathematically (using the LCAO method) to produce two molecular orbitals. The lower energy molecular orbital, or **bonding MO**, is the result of constructive interference of the original two atomic orbitals. The higher energy molecular orbital, or **antibonding MO**, is the result of destructive interference. Notice that the antibonding MO has one node, which explains why it is higher in energy. Both electrons occupy the bonding MO in order to achieve a lower energy state. This lowering in energy is the essence of the bond. For an H—H bond, the lowering in energy is equivalent to 436 kJ/mol. This energy corresponds with the bond strength of an H—H bond (as shown in Figure 1.1).

Now let's consider a molecule such as CH_3Br, which contains more than just one bond. Valence bond theory continues to view each bond separately, with each bond being formed from two overlapping atomic orbitals. In contrast, MO theory treats the bonding electrons as being associated with the entire molecule. The molecule has many molecular orbitals, each of which can be occupied by two electrons. Figure 1.16 illustrates one of the many molecular orbitals of CH_3Br.

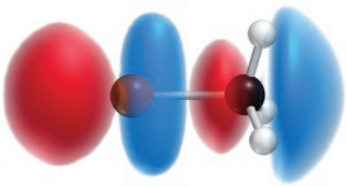


FIGURE 1.17
The LUMO of CH_3Br.

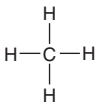
This molecular orbital is capable of accommodating up to two electrons. Red and blue regions indicate the different phases, as described in Section 1.7. As we saw with molecular hydrogen, not all molecular orbitals will be occupied. The bonding electrons will occupy the lower energy molecular orbitals (such as the one shown in Figure 1.16), while the higher energy molecular orbitals remain unoccupied. For every molecule, two of its molecular orbitals will be of particular interest: (1) the highest energy orbital from among the occupied orbitals is called the **highest occupied molecular orbital**, or **HOMO**, and (2) the lowest energy orbital from among the unoccupied orbitals is called the **lowest unoccupied molecular orbital**, or **LUMO**. For example, in Chapter 7, we will explore a reaction in which CH_3Br is attacked by a hydroxide ion (HO^-). In order for this process to occur, the hydroxide ion must transfer its electron density into the lowest energy, empty molecular orbital, or LUMO, of CH_3Br (Figure 1.17). The nature of the LUMO (i.e., number of nodes, location of nodes, etc.) will be useful in explaining the preferred direction from which the hydroxide ion will attack.

We will use MO theory several times in the chapters that follow. Most notably, in Chapter 16, we will investigate the structure of compounds containing several double bonds. To explain the unusual stability of those compounds, valence bond theory will be inadequate, and MO theory will provide a more meaningful understanding of the bonding structure. Throughout this textbook, we will continue to develop both valence bond theory and MO theory.

1.10 Hybrid Atomic Orbitals

Methane and sp^3 Hybridization

Let us now apply valence bond theory to the bonds in methane:



Methane

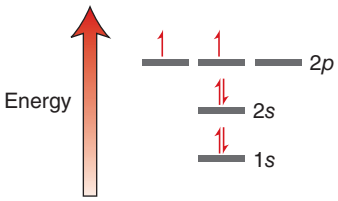


FIGURE 1.18
An energy diagram showing the electron configuration of carbon.

Recall the electron configuration of carbon (Figure 1.18). This electron configuration cannot satisfactorily describe the bonding structure of methane (CH_4), in which the carbon atom has four separate C—H bonds, because the electron configuration shows only two atomic orbitals capable of forming bonds (each of these orbitals has one unpaired electron). This would imply that the carbon atom will form only two bonds, but we know that it forms four bonds. We can solve this problem by imagining an excited state of carbon (Figure 1.19): a state in which a 2*s* electron has been promoted

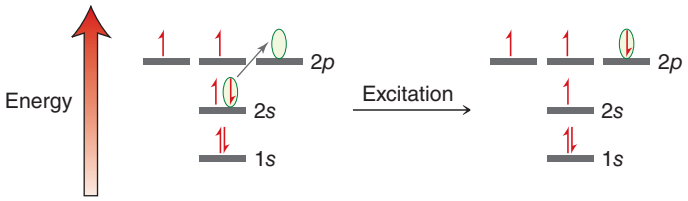


FIGURE 1.19
An energy diagram showing the electronic excitation of an electron in a carbon atom.

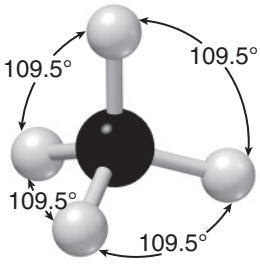


FIGURE 1.20
The tetrahedral geometry of methane. All bond angles are 109.5°.

to a higher energy 2*p* orbital. Now the carbon atom has four atomic orbitals capable of forming bonds, but there is yet another problem here. The geometry of the 2*s* and three 2*p* orbitals does not satisfactorily explain the observed three-dimensional geometry of methane (Figure 1.20). All bond angles are 109.5°, and the four bonds point away from each other in a perfect tetrahedron. This geometry cannot be explained by an excited state of carbon because the *s* orbital and the three *p* orbitals do not occupy a tetrahedral geometry. The *p* orbitals are separated from each other by only 90° (as seen in Figure 1.5) rather than 109.5°.

This problem was solved in 1931 by Linus Pauling, who suggested that the electronic configuration of the carbon atom in methane does not necessarily have to be the same as the electronic configuration of a free carbon atom. Specifically, Pauling mathematically averaged, or *hybridized*, the 2*s* orbital and the three 2*p* orbitals, giving four degenerate hybrid atomic orbitals (Figure 1.21). The hybridization process in Figure 1.21 does not represent a real physical process that the orbitals

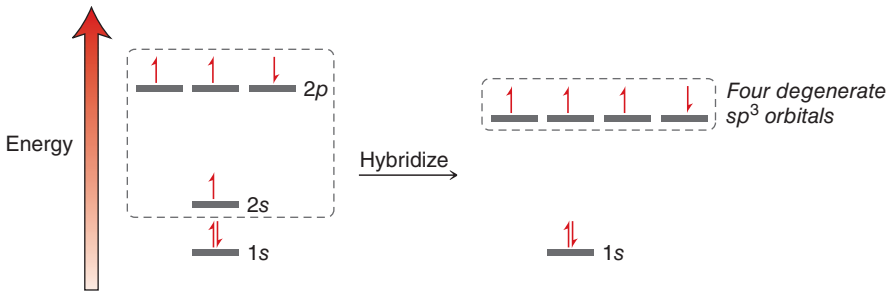


FIGURE 1.21
An energy diagram showing four degenerate hybrid atomic orbitals.

FIGURE 1.22
An illustration of an sp^3 hybrid atomic orbital.

undergo. Rather, it is a mathematical procedure that is used to arrive at a satisfactory description of the observed bonding. This procedure gives us four orbitals that were produced by averaging one *s* orbital and three *p* orbitals, and therefore we refer to these atomic orbitals as ***sp*^{3} hybrid orbitals**. Figure 1.22 shows an sp^3 hybrid orbital. If we use these hybrid atomic orbitals to describe the bonding of methane, we can successfully explain the observed geometry of the bonds. The four sp^3 hybrid orbitals are equivalent in energy (degenerate) and will therefore position themselves as far apart from each other as possible, achieving a tetrahedral geometry. Also notice that hybrid atomic orbitals are not symmetrical. That is, hybrid atomic orbitals have a larger front lobe (shown in red in Figure 1.22) and a smaller back lobe (shown in blue). The larger front lobe enables hybrid atomic orbitals to be more efficient than *p* orbitals in their ability to form bonds.

Using valence bond theory, each of the four bonds in methane is represented by the overlap between an sp^3 hybrid atomic orbital from the carbon atom and an *s* orbital from a hydrogen atom (Figure 1.23). For purposes of clarity the back lobes (blue) have been omitted from the images in Figure 1.23.

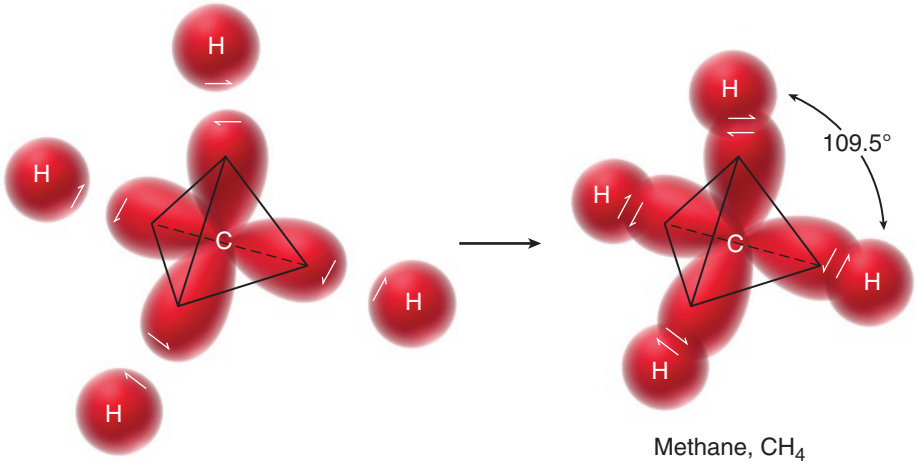
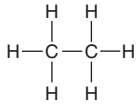


FIGURE 1.23
A tetrahedral carbon atom using each of its four sp^3 hybrid orbitals to form a bond.

The bonding in ethane is treated in much the same way:



Ethane

All bonds in this compound are single bonds, and therefore they are all σ bonds. Using the valence bond approach, each of the bonds in ethane can be treated individually and is represented by the overlap of atomic orbitals (Figure 1.24).

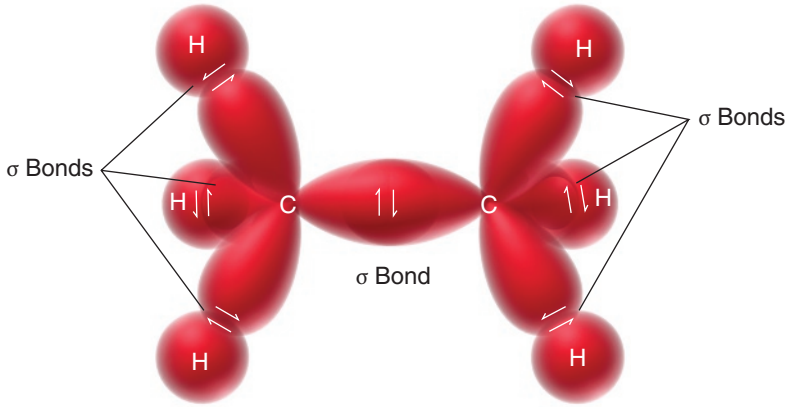
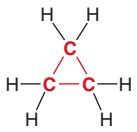


FIGURE 1.24
A valence bond picture of the bonding in ethane. Each carbon atom is sp^3 hybridized, and there are a total of seven sigma bonds.

CONCEPTUAL CHECKPOINT

1.16 Cyclopropane is a compound in which the carbon atoms form a three-membered ring:

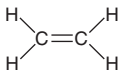


Cyclopropane

Each of the carbon atoms in cyclopropane is sp^3 hybridized. Cyclopropane is more reactive than other cyclic compounds (four-membered rings, five-membered rings, etc.). Analyze the bond angles in cyclopropane and explain why cyclopropane is so reactive.

Double Bonds and sp^2 Hybridization

Now let's consider the structure of a compound bearing a double bond. The simplest example is ethylene.



Ethylene

Ethylene exhibits a planar geometry (Figure 1.25). Once again, a satisfactory model for explaining this geometry can be achieved by the mathematical maneuver of hybridizing the *s* and *p* orbitals of the carbon atom to obtain hybrid atomic orbitals. When we did this procedure earlier to explain the bonding in methane, we hybridized the *s* orbital and all three *p* orbitals to produce four equivalent sp^3 hybrid orbitals. However, in the case of ethylene, each carbon atom only needs to form bonds with three atoms, not four. Therefore, each carbon atom only needs three hybrid orbitals. So in this case we will mathematically average the *s* orbital with only two of the three *p* orbitals (Figure 1.26). The remaining *p* orbital will remain unaffected by our mathematical procedure.

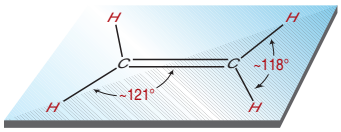


FIGURE 1.25
All six atoms of ethylene are in one plane.

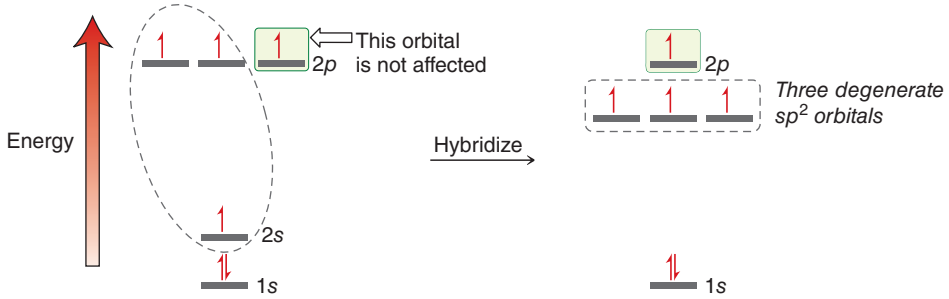


FIGURE 1.26
An energy diagram showing three degenerate sp^2 hybrid atomic orbitals.

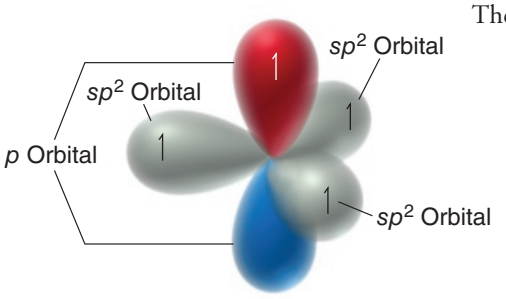


FIGURE 1.27
An illustration of an sp^2 hybridized carbon atom.

The result of this mathematical operation is a carbon atom with one p orbital and three ***sp*^{2} hybrid orbitals** (Figure 1.27). In Figure 1.27 the p orbital is shown in red and blue, and the hybrid orbitals are shown in gray (for clarity, only the front lobe of each hybrid orbital is shown). They are called sp^2 hybrid orbitals to indicate that they were obtained by averaging one s orbital and two p orbitals. As shown in Figure 1.27, each of the carbon atoms in ethylene is sp^2 hybridized, with three sp^2 hybrid orbitals arranged in a trigonal planar fashion and a p orbital that is orthogonal (perpendicular) to that plane.

Each carbon atom in ethylene has three sp^2 hybrid orbitals available to form σ bonds (Figure 1.28). One σ bond forms between the two carbon atoms, and then each carbon atom also forms a σ bond with each of its neighboring hydrogen atoms. In addition, each carbon atom has one p orbital (shown in Figure 1.28 with blue and red lobes).

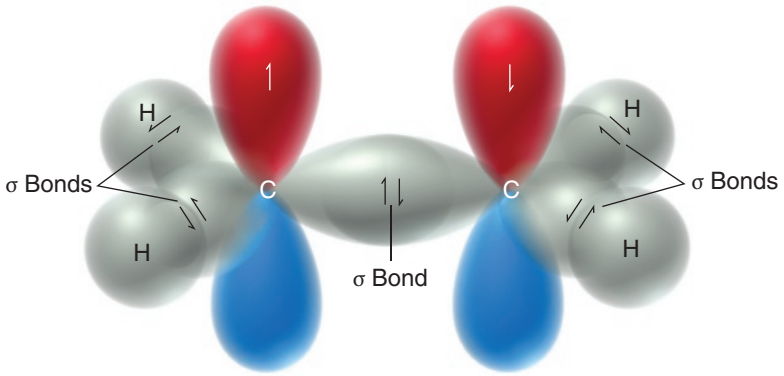


FIGURE 1.28
An illustration of the five σ bonds in ethylene.

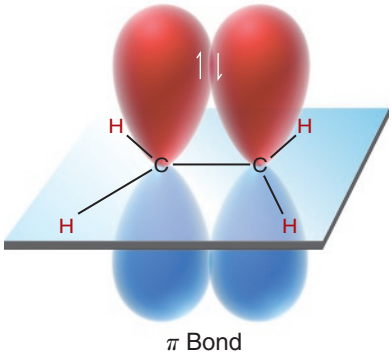


FIGURE 1.29
An illustration of the π bond in ethylene.

These p orbitals actually overlap with each other as well, which is a separate bonding interaction called a **pi (π) bond** (Figure 1.29). Although the π overlap occurs in two places—above the plane of the molecule (in red) and below the plane (in blue), these two regions of overlap represent only one interaction called a π bond.

The image of the π bond in Figure 1.29 is based on the valence bond approach (the p orbitals are simply drawn overlapping each other). Molecular orbital theory provides a fairly similar image of a π bond. Compare Figure 1.29 with the π bonding MO in Figure 1.30.

To summarize, we have seen that the carbon atoms of ethylene are connected via a σ bond and a π bond. The σ bond results from the overlap of sp^2 hybrid atomic orbitals, while the π bond results from the overlap of p orbitals. These two separate bonding interactions (σ and π) comprise the double bond of ethylene.

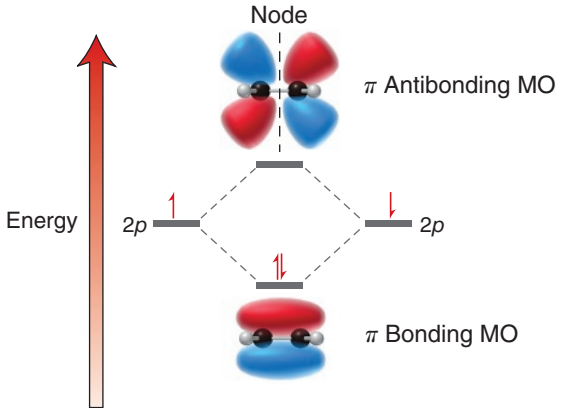
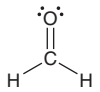


FIGURE 1.30
An energy diagram showing images of bonding and antibonding π molecular orbitals in ethylene.

CONCEPTUAL CHECKPOINT

1.17 Consider the structure of formaldehyde:

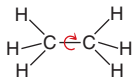


Formaldehyde

(a) Identify the type of bonds that form the C═O double bond.

(b) Identify the atomic orbitals that overlap to form each C—H bond.

1.18 Sigma bonds experience free rotation at room temperature:



In contrast, π bonds do not experience free rotation. Explain. (**Hint:** Compare Figures 1.24 and 1.29, focusing on the orbitals used in forming a σ bond and the orbitals used in forming a π bond. In each case, what happens to the orbital overlap during bond rotation?)

Triple Bonds and *sp* Hybridization

Now let's consider the bonding structure of a compound bearing a triple bond, such as acetylene:

H—C≡C—H

Acetylene

A triple bond is formed by ***sp* hybridized** carbon atoms. To achieve *sp* hybridization, one *s* orbital is mathematically averaged with only one *p* orbital (Figure 1.31). This leaves two *p* orbitals unaffected by the mathematical operation. As a result, an *sp* hybridized carbon atom has two *sp* hybrid orbitals and two unhybridized *p* orbitals (Figure 1.32).

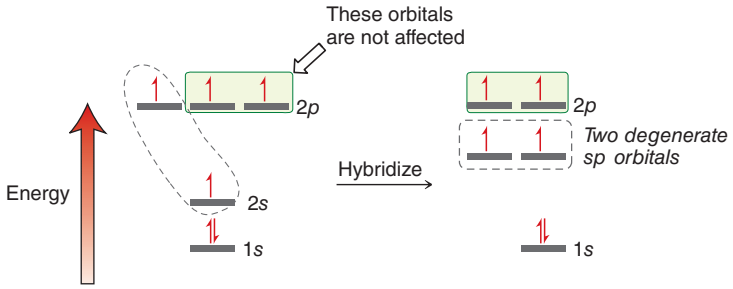


FIGURE 1.31
An energy diagram showing two degenerate *sp* hybrid atomic orbitals.

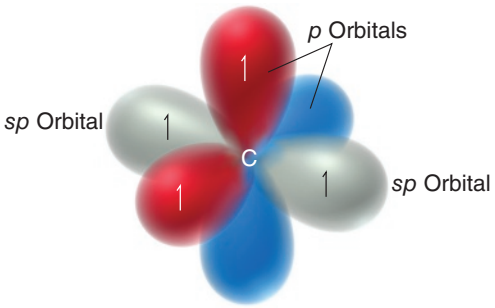


FIGURE 1.32
An illustration of an *sp*-hybridized carbon atom. The *sp* hybrid orbitals are shown in gray.

The two *sp* hybrid orbitals are available to form σ bonds (one on either side), and the two *p* orbitals are available to form π bonds, giving the bonding structure for acetylene shown in Figure 1.33. A triple bond between two carbon atoms is therefore the result of three separate bonding interactions: one σ bond and two π bonds. The σ bond results from the overlap of *sp* hybrid orbitals, while each of the two π bonds result from overlapping *p* orbitals. As shown in Figure 1.33, the geometry of the triple bond is linear.

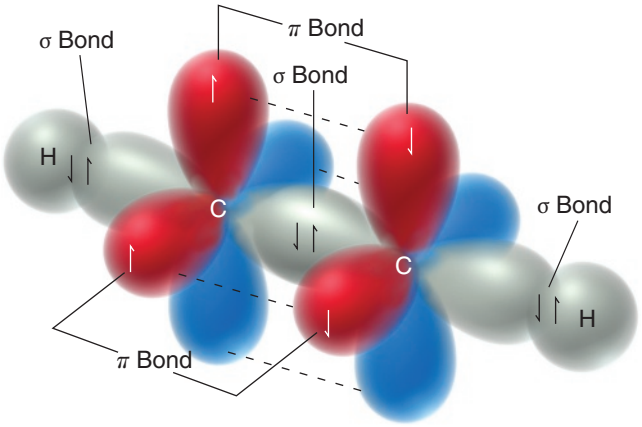
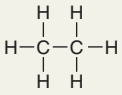
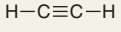


FIGURE 1.33
An illustration of the three σ bonds and two π bonds in acetylene.

Comparison of Hybridization States

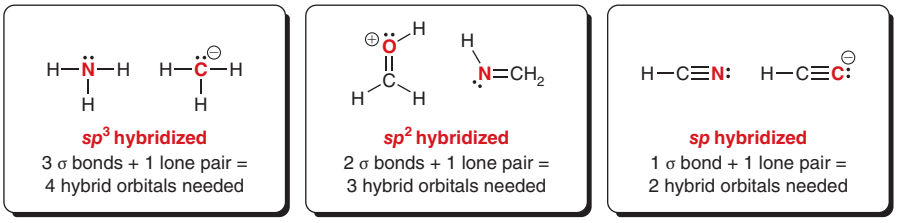
The atoms in organic compounds are joined together by σ bonds, and σ *bonds are formed by the overlap of hybrid orbitals*. As a result, the hybridization state of an uncharged carbon atom is dictated by the number of atoms to which it is attached. As summarized in Table 1.2, a carbon atom attached to four atoms has sp^3 hybridization, because an sp^3 hybridization state provides four hybrid orbitals to accommodate four σ bonds. A carbon atom attached to three atoms has three σ bonds, so it will be sp^2 hybridized. Finally, a carbon atom with two attached atoms will be *sp* hybridized.

TABLE 1.2 SUMMARY OF HYBRIDIZATION STATES

EXAMPLE TO ILLUSTRATE HYBRIDIZATION STATE	HYBRIDIZATION STATE	ORBITALS COMBINED				NUMBER OF RESULTING HYBRID ORBITALS
		s	*p*	*p*	*p*	
	sp^3	✔	✔	✔	✔	4
	sp^2	✔	✔	✔		3
	*sp*	✔	✔			2

It is helpful to note that the name of each hybridization state is directly related to the *number* of associated hybrid orbitals. Two *sp* hybrid orbitals are formed when two orbitals are combined (*s* and *p*), while three sp^2 hybrid orbitals are formed when three orbitals are combined (*s* and *p* and *p*), and four sp^3 hybrid orbitals are formed when four orbitals are combined (*s* orbital and all three *p* orbitals).

Hybrid orbitals are needed to form σ bonds, but they can also be used to accommodate lone pairs. To determine the hybridization of an atom bearing a lone pair of electrons, the lone pair is typically included when calculating the number of required hybrid orbitals. We will see many exceptions to this generalization, but shown below are some examples where we count the attached atoms (σ bonds) plus the lone pair to determine the number of required hybrid orbitals:



The s-Character of Hybrid Orbitals

The mathematical model of hybridization generates hybrid orbitals by "mixing" an *s* orbital with some number of *p* orbitals. Because the "recipe" for each hybrid orbital is different, there are differences between *sp*, sp^2 and sp^3 hybrid orbitals. These differences can be explained by using an analogy of mixing paint.

Let's use a can of red paint to represent an *s* orbital and a can of yellow paint for each *p* orbital. To envision the sp^3 hybridization state, which involves all four atomic orbitals (Table 1.2), we would

mix all four cans of paint. The result of the mixing is four hybrid cans of yellowish-orange paint (Figure 1.34):

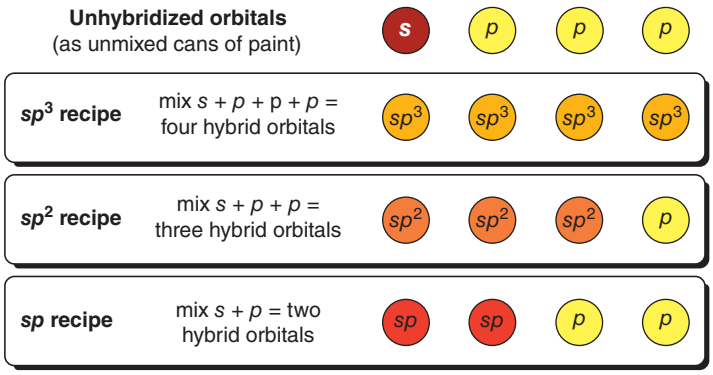


FIGURE 1.34
The mixing of cans of red and yellow paint can be used to illustrate hybridization states.

The "recipe" for sp^2 hybridization combines the can of *s* paint with only two of the *p* orbital paint cans. The sp^2 mixing also results in four cans of paint: three hybrid cans of orange paint, and one can of pure yellow paint. The third option, representing *sp* hybridization, is to mix only *two* of the original cans of paint (one red and one yellow), which produces two hybrid cans of reddish-orange paint and leaves two cans of yellow paint untouched.

The paint analogy illustrates two important features of hybridization: 1) In each case, the carbon atom starts out with four atomic orbitals, and it still has four atomic orbitals when hybridized; and 2) each type of hybrid orbital has different characteristics. By mixing paint in our analogy, we can see that each sp^3 hybrid can of paint has a lot of yellow character to it, because we used a lot of yellow paint to make it (three out of the four cans mixed). On the other hand, each *sp* hybrid can of paint has a much redder color. Compared to the other mixed cans, the *sp* paint more closely resembles the red paint, because the mixture is composed of 50% red paint (red was one out of the two cans that were combined).

We use similar language when we describe hybrid orbitals, by referring to how much a hybrid orbital resembles an *s* orbital. The **% s-character** describes the percentage of a hybrid orbital that was constructed from an *s* orbital. To construct the sp^3 orbitals, one s orbital was mathematically combined with three *p* orbitals. An *s* orbital was one out of the four combined orbitals (¼), so the sp^3 hybrid orbital is described as having 25% *s*-character (Figure 1.35). Likewise, sp^2 hybrid orbitals have 33% *s*-character, and *sp* hybrid orbitals have 50% *s*-character.

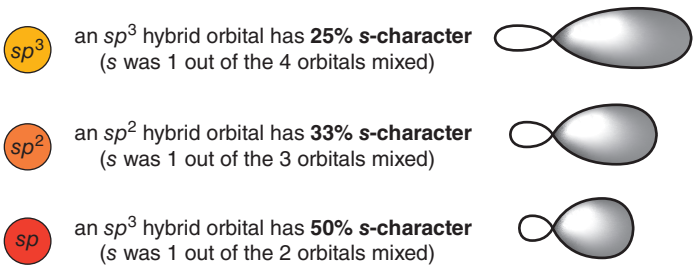


FIGURE 1.35
Just as cans of mixed paint have different colors, hybrid orbitals have different shapes.

Just like the different paint recipes resulted in different shades of orange, the varying percents of *s*-character impacts the extent to which a given hybrid orbital resembles the shape of an *s* orbital. All hybrid orbitals have two lobes (like a *p* orbital), but the greater the *s*-character, the more spherical the hybrid orbital. As a result, electrons in an *sp* hybrid orbital are held closer to the nucleus than electrons in an sp^3 hybrid orbital.

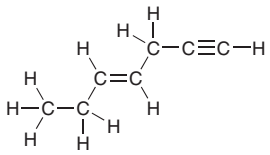
At times, predictions made using hybridization and valence bond theory are not consistent with all experimental observations. Like many scientific models, hybridization continues to be a subject of debate. However, hybridization is a very useful model that can help describe bonding and geometry. In the coming chapters, we will invoke hybridization states to explain additional properties of organic molecules.

SKILLBUILDER

1.6 IDENTIFYING HYBRIDIZATION STATES

LEARN the skill

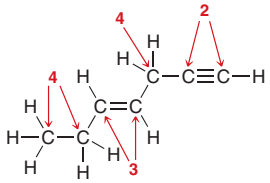
Identify the hybridization state of each carbon atom in the following compound:



SOLUTION

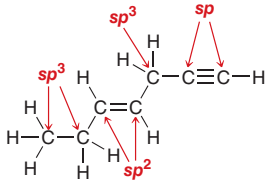
Determining the number of atoms attached to each carbon atom is the first step in identifying its hybridization state. Note that the number of attached atoms corresponds to the number of σ bonds around each carbon atom:

STEP 1
Determine the number of atoms attached to each carbon atom.



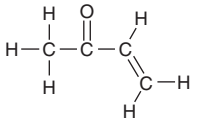
STEP 2
Determine the hybridization state of each carbon atom.

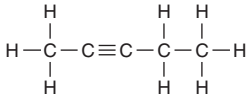
As described in Table 1.2, each carbon atom that is attached to four atoms requires four hybrid orbitals, so these carbon atoms must be sp^3 hybridized. Likewise, the carbon atoms with three σ bonds require sp^2 hybridization, and the carbon atoms with two attached atoms will be *sp* hybridized:

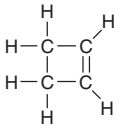


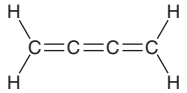
PRACTICE the skill

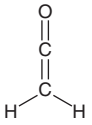
1.19 Determine the hybridization state of each carbon atom in the following compounds.


(a)


(b)


(c)

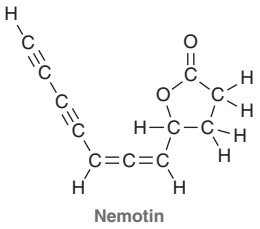

(d)


(e)

APPLY the skill

Organic compounds are isolated from a variety of sources (such as the mushroom pictured), and these *natural products* are then tested for biological activity.

1.20 Nemotin is a compound that was first isolated from the fungi *Poria tenuis* and *Poria corticola* in the 1940s and was shown to possess potent antibacterial activity. However, its structure was not verified until it was made in the laboratory much more recently.[8] Determine the hybridization state of each carbon atom in nemotin.



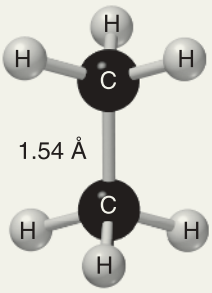
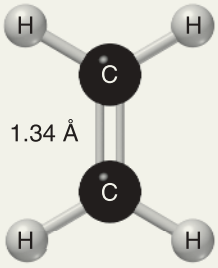
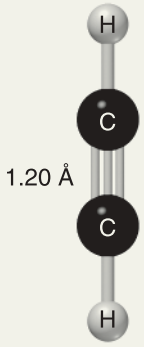
Nemotin

need more **PRACTICE?** **Try Problems 1.52, 1.53, 1.67, 1.73f, 1.73g, 1.74, 1.79a, 1.80b, 1.82a**

Bond Strength and Bond Length

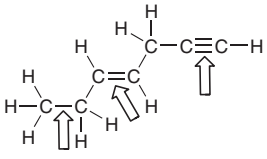
The information we have seen in this section allows us to compare single bonds, double bonds, and triple bonds. A single bond has only one bonding interaction (a σ bond), a double bond has two bonding interactions (one σ bond and one π bond), and a triple bond has three bonding interactions (one σ bond and two π bonds). Therefore, it is not surprising that a triple bond is stronger than a double bond, which in turn is stronger than a single bond. Compare the strengths and lengths of the C—C bonds in ethane, ethylene, and acetylene (Table 1.3).

TABLE 1.3 COMPARISON OF BOND LENGTHS AND BOND ENERGIES FOR ETHANE, ETHYLENE, AND ACETYLENE

	ETHANE	ETHYLENE	ACETYLENE
Structure			
C—C bond length	1.54 Å	1.34 Å	1.20 Å
Bond energy	368 kJ/mol	632 kJ/mol	820 kJ/mol

CONCEPTUAL CHECKPOINT

1.21 Rank the indicated bonds in terms of increasing bond length:



1.11 Predicting Molecular Geometry: VSEPR Theory

The shapes of small molecules can often be predicted if we presume that all electron pairs (whether bonding or nonbonding) repel each other, and as such, they arrange themselves in three-dimensional space so as to achieve maximal distance from each other. This approach, called **valence shell electron pair repulsion (VSEPR)** theory, enables us to make quick predictions about molecular geometry. In this section, we will encounter several different molecular shapes for small molecules, all of which are predicted accurately using the VSEPR model.

Tetrahedral Geometry

We begin our analysis with methane (CH_4), in which the carbon atom has four σ bonds and no lone pairs. VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting a **tetrahedral** arrangement. That is, the VSEPR model predicts that the four hydrogen atoms should be positioned at the four corners of a tetrahedron (Figure 1.36a). This prediction is consistent with sp^3 hybridization, as described by valence bond theory (Section 1.10), and it is also consistent with the observed bond angles of 109.5° (Figure 1.36b).

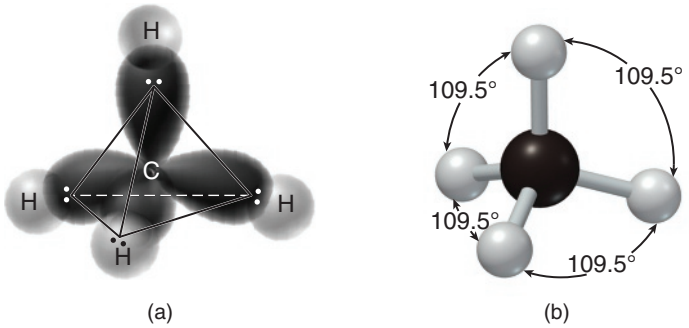


FIGURE 1.36
(a) The tetrahedral arrangement of electron pairs in CH_4.
(b) All bond angles in CH_4 are 109.5°.

Trigonal Pyramidal Geometry

Now let's apply the VSEPR model to ammonia (NH_3), in which the nitrogen atom has three σ bonds and one lone pair. The total number of bonded atoms and lone pairs, also called the **steric number**, is four in this case (as it was in the previous case as well). VSEPR theory presumes that all four regions of electron density will be positioned so as to achieve maximal distance from each other, suggesting once again a tetrahedral arrangement (Figure 1.37a). However, in this case, a lone pair is positioned at one corner of the tetrahedron. This predicted arrangement is observed to be accurate, and it is consistent with the valence bond approach, in which the nitrogen atom is sp^3 hybridized, and the lone pair occupies an sp^3 hybrid orbital. Note that the bonds in Figure 1.37b are drawn in different ways to show three-dimensionality. The wedge represents a bond that is projecting out of the page (toward you), and the dashed line represents a bond that is behind the page (pointing away from you). We will be using these conventions of wedged and dashed bonds throughout the coming chapters to represent 3D structures.

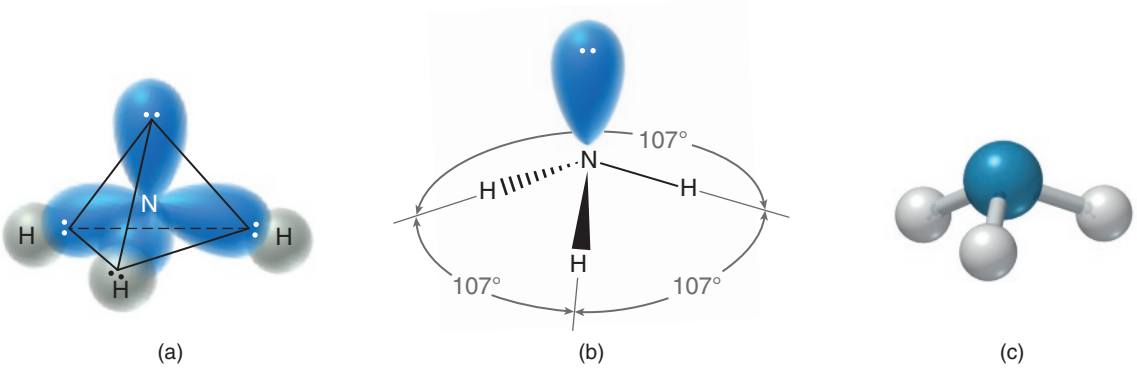


FIGURE 1.37
(a) The tetrahedral arrangement of electron pairs in NH_3.
(b) All bond angles in NH_3 are approximately 107°.
(c) NH_3 has trigonal pyramidal geometry.

As illustrated in Figure 1.37b, the bond angles for ammonia are observed to be 107°, rather than 109.5°. This shorter bond angle can be justified by VSEPR theory if we presume that lone pairs repel more strongly than σ bonds. Lone pair electrons are not bound between two nuclei, so they occupy more space than bonding electron pairs, causing the H—N—H bond angle to be less than 109.5°.

When we describe the geometry (or shape) of a molecule, we are referring to the arrangement *of atoms*. When we focus only on the positions of the atoms (ignoring the lone pair), the shape of ammonia is **trigonal pyramidal** (Figure 1.37c). "Trigonal" indicates the nitrogen atom is connected to three other atoms, and "pyramidal" indicates the compound is shaped like a pyramid, with the nitrogen atom sitting at the top of the pyramid.

Bent Geometry

Now let's apply the VSEPR model to water (H_2O), in which the oxygen atom has two σ bonds and two lone pairs. With a total of four regions of electron density to consider (2 atoms + 2 lone pairs = a steric number of 4), VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting once again a tetrahedral arrangement (Figure 1.38a). Notice that the VSEPR model predicts that the lone pairs should be positioned at two corners of the tetrahedral arrangement.

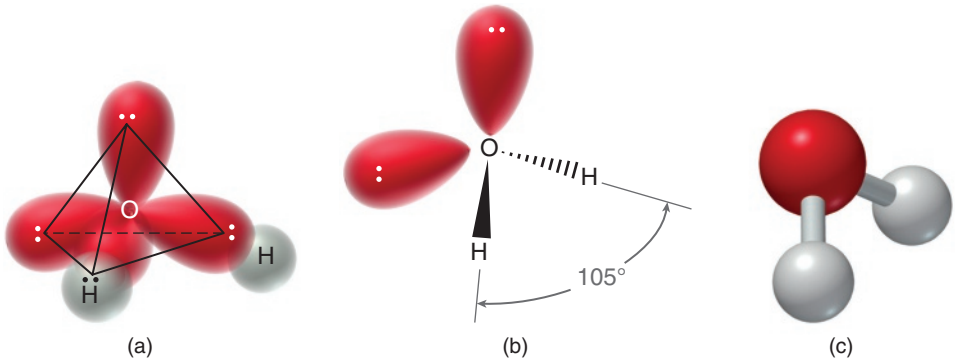
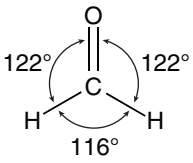


FIGURE 1.38
(a) The tetrahedral arrangement of electron pairs in H_2O, as predicted by VSEPR.
(b) The bond angle in H_2O is approximately 105°.
(c) H_2O has bent geometry.

Once again, VSEPR theory can explain the observed bond angle (105°) by considering the effect of two lone pairs (Figure 1.38b). Specifically, the lone pairs repel each other more strongly than σ bonds, causing the H—O—H bond angle to be even smaller than the bond angles in ammonia. In order to describe the geometry of H_2O, we focus on the arrangement of atoms, which gives a **bent** geometry (Figure 1.38c).

This analysis demonstrates that the VSEPR model correctly predicts the bent geometry of water, and the observed bond angle is even justified. However, VSEPR theory also predicts that the two lone pairs of H_2O should be at two corners of a tetrahedron and degenerate (the same energy), but this has proven to be false. Experiments conducted over 30 years ago strongly suggest that at least one lone pair occupies a *p* orbital, while the other lone pair occupies a lower-energy, hybrid orbital. Since one lone pair occupies a *p* orbital, the oxygen atom cannot be sp^3 hybridized, as would be predicted from a classical interpretation of valence bond theory and VSEPR theory. The VSEPR model fails in this case, because it assumes that steric repulsion of electrons is the only factor that determines electronic and molecular structures, but there are often additional relevant factors. Although VSEPR theory has correctly predicted the bent geometry of H_2O, it appears to have done so for the wrong reasons. This example illustrates that VSEPR is just a first approximation. It is just a model, incomplete and flawed (as most simple models are), but it is nevertheless useful, because it can be used to predict the molecular geometry of most small molecules with reasonable accuracy.

Thus far, we have seen three different molecular shapes: tetrahedral, trigonal pyramidal, and bent. We will now explore other common molecular shapes that are accurately predicted with VSEPR theory.



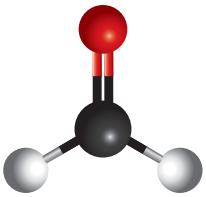


FIGURE 1.39
Formaldehyde has trigonal planar geometry, with bond angles of ~120°.

Trigonal Planar Geometry

Consider the structure of formaldehyde, O=CH_2. The carbon atom has three attached atoms (three sigma bonds), so three hybrid orbitals are needed. Applying valence bond theory, we expect the carbon atom to be sp^2 hybridized (with three sp^2 hybrid orbitals and one p orbital that is being used to form a pi bond to oxygen). As we saw in Section 1.10, sp^2 hybridization is associated with **trigonal planar** geometry, in which all bond angles are approximately 120° (Figure 1.39). The term "trigonal" indicates that the carbon atom is connected to three other atoms, and the term "planar" indicates that all atoms lie in the same plane.

Once again, the VSEPR model correctly predicts the trigonal planar geometry of formaldehyde. There are three electron pairs that are repelling each other (steric number = 3), and they are expected to position themselves in space so as to achieve maximal separation. This is only accomplished in a trigonal planar arrangement, with bond angles of approximately 120°, as observed.

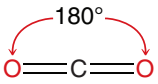


FIGURE 1.40
CO_2 has linear geometry, with a bond angle of 180°.

Linear Geometry

Consider the structure of CO_2. The carbon atom in carbon dioxide is attached to two atoms. The presence of two sigma bonds (and no lone pairs) indicates sp hybridization. Recall (Section 1.10) that sp hybridization is associated with **linear geometry** (Figure 1.40).
Once again, the VSEPR model correctly predicts the linear geometry of CO_2. There are two double bonds that are repelling each other (2 atoms and no lone pairs gives a steric number of 2), and they are expected to position themselves in space so as to achieve maximal separation. This is only accomplished in a linear arrangement, with a bond angle of 180°.

In summary, we have encountered five different molecular shapes, all of which are listed in Table 1.4.

TABLE 1.4 COMMON MOLECULAR SHAPES THAT CAN BE PREDICTED WITH VSEPR THEORY

EXAMPLE	ATTACHED ATOMS (σ BONDS)	NONBONDING ELECTRON PAIRS (LONE PAIRS)	STERIC NUMBER	PREDICTED ARRANGEMENT OF ELECTRON PAIRS	PREDICTED MOLECULAR GEOMETRY
CH_4	4	0	4	Tetrahedral	Tetrahedral
NH_3	3	1	4	Tetrahedral	Trigonal Pyramidal
H_2O	2	2	4	Tetrahedral	Bent
O=CH_2	3	0	3	Trigonal Planar	Trigonal Planar
CO_2	2	0	2	Linear	Linear

SKILLBUILDER

1.7 PREDICTING GEOMETRY

LEARN the skill

Using VSEPR theory, predict the geometry of a hydronium ion (H_3O^+):

SOLUTION

STEP 1
Determine the steric number.

We begin by counting the number of attached atoms and lone pairs on the oxygen atom. There are three atoms and one lone pair, giving a total of four regions of electron density around the oxygen atom (steric number = 4).

STEP 2
Identify the arrangement of electron pairs.

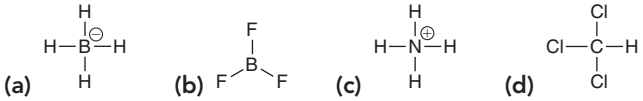
Next, identify the arrangement of the electron pairs in 3D space. According to VSEPR theory, we presume that all electron pairs will be positioned so as to achieve maximal distance from one another. With a steric number of 4, VSEPR theory predicts a tetrahedral arrangement of electron pairs.

STEP 3
Identify the geometry.

PRACTICE the skill

Recall that the geometry refers to the arrangement of the atoms only. In this case, a lone pair occupies one corner of the tetrahedron, giving rise to trigonal pyramidal geometry (just like NH_3).

1.22 Use VSEPR theory to predict the geometry for each of the following structures:



1.23 Compare the structures of a carbocation and a carbanion:

In one of these ions, the central carbon atom is trigonal planar, while the other is trigonal pyramidal. Using VSEPR theory, assign the correct geometry to each ion.

1.24 Ammonia (NH_3) will react with a strong acid, such as hydronium (H_3O^+), to give an ammonium ion, as shown below. This type of process is an acid-base reaction, which will be the topic of Chapter 3. Using VSEPR theory, determine whether you expect a change in bond angles when ammonia is converted into an ammonium ion. Explain.

APPLY the skill

1.25 When sand is coated with a layer of trimethylhydroxysilane, $(CH_3)_3SiOH$, it repels water and can no longer get wet. Hydrophobic sand (aka, magic sand) is fun to play with, but it can also have useful applications in agriculture to reduce water consumption.[9] Predict the geometry for the silicon atom in trimethylhydroxysilane.

The hydrophobic polymer coating on "magic sand" keeps it dry, even when submerged in water.

need more **PRACTICE?** **Try Problems 1.37, 1.45, 1.52, 1.53, 1.55, 1.63, 1.68, 1.73b, 1.77c, 1.77f, 1.79b, 1.80b, 1.81c, 1.82b, 1.82c**

1.12 Dipole Moments and Molecular Polarity

Recall that induction is caused by the presence of an electronegative atom, as we saw earlier in the case of chloromethane. In Figure 1.41a the arrow shows the inductive effect of the chlorine atom. Figure 1.41b is a map of the electron density, revealing that the molecule is polarized. Chloromethane is said to exhibit a dipole moment, because *the center of negative charge and the center of positive charge are separated from one another by a certain distance*. The **dipole moment** (μ) is used as an indicator of polarity, where μ is defined as the amount of partial charge (δ) on either end of the dipole multiplied by the distance of separation (d):

$$\mu = \delta \times d$$

Partial charges ($\delta+$ and $\delta-$) are given in electrostatic units (esu), and the distances are given in centimeters. The resulting dipole moments are extremely small numbers, so it is more convenient to report dipole moments with a new unit, called a **debye (D)**, where

$$1 \text{ debye} = 10^{-18} \text{ esu} \cdot \text{cm}$$

Using these units, the dipole moment of chloromethane is reported as 1.87 D. The debye unit is named after Dutch scientist Peter Debye, whose contributions to the fields of chemistry and physics earned him a Nobel Prize in 1936.

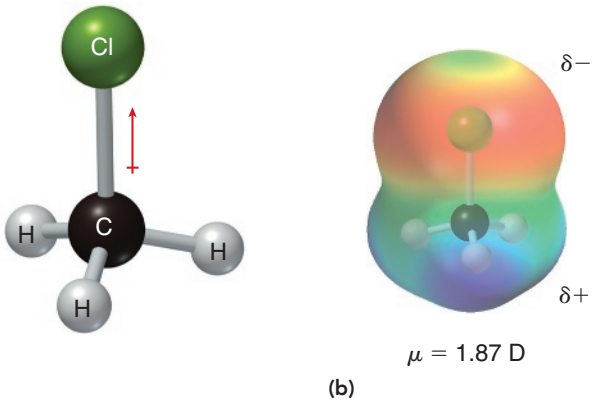


FIGURE 1.41
(a) Ball-and-stick model of chloromethane showing the dipole moment.
(b) An electrostatic potential map of chloromethane.

Chloromethane is a simple example, because it has only one polar bond. When dealing with a compound that has more than one polar bond, it is necessary to take the vector sum of the individual dipole moments. The vector sum is called the **molecular dipole moment**, and it takes into account both the magnitude and the direction of each individual dipole moment. For example, consider the structure of dichloromethane (Figure 1.42). Note that the tetrahedral shape is indicated by the given drawing: the wedge represents a hydrogen atom coming out of the page, and the dash represents a hydrogen atom behind the page. The individual dipole moments partially cancel, but not completely. The vector sum produces a dipole moment of 1.14 D, which is significantly smaller than the dipole moment of chloromethane because the two dipole moments here partially cancel each other.

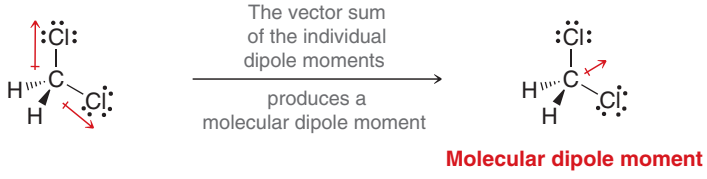


FIGURE 1.42
The molecular dipole moment of dichloromethane is the net sum of all dipole moments in the compound.

The presence of a lone pair has a significant effect on the molecular dipole moment. The two electrons of a lone pair are balanced by two positive charges in the nucleus, but the lone pair is separated from the nucleus by some distance. There is, therefore, a dipole moment associated with every lone pair. A common example is ammonia (Figure 1.43). In this way, the lone pair contributes significantly to the magnitude of the molecular dipole moment, although its direction is not altered. That is, the direction of the molecular dipole moment would be the same with or without the contribution of the lone pair.

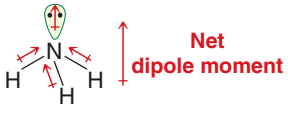


FIGURE 1.43
The net dipole moment of ammonia.

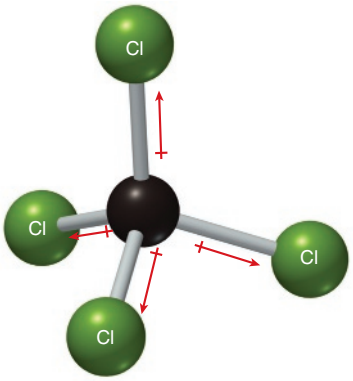
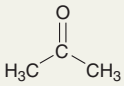


FIGURE 1.44
A ball-and-stick model of carbon tetrachloride. The individual dipole moments cancel to give a zero net dipole moment.

Table 1.5 shows experimentally observed molecular dipole moments for several common solvents. Notice that carbon tetrachloride (CCl_4) has no molecular dipole moment. In this case, the individual dipole moments cancel each other completely to give the molecule a zero net dipole moment ($\mu = 0$). This example (Figure 1.44) demonstrates that we must take geometry into account when assessing molecular dipole moments.

TABLE 1.5 DIPOLE MOMENTS FOR SOME COMMON SOLVENTS (AT 20°C)

COMPOUND	STRUCTURE	DIPOLE MOMENT	COMPOUND	STRUCTURE	DIPOLE MOMENT
Acetone		2.69 D	Ammonia	NH_3	1.47 D
Chloromethane	CH_3Cl	1.87 D	Diethyl ether	$CH_3CH_2OCH_2CH_3$	1.15 D
Water	H_2O	1.85 D	Methylene chloride	CH_2Cl_2	1.14 D
Methanol	CH_3OH	1.69 D	Pentane	$CH_3CH_2CH_2CH_2CH_3$	0 D
Ethanol	CH_3CH_2OH	1.66 D	Carbon tetrachloride	CCl_4	0 D

SKILLBUILDER

1.8 IDENTIFYING MOLECULAR DIPOLE MOMENTS

LEARN the skill

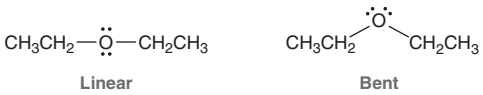
Identify whether each of the following compounds exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment:

(a) $CH_3CH_2OCH_2CH_3$ **(b)** CO_2

SOLUTION

(a) This molecule has two polar C—O bonds that can contribute to a molecular dipole moment. In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. Specifically, we need to know if the geometry around the oxygen atom is linear or bent:

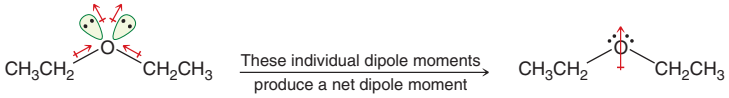
STEP 1
Predict the molecular geometry.



To make this determination, we use the method described in the previous SkillBuilder. The oxygen atom has two σ bonds and two lone pairs, so the steric number is 4. Since there are two lone pairs, VSEPR theory predicts bent geometry.

After determining the molecular geometry, now draw all dipole moments and determine whether they cancel each other. In this case, they do not fully cancel each other:

STEP 2
Identify the direction of all dipole moments.

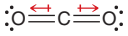


STEP 3
Draw the net dipole moment.

This compound does in fact have a net molecular dipole moment, and the direction of the moment is shown above.

(b) Carbon dioxide (CO_2) has two C═O bonds, each of which exhibits a dipole moment. In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. Once again, we use the method described in the previous SkillBuilder. The carbon atom has two attached atoms and no lone pairs, so

the steric number is two. Accordingly, VSEPR theory predicts linear geometry. Therefore, we expect the dipole moments to fully cancel each other:



In a similar way, the dipole moments associated with the lone pairs also cancel each other, and therefore CO_2 does not have a net molecular dipole moment.

PRACTICE the skill

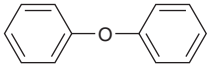
1.26 Identify whether each of the following compounds exhibits a molecular dipole moment. For compounds that do, indicate the direction of the net molecular dipole moment:

(a) $CHCl_3$ **(b)** CH_3OCH_3 **(c)** NH_3 **(d)** CCl_2Br_2

APPLY the skill

Tomatoes are a good source of vitamin C, and volatile organic compounds give rise to their aroma.

1.27 Volatile organic compounds (VOCs) contribute to the aroma of plants and can also be used for communication between plants. Diphenyl ether was identified as a minor VOC found in tomato plants.[10] Identify whether diphenyl ether exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment.



Diphenyl ether

need more **PRACTICE?** **Try Problems 1.34, 1.36, 1.39, 1.58–1.60, 1.75, 1.76**

1.13 Intermolecular Forces and Physical Properties

The physical properties of a compound are determined by the attractive forces between the individual molecules, called **intermolecular forces**. It is often difficult to use the molecular structure alone to predict a precise melting point or boiling point for a compound. However, a few simple trends will allow us to compare compounds to each other in a relative way, for example, to predict which compound will boil at a higher temperature.

All intermolecular forces are *electrostatic*—that is, these forces occur as a result of the attraction between opposite charges. The electrostatic interactions for neutral molecules (with no formal charges) are often classified as (1) **dipole-dipole interactions**, (2) hydrogen bonding, and (3) fleeting dipole-dipole interactions.

Dipole-Dipole Interactions

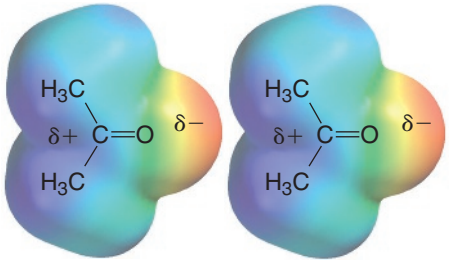
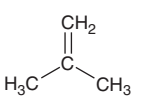


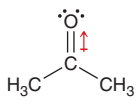
FIGURE 1.45
In the liquid state, the dipole moments in nearby molecules experience attractive forces.

Compounds with net dipole moments can act like magnets, either attracting or repelling each other, depending on how they approach each other in space. Molecules in the liquid phase are free to tumble, but they do tend to move in such a way so as to attract each other more often than they repel each other (Figure 1.45).

The resulting net attraction between the molecules results in an elevated boiling point. To illustrate this, compare the physical properties of isobutylene and acetone:



Isobutylene
Melting point = −140.3°C
Boiling point = −6.9°C



Acetone
Melting point = −94.9°C
Boiling point = 56.3°C

Isobutylene lacks a significant dipole moment, but acetone does have a strong net dipole moment. Therefore, acetone molecules will experience greater attractive interactions than isobutylene molecules. As a result, acetone has a higher boiling point than isobutylene. Predicting relative melting points is complicated, because molecular shape contributes to the efficiency of crystal packing, but in this case we can see that the more polar molecule also has a higher melting point.

Hydrogen Bonding

When a hydrogen atom is connected to a highly electronegative atom (O, N, or F), the hydrogen atom will bear a significant partial positive charge (δ+). This δ+ can then interact with a lone pair from an electronegative atom of another molecule or ion. The attractive interaction is so strong that a dashed line is used to represent the **hydrogen bond**—a significant link between the *hydrogen bond donor* (the molecule with an O—H or N—H group) and the *hydrogen bond acceptor* (the molecule with the lone pair). Figure 1.46 illustrates hydrogen bonding in both water and ammonia.

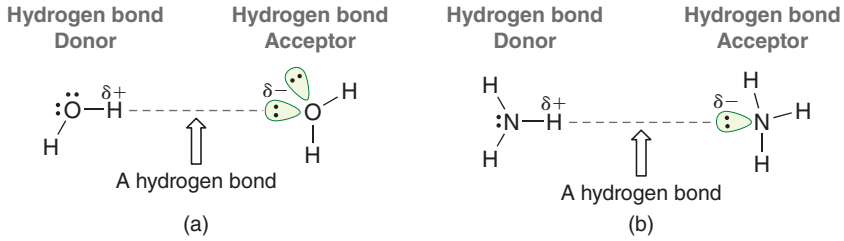


FIGURE 1.46
(a) Hydrogen bonding between molecules of water. **(b)** Hydrogen bonding between molecules of ammonia.

This attractive interaction is common among compounds that have an O—H bond or an N—H bond. For example, ethanol (CH_3CH_2OH) has an O—H bond, so it is also capable of forming hydrogen bonds (Figure 1.47).

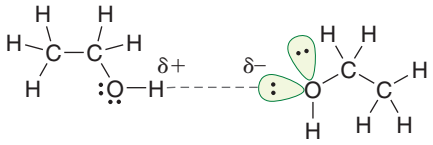
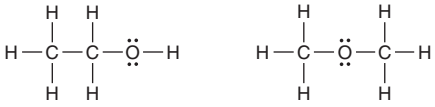


FIGURE 1.47
Hydrogen bonding between molecules of ethanol.

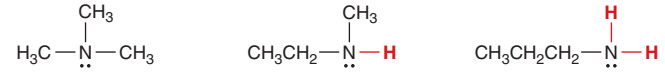
This type of interaction is quite strong because hydrogen is a relatively small atom, and as a result, the partial charges can get very close to each other. In fact, the effect of hydrogen bonding on physical properties is quite dramatic. In Section 1.2, we briefly mentioned the difference in properties between the following two constitutional isomers:



Ethanol
Boiling point = 78.4°C

Methoxymethane
Boiling point = −23°C

These compounds have the same molecular formula, but they have very different boiling points. Because the OH group in ethanol acts as both a hydrogen bond donor and a hydrogen bond acceptor, ethanol experiences intermolecular hydrogen bonding, giving rise to a very high boiling point. Methoxymethane, on the other hand, has no OH group, and therefore lacks a hydrogen bond donor (it has no δ+ hydrogen atom). As a result, methoxymethane cannot form hydrogen bonds between molecules, giving rise to a significantly lower boiling point. A similar trend can be seen in a comparison of the following isomeric amines:



Trimethylamine
Boiling point = 3.5°C

Ethylmethylamine
Boiling point = 37°C

Propylamine
Boiling point = 49°C

Once again, all three compounds have the same molecular formula (C_3H_9N), but they have very different properties as a result of hydrogen bonding. Trimethylamine, lacking a δ+ hydrogen atom directly attached to the nitrogen atom, does not exhibit any hydrogen bonding and has a relatively low boiling point. Ethylmethylamine does exhibit hydrogen bonding and therefore has a higher boiling point. Finally, propylamine, which has two N—H bonds and therefore exhibits even more hydrogen-bonding interactions, has the highest boiling point of the three compounds.

Hydrogen bonding is incredibly important in determining the shapes and interactions of biologically important compounds. Chapter 25 will focus on proteins, which are long molecules that coil up and fold into specific shapes that maximize intramolecular hydrogen bonding. These shapes ultimately determine the biological function of proteins. Similarly, hydrogen bonds hold together individual strands of DNA to form the familiar double-helix structure (Figure 1.48).

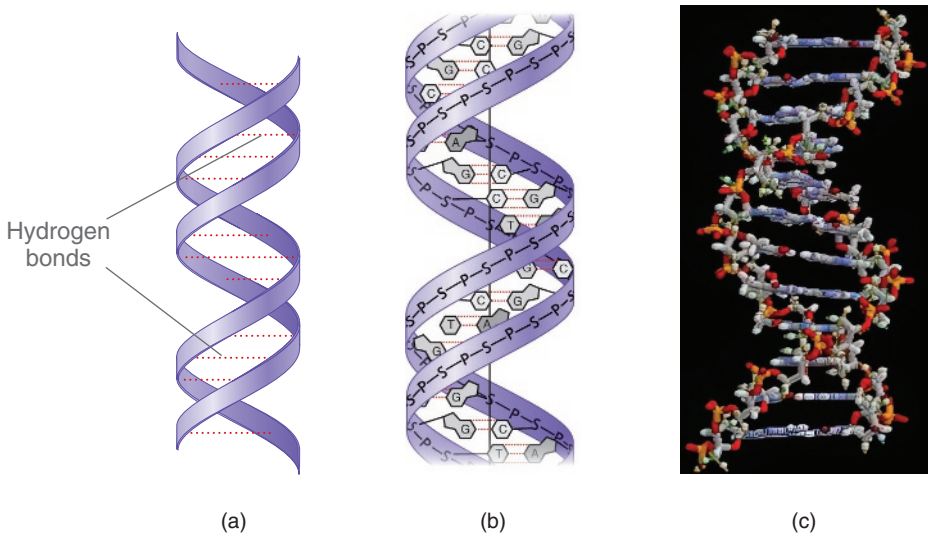


FIGURE 1.48
(a) The double helix in DNA, with hydrogen bonds connecting the two strands. (b) DNA image showing the individual base pairs that undergo hydrogen bonding. (c) Stick model of DNA illustrates "rungs" of the ladder formed by base pairs.

Each strand (illustrated as purple ribbons in Figure 1.48a and 1.48b) encodes genetic data that is "spelled out" by a specific sequence of four nucleotide bases—adenine (A), guanine (G), cytosine (C), and thymine (T)—that are attached to a sugar-phosphate backbone (Fig. 1.49). Compared to the English language this is a very small alphabet, but these letters are used to spell a code that is millions of letters long!

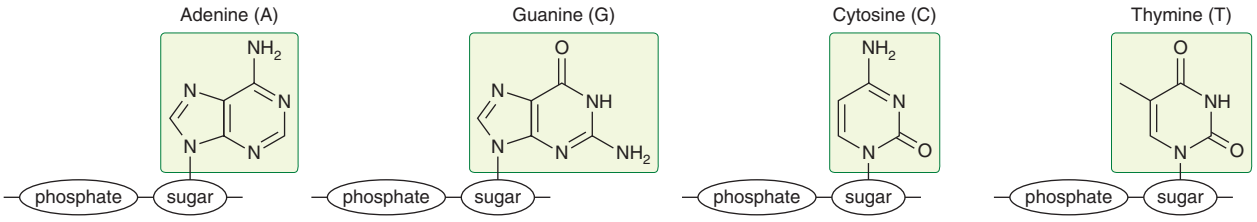


FIGURE 1.49
The four bases that make up the genetic code stored in DNA. The base-sugar-phosphate unit is called a nucleotide.

Each strand of DNA is paired with a second strand that has a complementary sequence—every adenine on one strand will align with a thymine on the other strand (described as an A—T base pair), and each guanine residue matches up with cytosine (a G—C base pair). As illustrated in Figure 1.50, the molecular structures of the complementary bases are perfectly aligned to match a hydrogen bond donor with a hydrogen bond acceptor, with each base pair making up a "rung" of the DNA ladder.

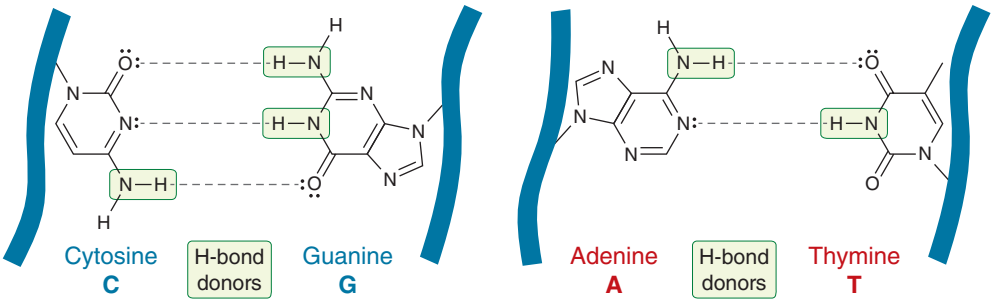


FIGURE 1.50
The hydrogen-bonding interactions that exist between complementary base pairs in DNA.

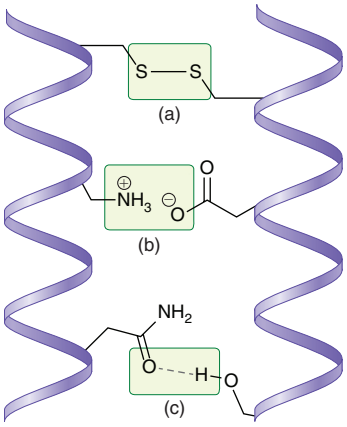
It is important to point out that the term "hydrogen bonding" is somewhat misleading. A hydrogen bond is not actually a "bond" but rather, it is a type of attractive interaction. To illustrate this, compare the energy of a covalent bond with the energy of a hydrogen-bonding interaction. A typical single bond (C—H, N—H, O—H) has a bond strength of approximately 400 kJ/mol. In contrast, a hydrogen-bonding interaction has an average strength of approximately 20 kJ/mol. This leaves us with the obvious question: Why do we call them hydrogen bonds instead of just hydrogen interactions? To answer this question, consider the double-helix structure of DNA (Figure 1.46). The two strands are joined by hydrogen-bonding interactions that function like rungs of a very long, twisted ladder. The net sum of these interactions contributes to the structure of the double helix, in which the hydrogen-bonding interactions appear as if they were actually bonds. Nevertheless, it is relatively easy to "unzip" the double helix and retrieve the individual strands. The structure of DNA is explored in more detail in Section 24.9.

BioLinks Hydrogen Bonding and Bad Hair Days

Wavy or straight or kinky or curly—each person has a certain type of hair as it grows naturally. And naturally, it's human nature for people with straight hair to wish it was curly, and for people with curls to prefer straight hair. Heat or water can be used to style hair, but sometimes it feels like hair has a mind of its own! Perhaps if we learn about some of the chemistry involved, we might have a better chance of avoiding bad hair days.

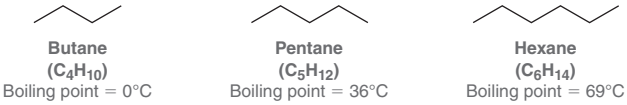
Hair fibers are made from long strands of α-keratin, a protein that has a shape like a coiled spring (called an α-helix). These long molecules are twisted together to make microscopically thin strands, which are then twisted together to make thicker filaments, and so on. Building the structure of a hair fiber is like intertwining threads to make a string, and then braiding the strings together to make a thick rope. The strands of keratin are held together with a variety of bonding and nonbonding interactions, as illustrated with two strands in the given figure. One of the strongest and most significant structural features is called a disulfide bond **(a)**, a covalent bond between two sulfur atoms that creates a connection between two keratin strands. The resulting cross-link provides stability to the keratin structure and contributes to the curl of the hair fiber. Many of the side chain groups in the keratin protein are charged, so ion-ion attractions described as salt bridges **(b)** are also present. The most frequently occurring links between keratin strands are hydrogen bonds **(c)**.

In order to add curls to straight hair, or to straighten curly hair, these intermolecular interactions must be disrupted. Chemical treatments, such as relaxers, straighteners and "perms" cleave the covalent S–S bonds and then rebuild new disulfide bridges after the hair is repositioned. Such changes are *permanent* and will not be undone by hair washing. Other methods for styling hair, such as setting wet hair in curlers and letting it dry, or using the heat of a curling iron or a flat iron, are *temporary*. Covalent disulfide bonds are not broken by heat or water, so adding heat or water does not permanently alter the molecular structure of keratin. Hydrogen bonds, on the other hand, *will* be disrupted with heat or by wetting hair, and after the hair is manipulated into a different shape and allowed to cool/dry, new hydrogen bonds will form to keep the hair fibers in the new position. The temporary nature of these styling methods becomes apparent when the hair is washed, and the style is completely undone. But sometimes when you try to style your hair, it doesn't hold throughout the day. You may have noticed that a hairstyle is likely to be especially fleeting on a rainy or humid day. Why is this so? Because the water molecules in the air will displace all the hydrogen bonds that were so carefully positioned between the strands of keratin. This causes your hair to revert to its natural state: curls will flatten out and straightened hair will become frizzy. Now that you have some expertise in hair structure and hydrogen bonding, you can avoid future frustration on rainy days by skipping the styling and instead tying your hair back or wearing a hat.



London Dispersion Forces

Some compounds have no permanent dipole moments, and yet analysis of boiling points indicates that they must have fairly strong intermolecular attractions. To illustrate this point, consider the following compounds:



Butane (C_4H_{10})
Boiling point = 0°C

Pentane (C_5H_{12})
Boiling point = 36°C

Hexane (C_6H_{14})
Boiling point = 69°C

These three compounds are hydrocarbons, compounds that contain only carbon and hydrogen atoms. If we compare the properties of the hydrocarbons above, an important trend becomes apparent. Specifically, the boiling point appears to increase with increasing molecular weight. This trend can be justified by considering the fleeting, or transient, dipole moments that are more prevalent in larger molecules. To understand the source of these temporary dipole moments, we consider the electrons to be in constant motion, and therefore, the center of negative charge is also constantly moving around within the molecule. On average, the center of negative charge coincides with the center of positive charge, resulting in a zero dipole moment. However, at any given instant, the center of negative charge and the center of positive charge might not coincide. The resulting transient dipole moment can then induce a separate transient dipole moment in a neighboring molecule, initiating a fleeting attraction between the two molecules (Figure 1.51). These attractive forces are called **London dispersion forces,** named after German-American physicist Fritz London. Large molecules have more surface area than smaller molecules and therefore experience these attractive forces to a larger extent.

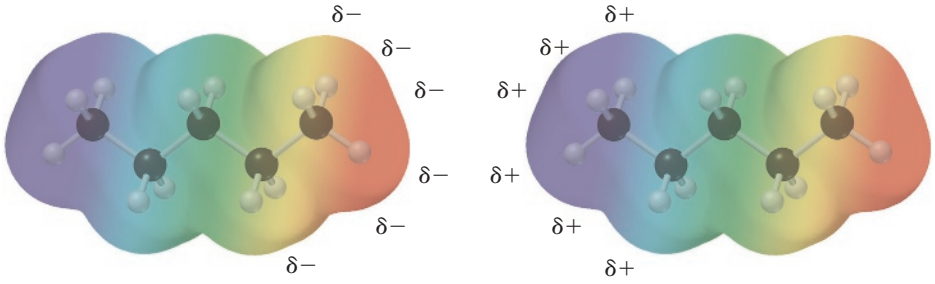


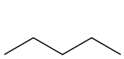
FIGURE 1.51
The fleeting attractive forces between two molecules of pentane.

London dispersion forces are stronger for higher molecular weight compounds because they have larger surface areas that can accommodate more interactions. As a result, compounds of higher molecular weight will generally boil at higher temperatures. Table 1.6 illustrates this trend.

TABLE 1.6 BOILING POINTS FOR HYDROCARBONS OF INCREASING MOLECULAR WEIGHT

STRUCTURE		BOILING POINT (°C)	STRUCTURE		BOILING POINT (°C)
CH_4	(CH_4)	−164		(C_6H_{14})	69
CH_3CH_3	(C_2H_6)	−89		(C_7H_{16})	98
$CH_3CH_2CH_3$	(C_3H_8)	−42		(C_8H_{18})	126
$CH_3CH_2CH_2CH_3$	(C_4H_{10})	0		(C_9H_{20})	151
$CH_3CH_2CH_2CH_2CH_3$	(C_5H_{12})	36		($C_{10}H_{22}$)	174

A branched hydrocarbon has a smaller surface area than its corresponding straight-chain isomer, and therefore, branching causes a decrease in boiling point. This trend can be seen by comparing the following constitutional isomers of C_5H_{12}:



Pentane
Boiling point = 36°C

2-Methylbutane
Boiling point = 28°C

2,2-Dimethylpropane
Boiling point = 10°C

WorldLinks Biomimicry and Gecko Feet

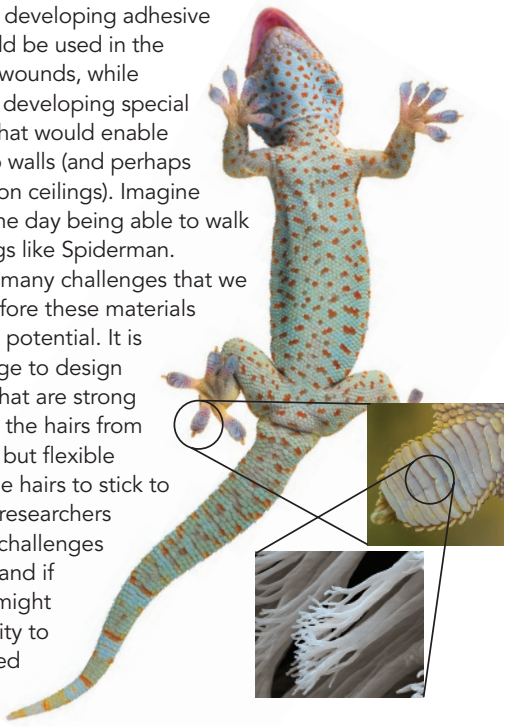
The term biomimicry describes the notion that scientists often draw creative inspiration from studying nature. By investigating some of nature's processes, it is possible to mimic those processes and to develop new technology. One such example is based on the way that geckos can scurry up walls and along ceilings. Until recently, scientists were baffled by the curious ability of geckos to walk upside down, even on very smooth surfaces such as polished glass.

As it turns out, geckos do not use any chemical adhesives, nor do they use suction. Instead, their abilities arise from the intermolecular forces of attraction between the molecules in their feet and the molecules in the surface on which they are walking. When you place your hand on a surface, there are certainly intermolecular forces of attraction between the molecules of your hand and the surface, but the microscopic topography of your hand is quite bumpy. As a result, your hand only makes contact with the surface at perhaps a few thousand points. In contrast, the foot of a gecko has approximately half a million microscopic flexible hairs, called *setae*, each of which has even smaller hairs.

When a gecko places its foot on a surface, the flexible hairs allow the gecko to make extraordinary contact with the surface, and the resulting London dispersion forces are collectively strong enough to support the gecko.

In the last decade, many research teams have drawn inspiration from geckos and have created materials with densely packed microscopic hairs. For example, some scientists are developing adhesive bandages that could be used in the healing of surgical wounds, while other scientists are developing special gloves and boots that would enable people to climb up walls (and perhaps walk upside down on ceilings). Imagine the possibility of one day being able to walk on walls and ceilings like Spiderman.

There are still many challenges that we must overcome before these materials will show their true potential. It is a technical challenge to design microscopic hairs that are strong enough to prevent the hairs from becoming tangled but flexible enough to allow the hairs to stick to any surface. Many researchers believe that these challenges can be overcome, and if they are right, we might have the opportunity to see the world turned literally upside down.



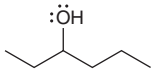
SKILLBUILDER

1.9 PREDICTING RELATIVE BOILING POINTS

LEARN the skill

Determine which compound has the higher boiling point, neopentane or 3-hexanol:

Neopentane



3-Hexanol

STEP 1
Identify all dipole-dipole interactions in both compounds.

STEP 2
Identify all H-bonding interactions in both compounds.

STEP 3
Identify the number of carbon atoms and extent of branching in both compounds.

SOLUTION

When comparing boiling points of compounds, we look for the following factors:

1. Are there any dipole-dipole interactions in either compound?

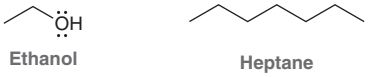
2. Will either compound form hydrogen bonds?

3a. How many carbon atoms are in each compound?

3b. How much branching is in each compound?

The second compound above (3-hexanol) is the winner in all of these categories. It has a dipole moment, while neopentane does not. It will experience hydrogen bonding, while neopentane will not. It has six carbon atoms, while neopentane only has five. And, finally, it has a straight chain, while neopentane is highly branched. Each of these factors alone would suggest that 3-hexanol should have a higher boiling point. When we consider all of these factors together, we expect that the boiling point of 3-hexanol will be significantly higher than neopentane.

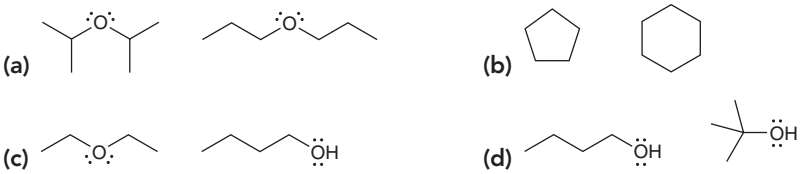
When comparing two compounds, it is important to consider all four factors. However, it is not always possible to make a clear prediction because in some cases there may be competing factors. For example, compare ethanol and heptane:



Ethanol will exhibit hydrogen bonding, but heptane has many more carbon atoms. Which factor dominates? It is not easy to predict. In this case, heptane has the higher boiling point, which is perhaps not what we would have guessed. In order to use the trends to make a prediction, there must be a clear winner.

PRACTICE the skill

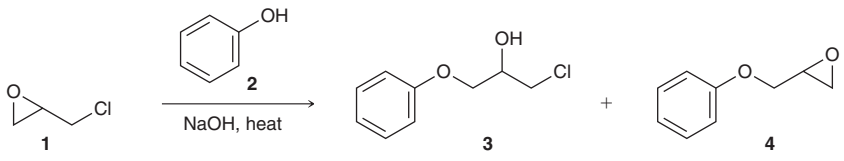
1.28 For each of the following pairs of compounds, identify the higher boiling compound and justify your choice:



APPLY the skill

Epoxy resins are used to make jewelry and art. This hummingbird window art was created by David Greenhalgh.

1.29 Epichlorohydrin (**1**) is an epoxide used in the production of plastic, epoxy glues, and resins (reactions of epoxides will be discussed in Chapter 13). When epichlorohydrin is treated with phenol (**2**), two products are formed (**3** and **4**).[11] These two products can be separated from each other via distillation, a process which exploits the difference in their boiling points. Which product (**3** or **4**) is expected to have the lower boiling point?



need more **PRACTICE?** **Try Problems 1.49, 1.50, 1.57, 1.61, 1.62, 1.65, 1.70, 1.73h**

1.14 Solubility

Solubility is based on the principle that "like dissolves like." In other words, polar compounds are soluble in polar solvents, while nonpolar compounds are soluble in nonpolar solvents. Why is this so? A polar compound experiences dipole-dipole interactions with the molecules of a polar solvent, allowing the compound to dissolve in the solvent. Similarly, a nonpolar compound experiences London dispersion forces with the molecules of a nonpolar solvent.

Water Solubility

The sugar-based, colored coating of a candy readily dissolves in water, but the palm-oil-based chewy center does not.

Water is an extremely polar solvent with an extensive network of hydrogen-bonding between water molecules. When a substrate dissolves in water, these hydrogen bonds will be disrupted, so the dissolved substrate (now called a **solute**) must experience very favorable interactions with water molecules in order to make the overall process energetically favorable. We know that many salts are soluble in water, such as the NaCl that is found in saltwater aquariums, saline IV fluid bags, and the brine used for pickling cucumbers. Sodium chloride readily dissolves in water (up to 360 grams per liter of water) because of the strong ion-dipole interactions that are formed between the Na^+ cations and Cl^- anions and the water molecules surrounding them (Figure 1.52).

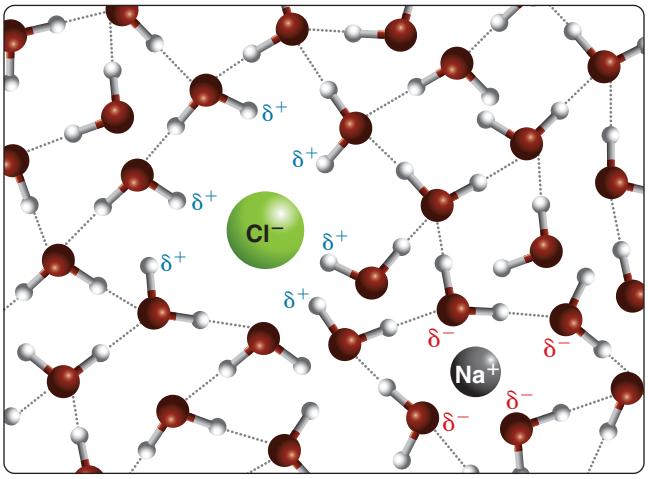


FIGURE 1.52
An aqueous solution of NaCl exhibits ion-dipole attractions (between ions and polar water molecules) and hydrogen-bonding attractions (between water molecules).

On the other hand, most organic compounds are *not* readily soluble in water. This can be observed every time we use an oil and vinegar salad dressing that separates into two layers. Fats and oils (also known as lipids, as seen in Chapter 26) are mixtures of compounds that have very long carbon chains. Because carbon-carbon bonds are nonpolar and carbon-hydrogen bonds are also described as nonpolar, fats and oils are nonpolar substances. Nonpolar compounds are not attracted to polar water molecules, so they are described as **hydrophobic** ("water-fearing") and they are **insoluble** in water (Figure 1.53).

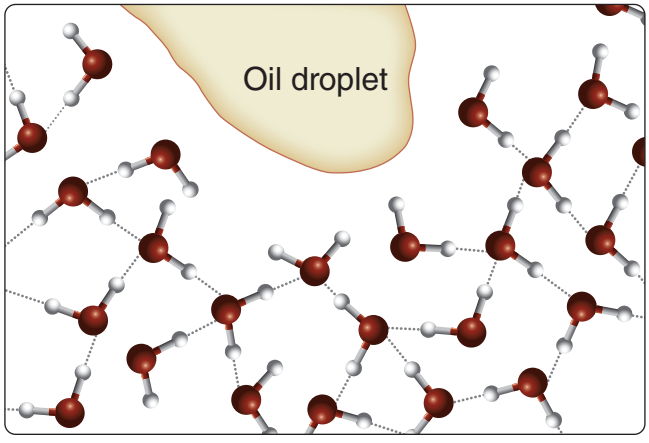
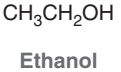


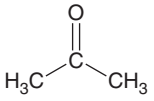
FIGURE 1.53
An oil droplet is hydrophobic and not soluble in water because nonpolar molecules have no favorable interactions with water, and their presence disrupts hydrogen bonding between water molecules.

Students at Cal Poly Pomona who are studying to be veterinarian technicians (aka vet techs) "learn by doing" as they work with a horse. DMSO is used in veterinary medicine to treat inflammation.

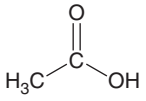
If an organic compound is sufficiently polar, it will have some degree of water solubility. Some organic compounds are so polar that they are **miscible** with water, which means that they can be mixed with water in any proportion (they will never separate into two layers like a mixture of water and oil). Examples include ethanol (found in beer, wine, tequila and hand sanitizer gels), acetone (found in nail polish remover), acetic acid (found in vinegar) and dimethyl sulfoxide (DMSO is used topically on horses to treat inflammation).



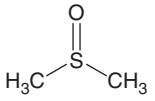
Ethanol
Found in alcoholic beverages and hand sanitizer gels



Acetone
Used in nail polish remover and to clean laboratory glassware



Acetic acid
Accounts for the characteristic odor and flavor of vinegar



DMSO
Readily absorbed through skin, used in veterinary medicine

Each of these **hydrophilic** (water-loving) compounds is polar and small enough to be fully surrounded by water molecules that are attracted to the compound. Intermolecular attractions include hydrogen bonding (as hydrogen bond acceptors, in the case of acetone and DMSO) and dipole-dipole interactions (Figure 1.54).

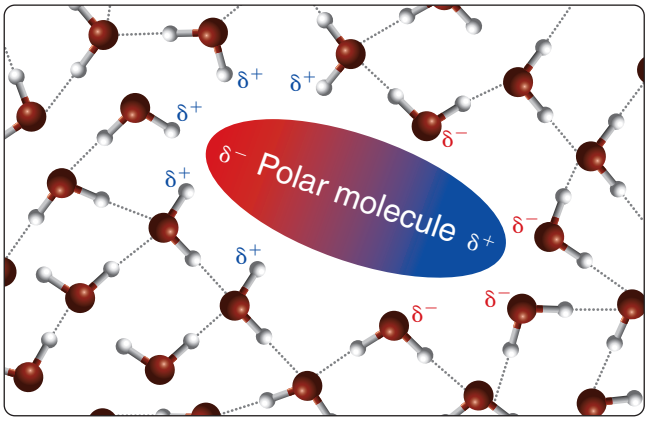
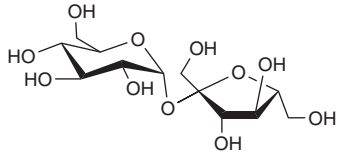
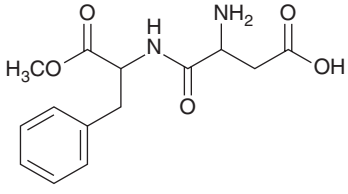


FIGURE 1.54
An aqueous solution of a polar organic molecule exhibits dipole-dipole attractions between solute and water molecules. In many cases, solute molecules can accept hydrogen bonds from water molecules as well.

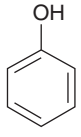
If an organic molecule is too large or if it has both polar and nonpolar regions, it may not be *miscible* with water, but it might still exhibit some water solubility. In other words, there will be a limit to how much of the compound will dissolve in a given amount of water (and at a given temperature). Some examples of polar organic compounds that are commonly encountered as aqueous solutions include sucrose (sugar found in soda), aspartame (artificial sweetener used in low-calorie drinks), and phenol (pain reliever found in throat spray).



Sucrose
(211 g per 100 mL water)
To dissolve 1 cup of sugar, less than 1/2 cup of water is needed!



Aspartame
(3 g per 100 mL water)
Sparingly soluble, but it is 200 times sweeter than sucrose, so very little is needed to sweeten a drink.



Phenol
(3 g per 100 mL water)
Relieves pain by numbing the area that is sprayed.

Sucrose (table sugar) is more soluble in hot tea than cold tea.

Sucrose is quite soluble, but when a packet of sugar is added to a glass of unsweetened iced tea, it takes a while to dissolve with stirring. On the other hand, if you add sugar to a cup of hot tea, it dissolves much more readily. Higher temperatures not only speed up the rate of dissolution, but they also increase the overall solubility. The solubilities given above are for 100 mL of water at room temperature. At that temperature (~20°C), sucrose is significantly more soluble in water than aspartame or phenol. The high solubility is attributed to the presence of several polar OH groups that can participate in hydrogen bonding with water (both as a hydrogen bond donor and acceptor). Aspartame and phenol have polar groups as well, but the 6-membered rings (called aromatic rings) are nonpolar regions that will not have favorable interactions with water, thus reducing the solubility of these molecules. We cannot predict how much of a given compound might dissolve in water, but we should be able to compare two structures and determine which would have the higher solubility based on each compound's hydrogen bonding capabilities and the relative size of any nonpolar regions.

Solubility in Organic Solvents

Nonpolar organic molecules will not dissolve in an extremely polar solvent such as water, but they are likely to be soluble in nonpolar solvents and organic solvents that are only slightly polar. Once again, the concept of "like dissolves like" can help us make predictions about solubility—we generally expect organic compounds to be soluble in organic solvents, because the solute molecules and solvent molecules will have similar polarities and favorable interactions. Figure 1.55 provides a list of some commonly encountered organic solvents, given in order of increasing polarity:

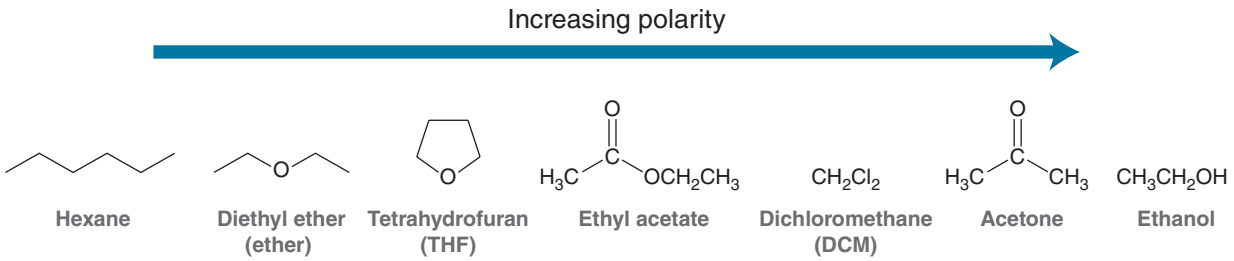


FIGURE 1.55
A sampling of common organic solvents, arranged according to increasing polarity.

The "like dissolves like" principle is applied in the laboratory when we use an extraction to separate the components of a mixture into aqueous and organic solvent layers, and it can also help us get out of some sticky situations! How can you remove gum that is stuck in your hair? Cover it with peanut butter, and the peanut oil will help soften the nonpolar gum base. The next time you are dealing with the sticky residue left behind from a label or a price tag on a nonporous surface, try using a nonpolar solvent such as mineral oil or WD-40 spray to remove it. In the process used by dry cleaners, a nonpolar organic solvent is used to effectively remove oils and greasy stains from clothing (because no *water* is used, the method is called "dry" cleaning). Likewise, to clean laboratory glassware joints that have been greased, a nonpolar solvent such as hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$, Figure 1.56) will work better than a polar solvent such as acetone.

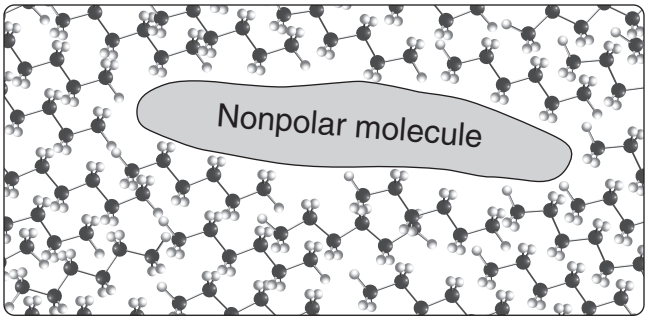
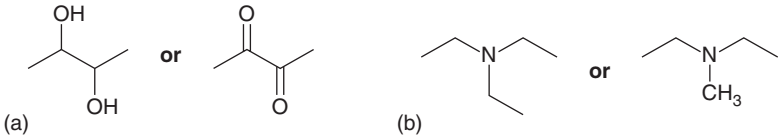


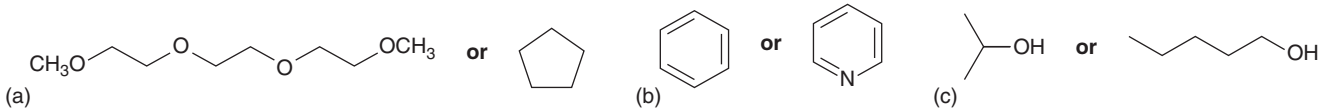
FIGURE 1.56
London dispersion forces cause an attraction between molecules of hexane (a nonpolar solvent) and allow for the favorable incorporation of nonpolar solutes, such as those found in greases and oils.

CONCEPTUAL CHECKPOINT

1.30 For each of the following pairs of compounds, determine which will be more soluble in water and explain your choice.



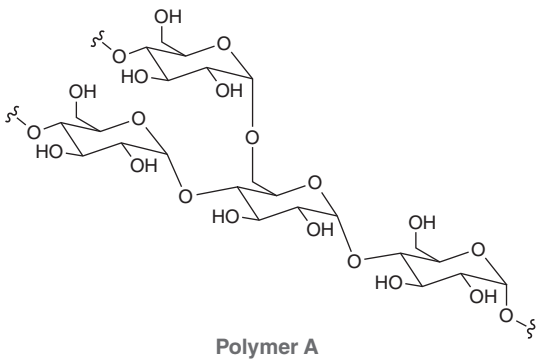
1.31 In each of the following pairs, only one of the compounds is miscible with water. Identify the miscible compound in each pair and explain your choice.



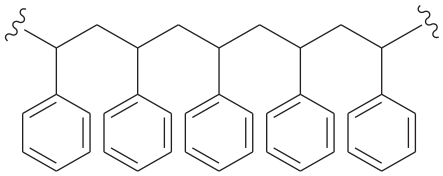
Green Chemistry

1.32 Traditional, lightweight packing peanuts are made from polystyrene, a hydrophobic plastic that persists for decades—or even centuries—as waste in landfills and our oceans. If you are looking for a more environmentally friendly option, consider using packing peanuts that are made with starch. This packing material is biodegradable and fully decomposes within a few months. When starch-based packing peanuts are moistened, they partially dissolve and become sticky, making them useful for creative art projects as well! Both polystyrene and starch are composed of very long molecules called polymers. Portions of each polymer are shown below, labeled as Polymer A and Polymer B. Based on the physical properties that have been described here, determine which structure is polystyrene and which is starch.

Packing peanuts made from starch are biodegradable and well suited for art projects.



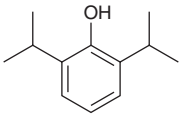
Polymer A



Polymer B

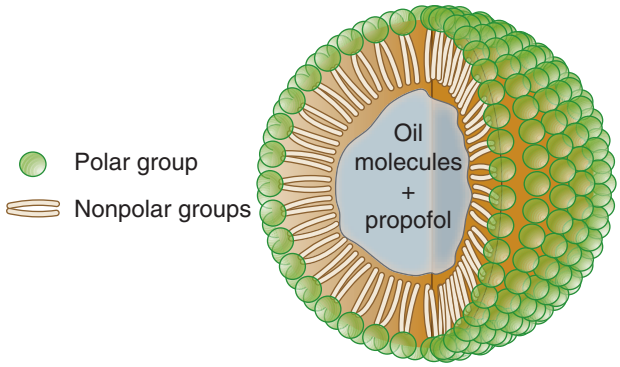
BioLinks Propofol: The Importance of Drug Solubility

The drug propofol received a lot of publicity in 2009 as one of the drugs implicated in the death of Michael Jackson:

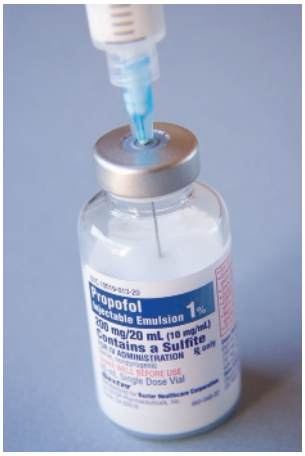


Propofol

Propofol is normally used for initiating and maintaining anesthesia during surgery. It is readily soluble in the hydrophobic (water-fearing) membranes of the brain, where it inhibits the firing (or excitation) of brain neurons. To be effective, propofol must be administered through intravenous injection, yet this poses a solubility problem. Specifically, the hydrophobic region of the drug is much larger than the hydrophilic (water-loving) region, and consequently, the drug does not readily dissolve in water (or in blood). Propofol does dissolve very well in soybean oil (a complex mixture of hydrophobic compounds, discussed in Section 26.3), but injecting a dose of soybean oil into the bloodstream would result in an oil globule, which could be fatal. To overcome this problem, compounds called lecithins (discussed in Section 26.5) are added to the mixture. Lecithins have enlongated hydrophobic regions as well as a hydrophilic region. When dissolved in water, lecithins assemble in such a way that the hydrophobic portions are grouped together inside a sphere called a micelle. The surface of the micelle is comprised of all the polar groups, rendering the micelle water-soluble. The nonpolar interior of the micelle enables the mixture of propofol and soybean oil to be encapsulated. This solution of micelles can then be injected into the bloodstream. The propofol readily passes out of the micelles, crosses the hydrophobic membranes of the brain, and reaches the target neurons.



The high concentration of micelles results in a solution that looks very much like milk, and ampules of propofol are sometimes referred to as "milk of amnesia."



1.15 Drug-Receptor Interactions

In this chapter, we have begun to investigate the structure and properties of organic compounds, and hopefully you are beginning to recognize that organic chemistry is deeply involved with the world around you, and within you! Its relevance to the medical field is especially strong, as most drugs are organic compounds. Now that you know how to interpret bond-line drawings, you can make sense of molecular structures on the literature that is packaged with prescription drugs.

In most situations, the physiological response produced by a drug is attributed to the interaction between the drug and a biological receptor site. A receptor is a region within a biological macromolecule that can serve as a pouch into which the drug molecule can fit (Figure 1.57).

Initially, this mechanism was considered to work much like a lock and key. That is, a drug molecule would function as a key, either fitting or not fitting into a particular receptor. Extensive research on drug-receptor interactions has forced scientists to modify this simple lock-and-key model. It is now understood that both the drug and the receptor are flexible, constantly changing their shapes. This flexibility is accounted for in the *induced-fit* model, which proposes that the initial binding of the drug can cause a change in the shape of the binding site. As such, drugs can bind to receptors with various levels of efficiency, with some drugs binding strongly and other drugs binding weakly.

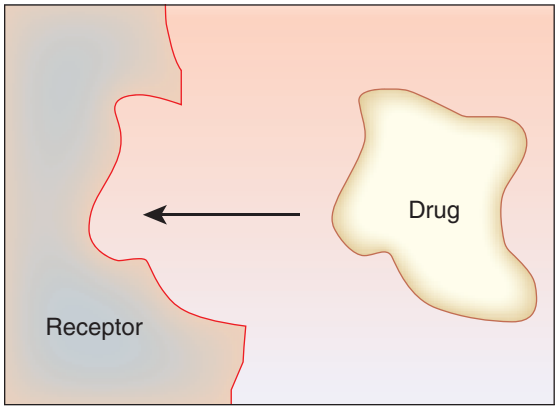


FIGURE 1.57
The therapeutic action of a small-molecule drug typically begins with the docking of the drug to a receptor site.

How does a drug bind to a receptor? In some cases, the drug molecule forms covalent bonds with the receptor. In such cases, the binding is indeed very strong (approximately 400 kJ/mol for each covalent bond) and therefore irreversible. We will see an example of irreversible binding when we explore a class of anticancer agents called nitrogen mustards (Chapter 13). For most drugs, however, the desired physiological response is meant to be temporary, which can only be accomplished if a drug can bind reversibly with its target receptor. This requires a weaker interaction between the drug and the receptor (at least weaker than a covalent bond). Examples of weak interactions include hydrogen bonding interactions (20 kJ/mol) and London dispersion forces (approximately 4 kJ/mol for each carbon atom participating in the interaction). As an example, consider the structure of a benzene ring, which is incorporated as a structural subunit in many drugs (Figure 1.58).

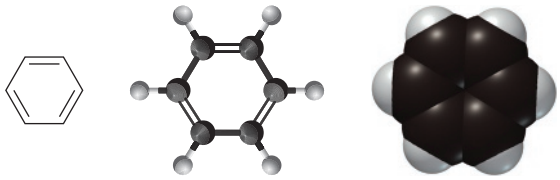


FIGURE 1.58
Three representations of benzene: (a) bond-line drawing; (b) ball-and-stick model; (c) space-filling model

In a benzene ring, each carbon is sp^2 hybridized and therefore trigonal planar. As a result, a benzene ring represents a flat surface. If the receptor also has a flat surface, the resulting London dispersion forces can contribute to the reversible binding of the drug to the receptor site (Figure 1.59).

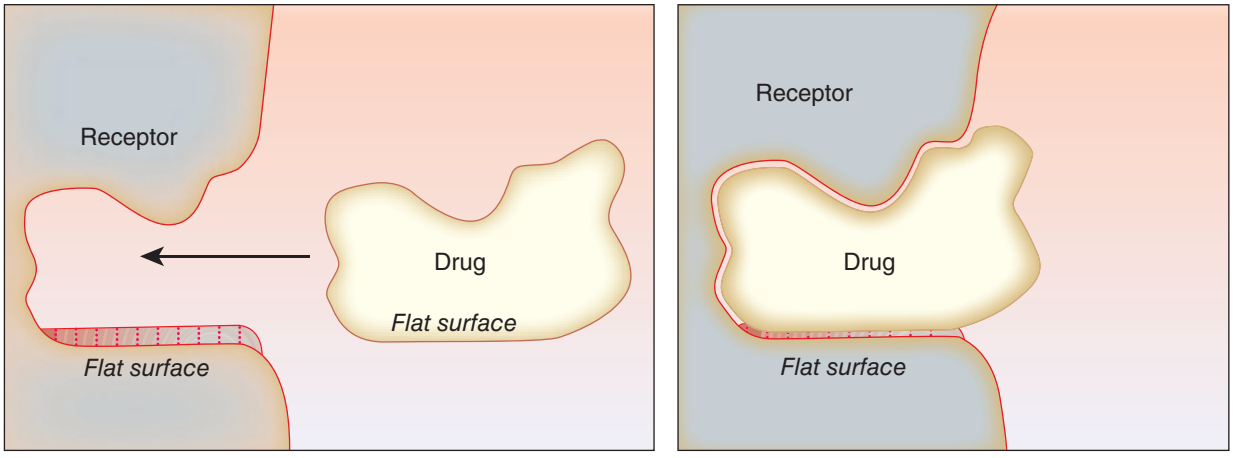


FIGURE 1.59
The flat surface of a drug can interact with the flat surface of a receptor via London dispersion forces.

This interaction is roughly equivalent to the strength of a single hydrogen-bonding interaction. The binding of a drug to a receptor is the result of the sum of the intermolecular forces of attraction between a portion of the drug molecule and the receptor site. We will have more to say about drugs and receptors in the upcoming chapters. In particular, we will see how drugs make their journey to the receptor, and we will explore how drugs flex and bend when interacting with a receptor site.

REVIEW OF CONCEPTS AND VOCABULARY

SECTION 1.1

- **Organic** compounds contain carbon atoms, while **inorganic** compounds generally lack carbon atoms.

SECTION 1.2

- **Constitutional isomers** share the same **molecular formula** but have different connectivity of atoms and different physical properties.

SECTION 1.3

- A **covalent bond** results when two atoms share a pair of electrons.
- Compounds can be illustrated using **Lewis structures**, in which all **valence electrons** are shown, and covalent bonds are represented as lines drawn between two atoms.
- Second-row elements generally obey the **octet rule**, bonding to achieve noble gas electron configuration.
- Each element will generally form a predictable number of bonds. Carbon is generally **tetravalent**, nitrogen **trivalent**, oxygen **divalent**, and hydrogen and the halogens **monovalent**.
- A pair of unshared electrons is called a **lone pair**.

SECTION 1.4

- A **formal charge** occurs when atoms do not exhibit the appropriate number of valence electrons; formal charges must be drawn in Lewis structures.

SECTION 1.5

- Bonds are classified as (1) **nonpolar covalent**, (2) **polar covalent**, or (3) **ionic**, depending on the difference in **electronegativity** values of the two bonded atoms. When two nonmetals are bonded together, two electrons are shared as a covalent bond. An ionic bond describes the attraction between a cation (a metal) and an anion (a nonmetal).
- Polar covalent bonds exhibit partial positive charges ($\delta+$) and partial negative charges ($\delta-$). **Electrostatic potential maps** present a visual illustration of partial charges.

SECTION 1.6

- In **bond-line structures**, carbon atoms and most hydrogen atoms are not drawn.

SECTION 1.7

- **Quantum mechanics** describes electrons in terms of their wavelike properties.
- A **wave equation** describes the total energy of an electron when in the vicinity of a proton. Solutions to wave equations are called **wavefunctions** (ψ), where ψ^2 represents the probability of finding an electron in a particular location.
- **Atomic orbitals** are represented visually by generating three-dimensional plots of ψ^2; **nodes** indicate that the value of ψ is zero.
- An occupied orbital can be thought of as a cloud of **electron density**.
- Electrons fill orbitals following three principles: (1) the **Aufbau principle**, (2) the **Pauli exclusion principle**, and (3) **Hund's rule**. Orbitals with the same energy level are described as **degenerate**.

SECTION 1.8

- **Valence bond theory** treats every bond as the sharing of electron density between two atoms as a result of the constructive interference of their atomic orbitals.
- **Sigma** (σ) **bonds** are formed when the electron density is located primarily on the bond axis.

SECTION 1.9

- **Molecular orbital theory** uses a mathematical method called the linear combination of atomic orbitals (LCAO) to form **molecular orbitals**. Each molecular orbital is associated with the entire molecule, rather than just two atoms.
- The **bonding MO** of molecular hydrogen results from constructive interference between its two atomic orbitals. The **antibonding MO** results from destructive interference.
- An **atomic orbital** is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule.
- Two molecular orbitals are the most important to consider: (1) the **highest occupied molecular orbital**, or **HOMO**, and (2) the **lowest unoccupied molecular orbital**, or **LUMO**.

SECTION 1.10

- Methane's tetrahedral geometry can be explained using four degenerate ***sp*^{3} hybrid orbitals** to achieve its four single bonds.
- Ethylene's planar geometry can be explained using three degenerate ***sp*^{2} hybrid orbitals** to achieve its three sigma (σ) bonds. The remaining *p* orbitals overlap to form a separate bonding interaction, called a **pi (π) bond**. The carbon atoms of ethylene are connected via a σ bond, resulting from the overlap of sp^2 hybrid atomic orbitals, and via a π bond, resulting from the overlap of *p* orbitals, both of which comprise the double bond of ethylene.
- Acetylene's linear geometry is achieved via ***sp*-hybridized** carbon atoms in which a triple bond is created from the bonding interactions of one σ bond, resulting from overlapping *sp* hybrid orbitals, and two π bonds, resulting from overlapping *p* orbitals.
- Triple bonds are stronger and shorter than double bonds, which are stronger and shorter than single bonds.

SECTION 1.11

- The geometry of small compounds can be predicted using valence shell electron pair repulsion (**VSEPR**) theory, which focuses on the number of σ bonds and lone pairs exhibited by each atom. The total, called the **steric number**, indicates the number of electron pairs that repel each other.
- A compound's geometry (the positions of its atoms) depends on the number of lone pairs and can be **tetrahedral, trigonal pyramidal, bent, trigonal planar**, or **linear**.

SECTION 1.12

- **Dipole moments** (μ) occur when the center of negative charge and the center of positive charge are separated from one another by a certain distance; the dipole moment is used as an indicator of polarity (measured in **debyes**).
- The vector sum of individual dipole moments in a compound determines the **molecular dipole moment**.

SECTION 1.13

- The physical properties of compounds are determined by **intermolecular forces**, the attractive forces between molecules.
- **Dipole-dipole interactions** occur between two molecules that possess permanent dipole moments. **Hydrogen bonding**, a type of attractive interaction, occurs when a lone pair of an electronegative atom (a **hydrogen bond acceptor**) interacts with an electron-poor hydrogen atom (NH or OH can act as a **hydrogen bond donor**). Compounds that exhibit hydrogen bonding have higher boiling points than similar compounds that lack hydrogen bonding.
- **London dispersion forces** result from the interaction between transient dipole moments and are stronger for larger molecules due to their larger surface area and ability to accommodate more interactions.

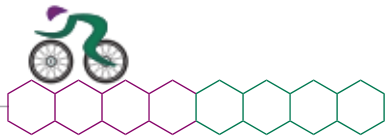
SECTION 1.14

- Solubility is based on the principle that "like dissolves like." Polar compounds are soluble in polar solvents; nonpolar compounds are soluble in nonpolar solvents.
- Ionic compounds and polar molecules are expected to have some amount of water solubility, while nonpolar compounds are **hydrophobic** and **insoluble** in water.
- Two liquids that are soluble in all proportions are described as **miscible**.

SECTION 1.15

- Drugs produce a physiological response by binding to a biological receptor site.
- The drug-receptor docking process typically involves nonbonding interactions, such as hydrogen bonding and London dispersion forces.

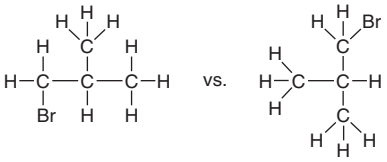
SKILLBUILDER REVIEW



1.1 IDENTIFYING CONSTITUTIONAL ISOMERS

EXAMPLE Evaluate two drawings and determine whether they represent the same compound or constitutional isomers.

STEP 1
Check the molecular formula.



C_4H_9Br C_4H_9Br

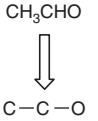
STEP 2
Determine the connectivity of the atoms.

✓ Same formula
✓ Same connectivity
✓ Same compound

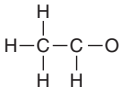
Try Problems **1.1, 1.2, 1.42, 1.64**

1.2 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

STEP 1
Connect atoms that form more than one bond.



STEP 2
Connect the hydrogen atoms.

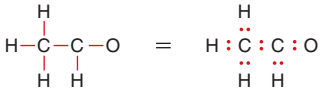


STEP 3
Determine the total number of valence electrons.

C × 2 = 8 electrons
O × 1 = 6 electrons
H × 4 = 4 electrons

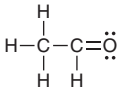
8 + 6 + 4 = 18 total valence electrons

STEP 4
Determine how many electrons have already been drawn.



6 bonds 12 electrons

STEP 5
Add remaining electrons so that each atom achieves an octet.

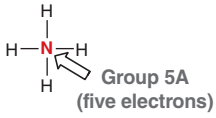


✓ *All atoms have octets*
✓ *18 total electrons shown*

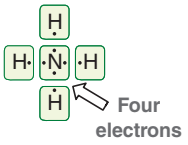
Try Problems **11.3–1.6, 1.35, 1.51**

1.3 CALCULATING FORMAL CHARGE

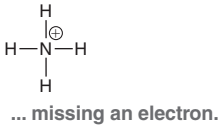
STEP 1 Determine appropriate number of valence electrons.



STEP 2 Determine the number of valence electrons in this case.



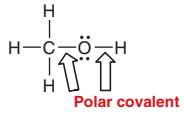
STEP 3 Assign a formal charge.



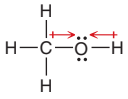
Try Problems 1.7–1.10, 1.66, 1.81a

1.4 LOCATING PARTIAL CHARGES

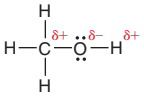
STEP 1 Identify all polar covalent bonds.



STEP 2 Determine the direction of each dipole.



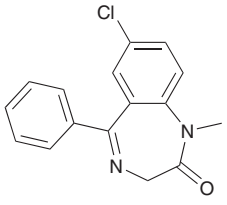
STEP 3 Indicate location of partial charges.



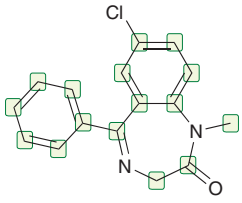
Try Problems 1.11–1.13, 1.33, 1.34, 1.43, 1.54

1.5 READING BOND-LINE STRUCTURES

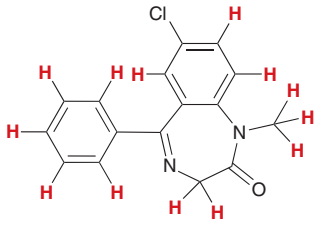
Identify all carbon atoms and hydrogen atoms.



STEP 1 The end of every line represents a carbon atom.



STEP 2 Each carbon atom will possess enough hydrogen atoms in order to achieve four bonds.



Try Problems 1.14, 1.15, 1.46, 1.47, 1.71

1.6 IDENTIFYING HYBRIDIZATION STATES

STEP 1 Determine the number of atoms attached to each carbon atom.

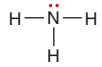
STEP 2 Determine the hybridization state of each carbon atom (number of σ bonds = number of hybrid orbitals).

four σ bonds	three σ bonds	two σ bonds
		
sp^3	sp^2	sp

Try Problems 1.19, 1.20, 1.52, 1.53, 1.67, 1.73f, 1.73g, 1.74, 1.79a, 1.80b, 1.82a

1.7 PREDICTING GEOMETRY

STEP 1 Determine the steric number by adding the number of σ bonds and lone pairs.



# of σ bonds = 3

# of lone pairs = 1

***Steric number* = 4**

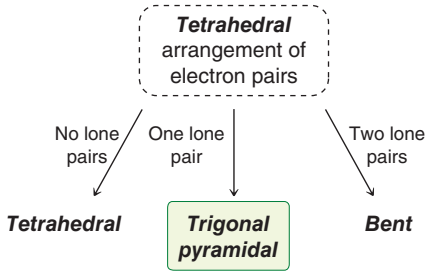
STEP 2 Use steric number to identify the arrangement of electron pairs.

4 → Tetrahedral

3 → Trigonal planar

2 → Linear

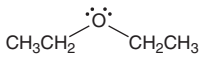
STEP 3 Identify the geometry.



Try Problems 1.22–1.25, 1.37, 1.45, 1.52, 1.53, 1.55, 1.63, 1.68, 1.73b, 1.77c, 1.77f, 1.79b, 1.80b, 1.81c, 1.82b, 1.82c

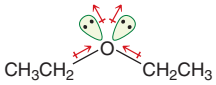
1.8 IDENTIFYING MOLECULAR DIPOLE MOMENTS

STEP 1 Predict geometry.

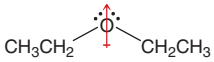


Bent

STEP 2 Identify direction of all dipole moments.



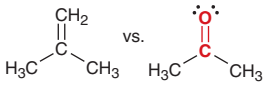
STEP 3 Draw net dipole moment.



Try Problems 1.26, 1.27, 1.34, 1.36, 1.39, 1.58–1.60, 1.75, 1.76

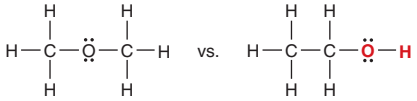
1.9 PREDICTING RELATIVE BOILING POINTS

STEP 1 Identify dipole-dipole interactions.



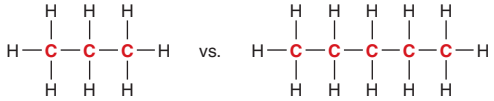
Higher boiling point

STEP 2 Identify H-bonding interactions.



Higher boiling point

STEP 3 Identify number of carbon atoms and extent of branching.



Higher boiling point

Try Problems 1.28, 1.29, 1.49, 1.50, 1.57, 1.61, 1.62, 1.65, 1.70, 1.73h

PRACTICE PROBLEMS

• **Included in Answers section**

1.33 For each compound below, identify any polar covalent bonds and indicate the direction of the dipole moment using the symbols δ+ and δ−:

(a) HBr (b) HCl (c) H_2O (d) CH_4O

1.34 For each pair of compounds below, identify the one that would be expected to have more ionic character. Explain your choice.

(a) NaBr or HBr (b) BrCl or FCl

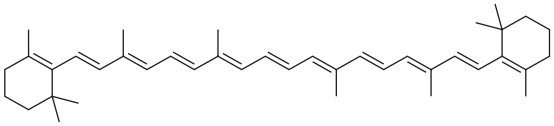
1.35 Draw a Lewis structure for each of the following compounds:

(a) CH_3CH_2OH (b) CH_3CN

1.36 Draw a Lewis structure for a compound with the molecular formula $C_4H_{11}N$ in which three of the carbon atoms are bonded to the nitrogen atom. What is the geometry of the nitrogen atom in this compound? Does this compound exhibit a molecular dipole moment? If so, indicate the direction of the dipole moment.

1.37 • Draw a Lewis structure of the anion $AlBr_4^-$ and determine its geometry.

1.38 Beta-carotene, shown below, is the organic compound that is responsible for the bright orange color of carrots. Would β-carotene be more soluble in water or in the solvent benzene (also shown below)? Explain.



β-Carotene

Benzene

1.39 Determine whether each compound below exhibits a molecular dipole moment:

(a) CH_4 (b) $N(CH_3)_3$ (c) H_2O

(d) CO_2 (e) CCl_4 (f) CH_2Br_2

1.40 Identify the neutral element that corresponds with each of the following electron configurations:

(a) $1s^2 2s^2 2p^4$ (b) $1s^2 2s^2 2p^5$ (c) $1s^2 2s^2 2p^2$

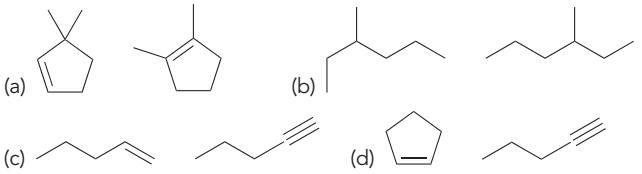
(d) $1s^2 2s^2 2p^3$ (e) $1s^2 2s^2 2p^6 3s^2 3p^5$

1.41 In the compounds below, classify each bond as nonpolar covalent, polar covalent, or ionic:

(a) NaBr (b) NaOH (c) $NaOCH_3$

(d) CH_3OH (e) CH_2O

1.42 Consider each pair of compounds below and determine whether the pair represents the same compound, constitutional isomers, or different compounds that are not isomeric at all:



1.43 For each type of bond below, determine the direction of the expected dipole moment:

(a) C—O (b) C—Mg (c) C—N (d) C—Li

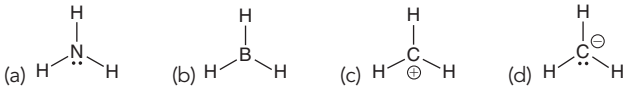
(e) C—Cl (f) C—Si (g) O—H (h) N—H

1.44 Predict the bond angles for all bonds in the following compounds:

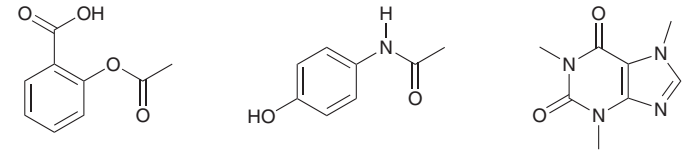
(a) CH_3CH_2OH (b) CH_2O (c) C_2H_4 (d) C_2H_2

(e) CH_3OCH_3 (f) CH_3NH_2 (g) C_3H_8 (h) CH_3CN

1.45 Identify the expected hybridization state and geometry for the central atom in each of the following structures:

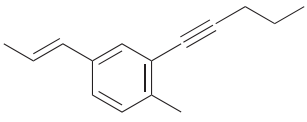


1.46 Draw all carbon atoms and hydrogen atoms for the following compounds.

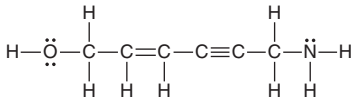


Acetylsalicylic acid (aspirin) Acetaminophen (Tylenol) Caffeine

1.47 Identify the number of carbon atoms and hydrogen atoms in the compound below:



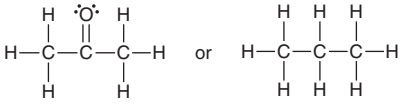
1.48 • Count the total number of σ bonds and π bonds in the compound below:



1.49 For each pair of compounds below, predict which compound will have the higher boiling point and explain your choice:

(a) $CH_3CH_2CH_2OCH_3$ or $CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CH_3$ or $CH_3CH_2CH_2CH_2CH_3$

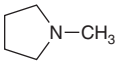
(c) 

1.50 Which of the following pure compounds will exhibit hydrogen bonding?

(a) CH_3CH_2OH (b) CH_2O

(c) C_3H_8 (d) CH_3F

(e) CH_3OCH_3 (f) CH_3NH_2

(g) NH_3 (h) 

1.51 For each case below, identify the most likely value for *x*:

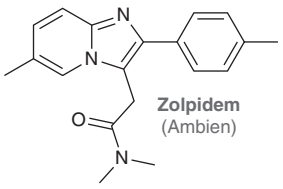
(a) BH_x (b) CH_x

(c) NH_x (d) CH_2Cl_x

1.52 Identify the hybridization state and geometry of each carbon atom in the following compounds:

(a)  (b) 

1.53 • Zolpidem, sold under the trade name Ambien, is a sedative used in the treatment of insomnia. It was discovered in 1982 and brought to market in 1992 (it takes a long time for new drugs to undergo the extensive testing required to receive approval from the Food and Drug Administration). Identify the hybridization state and geometry of each carbon atom in the structure of this compound:

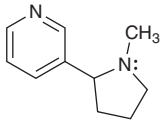


Zolpidem (Ambien)

1.54 Identify the most electronegative element in each of the following compounds:

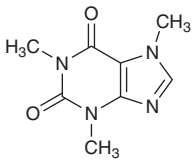
(a) $CH_3OCH_2CH_2NH_2$ (b) CH_2ClCH_2F (c) CH_3Li

1.55 Nicotine is an addictive substance found in tobacco. Identify the hybridization state and geometry of each of the nitrogen atoms in nicotine:



Nicotine

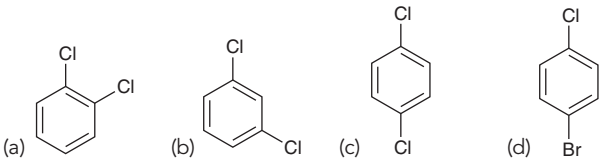
1.56 Below is the structure of caffeine, but its lone pairs are not shown. Identify the location of all lone pairs in this compound:



Caffeine

1.57 There are two different compounds with the molecular formula C_2H_6O. One of these isomers has a much higher boiling point than the other. Explain why.

1.58 Identify which compounds below possess a molecular dipole moment and indicate the direction of that dipole moment:



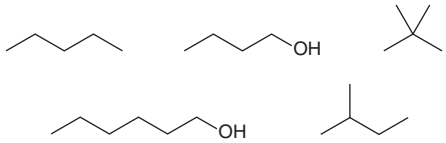
1.59 Methylene chloride (CH_2Cl_2) has fewer chlorine atoms than chloroform ($CHCl_3$). Nevertheless, methylene chloride has a larger molecular dipole moment than chloroform. Explain.

1.60 Which of the following compounds has the larger dipole moment? Explain your choice:

$CHCl_3$ or $CBrCl_3$

1.61 When the organic solvents ethanol (CH_3CH_2OH) and diethyl ether ($CH_3CH_2OCH_2CH_3$) are mixed, they form a single layer. They are miscible liquids, meaning they dissolve each other in all proportions. Draw one molecule of each compound, and illustrate the hydrogen bond that can form between them. Be sure to label the hydrogen bond donor and the hydrogen bond acceptor.

1.62 • Arrange the following compounds in order of increasing boiling point:



ACS-STYLE PROBLEMS (Multiple Choice)

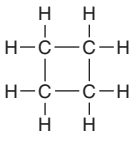
Problems 1.63–1.72 follow the style of the ACS organic chemistry exam. For each of these problems, there will be one correct answer and three distractors.

1.63 • Which is the correct hybridization state and geometry for the carbon atom in HCN?

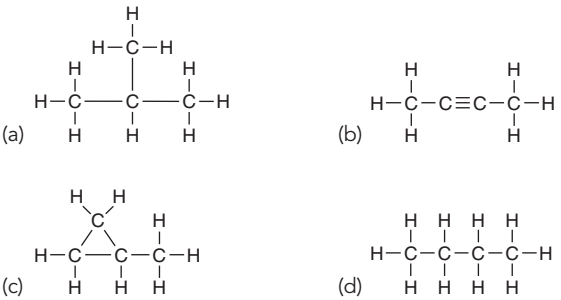
(a) *sp*, linear (b) sp^2, trigonal planar

(c) sp^3, tetrahedral (d) None of the above

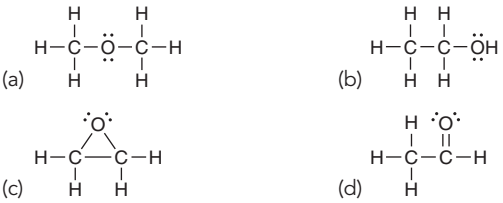
1.64 • Which of the following is a constitutional isomer of cyclobutane?



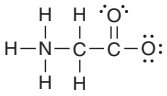
Cyclobutane



1.65 • Which of the following is expected to have the highest boiling point?



1.66 • The following structure has been drawn without formal charges. Which statement describes the missing formal charge(s)?



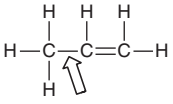
(a) This structure has one positive charge and one negative charge.

(b) This structure has one positive charge but no negative charges.

(c) This structure has one negative charge but no positive charges.

(d) This structure has no formal charges.

1.67 • The indicated σ bond results from the overlap of which orbitals?



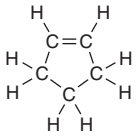
(a) sp^2–sp^2 (b) *sp*–sp^3 (c) *sp*–sp^2 (d) sp^2–sp^3

1.68 • Of the following molecular geometries, which has the largest bond angle?

(a) Pyramidal (b) Tetrahedral

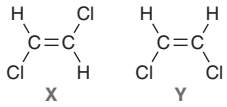
(c) Trigonal planar (d) Bent

1.69 • How many σ bonds are in the following compound?



(a) 8 (b) 9 (c) 13 (d) 14

1.70 • Which compound has the higher boiling point? Explain briefly.



X Y

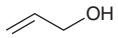
(a) **X**, because the dipole moments are far apart.

(b) **Y**, because the dipole moments do not fully cancel.

(c) **Y**, because it is less branched.

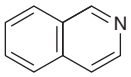
(d) **X**, because it is more linear.

1.71 • How many hydrogen atoms are in the compound represented by the following bond-line drawing?



(a) 5 (b) 6 (c) 7 (d) 8

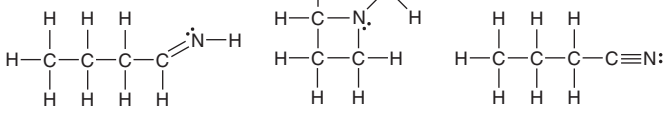
1.72 • The compound represented by the following bond-line drawing has how many carbon atoms and how many π bonds?



	C atoms	π bonds
(a)	10	6
(b)	10	5
(c)	9	6
(d)	9	5

INTEGRATED PROBLEMS

1.73 • Consider the three compounds shown below and then answer the questions that follow:



Compound A Compound B Compound C

(a) Which two compounds are constitutional isomers?

(b) Which compound contains a nitrogen atom with trigonal pyramidal geometry?

(c) Identify the compound with the greatest number of σ bonds.

(d) Identify the compound with the fewest number of σ bonds.

(e) Which compound contains more than one π bond?

(f) Which compound contains an sp^2-hybridized carbon atom?

(g) Which compound contains only sp^3-hybridized atoms (in addition to hydrogen atoms)?

(h) Which compound do you predict will have the highest boiling point? Explain.

1.74 Propose at least two different structures for a compound with six carbon atoms that exhibits the following features:

(a) All six carbon atoms are sp^2 hybridized.

(b) There is a ring, and all of the carbon atoms are sp^3 hybridized.

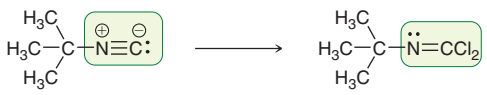
1.75 Silicon is the second most abundant element in the Earth's crust, and its compounds can be as ordinary as beach sand. However, silicon also plays an indispensable role in modern devices such as computers, cell phones, semiconductors, and solar panels. A recent technology incorporates silicon in nanometer-sized particles called quantum dots that act as luminescent labels for pancreatic cancer cells.[12] The experimental procedure for preparing the silicon quantum dots begins with using a CO_2 laser to heat silane (SiH_4).

(a) Draw a complete Lewis structure for silane, and be sure to determine if any formal charges need to be drawn.

(b) Is silane a polar or nonpolar molecule?

1.76 Bonds between carbon and oxygen (C—O) are more ploar than bonds between sulfur and oxygen (S—O). Nevertheless, sulfur dioxide (SO_2) exhibits a dipole moment while carbon dioxide (CO_2) does not. Explain this apparent anomaly.

1.77 Isonitriles (**A**) are an important class of compounds because of the versatile reactivity of the functional group, enabling the preparation of numerous new compounds and natural products. Isonitriles can be converted to isonitrile dihalides (**B**), which represents a useful procedure for temporarily hiding the reactivity of an isonitrile.[13]



A B

(a) Identify the hybridization state for each highlighted atom in **A**.

(b) One of the carbon atoms in **A** exhibits a lone pair. In what type of hybrid orbital does this lone pair reside?

(c) Predict the C—N—C bond angle in compound **A**.

(d) Identify the hybridization state for each highlighted atom in **B**.

(e) The nitrogen atom in **B** exhibits a lone pair. In what type of hybridized atomic orbital does this lone pair reside?

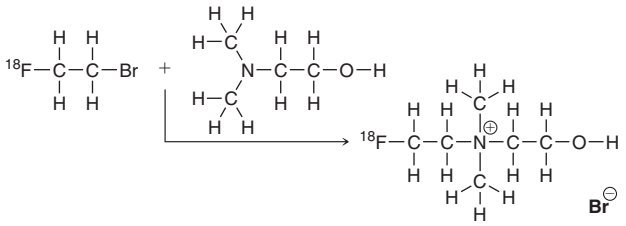
(f) Predict the C—N—C bond angle in compound **B**.

1.78 Consider the following table that provides bond lengths for a variety of C—X bonds (measured in Å).

	X = F	X = Cl	X = Br	X = I
	1.40	1.79	1.97	2.16
	1.34		1.88	2.10
	1.27	1.63	1.79	

Two trends emerge when we compare these data. First, notice that the bond length increases as the size of the halogen increases. This should make sense, since the valence electrons in iodine are farther away from the nucleus than the valence electrons in Br, so a C—I bond is longer than a C—Br bond. For the same reason, a C—Br bond is longer than a C—Cl bond, which in turn is longer than a C—F bond. Notice also that bond length decreases as the hybridization state goes from sp^3 to sp^2 to sp. This should also make sense, because sp-hybridized atoms hold their valence electrons closer to the nucleus (as seen in Table 1.2), and therefore form shorter bonds. These two trends are in conflict with each other when we compare a C_{sp^2}—Cl bond with a C_{sp}—I bond. The former bond is expected to be shorter because of the first trend (size of halogen), while the latter bond is expected to be shorter because of the second trend (hybridization state). Use the data provided to determine which bond is actually shorter, and explain your choice.

1.79 Positron emission tomography (PET) is a medical imaging technique that produces a three-dimensional picture of functional processes in the body, such as the brain uptake of glucose. PET imaging requires the introduction of [^{18}F]-fluorine (a radioactive isotope of fluorine) into molecules and can be achieved by several routes, such as the following:[14]

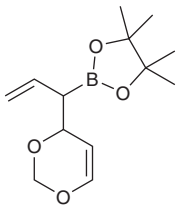


(a) Identify the hybridization for all atoms except for C, H, and O in the three compounds. We will soon see (Chapter 2) that lone pairs are often omitted from structural drawings, because they can be inferred by the presence or absence of formal charges. In this problem, none of the lone pairs have been drawn.

(b) Predict the bond angle of each C—N—C bond in the product.

CHALLENGE PROBLEMS

1.80 Phenalamide A_2 belongs to a class of natural products that are of interest because of their antibiotic, antifungal, and antiviral activity. In the first total synthesis of this compound, the following boronate ester was utilized:[15]



(a) Determine the hybridization state of the boron atom.

(b) Predict the O—B—O bond angle and then suggest a reason why the actual bond angle might deviate from the predicted value in this case.

(c) The lone pairs have not been drawn. Draw all of them. (**Hint:** Note that the structure has no formal charges.)

1.81 The formation of a variety of compounds called oxazolidinones is important for the synthesis of many different natural products and other compounds that have potential use as future medicines. One method[16] for preparing oxazolidinones involves the conversion of a hydroximoyl chloride, such as compound **1**, into a nitrile oxide, such as compound **2**:

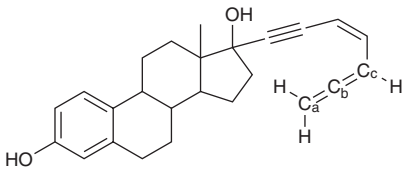
1 **2**

(a) Identify any formal charges that are missing from the structures of **1** and **2**.

(b) Determine which compound is expected to be more soluble in a polar solvent, and justify your choice.

(c) Determine the amount by which the C—C—N bond angle increases as a result of the conversion from **1** to **2**.

1.82 The following compound belongs to a class of compounds, called estradiol derivatives, which show promise in the treatment of breast cancer:[17]



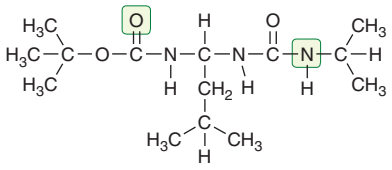
(a) Determine the hybridization state of C_a, C_b, and C_c.

(b) Determine the H—C_a—C_b bond angle.

(c) Determine the C_a—C_b—C_c bond angle.

(d) C_b exhibits two π bonds: one to C_a, and the other to C_c. Draw a picture of C_a, C_b, and C_c that shows the relative orientation of the two different p orbitals that C_b is utilizing to form its two π bonds. Also show the p orbitals on C_a and C_c that are being used by each of those atoms. Describe the relative orientation of the p orbitals on C_a and C_c.

1.83 The following structure shows promise for studying how enzymes (nature's catalysts) coil up into very discrete shapes that endow them with catalytic function:[18]

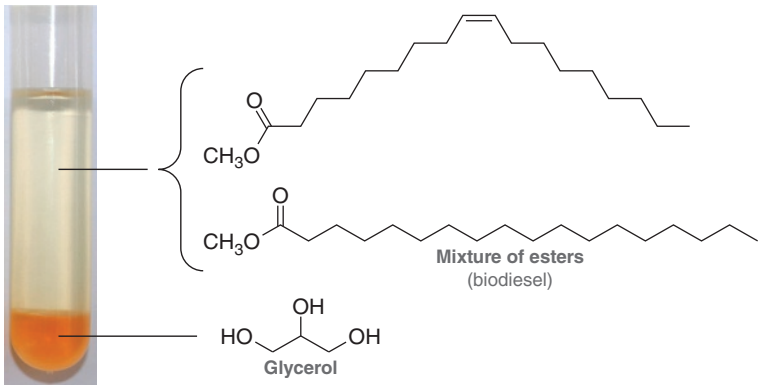


(a) This compound has two N—C—N units, with differing bond angles. Predict the difference in bond angles between these two units and explain the source of the difference.

(b) When this compound was prepared and investigated, it demonstrated a preference for adopting a three-dimensional shape in which the two highlighted regions were in close proximity. Describe the interaction that occurs and create a drawing that illustrates this interaction.

Green Chemistry

1.84 Vegetable oils can be converted to a fuel that is called biodiesel (because it comes from a renewable plant source).[19] Biodiesel production forms a liquid mixture of compounds called esters along with a liquid by-product, glycerol (also known as glycerin). The glycerol is immiscible with the ester mixture, forming two separate layers as shown in the test tube below.[20]



(a) Explain why the esters shown readily combine to form a solution.

(b) Explain why this mixture of esters is not soluble in the glycerol.

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