

CHAPTER 1

Structure and Bonding

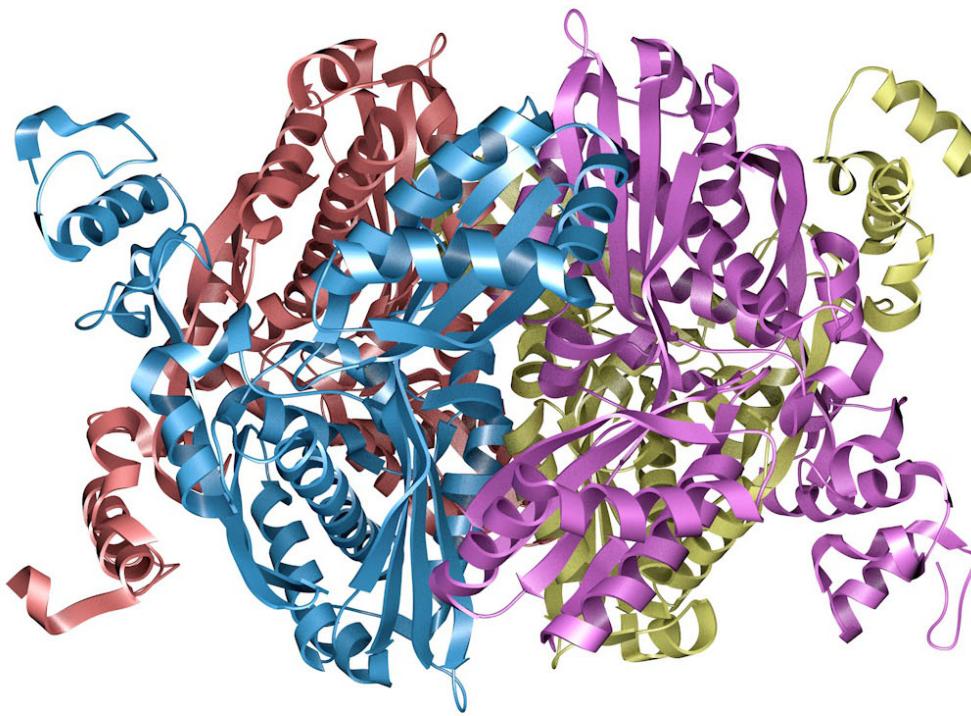


FIGURE 1.1 The enzyme HMG-CoA reductase, shown here as a so-called ribbon model, catalyzes a crucial step in the body's synthesis of cholesterol. Understanding how this enzyme functions has led to the development of drugs credited with saving millions of lives. (credit: image from the RCSB PDB (rcsb.org) of PBD ID 1HW9 (E.S. Istvan, J. Deisenhofer) (2001) Structural mechanism for statin inhibition of HMG-CoA reductase *Science* 292: 1160–1164/RCSB PDB, CC BY 1.0)

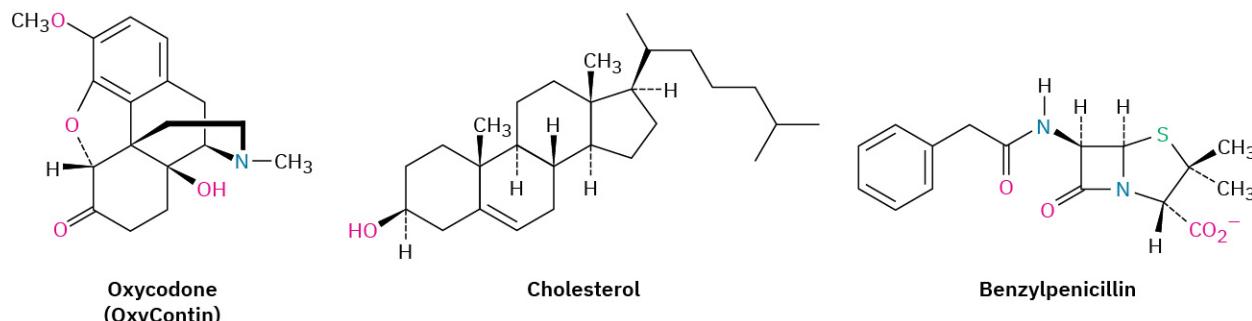
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WHY THIS CHAPTER? We'll ease into the study of organic chemistry by first reviewing some ideas about atoms, bonds, and molecular geometry that you may recall from your general chemistry course. Much of the material in this chapter and the next is likely to be familiar to you, but it's nevertheless a good idea to make sure you understand it before moving on.

What is organic chemistry, and why should you study it? The answers to these questions are all around you.

Every living organism is made of organic chemicals. The proteins that make up your hair, skin, and muscles; the DNA that controls your genetic heritage; the foods that nourish you; and the medicines that heal you are all organic chemicals. Anyone with a curiosity about life and living things, and anyone who wants to be a part of the remarkable advances taking place in medicine and the biological sciences, must first understand organic chemistry. Look at the following drawings for instance, which show the chemical structures of some molecules whose names might be familiar to you. Although the drawings may appear unintelligible at this point, don't worry. They'll make perfectly good sense before long, and you'll soon be drawing similar structures for any substance you're interested in.



Historically, the term *organic chemistry* dates to the mid-1700s, when it was used to mean the chemistry of substances found in living organisms. Little was known about chemistry at that time, and the behavior of the “organic” substances isolated from plants and animals seemed different from that of the “inorganic” substances found in minerals. Organic compounds were generally low-melting solids and were usually more difficult to isolate, purify, and work with than high-melting inorganic compounds.

By the mid-1800s, however, it was clear that there was no fundamental difference between organic and inorganic compounds. The only distinguishing characteristic of organic compounds is that all contain the element carbon.

Organic chemistry, then, is the study of carbon compounds. But why is carbon special? Why, of the more than 197 million presently known chemical compounds, do almost all of them contain carbon? The answers to these questions come from carbon’s electronic structure and its consequent position in the periodic table (**FIGURE 1.2**). As a group 4A element, carbon can share four valence electrons and form four strong covalent bonds. Furthermore, carbon atoms can bond to one another, forming long chains and rings. Carbon, alone of all elements, is able to form an immense diversity of compounds, from the simple methane, with one carbon atom, to the staggeringly complex DNA, which can have more than *100 million* carbons.

Group 1A																8A	
H	2A															He	
Li	Be																
Na	Mg																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

FIGURE 1.2 Carbon, hydrogen, and other elements commonly found in organic compounds are shown in the colors typically used to represent them.

Not all carbon compounds are derived from living organisms, however. Modern chemists have developed a remarkably sophisticated ability to design and synthesize new organic compounds in the laboratory—medicines, dyes, polymers, and a host of other substances. Organic chemistry touches the lives of

everyone. Its study can be a fascinating undertaking.

1.1 Atomic Structure: The Nucleus

As you might remember from your general chemistry course, an atom consists of a dense, positively charged nucleus surrounded at a relatively large distance by negatively charged electrons (**FIGURE 1.3**). The nucleus consists of subatomic particles called *neutrons*, which are electrically neutral, and *protons*, which are positively charged. Because an atom is neutral overall, the number of positive protons in the nucleus and the number of negative electrons surrounding the nucleus are the same.

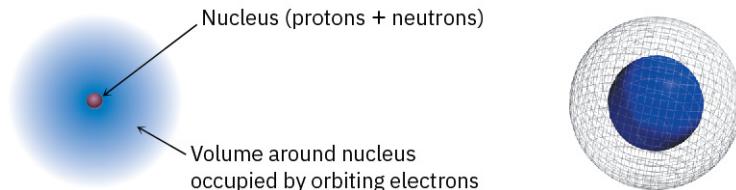


FIGURE 1.3 A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three-dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the **blue solid surface** than at the **gray mesh surface**.

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

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

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

1.2 Atomic Structure: Orbitals

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

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

What do orbitals look like? There are four different kinds of orbitals, denoted *s*, *p*, *d*, and *f*, each with a different shape. Of the four, we'll be concerned primarily with *s* and *p* orbitals because these are the most common in

organic and biological chemistry. An *s* orbital has a spherical shape, with the nucleus at its center; a *p* orbital has a dumbbell shape with two parts, or *lobes*; and four of the five *d* orbitals have a cloverleaf shape with four lobes, as shown in **FIGURE 1.4**. The fifth *d* orbital is shaped like an elongated dumbbell with a doughnut around its middle.

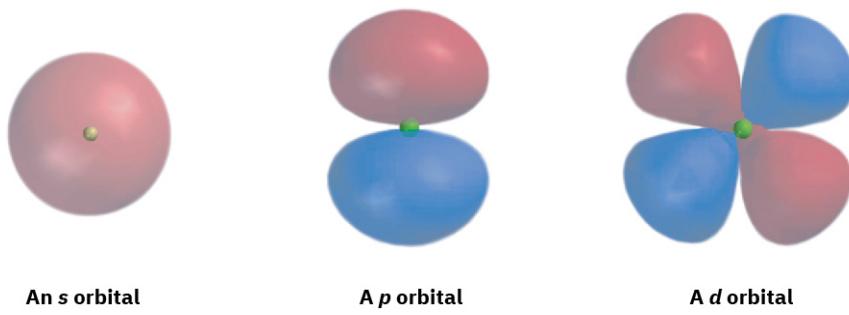


FIGURE 1.4 Representations of *s*, *p*, and *d* orbitals. An *s* orbital is spherical, a *p* orbital is dumbbell-shaped, and four of the five *d* orbitals are cloverleaf-shaped. Different lobes of *p* orbitals are often drawn for convenience as teardrops, but their actual shape is more like that of a doorknob, as indicated.

The orbitals in an atom are organized into different layers around the nucleus called **electron shells**, which are centered around the nucleus and have successively larger size and energy. Different shells contain different numbers and kinds of orbitals, and each orbital within a shell can be occupied by two electrons. The first shell contains only a single *s* orbital, denoted *1s*, and thus holds only 2 electrons. The second shell contains one *2s* orbital and three *2p* orbitals and thus holds a total of 8 electrons. The third shell contains a *3s* orbital, three *3p* orbitals, and five *3d* orbitals, for a total capacity of 18 electrons. These orbital groupings and their energy levels are shown in **FIGURE 1.5**.

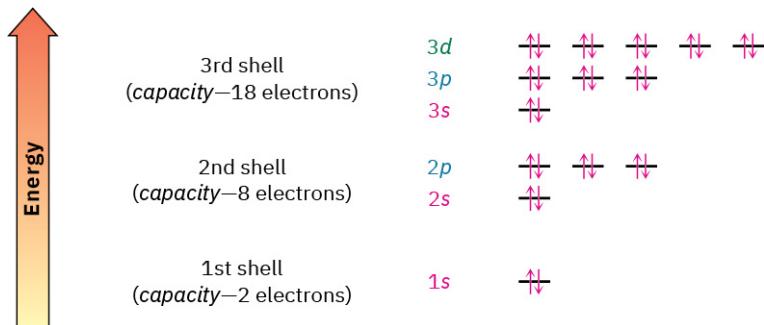


FIGURE 1.5 Energy levels of electrons in an atom. The first shell holds a maximum of 2 electrons in one *1s* orbital; the second shell holds a maximum of 8 electrons in one *2s* and three *2p* orbitals; the third shell holds a maximum of 18 electrons in one *3s*, three *3p*, and *3d* orbitals; and so on. The two electrons in each orbital are represented by five up and down arrows, $\uparrow\downarrow$. Although not shown, the energy level of the *4s* orbital falls between *3p* and *3d*.

The three different *p* orbitals within a given shell are oriented in space along mutually perpendicular directions, denoted *p_x*, *p_y*, and *p_z*. As shown in **FIGURE 1.6**, the two lobes of each *p* orbital are separated by a region of zero electron density called a **node**. Furthermore, the two orbital regions separated by the node have different algebraic signs, + and −, in the wave function, as represented by the different colors in **FIGURE 1.4** and **FIGURE 1.6**. As we'll see in **Section 1.11**, these algebraic signs for different orbital lobes have important consequences with respect to chemical bonding and chemical reactivity.

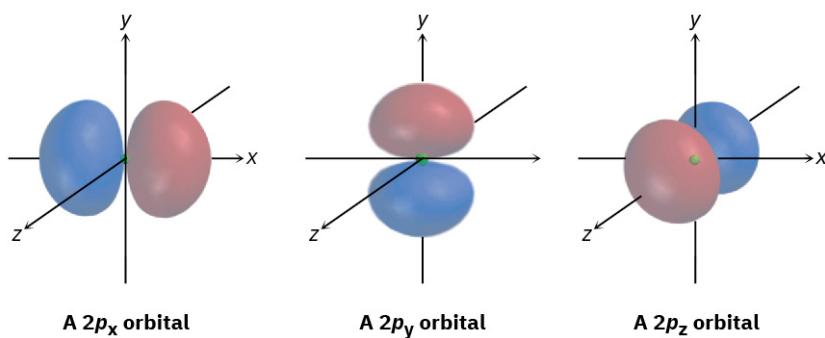


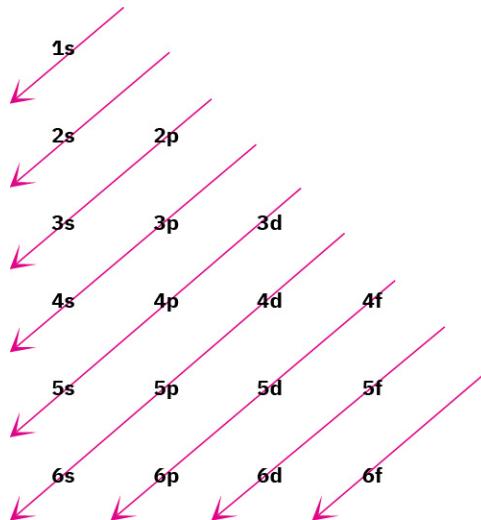
FIGURE 1.6 Shapes of the $2p$ orbitals. Each of the three mutually perpendicular, dumbbell-shaped orbitals has two lobes separated by a node. The **two lobes** have different algebraic signs in the corresponding wave function, as indicated by the different colors.

1.3 Atomic Structure: Electron Configurations

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

RULE 1

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



RULE 2

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

RULE 3

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

Some examples of how these rules apply are shown in **TABLE 1.1**. Hydrogen, for instance, has only one electron, which must occupy the lowest-energy orbital. Thus, hydrogen has a $1s$ ground-state configuration. Carbon has six electrons and the ground-state configuration $1s^2 2s^2 2p_x^1 2p_y^1$, and so forth. Note that a superscript is used to represent the number of electrons in a particular orbital.

TABLE 1.1 Ground-State Electron Configurations of Some Elements

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

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

- 1-1 (a)** Oxygen **(b)** Nitrogen **(c)** Sulfur

PROBLEM How many electrons does each of the following biological trace elements have in its outermost

- 1-2** electron shell?

- (a)** Magnesium **(b)** Cobalt **(c)** Selenium

1.4 Development of Chemical Bonding Theory

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

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

A representation of a tetrahedral carbon atom is shown in **FIGURE 1.7**. Note the conventions used to show three-dimensionality: solid lines represent bonds in the plane of the page, the heavy wedged line represents a bond coming out of the page toward the viewer, and the dashed line represents a bond receding back behind the page, away from the viewer. Get used to them; these representations will be used throughout the text.

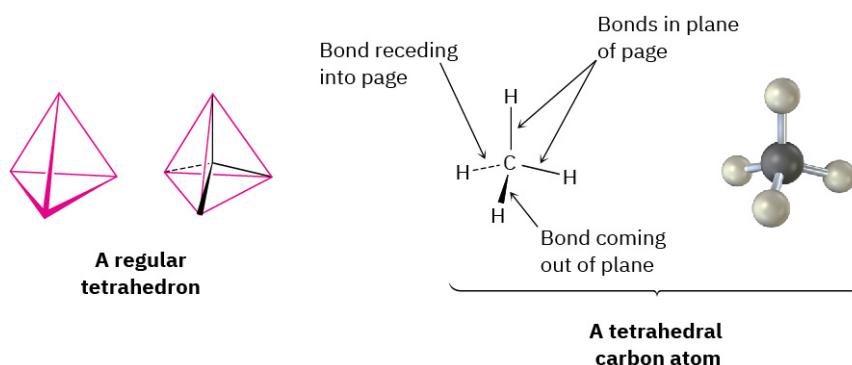


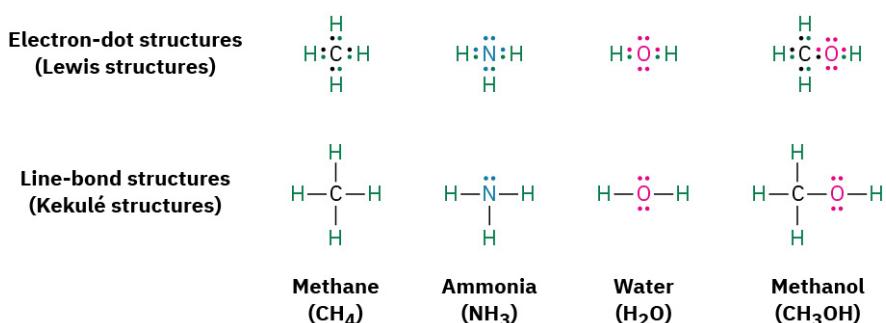
FIGURE 1.7 A representation of van't Hoff's tetrahedral carbon atom. The solid lines represent bonds in the plane of the paper, the heavy wedged line represents a bond coming out of the plane of the page toward the viewer, and the dashed line represents a bond going back behind the plane of the page away from the viewer.

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

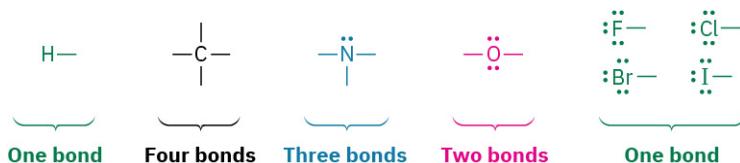
We know through observation that eight electrons (an electron *octet*) in an atom's outermost shell, or **valence shell**, impart special stability to the noble-gas elements in group 8A of the periodic table: Ne ($2 + 8$); Ar ($2 + 8 + 8$); Kr ($2 + 8 + 18 + 8$). We also know that the chemistry of the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

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

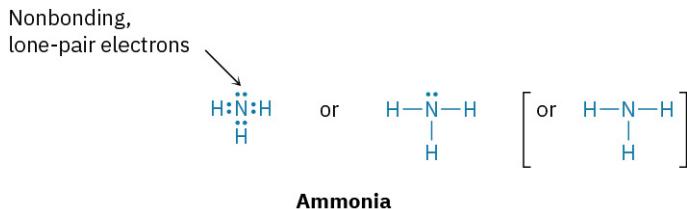
A simple way of indicating the covalent bonds in molecules is to use what are called **Lewis structures**, or **electron-dot structures**, in which the valence-shell electrons of an atom are represented as dots. Thus, hydrogen has one dot representing its $1s$ electron, carbon has four dots ($2s^2\ 2p^2$),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



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



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



WORKED EXAMPLE 1.1

Predicting the Number of Bonds Formed by Atoms in Molecules

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

Strategy

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

Solution

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



WORKED EXAMPLE 1.2

Drawing Electron-Dot and Line-Bond Structures

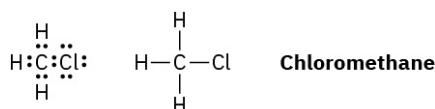
Draw both electron-dot and line-bond structures for chloromethane, CH₃Cl.

Strategy

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

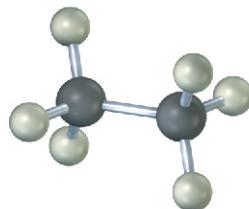
Solution

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



PROBLEM Draw a molecule of chloroform, CHCl_3 , using solid, wedged, and dashed lines to show its tetrahedral **1-3** geometry.

PROBLEM Convert the following representation of ethane, C_2H_6 , into a conventional drawing that uses solid, **1-4** wedged, and dashed lines to indicate tetrahedral geometry around each carbon (black = C, gray = H).



Ethane

PROBLEM What are likely formulas for the following substances?

- 1-5** (a) $\text{CCl}_?$ (b) $\text{AlH}_?$ (c) $\text{CH}_?\text{Cl}_2$ (d) SiF (e) $\text{CH}_3\text{NH}_?$

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

- 1-6** (a) CHCl_3 , chloroform (b) H_2S , hydrogen sulfide (c) CH_3NH_2 , methylamine
(d) CH_3Li , methyl lithium

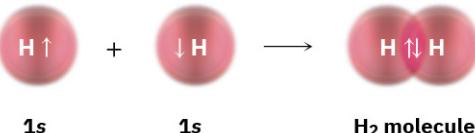
PROBLEM Why can't an organic molecule have the formula C_2H_7 ?

1-7

1.5 Describing Chemical Bonds: Valence Bond Theory

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

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



The overlapping orbitals in the H₂ molecule have the elongated egg shape we might get by pressing two spheres together. If a plane were to pass through the middle of the bond, the intersection of the plane and the overlapping orbitals would be a circle. In other words, the H–H bond is cylindrically symmetrical, as shown in **FIGURE 1.8**. Such bonds, which are formed by the head-on overlap of two atomic orbitals along a line drawn between the nuclei, are called **sigma (σ) bonds**.

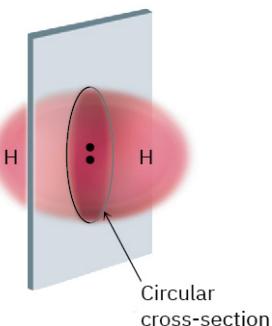


FIGURE 1.8 The cylindrical symmetry of the H–H σ bond in an H₂ molecule. The intersection of a plane cutting through the σ bond is a circle.

During the bond-forming reaction $2\text{H}\cdot \longrightarrow \text{H}_2$, 436 kJ/mol (104 kcal/mol) of energy is released. Because the product H₂ molecule has 436 kJ/mol less energy than the starting 2 H· atoms, the product is more stable than the reactant and we say that the H–H bond has a **bond strength** of 436 kJ/mol. In other words, we would have to put 436 kJ/mol of energy into the H–H bond to break the H₂ molecule apart into two H atoms (**FIGURE 1.9**). For convenience, we'll generally give energies in both kilocalories (kcal) and the SI unit kilojoules (kJ): 1 kJ = 0.2390 kcal; 1 kcal = 4.184 kJ.

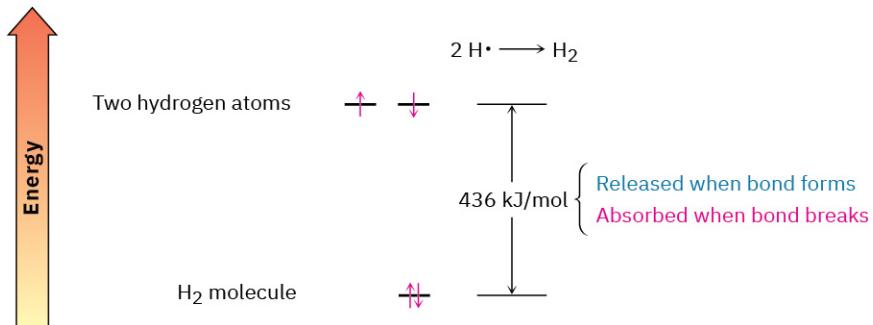


FIGURE 1.9 Relative energy levels of two H atoms and the H₂ molecule. The H₂ molecule has 436 kJ/mol (104 kcal/mol) less energy than the two separate H atoms, so 436 kJ/mol of energy is **released when the H–H bond forms**. Conversely, 436 kJ/mol is **absorbed when the H–H bond breaks**.

How close are the two nuclei in the H₂ molecule? If they are too close, they will repel each other because both are positively charged. Yet if they're too far apart, they won't be able to share the bonding electrons. Thus, there is an optimum distance between nuclei that leads to maximum stability (**FIGURE 1.10**). Called the **bond length**, this distance is 74 pm in the H–H molecule. Every covalent bond has both a characteristic bond strength and bond length.

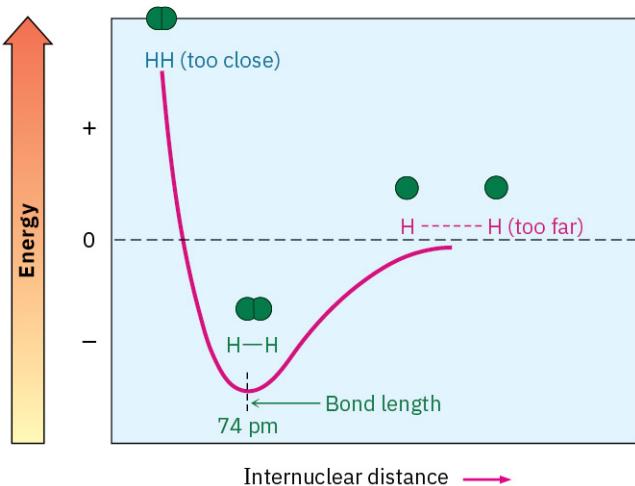


FIGURE 1.10 A plot of energy versus internuclear distance for two hydrogen atoms. The distance between nuclei at the minimum energy point is the **bond length**.

1.6 sp^3 Hybrid Orbitals and the Structure of Methane

The bonding in the hydrogen molecule is fairly straightforward, but the situation is more complicated in organic molecules with tetravalent carbon atoms. Take methane, CH_4 , for instance. As we've seen, carbon has four valence electrons ($2s^2 2p^2$) and forms four bonds. Because carbon uses two kinds of orbitals for bonding, $2s$ and $2p$, we might expect methane to have two kinds of C–H bonds. In fact, though, all four C–H bonds in methane are identical and are spatially oriented toward the corners of a regular tetrahedron, as shown previously in **FIGURE 1.7**. How can we explain this?

An answer was provided in 1931 by Linus Pauling, who showed mathematically how an s orbital and three p orbitals on an atom can combine, or *hybridize*, to form four equivalent atomic orbitals with tetrahedral orientation. Shown in **FIGURE 1.11**, these tetrahedrally oriented orbitals are called **sp^3 hybrid orbitals**. Note that the superscript 3 in the name sp^3 tells how many of each type of atomic orbital combine to form the hybrid, not how many electrons occupy it.

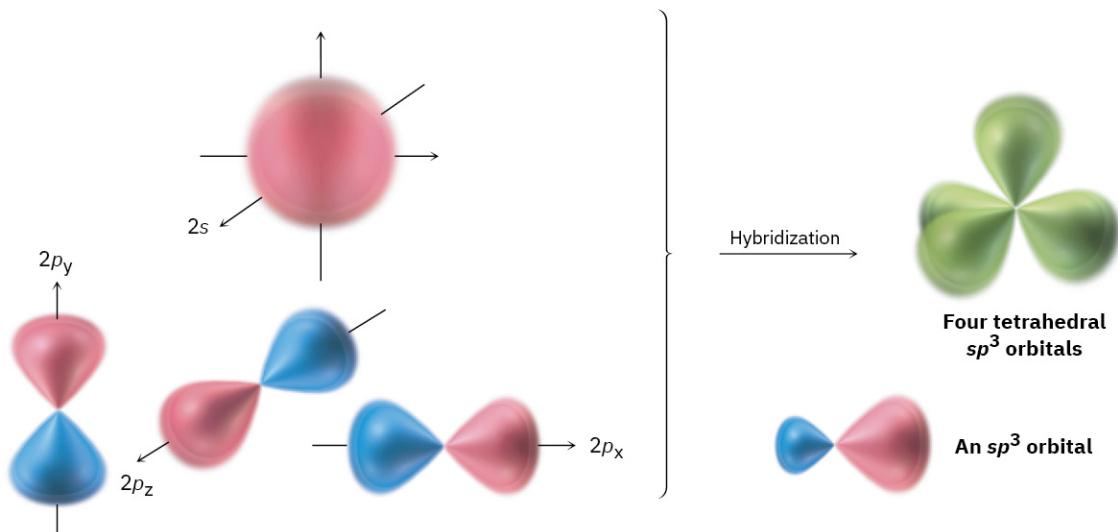


FIGURE 1.11 Four sp^3 hybrid orbitals, oriented toward the corners of a regular tetrahedron, are formed by the combination of an **s orbital** and three **p orbitals (red/blue).** The sp^3 hybrids have two lobes and are unsymmetrical about the nucleus, giving them a directionality and allowing them to form strong bonds to other atoms.

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

sp^3 hybrid orbitals form stronger bonds than do unhybridized s or p orbitals.

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

When each of the four identical sp^3 hybrid orbitals of a carbon atom overlaps with the $1s$ orbital of a hydrogen atom, four identical C–H bonds are formed and methane results. Each C–H bond in methane has a strength of 439 kJ/mol (105 kcal/mol) and a length of 109 pm. Because the four bonds have a specific geometry, we also can define a property called the **bond angle**. The angle formed by each H–C–H is 109.5° , the so-called tetrahedral angle. Methane thus has the structure shown in **FIGURE 1.12**.

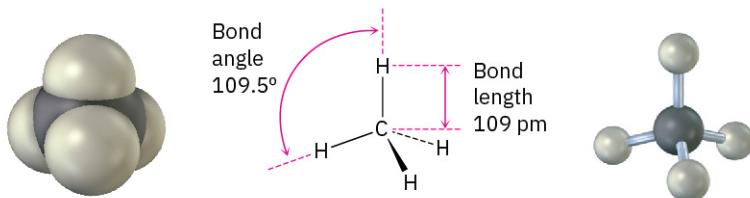
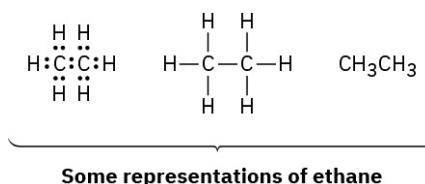


FIGURE 1.12 The structure of methane, showing its 109.5° bond angles.

1.7 sp^3 Hybrid Orbitals and the Structure of Ethane

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



We can picture the ethane molecule by imagining that the two carbon atoms bond to each other by head-on sigma (σ) overlap of an sp^3 hybrid orbital from each (**FIGURE 1.13**). The remaining three sp^3 hybrid orbitals on each carbon overlap with the $1s$ orbitals of three hydrogens to form the six C–H bonds. The C–H bonds in ethane are similar to those in methane, although a bit weaker: 421 kJ/mol (101 kcal/mol) for ethane versus 439 kJ/mol for methane. The C–C bond is 153 pm in length and has a strength of 377 kJ/mol (90 kcal/mol). All the bond angles of ethane are near, although not exactly at, the tetrahedral value of 109.5° .

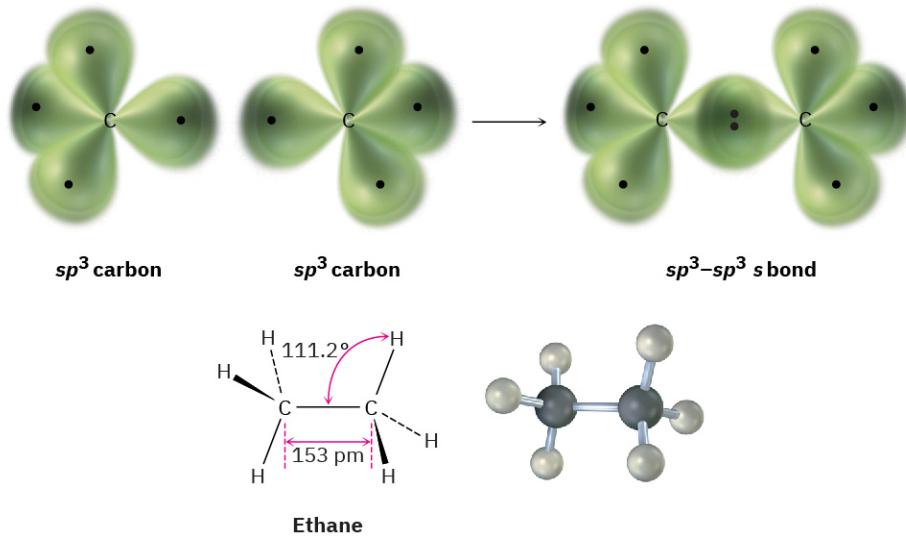
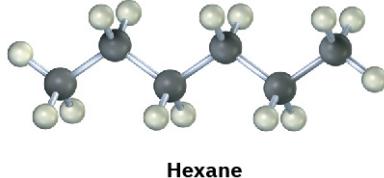


FIGURE 1.13 The structure of ethane. The carbon–carbon bond is formed by σ overlap of two sp^3 hybrid orbitals. For clarity, the smaller

lobes of the sp^3 hybrid orbitals are not shown.

PROBLEM Draw a line-bond structure for propane, $\text{CH}_3\text{CH}_2\text{CH}_3$. Predict the value of each bond angle, and **1-8** indicate the overall shape of the molecule.

PROBLEM Convert the following molecular model of hexane, a component of gasoline, into a line-bond **1-9** structure (black = C, gray = H).



1.8 sp^2 Hybrid Orbitals and the Structure of Ethylene

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

How are multiple bonds described by valence bond theory? When we discussed sp^3 hybrid orbitals in **Section 1.6**, we said that the four valence-shell atomic orbitals of carbon combine to form four equivalent sp^3 hybrids. Imagine instead that the $2s$ orbital combines with only *two* of the three available $2p$ orbitals. Three **sp^2 hybrid orbitals** result, and one $2p$ orbital remains unchanged. Like sp^3 hybrids, sp^2 hybrid orbitals are unsymmetrical about the nucleus and are strongly oriented in a specific direction so they can form strong bonds. The three sp^2 orbitals lie in a plane at angles of 120° to one another, with the remaining p orbital perpendicular to the sp^2 plane, as shown in **FIGURE 1.14**.

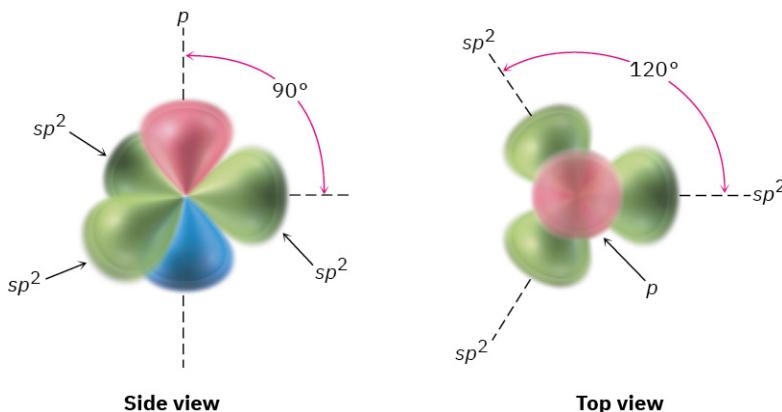


FIGURE 1.14 sp^2 Hybridization. The three equivalent **sp^2 hybrid orbitals** lie in a plane at angles of 120° to one another, and a single unhybridized **p orbital** (red/blue) is perpendicular to the sp^2 plane.

When two carbons with sp^2 hybridization approach each other, they form a strong σ bond by sp^2-sp^2 head-on overlap. At the same time, the unhybridized p orbitals interact by sideways overlap to form what is called a **pi (π) bond**. The combination of an sp^2-sp^2 σ bond and a $2p-2p$ π bond results in the sharing of four electrons and the formation of a carbon–carbon double bond (**FIGURE 1.15**). Note that the electrons in the σ bond occupy the region centered between nuclei, while the electrons in the π bond occupy regions above and below a line drawn between nuclei.

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

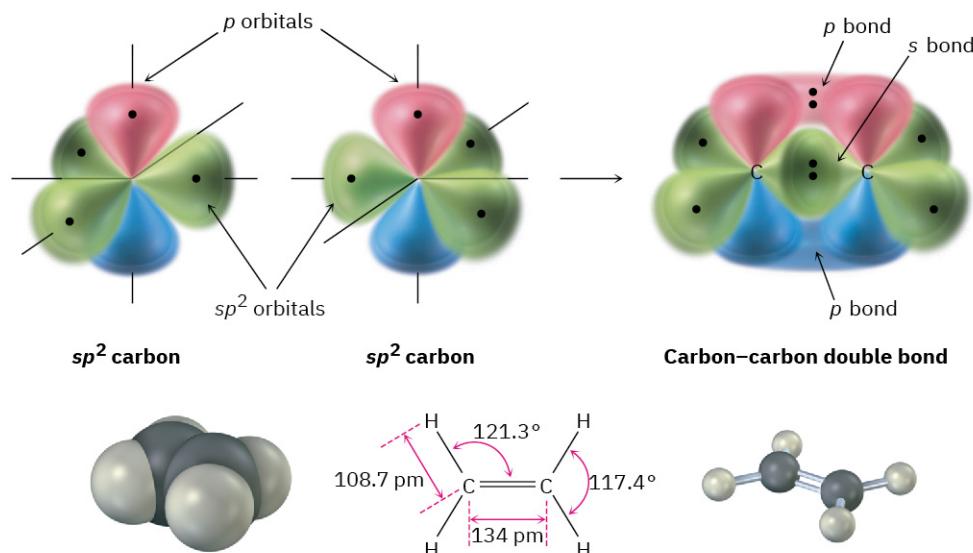


FIGURE 1.15 The structure of ethylene. One part of the double bond in ethylene results from σ (head-on) overlap of sp^2 hybrid orbitals, and the other part results from π (sideways) overlap of unhybridized **p orbitals** (red/blue). The π bond has regions of electron density above and below a line drawn between nuclei.

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



WORKED EXAMPLE 1.3

Drawing Electron-Dot and Line-Bond Structures

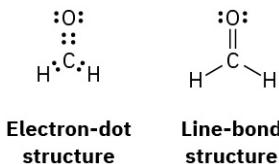
Commonly used in biology as a tissue preservative, formaldehyde, CH₂O, contains a carbon–oxygen double bond. Draw electron-dot and line-bond structures of formaldehyde, and indicate the hybridization of the carbon orbitals.

Strategy

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

Solution

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

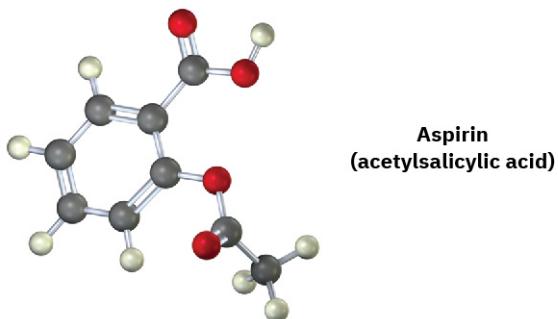


Like the carbon atoms in ethylene, the carbon atom in formaldehyde is in a double bond and its orbitals are therefore sp^2 -hybridized.

PROBLEM Draw a line-bond structure for propene, CH₃CH=CH₂. Indicate the hybridization of the orbitals on **1-10** each carbon, and predict the value of each bond angle.

PROBLEM Draw a line-bond structure for 1,3-butadiene, H₂C=CH–CH=CH₂. Indicate the hybridization of the orbitals on each carbon, and predict the value of each bond angle.

PROBLEM A molecular model of aspirin (acetylsalicylic acid) is shown. Identify the hybridization of the **1-12** orbitals on each carbon atom in aspirin, and tell which atoms have lone pairs of electrons (black = C, red = O, gray = H).



1.9 *sp* Hybrid Orbitals and the Structure of Acetylene

In addition to forming single and double bonds by sharing two and four electrons, respectively, carbon can also form a *triple bond* by sharing six electrons. To account for the triple bond in a molecule such as acetylene, H–C≡C–H, we need a third kind of hybrid orbital, an ***sp* hybrid**. Imagine that, instead of combining with two or three *p* orbitals, a carbon 2s orbital hybridizes with only a single *p* orbital. Two *sp* hybrid orbitals result, and two *p* orbitals remain unchanged. The two *sp* orbitals are oriented 180° apart on the right-left (*x*) axis, while the *p* orbitals are perpendicular on the up-down (*y*) axis and the in-out (*z*) axis, as shown in **FIGURE 1.16**.

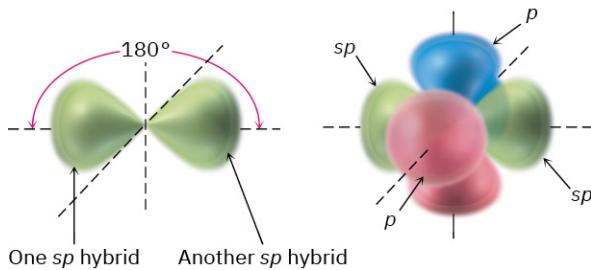


FIGURE 1.16 *sp* Hybridization. The two ***sp* hybrid orbitals** are oriented 180° away from each other, perpendicular to the two remaining *p* orbitals (red/blue).

When two *sp*-hybridized carbon atoms approach each other, *sp* hybrid orbitals on each carbon overlap head-on to form a strong *sp-sp* σ bond. At the same time, the p_z orbitals from each carbon form a p_z-p_z π bond by sideways overlap, and the p_y orbitals overlap similarly to form a p_y-p_y π bond. The net effect is the sharing of six electrons and formation of a carbon–carbon triple bond. Each of the two remaining *sp* hybrid orbitals forms a σ bond with hydrogen to complete the acetylene molecule (**FIGURE 1.17**).

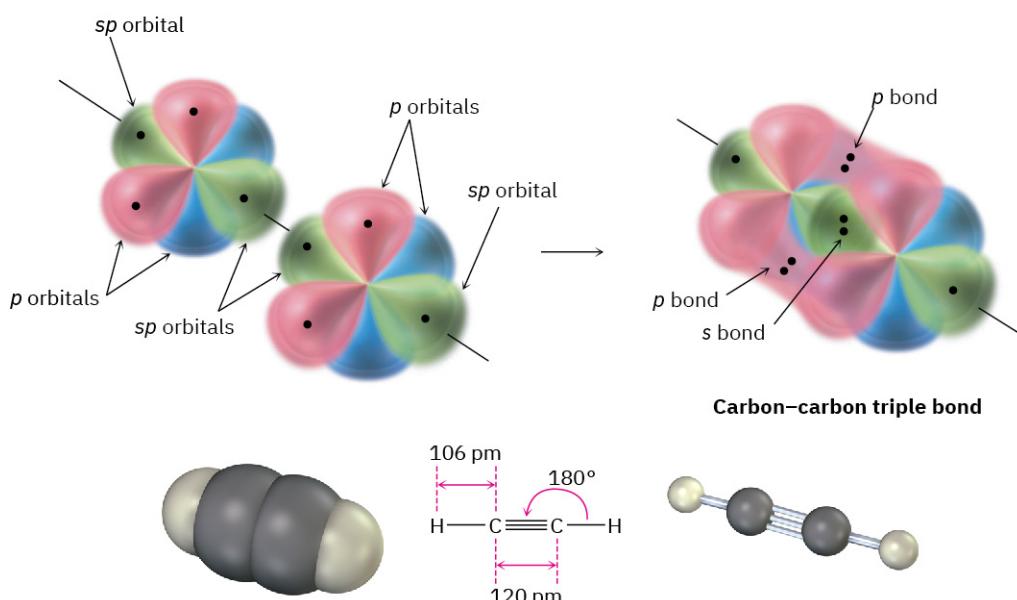


FIGURE 1.17 The structure of acetylene. The two carbon atoms are joined by one sp - sp σ bond and two p - p π bonds.

As suggested by sp hybridization, acetylene is a linear molecule with H-C-C bond angles of 180° . The C-H bonds have a length of 106 pm and a strength of 558 kJ/mol (133 kcal/mol). The C-C bond length in acetylene is 120 pm, and its strength is about 965 kJ/mol (231 kcal/mol), making it the shortest and strongest of any carbon–carbon bond. A comparison of sp , sp^2 , and sp^3 hybridization is given in **TABLE 1.2**.

TABLE 1.2 Comparison of C–C and C–H Bonds in Methane, Ethane, Ethylene, and Acetylene

Molecule	Bond	Bond strength		Bond length (pm)
		(kJ/mol)	(kcal/mol)	
Methane, CH ₄	(sp^3) C–H	439	105	109
Ethane, CH ₃ CH ₃	(sp^3) C–C (sp^3)	377	90	153
	(sp^3) C–H	421	101	109
Ethylene, H ₂ C=CH ₂	(sp^2) C=C (sp^2)	728	174	134
	(sp^2) C–H	464	111	109
Acetylene, HC≡CH	(sp) C≡C (sp)	965	231	120
	(sp) C–H	558	133	106

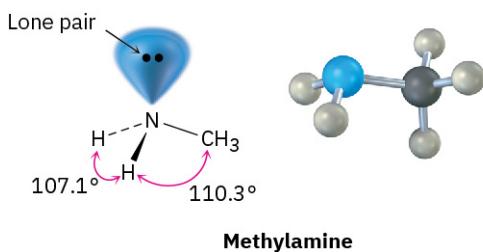
PROBLEM Draw a line-bond structure for propyne, CH₃C≡CH. Indicate the hybridization of the orbitals on **1-13** each carbon, and predict a value for each bond angle.

1.10 Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

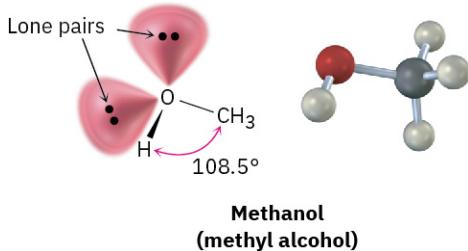
The valence-bond concept of orbital hybridization described in the previous four sections is not limited to carbon. Covalent bonds formed by other elements can also be described using hybrid orbitals. Look, for instance, at the nitrogen atom in methylamine (CH₃NH₂), an organic derivative of ammonia (NH₃) and the substance responsible for the odor of rotting fish.

The experimentally measured H–N–H bond angle in methylamine is 107.1° , and the C–N–H bond angle is

110.3° , both of which are close to the 109.5° tetrahedral angle found in methane. We therefore assume that nitrogen forms four sp^3 -hybridized orbitals, just as carbon does. One of the four sp^3 orbitals is occupied by two nonbonding electrons (a lone pair), and the other three hybrid orbitals have one electron each. Overlap of these three half-filled nitrogen orbitals with half-filled orbitals from other atoms (C or H) gives methylamine. Note that the unshared lone pair of electrons in the fourth sp^3 hybrid orbital of nitrogen occupies as much space as an N–H bond does and is very important to the chemistry of methylamine and other nitrogen-containing organic molecules.

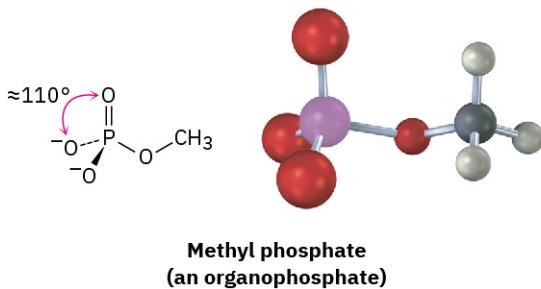


Like the carbon atom in methane and the nitrogen atom in methylamine, the oxygen atom in methanol (methyl alcohol) and many other organic molecules can be described as sp^3 -hybridized. The C–O–H bond angle in methanol is 108.5° , very close to the 109.5° tetrahedral angle. Two of the four sp^3 hybrid orbitals on oxygen are occupied by nonbonding electron lone pairs, and two are used to form bonds.

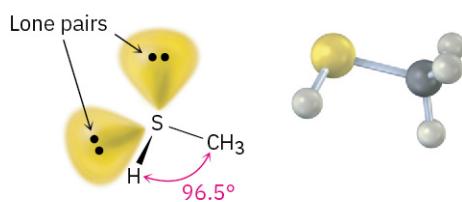


In the periodic table, phosphorus and sulfur are the third-row analogs of nitrogen and oxygen, and the bonding in both can be described using hybrid orbitals. Because of their positions in the third row, however, both phosphorus and sulfur can expand their outer-shell octets and form more than the typical number of covalent bonds. Phosphorus, for instance, often forms five covalent bonds, and sulfur often forms four.

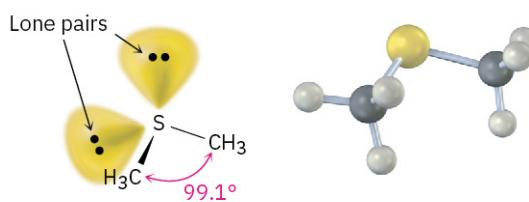
Phosphorus is most commonly encountered in biological molecules in compounds called *organophosphates*, which contain a phosphorus atom bonded to four oxygens, with one of the oxygens also bonded to carbon. Methyl phosphate, $\text{CH}_3\text{OPO}_3^{2-}$, is the simplest example. The O–P–O bond angle in such compounds is typically in the range 110° to 112° , implying sp^3 hybridization for phosphorus orbitals.



Sulfur is most commonly encountered in biological molecules either in compounds called *thiols*, which have a sulfur atom bonded to one hydrogen and one carbon, C–S–H or in *sulfides*, which have a sulfur atom bonded to two carbons, C–S–C. Produced by some bacteria, methanethiol (CH_3SH) is the simplest example of a thiol, and dimethyl sulfide, $\text{H}_3\text{C}-\text{S}-\text{CH}_3$, is the simplest example of a sulfide. Both can be described by approximate sp^3 hybridization around sulfur, although both have significant deviation from the 109.5° tetrahedral angle.



Methanethiol

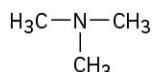


Dimethyl sulfide

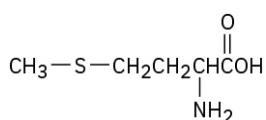
PROBLEM Identify all nonbonding lone pairs of electrons in the following molecules, and tell what geometry

1-14 you expect for each of the indicated atoms.

- (a) The oxygen atom in dimethyl ether, CH₃-O-CH₃ (b) The nitrogen atom in trimethylamine,



- (c) The phosphorus atom in phosphine, PH₃
 (d) The sulfur atom in the amino acid methionine,



1.11 Describing Chemical Bonds: Molecular Orbital Theory

We said in [Section 1.5](#) that chemists use two models for describing covalent bonds: valence bond theory and molecular orbital theory. Having now seen the valence bond approach, which uses hybrid atomic orbitals to account for geometry and assumes the overlap of atomic orbitals to account for electron sharing, let's look briefly at the molecular orbital approach to bonding. We'll return to this topic in Chapters 14, 15, and 30 for a more in-depth discussion.

Molecular orbital (MO) theory describes covalent bond formation as arising from a mathematical combination of atomic orbitals (wave functions) on different atoms to form *molecular orbitals*, so called because they belong to the entire molecule rather than to an individual atom. Just as an *atomic* orbital, whether unhybridized or hybridized, describes a region of space around an *atom* where an electron is likely to be found, so a *molecular* orbital describes a region of space in a *molecule* where electrons are most likely to be found.

Like an atomic orbital, a molecular orbital has a specific size, shape, and energy. In the H₂ molecule, for example, two singly occupied 1s atomic orbitals combine to form two molecular orbitals. There are two ways for the orbital combination to occur—an additive way and a subtractive way. The additive combination leads to formation of a molecular orbital that is lower in energy and roughly egg-shaped, while the subtractive combination leads to a molecular orbital that is higher in energy and has a node between nuclei ([FIGURE 1.18](#)). Note that the additive combination is a single, egg-shaped, molecular orbital; it is not the same as the two overlapping 1s atomic orbitals of the valence bond description. Similarly, the subtractive combination is a single molecular orbital with the shape of an elongated dumbbell.

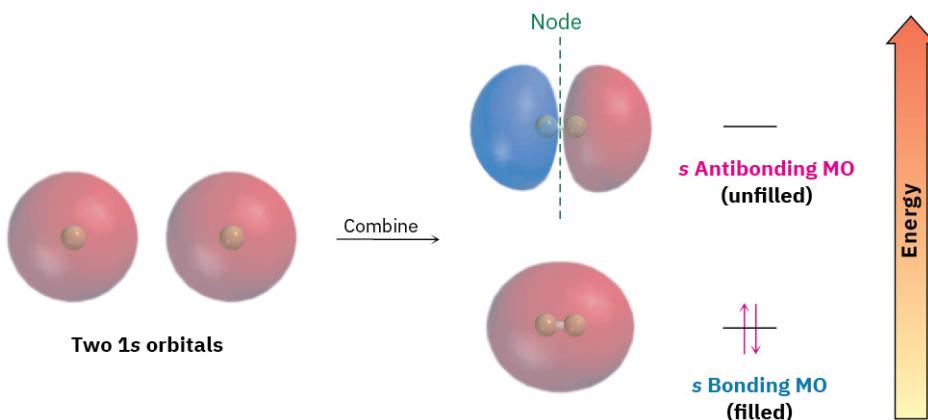


FIGURE 1.18 Molecular orbitals of H_2 . Combination of two hydrogen 1s atomic orbitals leads to two H_2 molecular orbitals. The lower-energy, **bonding MO** is filled, and the higher-energy, **antibonding MO** is unfilled.

The additive combination is lower in energy than the two hydrogen 1s atomic orbitals and is called a **bonding MO** because electrons in this MO spend most of their time in the region between the two nuclei, thereby bonding the atoms together. The subtractive combination is higher in energy than the two hydrogen 1s orbitals and is called an **antibonding MO** because any electrons it contains *can't* occupy the central region between the nuclei, where there is a node, and thus can't contribute to bonding. The two nuclei therefore repel each other.

Just as bonding and antibonding σ molecular orbitals result from the head-on combination of two s atomic orbitals in H_2 , so bonding and antibonding π molecular orbitals result from the sideways combination of two p atomic orbitals in ethylene. As shown in **FIGURE 1.19**, the lower-energy, π bonding MO has no node between nuclei and results from the combination of p orbital lobes with the same algebraic sign. The higher-energy, π antibonding MO has a node between nuclei and results from the combination of lobes with opposite algebraic signs. Only the bonding MO is occupied; the higher-energy, antibonding MO is vacant. We'll see in Chapters 14, 15, and 30 that molecular orbital theory is particularly useful for describing π bonds in compounds that have more than one double bond.

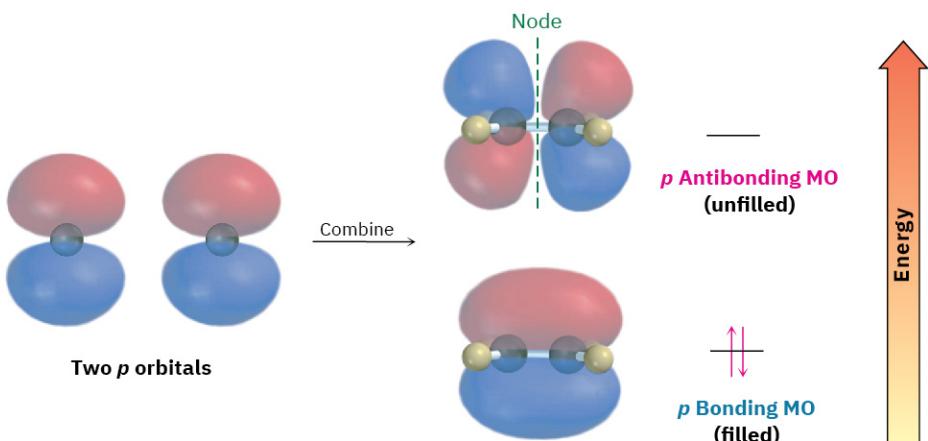
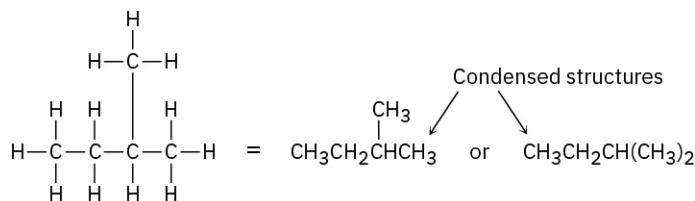


FIGURE 1.19 A molecular orbital description of the C–C π bond in ethylene. The lower-energy, π bonding MO results from an additive combination of p orbital lobes with the same algebraic sign and is filled. The higher-energy, π antibonding MO results from a subtractive combination of p orbital lobes with opposite algebraic signs and is unfilled.

1.12 Drawing Chemical Structures

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



2-Methylbutane

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

Even simpler than condensed structures are **skeletal structures** such as those shown in **TABLE 1.3**. The rules for drawing skeletal structures are straightforward.

RULE 1

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

RULE 2

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

RULE 3

Atoms other than carbon and hydrogen are shown.

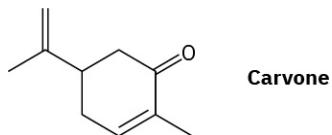
One further comment: Although such groupings as $-\text{CH}_3$, $-\text{OH}$, and $-\text{NH}_2$ are usually written with the C, O, or N atom first and the H atom second, the order of writing is sometimes inverted to $\text{H}_3\text{C}-$, $\text{HO}-$, and $\text{H}_2\text{N}-$ if needed to make the bonding connections clearer. Larger units such as $-\text{CH}_2\text{CH}_3$ are not inverted, though; we don't write H_3CH_2- because it would be confusing. There are, however, no well-defined rules that cover all cases; it's largely a matter of preference.

TABLE 1.3 Line-bond and Skeletal Structures for Some Compounds

Compound	Line-bond structure	Skeletal structure
Isoprene, C_5H_8		
Methylcyclohexane, C_7H_{14}		
Phenol, $\text{C}_6\text{H}_6\text{O}$		

**WORKED EXAMPLE 1.4****Interpreting a Line-Bond Structure**

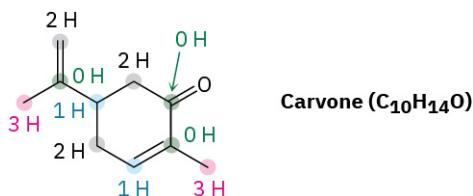
Carvone, a substance responsible for the odor of spearmint, has the following structure. Tell how many hydrogens are bonded to each carbon, and give the molecular formula of carvone.



Carvone

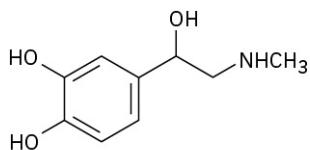
Strategy

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

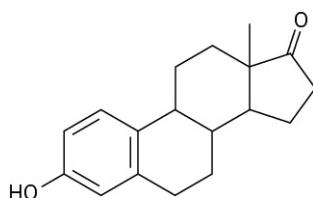
Solution

PROBLEM How many hydrogens are bonded to each carbon in the following compounds, and what is the
1-15 molecular formula of each substance?

(a)



(b)



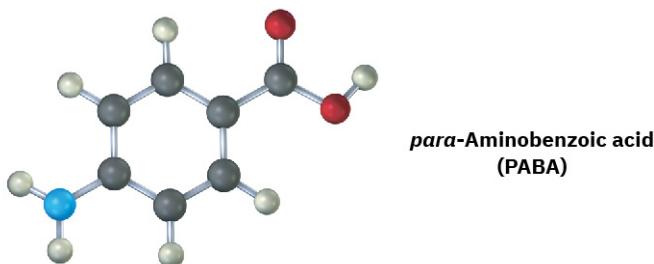
Adrenaline

Estrone (a hormone)

PROBLEM Propose skeletal structures for compounds that satisfy the following molecular formulas: There is
1-16 more than one possibility in each case.

- (a) C_5H_{12} (b) $\text{C}_2\text{H}_7\text{N}$ (c) $\text{C}_3\text{H}_6\text{O}$ (d) $\text{C}_4\text{H}_9\text{Cl}$

PROBLEM The following molecular model is a representation of *para*-aminobenzoic acid (PABA), the active
1-17 ingredient in many sunscreens. Indicate the positions of the multiple bonds, and draw a skeletal
structure (black = C, red = O, blue = N, gray = H).

para-Aminobenzoic acid
(PABA)



CHEMISTRY MATTERS

Organic Foods: Risk versus Benefit

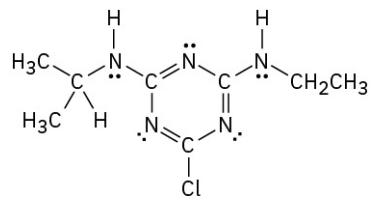
Contrary to what you may hear in supermarkets or on television, all foods are organic—that is, complex mixtures of organic molecules. Even so, when applied to food, the word *organic* has come to mean an absence of synthetic chemicals, typically pesticides, antibiotics, and preservatives. How concerned should we be about traces of pesticides in the food we eat? Or toxins in the water we drink? Or pollutants in the air we breathe?

Life is not risk-free—we all take many risks each day without even thinking about it. We decide to ride a bike rather than drive, even though there is a ten times greater likelihood per mile of dying in a bicycling accident than in a car. We decide to walk down stairs rather than take an elevator, even though 32,000 people die from falls each year in the United States. Some of us decide to smoke cigarettes, even though it increases our chance of getting cancer by 50%. But what about risks from chemicals like pesticides?



FIGURE 1.20 How dangerous is the pesticide being sprayed on this crop? (credit: “NRCSAR83001(265)” by USDA Natural Resources Conservation Service/Wikimedia Commons, Public Domain)

One thing is certain: without pesticides, whether they target weeds (herbicides), insects (insecticides), or molds and fungi (fungicides), crop production would drop significantly, food prices would increase, and famines would occur in less developed parts of the world. Take the herbicide atrazine, for instance. In the United States alone, approximately 100 million pounds of atrazine are used each year to kill weeds in corn, sorghum, and sugarcane fields, greatly improving the yields of these crops. Nevertheless, the use of atrazine continues to be a concern because traces persist in the environment. Indeed, heavy atrazine exposure *can* pose health risks to humans and some animals. Because of these risks, the United States Environmental Protection Agency (EPA) has decided not to ban its use because doing so would result in lower crop yields and increased food costs, and because there is no suitable alternative herbicide available.



Atrazine

How can the potential hazards from a chemical like atrazine be determined? Risk evaluation of chemicals is carried out by exposing test animals, usually mice or rats, to the chemical and then monitoring the animals for signs of harm. To limit the expense and time needed, the amounts administered are typically hundreds or thousands of times greater than those a person might normally encounter. The results obtained in animal tests are then distilled into a single number called an LD₅₀, the amount of substance per kilogram of body weight that

is a lethal dose for 50% of the test animals. For atrazine, the LD₅₀ value is between 1 and 4 g/kg depending on the animal species. Aspirin, for comparison, has an LD₅₀ of 1.1 g/kg, and ethanol (ethyl alcohol) has an LD₅₀ of 10.6 g/kg.

TABLE 1.4 lists the LD₅₀ for some other familiar substances. The lower the value, the more toxic the substance. Note, though, that LD₅₀ values only pertain to the effects of heavy exposure for a relatively short time. They say nothing about the risks of long-term exposure, such as whether the substance can cause cancer or interfere with development in the unborn.

TABLE 1.4 Some LD₅₀ Values

Substance	LD ₅₀ (g/kg)	Substance	LD ₅₀ (g/kg)
Strychnine	0.005	Chloroform	1.2
Arsenic trioxide	0.015	Iron(II) sulfate	1.5
DDT	0.115	Ethyl alcohol	10.6
Aspirin	1.1	Sodium cyclamate	17

So, should we still use atrazine? All decisions involve tradeoffs, and the answer is rarely obvious. Does the benefit of increased food production outweigh possible health risks of a pesticide? Do the beneficial effects of a new drug outweigh a potentially dangerous side effect in a small number of users? Different people will have different opinions, but an honest evaluation of facts is surely the best way to start. As of June 2022, atrazine was still approved for continued use in the United States because the EPA believes that the benefits of increased food production outweigh possible health risks. At the same time, atrazine is little used, though not banned, in the European Union.

Key Terms

- antibonding MO
- atomic number (Z)
- Aufbau principle
- bond angle
- bond length
- bond strength
- bonding MO
- condensed structure
- covalent bond
- electron shell
- electron-dot structure
- ground-state electron configuration
- Hund's rule
- ionic bond
- isotope
- Kekulé structure
- Lewis structure
- line-bond structure
- lone-pair electrons
- mass number (A)
- molecular orbital (MO) theory
- molecule
- node
- nonbonding electron
- orbital
- organic chemistry
- Pauli exclusion principle
- pi (π) bond
- sigma (σ) bond
- skeletal structure
- sp hybrid orbital
- sp^2 hybrid orbital
- sp^3 hybrid orbital
- valence bond (VB) theory
- valence shell

Summary

The purpose of this chapter has been to get you up to speed—to review some ideas about atoms, bonds, and molecular geometry. As we've seen, **organic chemistry** is the study of carbon compounds. Although a division into organic and inorganic chemistry occurred historically, there is no scientific reason for the division.

An atom consists of a positively charged nucleus surrounded by one or more negatively charged electrons. The electronic structure of an atom can be described by a quantum mechanical wave equation, in which electrons are considered to occupy **orbitals** around the nucleus. Different orbitals have different energy levels and different shapes. For example, *s* orbitals are spherical and *p* orbitals are dumbbell-shaped. The **ground-state electron configuration** of an atom can be found by assigning electrons to the proper orbitals, beginning with the lowest-energy ones.

A **covalent bond** is formed when an electron pair is shared between atoms. According to **valence bond (VB) theory**, electron sharing occurs by the overlap of two atomic orbitals. According to **molecular orbital (MO) theory**, bonds result from the mathematical combination of atomic orbitals to give molecular orbitals, which belong to the entire molecule. Bonds that have a circular cross-section and are formed by head-on interaction are called **sigma (*σ*) bonds**; bonds formed by sideways interaction of *p* orbitals are called **pi (*π*) bonds**.

In the valence bond description, carbon uses hybrid orbitals to form bonds in organic molecules. When forming only single bonds with tetrahedral geometry, carbon uses four equivalent ***sp*³ hybrid orbitals**. When forming a double bond with planar geometry, carbon uses three equivalent ***sp*² hybrid orbitals** and one unhybridized *p* orbital. When forming a triple bond with linear geometry, carbon uses two equivalent ***sp* hybrid orbitals** and two unhybridized *p* orbitals. Other atoms such as nitrogen, phosphorus, oxygen, and sulfur also use hybrid orbitals to form strong, oriented bonds.

Organic molecules are usually drawn using either condensed structures or skeletal structures. In **condensed structures**, carbon–carbon and carbon–hydrogen bonds aren't shown. In **skeletal structures**, only the bonds and not the atoms are shown. A carbon atom is assumed to be at the ends and at the junctions of lines (bonds), and the correct number of hydrogens is supplied mentally.

WHY YOU SHOULD WORK PROBLEMS

There's no surer way to learn organic chemistry than by working problems. Although careful reading and rereading of this text are important, reading alone isn't enough. You must also be able to use the information you've read and be able to apply your knowledge in new situations. Working problems gives you practice at doing this.

Each chapter in this book provides many problems of different sorts. The in-chapter problems are placed for immediate reinforcement of ideas just learned, while end-of-chapter problems provide additional practice and come in several forms. They often begin with a short section called "Visualizing Chemistry," which helps you see the microscopic world of molecules and provides practice for working in three dimensions. After the visualizations are many further problems, which are organized by topic. Early problems are primarily of the drill type, providing an opportunity for you to practice your command of the fundamentals. Later problems tend to be more thought-provoking, and some are real challenges.

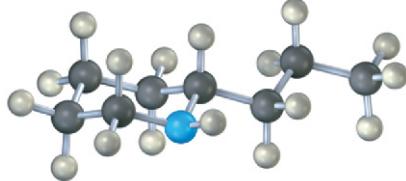
As you study organic chemistry, take the time to work the problems. Do the ones you can, and ask for help on the ones you can't. If you're stumped by a particular problem, check the accompanying *Study Guide* and *Student Solutions Manual* for an explanation that should help clarify the difficulty. Working problems takes effort, but the payoff in knowledge and understanding is immense.

Additional Problems

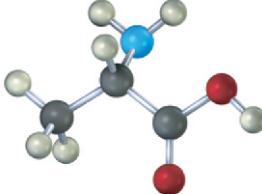
Visualizing Chemistry

PROBLEM Convert each of the following molecular models into a skeletal structure, and give the formula of **1-18** each. Only the connections between atoms are shown; multiple bonds are not indicated (black = C, red = O, blue = N, gray = H).

(a)

Coniine (the toxic substance
in poison hemlock)

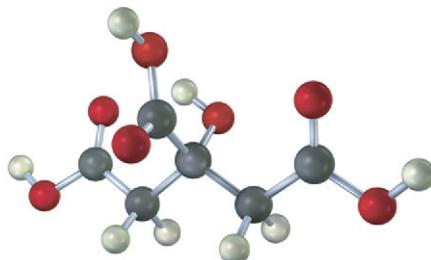
(b)



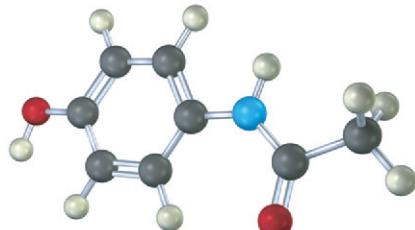
Alanine (an amino acid)

PROBLEM The following model is a representation of citric acid, the key substance in the so-called citric acid

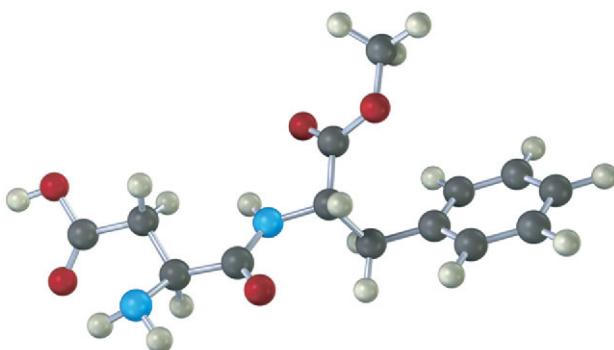
- 1-19** cycle, by which food molecules are metabolized in the body. Only the connections between atoms are shown; multiple bonds are not indicated. Complete the structure by indicating the positions of multiple bonds and lone-pair electrons (black = C, red = O, gray = H).

**PROBLEM** The following model is a representation of acetaminophen, a pain reliever sold in drugstores

- 1-20** under a variety of names, including Tylenol. Identify the hybridization of each carbon atom in acetaminophen, and tell which atoms have lone pairs of electrons (black = C, red = O, blue = N, gray = H).

**PROBLEM** The following model is a representation of aspartame, C₁₄H₁₈N₂O₅, known commercially under

- 1-21** many names, including NutraSweet. Only the connections between atoms are shown; multiple bonds are not indicated. Complete the structure for aspartame, and indicate the positions of multiple bonds (black = C, red = O, blue = N, gray = H).



Electron Configurations

PROBLEM How many valence electrons does each of the following dietary trace elements have?

- 1-22 (a) Zinc (b) Iodine (c) Silicon (d) Iron

PROBLEM Give the ground-state electron configuration for each of the following elements:

- 1-23 (a) Potassium (b) Arsenic (c) Aluminum (d) Germanium

Electron-Dot and Line-Bond Structures

PROBLEM What are likely formulas for the following molecules?

- 1-24 (a) NH₂OH (b) AlCl₃ (c) CF₂Cl₂ (d) CH₂O

PROBLEM Why can't molecules with the following formulas exist?

- 1-25 (a) CH₅ (b) C₂H₆N (c) C₃H₅Br₂

PROBLEM Draw an electron-dot structure for acetonitrile, C₂H₃N, which contains a carbon–nitrogen triple bond.

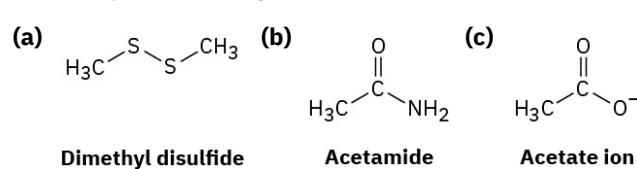
- 1-26 How many electrons does the nitrogen atom have in its outer shell? How many are bonding, and how many are nonbonding?

PROBLEM Draw a line-bond structure for vinyl chloride, C₂H₃Cl, the starting material from which PVC

- 1-27 poly(vinyl chloride) plastic is made.

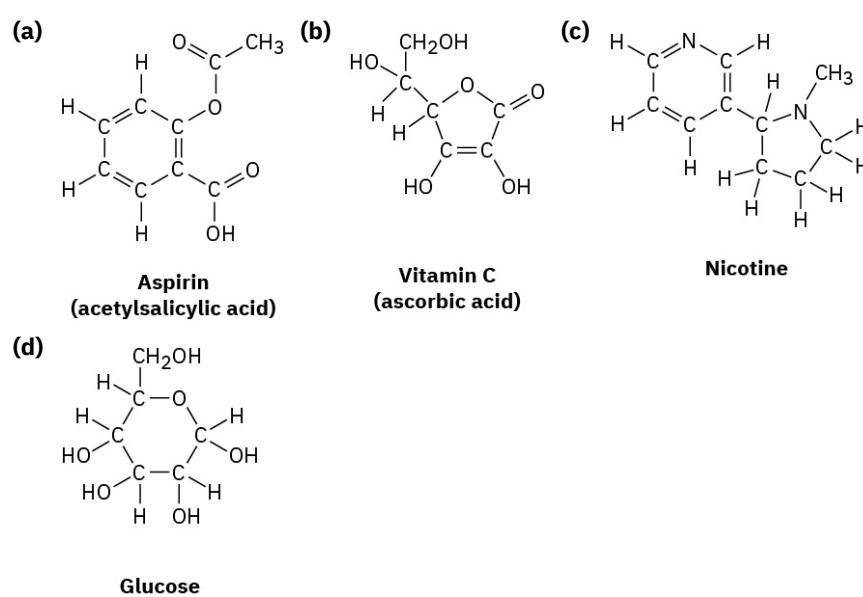
PROBLEM Fill in any nonbonding valence electrons that are missing from the following structures:

1-28



PROBLEM Convert the following line-bond structures into molecular formulas:

1-29



PROBLEM Convert the following molecular formulas into line-bond structures that are consistent with valence

- 1-30 rules:

- (a) C₃H₈ (b) CH₅N (c) C₂H₆O (2 possibilities) (d) C₃H₇Br (2 possibilities)
(e) C₂H₄O (3 possibilities) (f) C₃H₉N (4 possibilities)

PROBLEM Draw a three-dimensional representation of the oxygen-bearing carbon atom in ethanol,

- 1-31 CH₃CH₂OH, using the standard convention of solid, wedged, and dashed lines.

PROBLEM Oxaloacetic acid, an important intermediate in food metabolism, has the formula C₄H₄O₅ and
1-32 contains three C=O bonds and two O—H bonds. Propose two possible structures.

PROBLEM Draw structures for the following molecules, showing lone pairs:

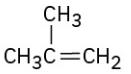
- 1-33** (a) Acrylonitrile, C₃H₃N, which contains a carbon–carbon double bond and a carbon–nitrogen triple bond
 (b) Ethyl methyl ether, C₃H₈O, which contains an oxygen atom bonded to two carbons
 (c) Butane, C₄H₁₀, which contains a chain of four carbon atoms
 (d) Cyclohexene, C₆H₁₀, which contains a ring of six carbon atoms and one carbon–carbon double bond

Hybridization

PROBLEM What is the hybridization of each carbon atom in acetonitrile (Problem 1-26)?

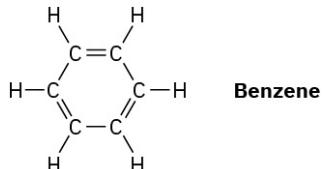
1-34

PROBLEM What kind of hybridization do you expect for each carbon atom in the following molecules?

- 1-35** (a) Propane, CH₃CH₂CH₃ (b) 2-Methylpropene,  (c) But-1-en-3-yne, H₂C=CH—C≡CH
 (d) Acetic acid, 

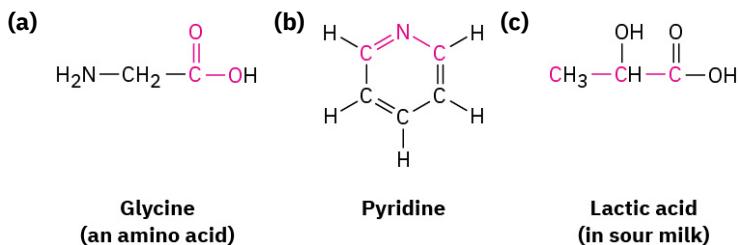
PROBLEM What is the shape of benzene, and what hybridization do you expect for each carbon?

1-36



PROBLEM What bond angle do you expect for each of the indicated atoms, and what kind of hybridization do

- 1-37** you expect for the central atom in each molecule?

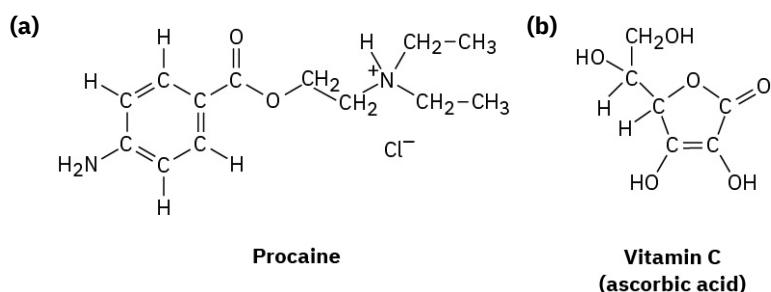


PROBLEM Propose structures for molecules that meet the following descriptions:

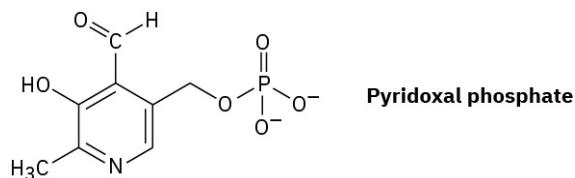
- 1-38** (a) Contains two sp²-hybridized carbons and two sp³-hybridized carbons
 (b) Contains only four carbons, all of which are sp²-hybridized
 (c) Contains two sp-hybridized carbons and two sp²-hybridized carbons

PROBLEM What kind of hybridization do you expect for each carbon atom in the following molecules?

1-39

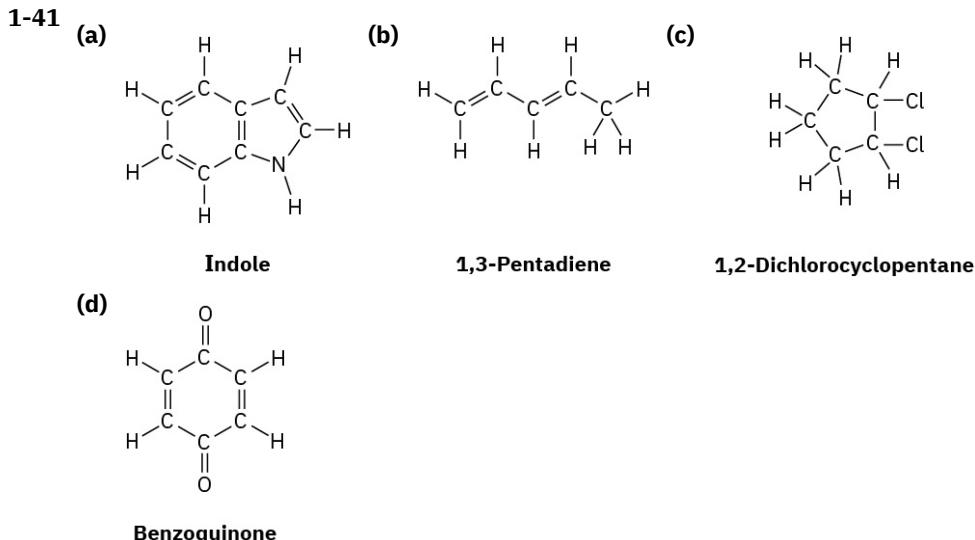


PROBLEM Pyridoxal phosphate, a close relative of vitamin B₆, is involved in a large number of metabolic reactions. What is the hybridization and the bond angle for each nonterminal atom?

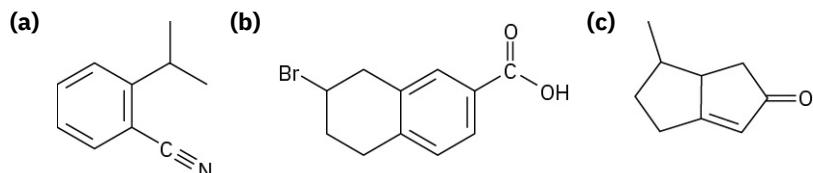


Skeletal Structures

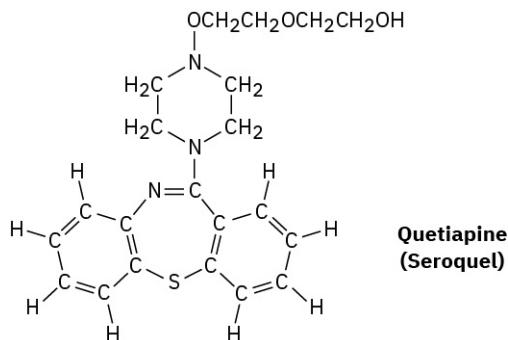
PROBLEM Convert the following structures into skeletal drawings:



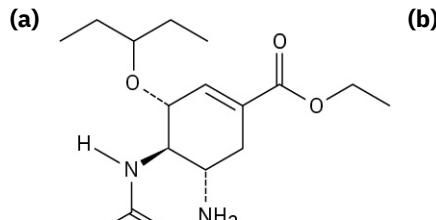
PROBLEM How many hydrogens are bonded to each carbon atom in the following substances, and what is the molecular formula of each?



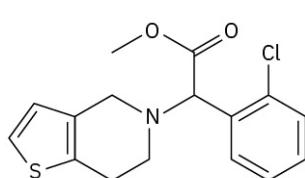
PROBLEM Quetiapine, marketed as Seroquel, is a heavily prescribed antipsychotic drug used in the treatment of schizophrenia and bipolar disorder. Convert the following representation into a skeletal structure, and give the molecular formula of quetiapine.



PROBLEM How many hydrogens are bonded to each carbon atom in (a) the antinfluenza agent oseltamivir, **1-44** marketed as Tamiflu, and (b) the platelet aggregation inhibitor clopidogrel, marketed as Plavix? Give the molecular formula of each.



Oseltamivir
(Tamiflu)



Clopidogrel
(Plavix)

General Problems

PROBLEM Why do you suppose no one has ever been able to make cyclopentyne as a stable molecule?

1-45

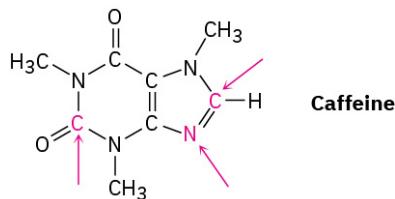


Cyclopentyne

PROBLEM Allene, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, has two adjacent double bonds. Draw a picture showing the orbitals involved **1-46** in the σ and π bonds of allene. Is the central carbon atom sp^2 - or sp -hybridized? What about the hybridization of the terminal carbons? What shape do you predict for allene?

PROBLEM Allene (see Problem 1-46) is structurally related to carbon dioxide, CO_2 . Draw a picture showing the **1-47** orbitals involved in the σ and π bonds of CO_2 , and identify the likely hybridization of carbon.

PROBLEM Complete the electron-dot structure of caffeine, showing all lone-pair electrons, and identify the **1-48** hybridization of the indicated atoms.



PROBLEM Most stable organic species have tetravalent carbon atoms, but species with trivalent carbon atoms **1-49** also exist. Carbocations are one such class of compounds.



(a) How many valence electrons does the positively charged carbon atom have?

(b) What hybridization do you expect this carbon atom to have?

(c) What geometry is the carbocation likely to have?

PROBLEM A carbanion is a species that contains a negatively charged, trivalent carbon.

1-50



(a) What is the electronic relationship between a carbanion and a trivalent nitrogen compound such as NH_3 ?

(b) How many valence electrons does the negatively charged carbon atom have?

(c) What hybridization do you expect this carbon atom to have?

(d) What geometry is the carbanion likely to have?

PROBLEM Divalent carbon species called *carbenes* are capable of fleeting existence. For example, methylene,

1-51 : CH_2 , is the simplest carbene. The two unshared electrons in methylene can be either paired in a single orbital or unpaired in different orbitals. Predict the type of hybridization you expect carbon to adopt in singlet (spin-paired) methylene and triplet (spin-unpaired) methylene. Draw a picture of each, and identify the valence orbitals on carbon.

PROBLEM Two different substances have the formula C_4H_{10} . Draw both, and tell how they differ.

1-52

PROBLEM Two different substances have the formula C_3H_6 . Draw both, and tell how they differ.

1-53

PROBLEM Two different substances have the formula $\text{C}_2\text{H}_6\text{O}$. Draw both, and tell how they differ.

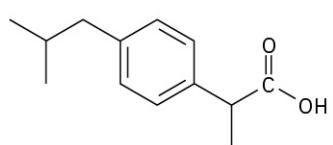
1-54

PROBLEM Three different substances contain a carbon–carbon double bond and have the formula C_4H_8 . Draw

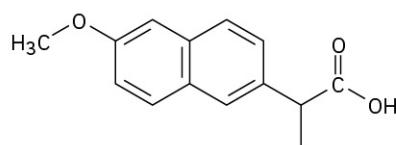
1-55 them, and tell how they differ.

PROBLEM Among the most common over-the-counter drugs you might find in a medicine cabinet are mild

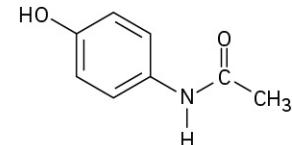
1-56 pain relievers such ibuprofen (Advil, Motrin), naproxen (Aleve), and acetaminophen (Tylenol).



Ibuprofen



Naproxen



Acetaminophen

(a) How many sp^3 -hybridized carbons does each molecule have?

(b) How many sp^2 -hybridized carbons does each molecule have?

(c) What similarities can you see in their structures?