

# 1

## Structure and Bonding

### Organic KNOWLEDGE TOOLS

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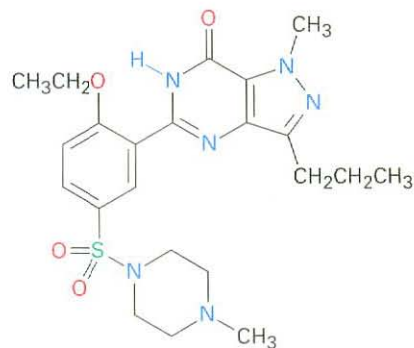


Online homework for this and other chapters may be assigned in Organic OWL.

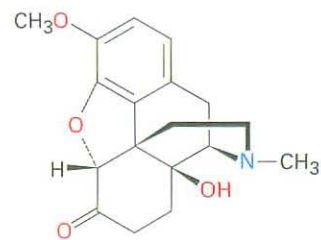
What is organic chemistry, and why should you study it? The answers to these questions are all around you. Every living organism is made of organic chemicals. The proteins that make up your hair, skin, and muscles; the DNA that controls your genetic heritage; the foods that nourish you; and the medicines 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 many exciting developments now happening 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



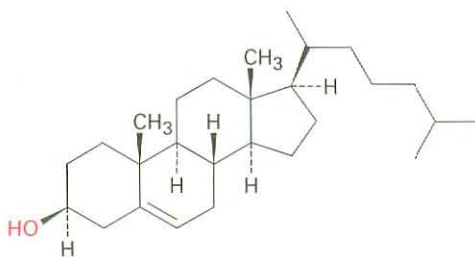
**Rofecoxib**  
(Vioxx)



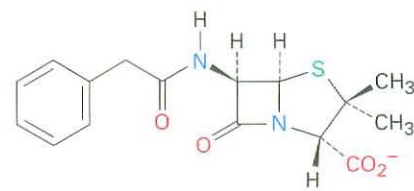
**Sildenafil**  
(Viagra)



**Oxycodone**  
(OxyContin)



**Cholesterol**



**Benzylpenicillin**

Although the drawings may appear unintelligible at this point, don't worry. Before long they'll make perfectly good sense and you'll be drawing similar structures for any substance you're interested in.

The foundations of organic chemistry date from the mid-1700s, when chemistry was evolving from an alchemist's art into a modern science. At that time, unexplainable differences were noted between substances obtained from living sources and those obtained from minerals. Compounds obtained from plants and animals were often difficult to isolate and purify. Even when pure, they were often difficult to work with, and they tended to decompose more easily than compounds obtained from minerals. The Swedish chemist Torbern Bergman in 1770 was the first to express this difference between "organic" and "inorganic" substances, and the term *organic chemistry* soon came to mean the chemistry of compounds found in living organisms.

To many chemists of the time, the only explanation for the differences in behavior between organic and inorganic compounds was that organic compounds must contain a peculiar "vital force" as a result of their origin in living sources. One consequence of this vital force, chemists believed, was that organic compounds could not be prepared and manipulated in the laboratory as could inorganic compounds. As early as 1816, however, this vitalistic theory received a heavy blow when Michel Chevreul found that soap, prepared by the reaction of alkali with animal fat, could be separated into several pure organic compounds, which he termed *fatty acids*. For the first time, one organic substance (fat) was converted into others (fatty acids plus glycerin) without the intervention of an outside vital force.

### Michel-Eugène Chevreul

#### Michel-Eugène Chevreul

(1786–1889) was born in Angers, France. After studies at the Collège de France in Paris, he became professor of physics at the Lycée Charlemagne in 1813 and professor of chemistry in 1830. Chevreul's studies of soaps and waxes led him to patent a method for manufacturing candles. He also published work on the psychology of color perception and of aging. All France celebrated his 100th birthday in 1886.

### Friedrich Wöhler

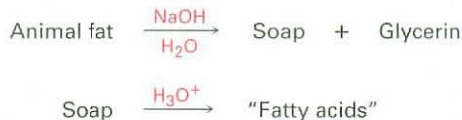
#### Friedrich Wöhler (1800–1882)

was born in Eschersheim, Germany, and studied at Heidelberg under Leopold Gmelin. From 1836 to 1882, he was professor of chemistry at Göttingen. Wöhler developed the first industrial method for preparing aluminum metal, and he discovered several new elements. In addition, he wrote textbooks about both inorganic and organic chemistry.

### William Thomas Brande

#### William Thomas Brande

(1788–1866) was born in London, England. Trained as an apothecary, he became a lecturer in chemistry at the University of London in 1808 and was a professor at the Royal Institution from 1813 to 1852. His scientific achievements were modest, although he was the first person to discover naphthalene, now used in mothballs.



Little more than a decade later, the vitalistic theory suffered still further when Friedrich Wöhler discovered in 1828 that it was possible to convert the "inorganic" salt ammonium cyanate into the "organic" substance urea, which had previously been found in human urine.



By the mid-1800s, the weight of evidence was clearly against the vitalistic theory. As William Brande wrote in 1848, "No definite line can be drawn between organic and inorganic chemistry. . . . Any distinctions . . . must for the present be merely considered as matters of practical convenience calculated to further the progress of students." Chemistry today is unified, and the same principles explain the behaviors of all substances, regardless of origin or complexity. The only distinguishing characteristic of organic chemicals 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 30 million presently known chemical compounds, do more than 99% of them contain carbon? The answers to these questions come from carbon's electronic structure and its consequent position in the periodic table (Figure 1.1). 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 to the staggeringly complex—from methane, with one carbon atom, to DNA, which can have more than *100 hundred million* carbons.

**Figure 1.1** The position of carbon in the periodic table. Other elements commonly found in organic compounds are shown in the colors typically used to represent them.

Group 1A												3A 4A 5A 6A 7A					8A
H												B	C	N	O	F	He
Li	Be																Ne
Na	Mg											Al	Si	P	S	Cl	Ar
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															

Not all carbon compounds are derived from living organisms, of course, and chemists over the years have developed a remarkably sophisticated ability to design and synthesize new organic compounds. Medicines, dyes, polymers, food additives, pesticides, and a host of other substances are now prepared in the laboratory. Organic chemistry touches the lives of everyone. Its study is a fascinating undertaking.

## 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 going on.

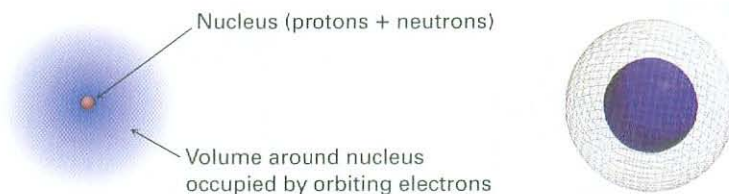
## 1.1 Atomic Structure: The Nucleus

As you probably know, an atom consists of a dense, positively charged *nucleus* surrounded at a relatively large distance by negatively charged *electrons* (Figure 1.2). 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.

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  $2 \times 10^{-10}$  m, or 200 *picometers* (pm), where  $1 \text{ pm} = 10^{-12} \text{ m}$ . To give you an idea of how small this is, a thin pencil line is about 3 million carbon atoms wide. Many organic chemists and biochemists, particularly in the United States, still use the unit *angstrom* ( $\text{\AA}$ ) to express atomic distances, where  $1 \text{ \AA} = 10^{-10} \text{ m} = 100 \text{ pm}$ , but we'll stay with the SI unit picometer in this book.

**Figure 1.2** 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.



A specific atom is described by its *atomic number* ( $Z$ ), which gives the number of protons in the atom's nucleus, and its *mass number* ( $A$ ), which gives the total of protons plus 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 weighted average mass in atomic mass units (amu) of an element's naturally occurring isotopes is called the element's *atomic mass* (or *atomic weight*)—1.008 amu for hydrogen, 12.011 amu for carbon, 30.974 amu for phosphorus, and so on.

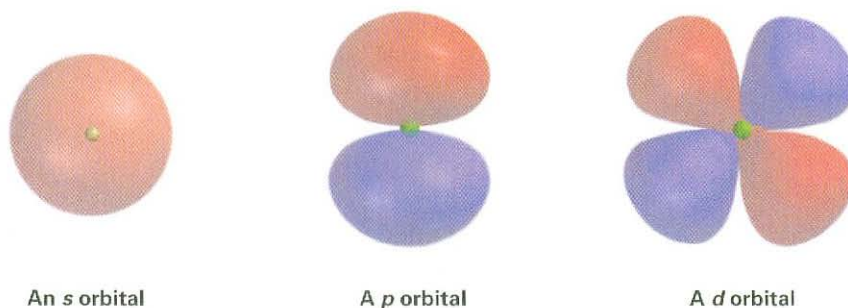
## 1.2 Atomic Structure: Orbitals

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 sort 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 Greek letter psi,  $\psi$ .

By plotting the square of the wave function,  $\psi^2$ , in three-dimensional space, the 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. The orbital would appear as a blurry cloud indicating the region of space around the nucleus 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 most (90%–95%) of its time.

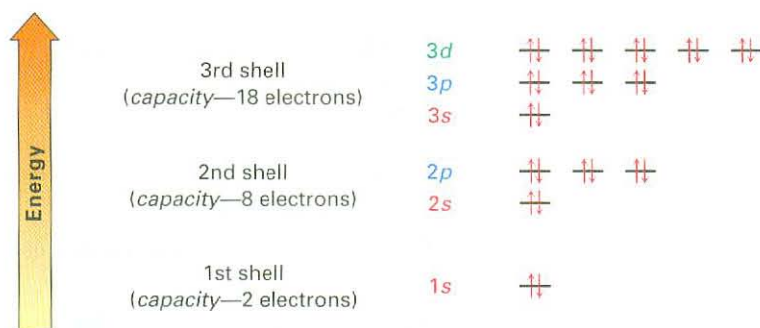
What do orbitals look like? There are four different kinds of orbitals, denoted  $s$ ,  $p$ ,  $d$ , and  $f$ , each with a different shape. Of the four, we'll be concerned primarily with  $s$  and  $p$  orbitals because these are the most common in organic and biological chemistry. The  $s$  orbitals are spherical, with the nucleus at their center;  $p$  orbitals are dumbbell-shaped; and four of the five  $d$  orbitals are cloverleaf-shaped, as shown in Figure 1.3. The fifth  $d$  orbital is shaped like an elongated dumbbell with a doughnut around its middle.

**Figure 1.3** Representations of  $s$ ,  $p$ , and  $d$  orbitals. The  $s$  orbitals are spherical, the  $p$  orbitals are 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 true shape is more like that of a doorknob, as indicated.



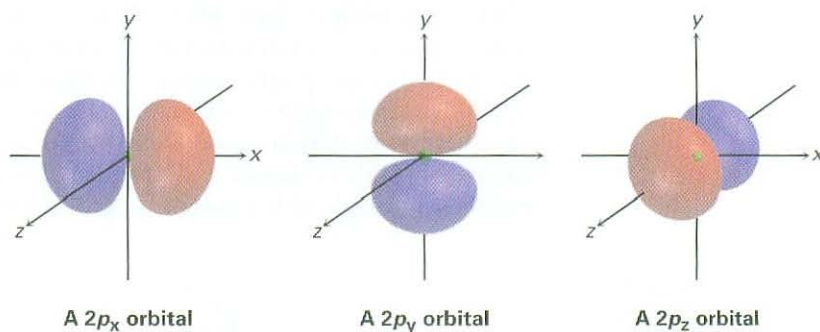
The orbitals in an atom are organized into different layers, or **electron shells**, of successively larger size and energy. Different shells contain different numbers and kinds of orbitals, and each orbital within a shell can be occupied by two electrons. The first shell contains only a single  $s$  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 1.4.

**Figure 1.4** The 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 five  $3d$  orbitals; and so on. The two electrons in each orbital are represented by 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 1.5, 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 we'll see in Section 1.11, the algebraic signs of the different orbital lobes have important consequences with respect to chemical bonding and chemical reactivity.

**Figure 1.5** 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 listing 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, according to the order  $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$ , a statement called the *aufbau principle*. Note that the  $4s$  orbital lies between the  $3p$  and  $3d$  orbitals in energy.
- Rule 2** Electrons act as if they were spinning around an axis, in much the same way that 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 be of opposite spin, 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	Element	Atomic number	Configuration
Hydrogen	1	$1s$ $\uparrow$	Phosphorus	15	$3p$ $\uparrow$ $\uparrow$ $\uparrow$
					$3s$ $\uparrow\downarrow$
Carbon	6	$2p$ $\uparrow$ $\uparrow$ —			$2p$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$
		$2s$ $\uparrow\downarrow$			$2s$ $\uparrow\downarrow$
		$1s$ $\uparrow\downarrow$			$1s$ $\uparrow\downarrow$

- Problem 1.1** Give the ground-state electron configuration for each of the following elements:  
 (a) Oxygen    (b) Silicon    (c) Sulfur

- Problem 1.2** How many electrons does each of the following elements have in its outermost electron shell?  
 (a) Magnesium      (b) Molybdenum      (c) Selenium

## 1.4 Development of Chemical Bonding Theory

### Friedrich August Kekulé

**Friedrich August Kekulé** (1829–1896) was born in Darmstadt, Germany. He entered the University of Giessen in 1847 intending to become an architect but soon switched to chemistry. After receiving his doctorate under Liebig and doing further study in Paris, Kekulé became a lecturer at Heidelberg in 1855 and a professor of chemistry at Ghent (1858) and Bonn (1867). His realization that carbon can form rings of atoms is said to have come to him in a dream in which he saw a snake biting its tail.

By the mid-1800s, the new science of chemistry was developing rapidly and chemists had begun to probe the forces holding compounds together. In 1858, August Kekulé and Archibald Couper independently proposed that, in all its 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.

Shortly after the tetravalent nature of carbon was proposed, extensions to the Kekulé–Couper theory were made when the possibility of *multiple* bonding between atoms was suggested. Emil Erlenmeyer proposed a carbon–carbon triple bond for acetylene, and Alexander Crum Brown proposed a carbon–carbon double bond for ethylene. 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, Jacobus van't Hoff and 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

Archibald Scott Couper	Richard A. C. E. Erlenmeyer	Alexander Crum Brown	Jacobus Hendricus van't Hoff
<p><b>Archibald Scott Couper</b> (1831–1892) was born in Kirkintilloch, Scotland, and studied at the universities of Glasgow, Edinburgh, and Paris. Although his scientific paper about the ability of carbon to form four bonds was submitted prior to a similar paper by Kekulé, Couper never received credit for his work. His health began to decline after the rejection of his achievements, and he suffered a nervous breakdown in 1858. He then retired from further scientific work and spent the last 30 years of his life in the care of his mother.</p>	<p><b>Richard A. C. E. Erlenmeyer</b> (1825–1909) was born in Wehen, Germany. He studied in Giessen and in Heidelberg, intending originally to be a pharmacist, and was professor of chemistry at Munich Polytechnicum from 1868 to 1883. Much of his work was carried out with biological molecules, and he was the first to prepare the amino acid tyrosine.</p>	<p><b>Alexander Crum Brown</b> (1838–1922) was born in Edinburgh, the son of a Presbyterian minister. He studied at Edinburgh, Heidelberg, and Marburg and was professor of chemistry at Edinburgh from 1869 to 1908. Crum Brown's interests were many. He studied the physiology of the canals in the inner ear, he was proficient in Japanese, and he had a lifelong interest in knitting.</p>	<p><b>Jacobus Hendricus van't Hoff</b> (1852–1911) was born in Rotterdam, Netherlands, and studied at Delft, Leyden, Bonn, Paris, and Utrecht. Widely educated, he served as professor of chemistry, mineralogy, and geology at the University of Amsterdam from 1878 to 1896 and later became professor at Berlin. In 1901, he received the first Nobel Prize in chemistry for his work on chemical equilibrium and osmotic pressure.</p>

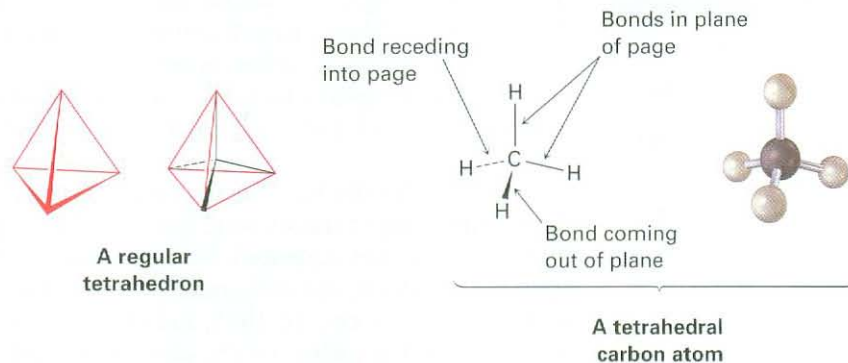
## Joseph Achille Le Bel

**Joseph Achille Le Bel** (1847–1930) was born in Pêchebronn, France, and studied at the École Polytechnique and the Sorbonne in Paris. Freed by his family's wealth from the need to earn a living, he established his own private laboratory.

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 1.6. 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. These representations will be used throughout the text.

**Figure 1.6** A representation of Van't Hoff's tetrahedral carbon atom. The solid lines are in the plane of the paper, the heavy wedged line comes out of the plane of the page, and the dashed line goes back behind the plane of the page.



Why, though, do atoms bond together, and how can bonds be described electronically? The *why* question is relatively easy to answer. Atoms bond together because the compound that results is lower in energy, and thus more stable, than the separate atoms. Energy (usually as heat) always flows out of the chemical system when a chemical bond forms. Conversely, energy must be put into the system to break a chemical bond. 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 main-group elements is governed by their tendency to take on the electron configuration of the nearest noble gas. The alkali metals 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 in group 7A achieve a noble-gas configuration by gaining a *p* electron to fill their valence shell, thereby forming an anion. The resultant ions are held together in compounds like  $\text{Na}^+ \text{Cl}^-$  by an electrostatic attraction that we call an *ionic bond*.

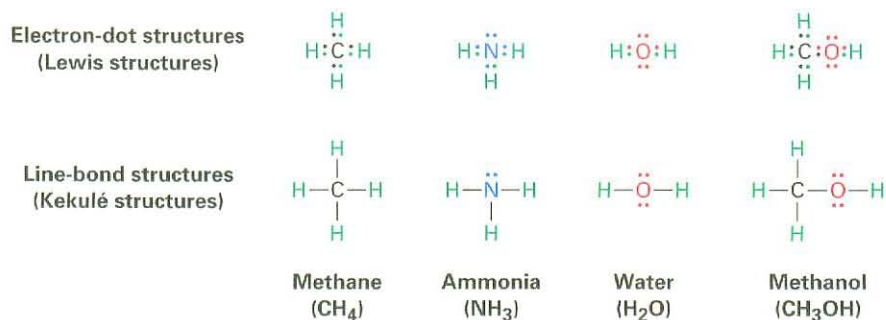
But how do elements closer to the middle of the periodic table form bonds? Look at methane,  $\text{CH}_4$ , the main constituent of natural gas, for example. The bonding in methane is not ionic because it would take too much energy for carbon ( $1s^2 2s^2 2p^2$ ) either to gain or lose four electrons to achieve a noble-gas configuration. As a result, 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 G. N. Lewis, is called a **covalent bond**. The neutral collection of atoms held together by covalent bonds is called a **molecule**.

## Gilbert Newton Lewis

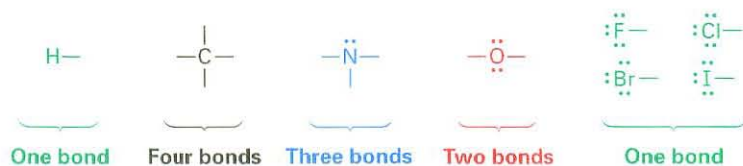
**Gilbert Newton Lewis** (1875–1946) was born in Weymouth, Massachusetts, and received his Ph.D. at Harvard in 1899. After a short time as professor of chemistry at the Massachusetts Institute of Technology (1905–1912), he spent the rest of his career at the University of California at Berkeley (1912–1946). In addition to his work on structural theory, Lewis was the first to prepare "heavy water,"  $\text{D}_2\text{O}$ , in which the two hydrogens of water are the  $^2\text{H}$  isotope, deuterium.



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 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 is achieved for all the atoms—eight dots (an octet) for main-group atoms or two dots for hydrogen. Simpler still is the use of *Kekulé structures*, or **line-bond structures**, in which a two-electron covalent bond is indicated as a line 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 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 are called **lone-pair electrons**, or *nonbonding electrons*. The nitrogen atom in ammonia, for instance, shares six valence electrons in three covalent bonds and has its remaining two valence electrons 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 a Molecule**

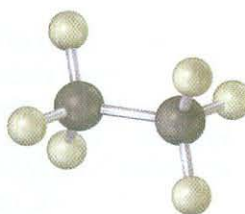
How many hydrogen atoms does phosphorus bond to in forming phosphine,  $\text{PH}_3$ ?

**Strategy** Identify the periodic group of phosphorus, and tell 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  $\text{PH}_3$ .

**Problem 1.3** Draw a molecule of chloroform,  $\text{CHCl}_3$ , using solid, wedged, and dashed lines to show its tetrahedral geometry.

**Problem 1.4** Convert the following representation of ethane,  $\text{C}_2\text{H}_6$ , into a conventional drawing that uses solid, wedged, and dashed lines to indicate tetrahedral geometry around each carbon (gray = C, ivory = H).



Ethane

**Problem 1.5** What are likely formulas for the following substances?  
 (a)  $\text{GeCl}_?$       (b)  $\text{AlH}_?$       (c)  $\text{CH}_? \text{Cl}_2$       (d)  $\text{SiF}_?$       (e)  $\text{CH}_3\text{NH}_?$

**Problem 1.6** Write line-bond structures for the following substances, showing all nonbonding electrons:

(a)  $\text{CHCl}_3$ , chloroform      (b)  $\text{H}_2\text{S}$ , hydrogen sulfide  
 (c)  $\text{CH}_3\text{NH}_2$ , methylamine      (d)  $\text{CH}_3\text{Li}$ , methyllithium

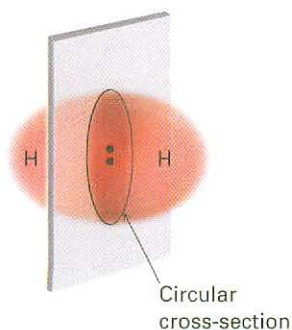
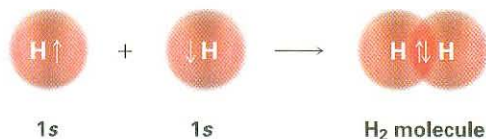
**Problem 1.7** Why can't an organic molecule have the formula  $\text{C}_2\text{H}_7$ ?

## 1.5 The Nature of 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 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  $\text{H}_2$  molecule, for example, the H–H bond results from the overlap of two singly occupied hydrogen 1s orbitals.

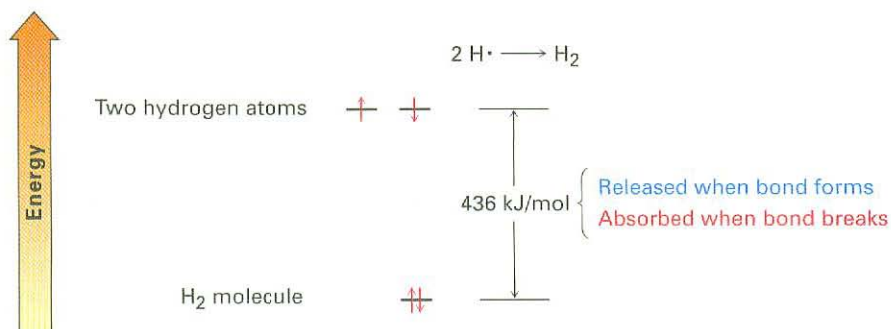


**Figure 1.7** The cylindrical symmetry of the H–H  $\sigma$  bond in an  $\text{H}_2$  molecule. The intersection of a plane cutting through the  $\sigma$  bond is a circle.

The overlapping orbitals in the  $\text{H}_2$  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 1.7. Such bonds, which are formed by the head-on overlap of two atomic orbitals along a line drawn between the nuclei, are called **sigma ( $\sigma$ ) bonds**.

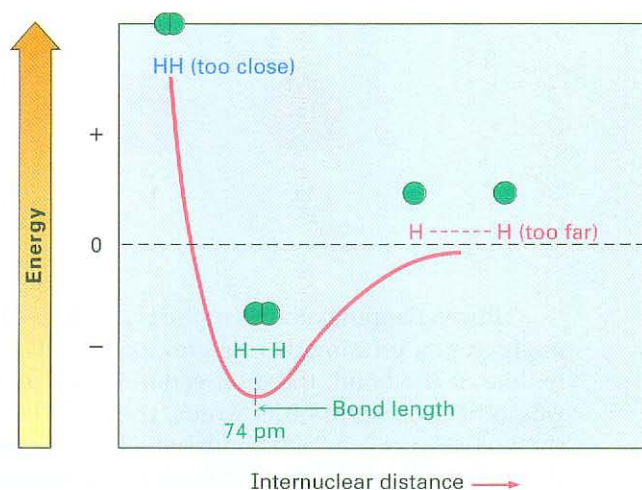
During the bond-forming reaction  $2 \text{H}\cdot \rightarrow \text{H}_2$ , 436 kJ/mol (104 kcal/mol) of energy is released. Because the product  $\text{H}_2$  molecule has 436 kJ/mol less energy than the starting  $2 \text{H}\cdot$  atoms, we say that the product is more stable than the reactant and 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  $\text{H}_2$  molecule apart into H atoms (Figure 1.8.) [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 1.8** Relative energy levels of H atoms and the  $\text{H}_2$  molecule. The  $\text{H}_2$  molecule has 436 kJ/mol (104 kcal/mol) less energy than the two H atoms, so 436 kJ/mol of energy is released when the H–H bond forms. Conversely, 436 kJ/mol must be added to the  $\text{H}_2$  molecule to break the H–H bond.



How close are the two nuclei in the  $\text{H}_2$  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 1.9). Called the **bond length**, this distance is 74 pm in the  $\text{H}_2$  molecule. Every covalent bond has both a characteristic bond strength and bond length.

**Figure 1.9** 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

### Linus Carl Pauling

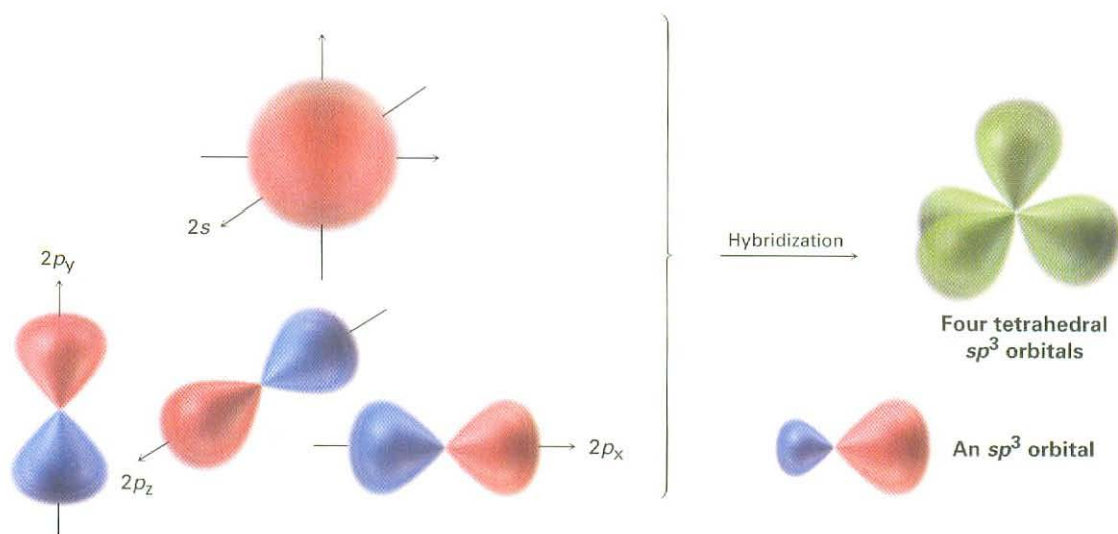
**Linus Carl Pauling** (1901–1994) was born in Portland, Oregon, the son of a pharmacist. After obtaining a B.S. degree at Oregon State University, he received a Ph.D. from the California Institute of Technology in 1925. He was professor of chemistry from 1925 to 1967 at the California Institute of Technology and then from 1974 to 1994 at the University of California in San Diego and Stanford University.

Pauling was a scientific giant, who made fundamental discoveries in fields ranging from chemical bonding to molecular biology to medicine. A lifelong pacifist, Pauling is the only solo winner of two Nobel Prizes in different fields: the first in 1954 for chemistry and the second in 1962 for peace.

The bonding in the hydrogen molecule is fairly straightforward, but the situation is more complicated in organic molecules with tetravalent carbon atoms. Take methane,  $\text{CH}_4$ , 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 (Figure 1.6). How can we explain this?

An answer was provided in 1931 by Linus Pauling, who showed how an  $s$  orbital and three  $p$  orbitals on an atom can combine mathematically, or *hybridize*, to form four equivalent atomic orbitals with tetrahedral orientation. Shown in Figure 1.10, these tetrahedrally oriented orbitals are called  $sp^3$  hybrids. 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.

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. When an  $s$  orbital hybridizes with three  $p$  orbitals, the resultant  $sp^3$  hybrid orbitals are unsymmetrical about the nucleus. One of the two



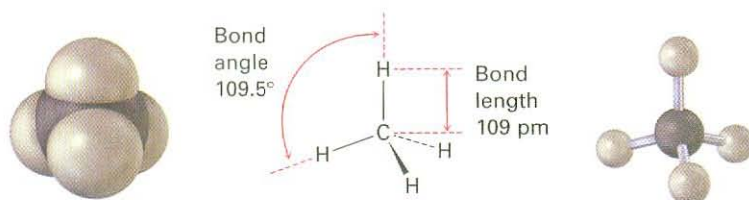
**Active Figure 1.10** Four  $sp^3$  hybrid orbitals (green), oriented to the corners of a regular tetrahedron, are formed by combination of an  $s$  orbital (red) and three  $p$  orbitals (red/blue). The  $sp^3$  hybrids have two lobes and are unsymmetrical about the nucleus, giving them a directionality and allowing them to form strong bonds to other atoms. Sign in at [www.thomsonedu.com](http://www.thomsonedu.com) to see a simulation based on this figure and to take a short quiz.

lobes is much larger than the other and can therefore overlap more effectively with an orbital from another atom when it forms 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  $-$ . 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.

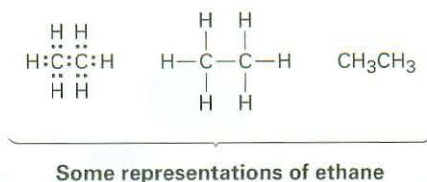
When each of the four identical  $sp^3$  hybrid orbitals of a carbon atom overlaps with the  $1s$  orbital of a hydrogen atom, four identical C–H bonds are formed and methane results. Each C–H bond in methane has a strength of 436 kJ/mol (104 kcal/mol) and a length of 109 pm. Because the four bonds have a specific geometry, we also can define a property called the **bond angle**. The angle formed by each H–C–H is  $109.5^\circ$ , the so-called tetrahedral angle. Methane thus has the structure shown in Figure 1.11.

**Active Figure 1.11** The structure of methane, showing its  $109.5^\circ$  bond angles. Sign in at [www.thomsonedu.com](http://www.thomsonedu.com) to see a simulation based on this figure and to take a short quiz.



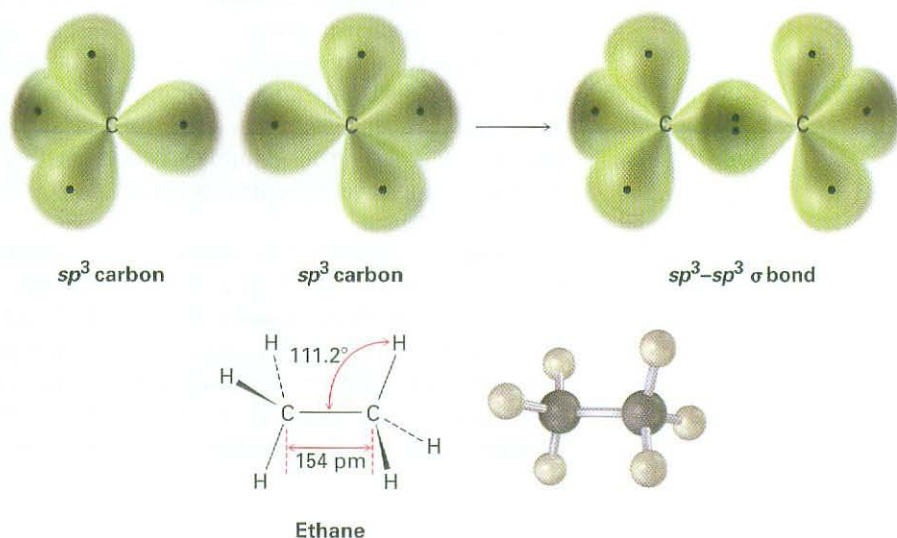
## 1.7 $sp^3$ Hybrid Orbitals and the Structure of Ethane

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.



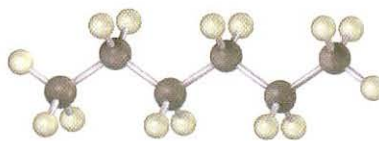
We can picture the ethane molecule by imagining that the two carbon atoms bond to each other by  $\sigma$  overlap of an  $sp^3$  hybrid orbital from each (Figure 1.12). The remaining three  $sp^3$  hybrid orbitals of each carbon overlap with the  $1s$  orbitals of three hydrogens to form the six C-H bonds. The C-H bonds in ethane are similar to those in methane, although a bit weaker—423 kJ/mol (101 kcal/mol) for ethane versus 436 kJ/mol for methane. The C-C bond is 154 pm long and has a strength of 376 kJ/mol (90 kcal/mol). All the bond angles of ethane are near, although not exactly at, the tetrahedral value of  $109.5^\circ$ .

**Figure 1.12** The structure of ethane. The carbon-carbon bond is formed by  $\sigma$  overlap of two carbon  $sp^3$  hybrid orbitals. For clarity, the smaller lobes of the  $sp^3$  hybrid orbitals are not shown.



**Problem 1.8** Draw a line-bond structure for propane,  $CH_3CH_2CH_3$ . Predict the value of each bond angle, and indicate the overall shape of the molecule.

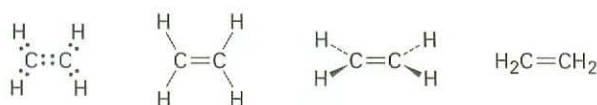
**Problem 1.9** Convert the following molecular model of hexane, a component of gasoline, into a line-bond structure (gray = C, ivory = H).



Hexane

## 1.8 $sp^2$ Hybrid Orbitals and the Structure of Ethylene

Although  $sp^3$  hybridization is the most common electronic state of carbon, it's not the only possibility. Look at ethylene,  $C_2H_4$ , for example. It was recognized more than 100 years ago that ethylene carbons can be tetravalent only if they share *four* electrons and are linked by a *double* bond. Furthermore, ethylene is planar (flat) and has bond angles of approximately  $120^\circ$  rather than  $109.5^\circ$ .



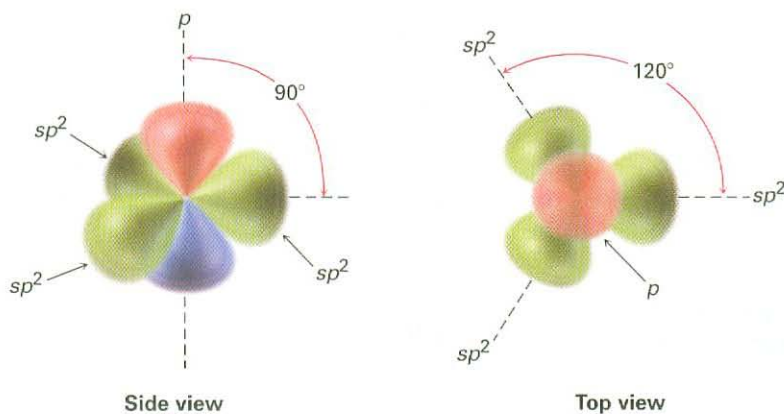
Top view

Side view

Some representations of ethylene

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. The three  $sp^2$  orbitals lie in a plane at angles of  $120^\circ$  to one another, with the remaining  $p$  orbital perpendicular to the  $sp^2$  plane, as shown in Figure 1.13.

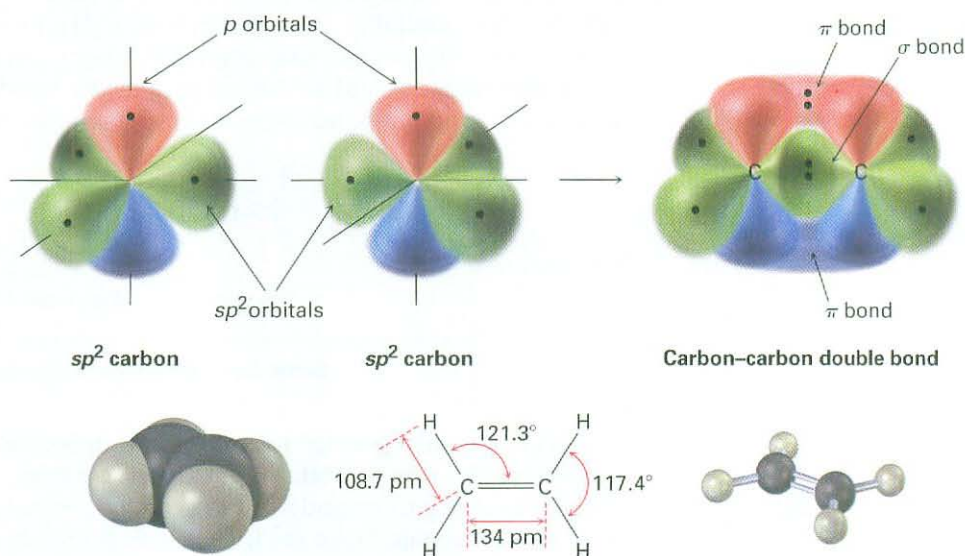
**Figure 1.13** An  $sp^2$ -hybridized carbon. The three equivalent  $sp^2$  hybrid orbitals (green) lie in a plane at angles of  $120^\circ$  to one another, and a single unhybridized  $p$  orbital (red/blue) is perpendicular to the  $sp^2$  plane.



When two  $sp^2$ -hybridized carbons approach each other, they form a  $\sigma$  bond by  $sp^2$ - $sp^2$  head-on overlap. At the same time, the unhybridized  $p$  orbitals approach with the correct geometry for *sideways* overlap, leading to the formation of what is called a **pi ( $\pi$ ) bond**. The combination of an  $sp^2$ - $sp^2$   $\sigma$  bond and a  $2p$ - $2p$   $\pi$  bond results in the sharing of four electrons and the formation of a carbon-carbon double bond (Figure 1.14). Note that the electrons in the  $\sigma$  bond occupy the region centered between nuclei, while the electrons in the  $\pi$  bond occupy regions on either side of a line drawn between nuclei.

To complete the structure of ethylene, four hydrogen atoms form  $\sigma$  bonds with the remaining four  $sp^2$  orbitals. Ethylene thus has a planar structure, with H-C-H and H-C-C bond angles of approximately  $120^\circ$ . (The actual values are  $117.4^\circ$  for the H-C-H bond angle and  $121.3^\circ$  for the H-C-C bond angle.) Each C-H bond has a length of 108.7 pm and a strength of 465 kJ/mol (111 kcal/mol).

**Figure 1.14** The structure of ethylene. Orbital overlap of two  $sp^2$ -hybridized carbons forms a carbon-carbon double bond. One part of the double bond results from  $\sigma$  (head-on) overlap of  $sp^2$  orbitals (green), and the other part results from  $\pi$  (sideways) overlap of unhybridized  $p$  orbitals (red/blue). The  $\pi$  bond has regions of electron density on either side of 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 154 pm and a strength of 376 kJ/mol for ethane. Note that the carbon-carbon double bond is less than twice as strong as a single bond because the overlap in the  $\pi$  part of the double bond is not as effective as the overlap in the  $\sigma$  part.

### WORKED EXAMPLE 1.2

#### Predicting the Structures of Simple Organic Molecules from Their Formulas

Commonly used in biology as a tissue preservative, formaldehyde,  $\text{CH}_2\text{O}$ , contains a carbon-oxygen double bond. Draw the line-bond structure of formaldehyde, and indicate the hybridization of the carbon atom.



**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:

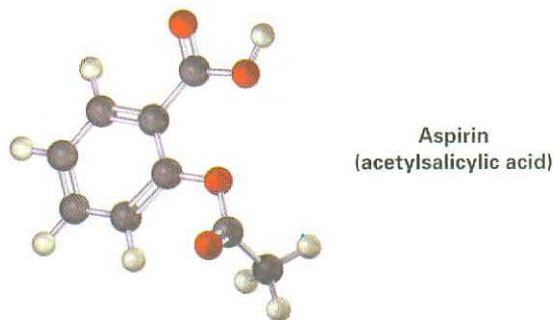


Like the carbon atoms in ethylene, the carbon atom in formaldehyde is in a double bond and therefore  $sp^2$ -hybridized.

**Problem 1.10** Draw a line-bond structure for propene,  $\text{CH}_3\text{CH}=\text{CH}_2$ ; indicate the hybridization of each carbon; and predict the value of each bond angle.

**Problem 1.11** Draw a line-bond structure for 1,3-butadiene,  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ ; indicate the hybridization of each carbon; and predict the value of each bond angle.

**Problem 1.12** Following is a molecular model of aspirin (acetylsalicylic acid). Identify the hybridization of each carbon atom in aspirin, and tell which atoms have lone pairs of electrons (gray = C, red = O, ivory = H).

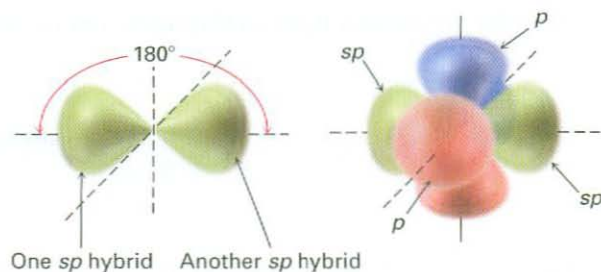


## 1.9 $sp$ Hybrid Orbitals and the Structure of Acetylene

In addition to forming single and double bonds by sharing two and four electrons, respectively, carbon also can form a *triple* bond by sharing six electrons. To account for the triple bond in a molecule such as acetylene,  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ , 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  $180^\circ$  apart on the  $x$ -axis, while the

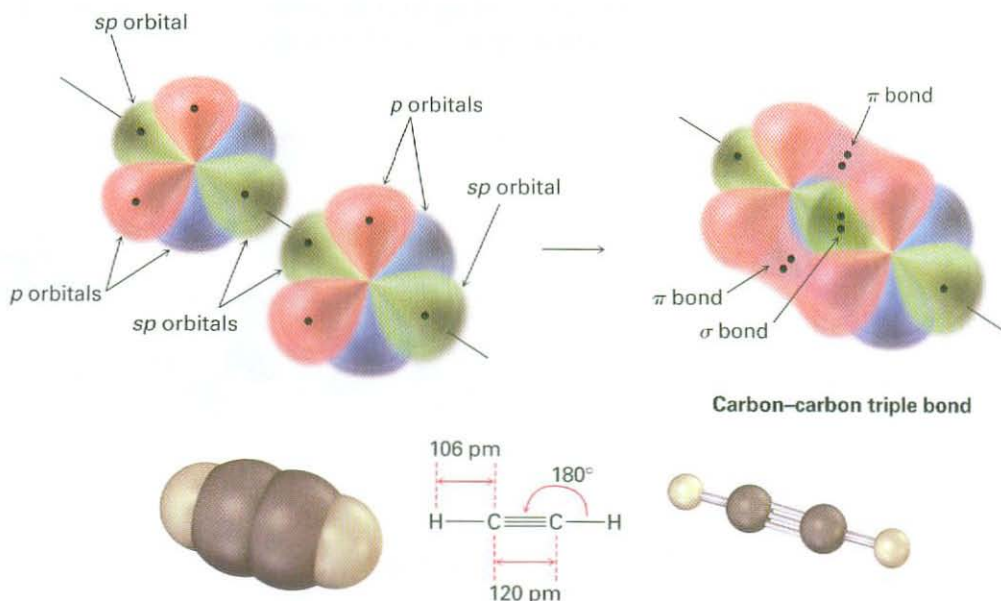
remaining two  $p$  orbitals are perpendicular on the  $y$ -axis and the  $z$ -axis, as shown in Figure 1.15.

**Figure 1.15** An  $sp$ -hybridized carbon atom. The two  $sp$  hybrid orbitals (green) are oriented  $180^\circ$  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  $sp$ - $sp$   $\sigma$  bond. In addition, the  $p_z$  orbitals from each carbon form a  $p_z$ - $p_z$   $\pi$  bond by sideways overlap and the  $p_y$  orbitals overlap similarly to form a  $p_y$ - $p_y$   $\pi$  bond. The net effect is the sharing of six electrons and formation of a carbon-carbon triple bond. The two remaining  $sp$  hybrid orbitals each form a  $\sigma$  bond with hydrogen to complete the acetylene molecule (Figure 1.16).

**Figure 1.16** The structure of acetylene. The two  $sp$ -hybridized carbon atoms are joined by one  $sp$ - $sp$   $\sigma$  bond and two  $p$ - $p$   $\pi$  bonds.



As suggested by  $sp$  hybridization, acetylene is a linear molecule with  $\text{H}-\text{C}-\text{C}$  bond angles of  $180^\circ$ . The  $\text{C}-\text{H}$  bonds have a length of 106 pm and a strength of 556 kJ/mol (133 kcal/mol). The  $\text{C}-\text{C}$  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 <sub>4</sub>	(sp <sup>3</sup> ) C—H	436	104	109
Ethane, CH <sub>3</sub> CH <sub>3</sub>	(sp <sup>3</sup> ) C—C (sp <sup>3</sup> )	376	90	154
	(sp <sup>3</sup> ) C—H	423	101	109
Ethylene, H <sub>2</sub> C=CH <sub>2</sub>	(sp <sup>2</sup> ) C—C (sp <sup>2</sup> )	728	174	134
	(sp <sup>2</sup> ) C—H	465	111	109
Acetylene, HC≡CH	(sp) C≡C (sp)	965	231	120
	(sp) C—H	556	133	106

**Problem 1.13** Draw a line-bond structure for propyne, CH<sub>3</sub>C≡CH; indicate the hybridization of each carbon; and predict a value for each bond angle.

## 1.10 Hybridization of Nitrogen, Oxygen, Phosphorus, and Sulfur

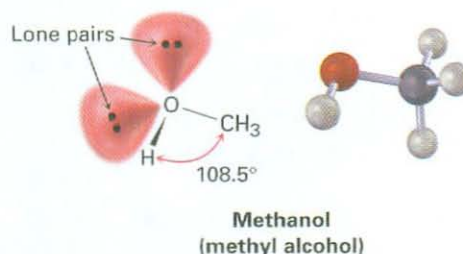
The valence-bond concept of orbital hybridization described in the previous four sections is not limited to carbon compounds. Covalent bonds formed by other elements can also be described using hybrid orbitals. Look, for instance, at the nitrogen atom in methylamine, CH<sub>3</sub>NH<sub>2</sub>, an organic derivative of ammonia (NH<sub>3</sub>) 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 hybridizes to form four sp<sup>3</sup> orbitals, just as carbon does. One of the four sp<sup>3</sup> orbitals is occupied by two nonbonding electrons, and the other three hybrid orbitals have one electron each. Overlap of these 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<sup>3</sup> 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.



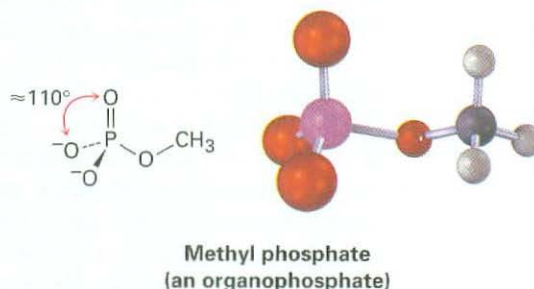
Like the carbon atom in methane and the nitrogen atom in methylamine, the oxygen atom in methanol (methyl alcohol) and many other organic molecules can also be described as sp<sup>3</sup>-hybridized. The C—O—H bond angle in methanol is 108.5°, very close to the 109.5° tetrahedral angle. Two of the four sp<sup>3</sup> hybrid

orbitals on oxygen are occupied by nonbonding electron lone pairs, and two are used to form bonds.



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 occasionally forms four.

Phosphorus is most commonly encountered in biological molecules in *organophosphates*, compounds that contain a phosphorus atom bonded to four oxygens, with one of the oxygens also bonded to carbon. Methyl phosphate, CH<sub>3</sub>OPO<sub>3</sub><sup>2-</sup> is the simplest example. The O-P-O bond angle in such compounds is typically in the range 110 to 112°, implying *sp*<sup>3</sup> hybridization for the phosphorus.



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, or in *sulfides*, which have a sulfur atom bonded to two carbons. Produced by some bacteria, methanethiol (CH<sub>3</sub>SH) is the simplest example of a thiol, and dimethyl sulfide [(CH<sub>3</sub>)<sub>2</sub>S] is the simplest example of a sulfide. Both can be described by approximate *sp*<sup>3</sup> hybridization around sulfur, although both have significant deviation from the 109.5° tetrahedral angle.

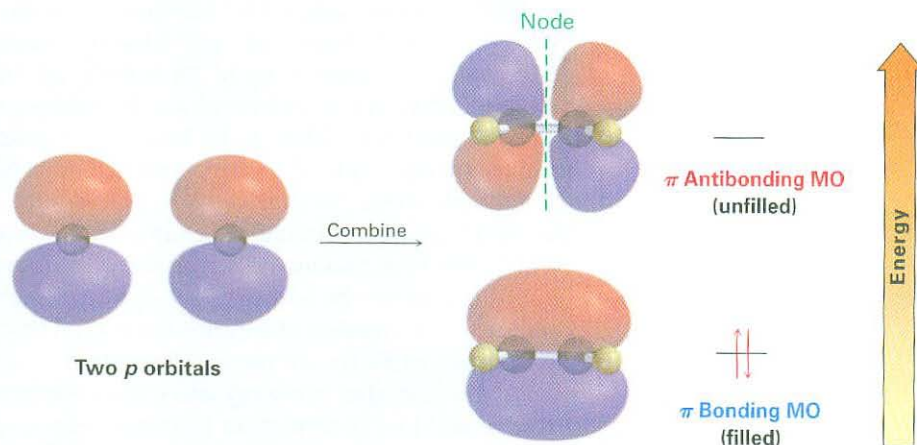


**ThomsonNOW** Click *Organic Interactive* to learn how to identify hybridization in a variety of organic molecules.



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 can't contribute to bonding. The two nuclei therefore repel each other.

Just as bonding and antibonding  $\sigma$  molecular orbitals result from the combination of two  $s$  atomic orbitals in  $H_2$ , so bonding and antibonding  $\pi$  molecular orbitals result from the combination of two  $p$  atomic orbitals in ethylene. As shown in Figure 1.18, the lower-energy,  $\pi$  bonding MO has no node between nuclei and results from combination of  $p$  orbital lobes with the same algebraic sign. The higher-energy,  $\pi$  antibonding MO has a node between nuclei and results from 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 and 15 that molecular orbital theory is particularly useful for describing  $\pi$  bonds in compounds that have more than one double bond.

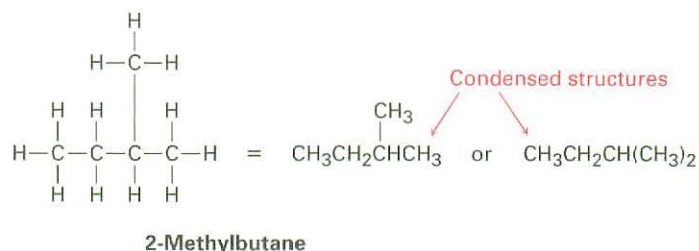


**Figure 1.18** A molecular orbital description of the  $C=C$   $\pi$  bond in ethylene. The lower-energy,  $\pi$  bonding MO results from a combination of  $p$  orbital lobes with the same algebraic sign and is filled. The higher-energy,  $\pi$  antibonding MO results from a combination of  $p$  orbital lobes with the opposite algebraic signs and is unfilled.

## 1.12 Drawing Chemical Structures

Let's cover 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  $\text{CH}_2$ ; and so on. The compound called 2-methylbutane, for example, is written as follows:

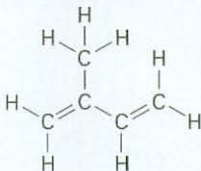
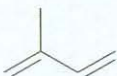
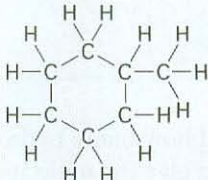

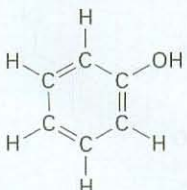
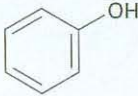


Notice that the horizontal bonds between carbons aren't shown in condensed structures—the  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  units are simply placed next to each other—but the vertical carbon-carbon bond in the first of the condensed structures drawn above is shown for clarity. Notice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

Even simpler than condensed structures is the use of **skeletal structures** such as those shown in Table 1.3. The rules for drawing skeletal structures are straightforward.

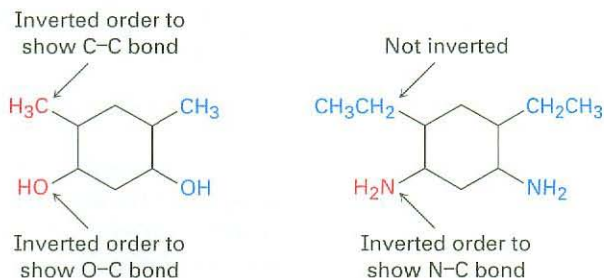
- Rule 1** Carbon atoms aren't usually shown. Instead, a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Occasionally, a carbon atom might be indicated for emphasis or clarity.
- Rule 2** Hydrogen atoms bonded to carbon aren't shown. Since carbon always 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.

**Table 1.3** Kekulé and Skeletal Structures for Some Compounds

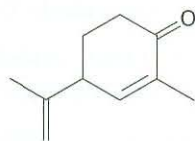
Compound	Kekulé structure	Skeletal structure
Isoprene, $\text{C}_5\text{H}_8$		
Methylcyclohexane, $\text{C}_7\text{H}_{14}$		
Phenol, $\text{C}_6\text{H}_6\text{O}$		

**ThomsonNOW** Click *Organic Interactive* to learn how to **interconvert skeletal structures, condensed structures, and molecular models.**

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 in a molecule clearer. Larger units such as  $-\text{CH}_2\text{CH}_3$  are not inverted, though; we don't write  $\text{H}_3\text{CH}_2\text{C}-$  because it would be confusing. There are, however, no well-defined rules that cover all cases; it's largely a matter of preference.

**WORKED EXAMPLE 1.3****Interpreting Line-Bond Structures**

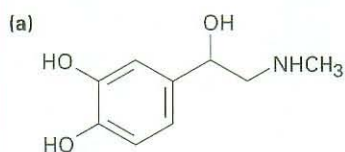
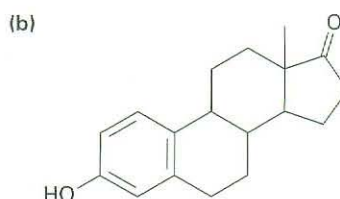
Carvone, a substance responsible for the odor of spearmint, has the following structure. Tell how many hydrogens are bonded to each carbon, and give the molecular formula of carvone.

**Carvone**

**Strategy** The end of a line represents a carbon atom with 3 hydrogens,  $\text{CH}_3$ ; a two-way intersection is a carbon atom with 2 hydrogens,  $\text{CH}_2$ ; a three-way intersection is a carbon atom with 1 hydrogen,  $\text{CH}$ ; and a four-way intersection is a carbon atom with no attached hydrogens.

**Solution****Carvone,  $\text{C}_{10}\text{H}_{14}\text{O}$** 

**Problem 1.15** Tell how many hydrogens are bonded to each carbon in the following compounds, and give the molecular formula of each substance:

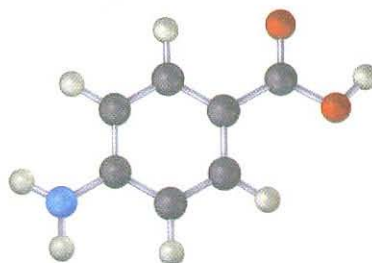
**Adrenaline****Estrone (a hormone)**



**Problem 1.16** Propose skeletal structures for compounds that satisfy the following molecular formulas. There is more than one possibility in each case.

(a)  $C_5H_{12}$     (b)  $C_2H_7N$     (c)  $C_3H_6O$     (d)  $C_4H_9Cl$

**Problem 1.17** The following molecular model is a representation of *para*-aminobenzoic acid (PABA), the active ingredient in many sunscreens. Indicate the positions of the multiple bonds, and draw a skeletal structure (gray = C, red = O, blue = N, ivory = H).



*para*-Aminobenzoic acid  
(PABA)

## Focus On . . .

### Chemicals, Toxicity, and Risk



© Keith Larnett/AP Photo

We all take many risks each day, some much more dangerous than others.

We hear and read a lot these days about the dangers of “chemicals”—about pesticide residues on our food, toxic wastes on our land, unsafe medicines, and so forth. What’s a person to believe?

Life is not risk-free; we all take many risks each day. 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 7000 people die from falls each year in the United States. We decide to smoke cigarettes, even though it increases our chance of getting cancer by 50%. Making decisions that affect our health is something we do routinely without even thinking about it.

What about risks from chemicals? Risk evaluation of chemicals is carried out by exposing test animals (usually rats) to the chemical and then monitoring for signs of harm. To limit the expense and time needed, the amounts administered are hundreds or thousands of times greater than those a person might normally encounter. Data are then reduced to a single number called an  $LD_{50}$ , the amount of a substance per kilogram body weight that is lethal to

(continued)

50% of the test animals. The  $LD_{50}$ 's of some common substances are shown in Table 1.4. The lower the value, the more toxic the substance.

**Table 1.4** Some  $LD_{50}$  Values

Substance	$LD_{50}$ (g/kg)	Substance	$LD_{50}$ (g/kg)
Strychnine	0.005	Iron(II) sulfate	1.5
Arsenic trioxide	0.015	Chloroform	3.2
DDT	0.115	Ethyl alcohol	10.6
Aspirin	1.1	Sodium cyclamate	17

Even with animal data available, risk is still hard to assess. If a substance is harmful to animals, is it necessarily harmful to humans? How can a large dose for a small animal be translated into a small dose for a large human? All substances are toxic to some organisms to some extent, and the difference between help and harm is often a matter of degree. Vitamin A, for example, is necessary for vision, yet it can promote cancer at high dosages. Arsenic trioxide is the most classic of poisons, yet recent work has shown it to be effective at inducing remissions in some types of leukemia. Even water can be toxic if drunk in large amounts because it dilutes the salt in body fluids and causes a potentially life-threatening condition called *hyponatremia*. Furthermore, how we evaluate risk is strongly influenced by familiarity. Many foods contain natural ingredients far more toxic than synthetic additives or pesticide residues, but the ingredients are ignored because the foods are familiar.

All decisions involve tradeoffs. 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 fraction of users? The answers are rarely obvious, but we should at least try to base our responses on facts.

## SUMMARY AND KEY WORDS

**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

antibonding MO, 22

bond angle, 13

bond length, 12

bond strength, 11

bonding MO, 22

condensed structure, 22

covalent bond, 8

electron-dot structure, 9  
 electron shell, 5  
 ground-state electron configuration, 6  
 isotope, 4  
 line-bond structure, 9  
 lone-pair electrons, 9  
 molecular orbital (MO) theory, 21  
 molecule, 8  
 node, 5  
 orbital, 4  
 organic chemistry, 3  
 pi ( $\pi$ ) bond, 16  
 sigma ( $\sigma$ ) bond, 11  
 skeletal structure, 23  
 sp hybrid orbital, 17  
 sp<sup>2</sup> hybrid orbital, 15  
 sp<sup>3</sup> hybrid orbital, 12  
 valence bond theory, 11  
 valence shell, 8

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 theory**, electron sharing occurs by 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 ( $\sigma$ ) bonds**; bonds formed by sideways interaction of *p* orbitals are called **pi ( $\pi$ ) 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<sup>3</sup> hybrid orbitals**. When forming a double bond with planar geometry, carbon uses three equivalent **sp<sup>2</sup> 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 mentally supplied.

### Working Problems

There is 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 are of several types. They 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 "Additional Problems." 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 Solutions Manual* for an explanation that will help clarify the difficulty. Working problems takes effort, but the payoff in knowledge and understanding is immense.

## EXERCISES

## Organic KNOWLEDGE TOOLS

**ThomsonNOW** Sign in at [www.thomsonedu.com](http://www.thomsonedu.com) to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.



Online homework for this chapter may be assigned in Organic OWL.

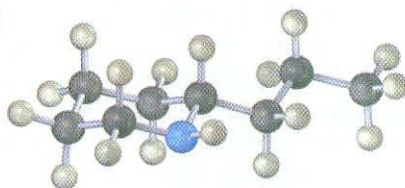
■ indicates problems assignable in Organic OWL.

## VISUALIZING CHEMISTRY

(Problems 1.1–1.17 appear within the chapter.)

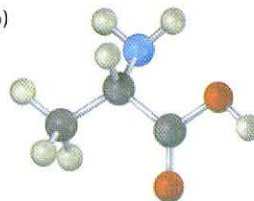
**1.18** ■ Convert each of the following molecular models into a skeletal structure, and give the formula of each. Only the connections between atoms are shown; multiple bonds are not indicated (gray = C, red = O, blue = N, ivory = H).

(a)



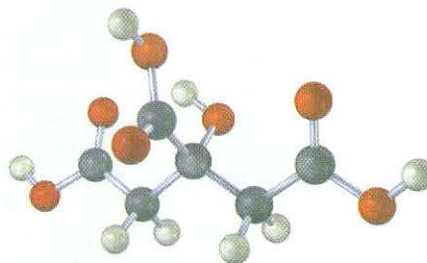
Coniine (the toxic substance in poison hemlock)

(b)

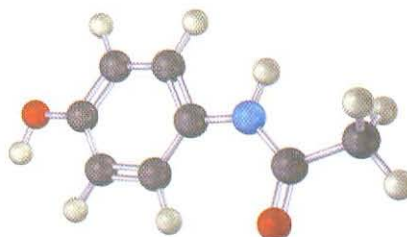


Alanine (an amino acid)

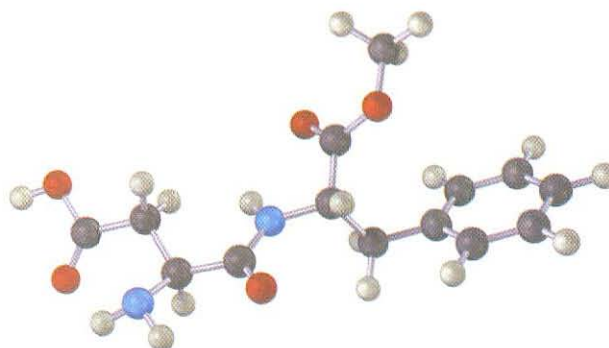
**1.19** ■ The following model is a representation of citric acid, the key substance in the so-called citric acid cycle by which food molecules are metabolized in the body. Only the connections between atoms are shown; multiple bonds are not indicated. Complete the structure by indicating the positions of multiple bonds and lone-pair electrons (gray = C, red = O, ivory = H).



- 1.20 ■ The following model is a representation of acetaminophen, a pain reliever sold in drugstores as Tylenol. Identify the hybridization of each carbon atom in acetaminophen, and tell which atoms have lone pairs of electrons (gray = C, red = O, blue = N, ivory = H).



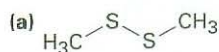
- 1.21 The following model is a representation of aspartame,  $C_{14}H_{18}N_2O_5$ , known commercially as NutraSweet. Only the connections between atoms are shown; multiple bonds are not indicated. Complete the structure by indicating the positions of multiple bonds (gray = C, red = O, blue = N, ivory = H).



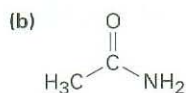
## ADDITIONAL PROBLEMS

- 1.22 ■ How many valence electrons does each of the following dietary trace elements have?  
 (a) Zinc      (b) Iodine      (c) Silicon      (d) Iron
- 1.23 ■ Give the ground-state electron configuration for each of the following elements:  
 (a) Potassium      (b) Arsenic      (c) Aluminum      (d) Germanium
- 1.24 ■ What are likely formulas for the following molecules?  
 (a)  $NH_2OH$       (b)  $AlCl_7$       (c)  $CF_2Cl_7$       (d)  $CH_7O$
- 1.25 Draw an electron-dot structure for acetonitrile,  $C_2H_3N$ , which contains a carbon–nitrogen triple bond. How many electrons does the nitrogen atom have in its outer shell? How many are bonding, and how many are non-bonding?
- 1.26 What is the hybridization of each carbon atom in acetonitrile (Problem 1.25)?
- 1.27 ■ Draw a line-bond structure for vinyl chloride,  $C_2H_3Cl$ , the starting material from which PVC [poly(vinyl chloride)] plastic is made.

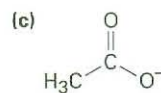
1.28 ■ Fill in any nonbonding valence electrons that are missing from the following structures:



Dimethyl disulfide

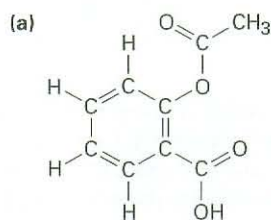


Acetamide

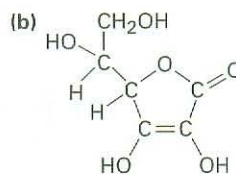


Acetate ion

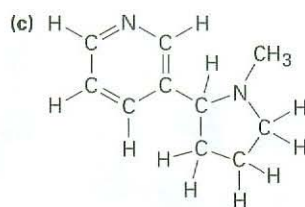
1.29 Convert the following line-bond structures into molecular formulas:



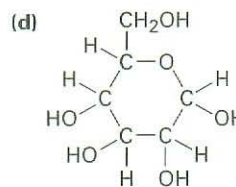
Aspirin  
(acetylsalicylic acid)



Vitamin C  
(ascorbic acid)

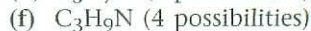
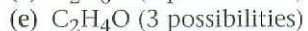
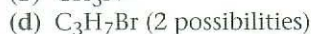
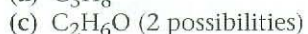
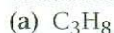


Nicotine

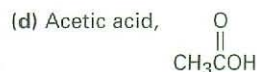
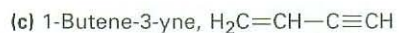
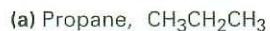


Glucose

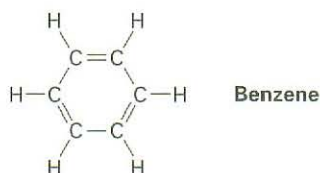
1.30 Convert the following molecular formulas into line-bond structures that are consistent with valence rules:



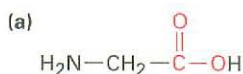
1.31 ■ What kind of hybridization do you expect for each carbon atom in the following molecules?



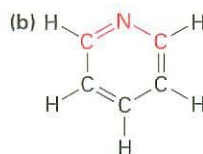
1.32 What is the shape of benzene, and what hybridization do you expect for each carbon?



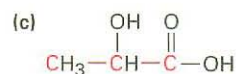
1.33 ■ What bond angles do you expect for each of the following, and what kind of hybridization do you expect for the central atom in each?



**Glycine**  
(an amino acid)

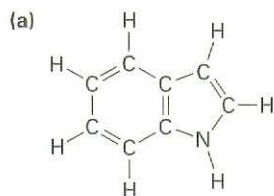


**Pyridine**

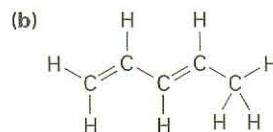


**Lactic acid**  
(in sour milk)

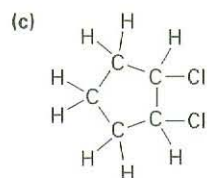
1.34 ■ Convert the following structures into skeletal drawings:



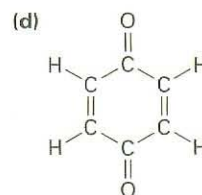
**Indole**



**1,3-Pentadiene**

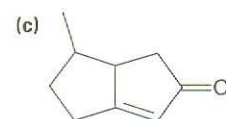
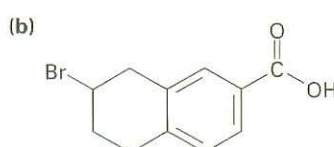
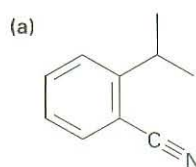


**1,2-Dichlorocyclopentane**

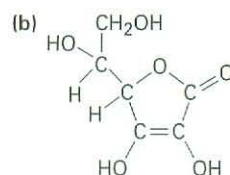
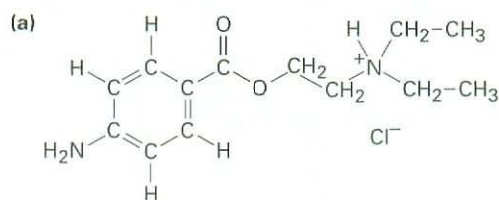


**Benzoquinone**

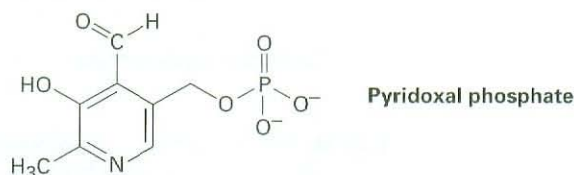
1.35 ■ Tell the number of hydrogens bonded to each carbon atom in the following substances, and give the molecular formula of each:



- 1.36** Propose structures for molecules that meet the following descriptions:  
 (a) Contains two  $sp^2$ -hybridized carbons and two  $sp^3$ -hybridized carbons  
 (b) Contains only four carbons, all of which are  $sp^2$ -hybridized  
 (c) Contains two  $sp$ -hybridized carbons and two  $sp^2$ -hybridized carbons
- 1.37** ■ Why can't molecules with the following formulas exist?  
 (a)  $CH_5$  (b)  $C_2H_6N$  (c)  $C_3H_5Br_2$
- 1.38** Draw a three-dimensional representation of the oxygen-bearing carbon atom in ethanol,  $CH_3CH_2OH$ , using the standard convention of solid, wedged, and dashed lines.
- 1.39** Oxaloacetic acid, an important intermediate in food metabolism, has the formula  $C_4H_4O_5$  and contains three  $C=O$  bonds and two  $O-H$  bonds. Propose two possible structures.
- 1.40** ■ Draw structures for the following molecules, showing lone pairs:  
 (a) Acrylonitrile,  $C_3H_3N$ , which contains a carbon-carbon double bond and a carbon-nitrogen triple bond  
 (b) Ethyl methyl ether,  $C_3H_8O$ , which contains an oxygen atom bonded to two carbons  
 (c) Butane,  $C_4H_{10}$ , which contains a chain of four carbon atoms  
 (d) Cyclohexene,  $C_6H_{10}$ , which contains a ring of six carbon atoms and one carbon-carbon double bond
- 1.41** Potassium methoxide,  $KOCH_3$ , contains both covalent and ionic bonds. Which do you think is which?
- 1.42** What kind of hybridization do you expect for each carbon atom in the following molecules?



- 1.43** Pyridoxal phosphate, a close relative of vitamin  $B_6$ , is involved in a large number of metabolic reactions. Tell the hybridization, and predict the bond angles for each nonterminal atom.



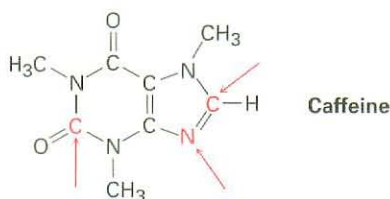
- 1.44** Why do you suppose no one has ever been able to make cyclopentyne as a stable molecule?



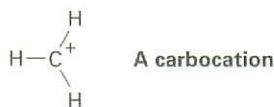
Cyclopentyne



- 1.45 What is wrong with the following sentence? "The  $\pi$  bonding molecular orbital in ethylene results from sideways overlap of two  $p$  atomic orbitals."
- 1.46 Allene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ , is somewhat unusual in that it has two adjacent double bonds. Draw a picture showing the orbitals involved in the  $\sigma$  and  $\pi$  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?
- 1.47 Allene (see Problem 1.46) is related structurally to carbon dioxide,  $\text{CO}_2$ . Draw a picture showing the orbitals involved in the  $\sigma$  and  $\pi$  bonds of  $\text{CO}_2$ , and identify the likely hybridization of carbon.
- 1.48 Complete the electron-dot structure of caffeine, showing all lone-pair electrons, and identify the hybridization of the indicated atoms.



- 1.49 Almost all stable organic species have tetravalent carbon atoms, but species with trivalent carbon atoms also exist. *Carbocations* are one such class of compounds.

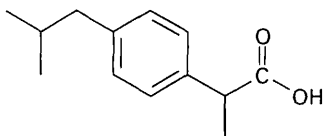


- (a) How many valence electrons does the positively charged carbon atom have?  
 (b) What hybridization do you expect this carbon atom to have?  
 (c) What geometry is the carbocation likely to have?
- 1.50 A *carbanion* is a species that contains a negatively charged, trivalent carbon.

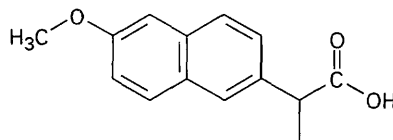


- (a) What is the electronic relationship between a carbanion and a trivalent nitrogen compound such as  $\text{NH}_3$ ?  
 (b) How many valence electrons does the negatively charged carbon atom have?  
 (c) What hybridization do you expect this carbon atom to have?  
 (d) What geometry is the carbanion likely to have?
- 1.51 Divalent carbon species called *carbenes* are capable of fleeting existence. For example, methylene,  $:\text{CH}_2$ , is the simplest carbene. The two unshared electrons in methylene can be either spin-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.
- 1.52 There are two different substances with the formula  $\text{C}_4\text{H}_{10}$ . Draw both, and tell how they differ.

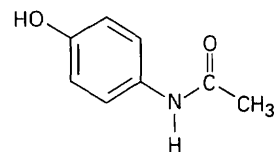
- 1.53** There are two different substances with the formula  $C_3H_6$ . Draw both, and tell how they differ.
- 1.54** There are two different substances with the formula  $C_2H_6O$ . Draw both, and tell how they differ.
- 1.55** There are three different substances that contain a carbon-carbon double bond and have the formula  $C_4H_8$ . Draw them, and tell how they differ.
- 1.56** Among the most common over-the-counter drugs you might find in a medicine cabinet are mild 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) Can you spot any similarities in their structures?