

Prologue

What is organic chemistry?
Some representative organic
molecules
Organic chemistry in the
marine environment

Organic chemistry. You might wonder how a discipline that conjures up images of eccentric old scientists working in basement laboratories is relevant to you, a student in the twenty-first century.

Consider for a moment the activities that occupied your past 24 hours. You likely showered with soap, drank a caffeinated beverage, ate at least one form of starch, took some medication, read a newspaper, listened to a CD, and traveled in a vehicle that had rubber tires and was powered by fossil fuels. If you did any *one* of these, your life was touched by organic chemistry.

What Is Organic Chemistry?

- **Organic chemistry is the chemistry of compounds that contain the element carbon.**

It is one branch in the entire field of chemistry, which encompasses many classical subdisciplines including inorganic, physical, and analytical chemistry, and newer fields such as bioinorganic chemistry, physical biochemistry, polymer chemistry, and materials science.

Organic chemistry was singled out as a separate discipline for historical reasons. Originally, it was thought that compounds in living things, termed *organic compounds*, were fundamentally different from those in nonliving things, called *inorganic compounds*. Although we have known for more than 150 years that this distinction is artificial, the name *organic* persists. Today the term refers to the study of the compounds that contain carbon, many of which, incidentally, are found in living organisms.

It may seem odd that a whole discipline is devoted to the study of a single element in the periodic table, when more than 100 elements exist. It turns out, though, that there are far more organic compounds than any other type. **Organic chemicals affect virtually every facet of our lives, and for this reason, it is important and useful to know something about them.**

Clothes, foods, medicines, gasoline, refrigerants, and soaps are composed almost solely of organic compounds. Some, like cotton, wool, or silk are naturally occurring; that is, they can be isolated directly from natural sources. Others, such as nylon and polyester, are synthetic, meaning they are produced by chemists in the laboratory. By studying the principles and concepts of organic chemistry, you can learn more about compounds such as these and how they affect the world around you.

Realize, too, what organic chemistry has done for us. Organic chemistry has made available both comforts and necessities that were previously nonexistent, or reserved for only the wealthy. We have seen an enormous increase in life span, from 47 years in 1900 to over 70 years currently. To a large extent this is due to the isolation and synthesis of new drugs to fight infections and the availability of vaccines for childhood diseases. Chemistry has also given us the tools to control insect populations that spread disease, and there is more food for all because of fertilizers, pesticides, and herbicides. Our lives would be vastly different today without the many products that result from organic chemistry (Figure 1).

Figure 1

Products of organic chemistry used in medicine

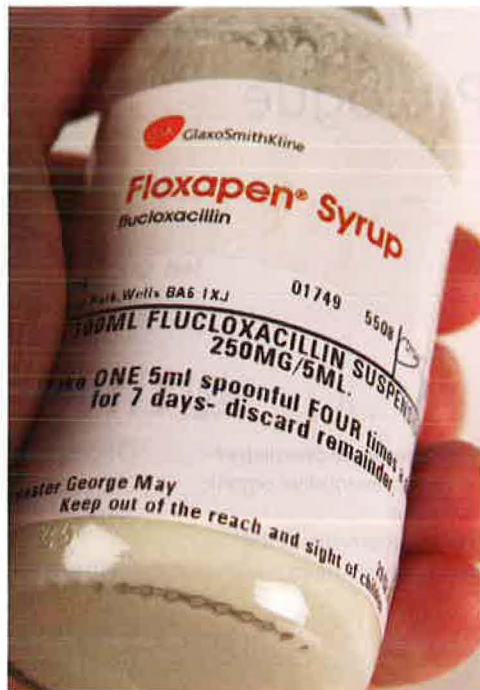
a. Oral contraceptives



b. Plastic syringes



c. Antibiotics



d. Synthetic heart valves



- Organic chemistry has given us contraceptives, plastics, antibiotics, and the knitted material used in synthetic heart valves.

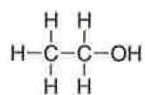
Some Representative Organic Molecules

Perhaps the best way to appreciate the variety of organic molecules is to look at a few. Three simple organic compounds are **methane**, **ethanol**, and **trichlorofluoromethane**.



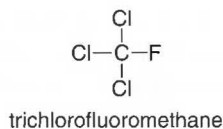
methane

- Methane**, the simplest of all organic compounds, contains one carbon atom. Methane—the main component of natural gas—occurs widely in nature. Like other hydrocarbons—organic compounds that contain only carbon and hydrogen—**methane is combustible**; that is, it burns in the presence of oxygen. Methane is the product of the anaerobic (without air) decomposition of organic matter by bacteria. The natural gas we use today was formed by the decomposition of organic material millions of years ago. Hydrocarbons such as methane are discussed in Chapter 4.



ethanol

- Ethanol**, the alcohol present in beer, wine, and other alcoholic beverages, is formed by the fermentation of sugar, quite possibly the oldest example of organic synthesis. Ethanol can also be made in the lab by a totally different process, but **the ethanol produced in the lab is identical to the ethanol produced by fermentation**. Alcohols including ethanol are discussed in Chapter 9.

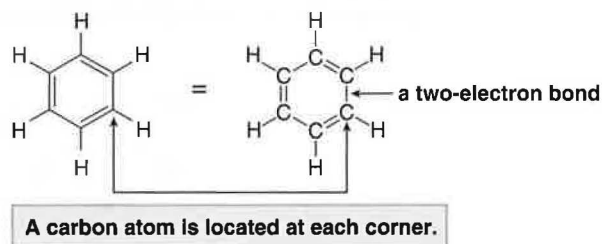


- **Trichlorofluoromethane** is a member of a class of molecules called **chlorofluorocarbons** or **CFCs**, which contain one or two carbon atoms and several halogens. Trichlorofluoromethane is an unusual organic molecule in that **it contains no hydrogen atoms**. Because it has a low molecular weight and is easily vaporized, trichlorofluoromethane has been used as an aerosol propellant and refrigerant. It and other CFCs have been implicated in the destruction of the stratospheric ozone layer, as is discussed in Chapter 15.

Because more complicated organic compounds contain many carbon atoms, organic chemists have devised a shorthand to draw them. Keep in mind the following when examining these structures:

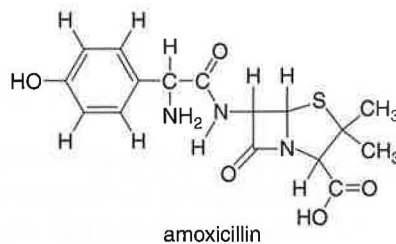
- Each solid line represents a two-electron covalent bond.
- When no atom is drawn at the corner of a ring, an organic chemist assumes it to be carbon.

For example, in the six-membered ring drawn, there is one carbon atom at each corner of the hexagon.

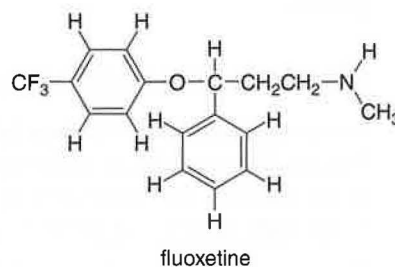


Three complex organic molecules that are important medications are **amoxicillin**, **fluoxetine**, and **AZT**.

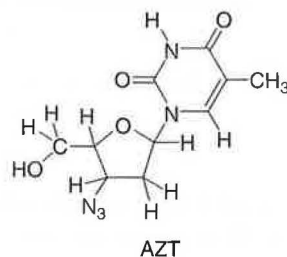
- **Amoxicillin** is one of the most widely used antibiotics in the penicillin family. The discovery and synthesis of such antibiotics in the twentieth century have made routine the treatment of infections that were formerly fatal. You were likely given some amoxicillin to treat an ear infection when you were a child. The penicillin antibiotics are discussed in Chapter 22.



- **Fluoxetine** is the generic name for the antidepressant **Prozac**. Prozac was designed and synthesized by chemists in the laboratory, and is now produced on a large scale in chemical factories. Because it is safe and highly effective in treating depression, Prozac is widely prescribed. Over 40 million individuals worldwide have used Prozac since 1986.

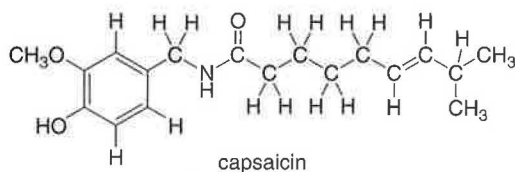


- **AZT**, **azidodeoxythymidine**, is a drug that treats human immunodeficiency virus (HIV), the virus that causes acquired immune deficiency syndrome (AIDS). Also known by its generic name **zidovudine**, AZT represents a chemical success to a different challenge: synthesizing agents that combat viral infections.

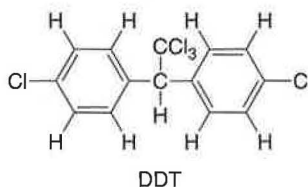


Other complex organic compounds having interesting properties are **capsaicin** and **DDT**.

- **Capsaicin**, one member of a group of compounds called *vanilloids*, is responsible for the characteristic spiciness of hot peppers. It is the active ingredient in pepper sprays used for personal defense and topical creams used for pain relief.



- **DDT**, **dichlorodiphenyltrichloroethane**, is a pesticide once called “miraculous” by Winston Churchill because of the many lives it saved by killing disease-carrying mosquitoes. DDT use is now banned in the United States and many developed countries because it is a non-specific insecticide that persists in the environment.



What are the common features of these organic compounds?

- All organic compounds contain carbon atoms and most contain hydrogen atoms.
- All the carbon atoms have four bonds. A stable carbon atom is said to be *tetravalent*.
- Other elements may also be present. Any atom that is not carbon or hydrogen is called a *heteroatom*. Common heteroatoms include N, O, S, P, and the halogens.
- Some compounds have chains of atoms and some compounds have rings.

These features explain why there are so many organic compounds: **Carbon forms four strong bonds with itself and other elements. Carbon atoms combine together to form rings and chains.**

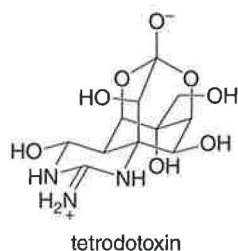
Organic Chemistry in the Marine Environment

Nature has generously supplied the organic chemist with a wide variety of complex molecules, biologically active drugs, and curious ecological adaptations. In the past 40 years, the chemistry of the marine environment has proven to be especially fruitful in producing unique chemical compounds and unusual behaviors.

For example, two complex molecules isolated from marine organisms are tetrodotoxin and tetrodotoxin (Figure 2).

Figure 2

Tetrodotoxin and trabectedin, natural products from marine sources

*Fugu niphobles**Ecteinascidia turbinata*

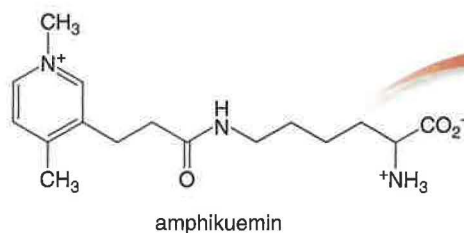
- Hydrogen atoms bonded to ring carbons are omitted in the structures of tetrodotoxin and trabectedin, a convention described in Section 1.8.

- **Tetrodotoxin**, a neurotoxin, is found in puffer fish of the genus *Fugu*. Puffer fish, a culinary delicacy in Japan, must be carefully prepared to remove organs such as the liver and ovaries that contain unsafe levels of this potent poison.
- **Trabectedin**, isolated from the sea squirt *Ecteinascidia turbinata*, is a novel anticancer drug recently approved in Europe for the treatment of ovarian cancer and soft tissue carcinoma. Trabectedin, also known as ecteinascidin 743, is marketed under the trade name Yondelis.

Finally, the complex chemistry that allows an anemonefish to live among the stinging tentacles of a sea anemone has attracted the attention of chemists, biochemists, and chemical biologists (Figure 3). Over the last 25 years, it has been shown that anemonefish are covered in a mucous

Figure 3

The attractant amphikuemin, secreted by the sea anemone *Heteractis crispa*

*sea anemone Heteractis crispa and the anemonefish Amphiprion perideraion*

- Hydrogen atoms bonded to carbon are omitted on the ring carbons and carbon chain in the structure of amphikuemin (Section 1.8).

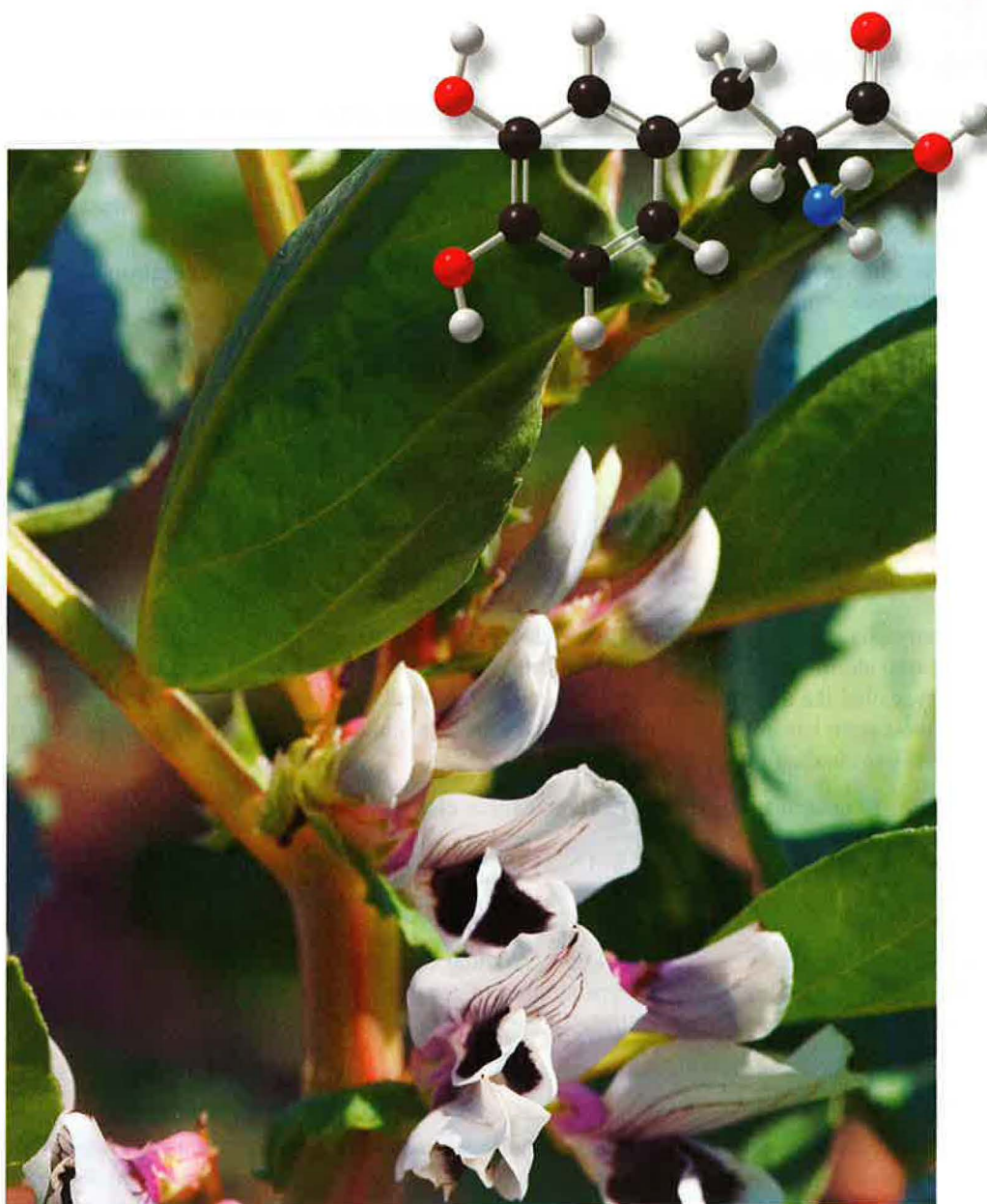
coating that protects them from the protein neurotoxin used by the sea anemone to ward off predators and kill prey. Moreover, the symbiosis between the sea anemone *Heteractis crispa* and the pink anemonefish *Amphiprion perideraion* is initiated by the secretion of **amphikuemin**, a compound of molecular formula $C_{16}H_{26}N_3O_3$ derived from the amino acid lysine (Chapter 29). The details of many of the chemical phenomena in this intricate biological system are as yet unknown and awaiting discovery.

In this introduction, we have seen a variety of molecules that have diverse structures. They represent a miniscule fraction of the organic compounds currently known and the many thousands that are newly discovered or synthesized each year. The principles you learn in organic chemistry will apply to all of these molecules, from simple ones like methane and ethanol, to complex ones like capsaicin and trabectedin. It is these beautiful molecules, their properties, and their reactions that we will study in organic chemistry.

WELCOME TO THE WORLD OF ORGANIC CHEMISTRY!

Structure and Bonding

1



- 1.1 The periodic table
- 1.2 Bonding
- 1.3 Lewis structures
- 1.4 Isomers
- 1.5 Exceptions to the octet rule
- 1.6 Resonance
- 1.7 Determining molecular shape
- 1.8 Drawing organic structures
- 1.9 Hybridization
- 1.10 Ethane, ethylene, and acetylene
- 1.11 Bond length and bond strength
- 1.12 Electronegativity and bond polarity
- 1.13 Polarity of molecules
- 1.14 L-Dopa—A representative organic molecule

L-Dopa, also called levodopa, was first isolated from seeds of the broad bean plant *Vicia faba* in 1913. Since 1967 it has been the drug of choice for the treatment of Parkinson's disease, a debilitating illness that results from the degeneration of neurons that produce the neurotransmitter dopamine in the brain. L-Dopa is an oral medication that is transported to the brain by the bloodstream, where it is converted to dopamine. Since L-dopa must be taken in large doses with some serious side effects, today it is often given with other drugs that lessen its negative impact on an individual. In Chapter 1, we learn about the structure, bonding, and properties of organic molecules like L-dopa.

Before examining organic molecules in detail, we must review some important features about structure and bonding learned in previous chemistry courses. We will discuss these concepts primarily from an organic chemist's perspective, and spend time on only the particulars needed to understand organic compounds.

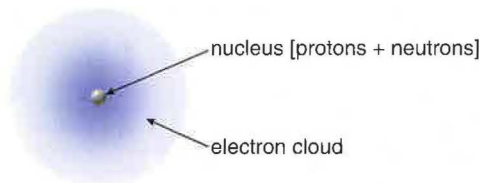
Important topics in Chapter 1 include drawing Lewis structures, predicting the shape of molecules, determining what orbitals are used to form bonds, and how electronegativity affects bond polarity. Equally important is Section 1.8 on drawing organic molecules, both shorthand methods routinely used for simple and complex compounds, as well as three-dimensional representations that allow us to more clearly visualize them.

1.1 The Periodic Table

All matter is composed of the same building blocks called **atoms**. There are two main components of an atom.

- The **nucleus** contains positively charged **protons** and uncharged **neutrons**. Most of the mass of the atom is contained in the nucleus.
- The **electron cloud** is composed of negatively charged **electrons**. The electron cloud comprises most of the volume of the atom.

Schematic of an atom



The charge on a proton is equal in magnitude but opposite in sign to the charge on an electron. In a neutral atom, the **number of protons in the nucleus equals the number of electrons**. This quantity, called the **atomic number**, is unique to a particular element. For example, every neutral carbon atom has an atomic number of six, meaning it has six protons in its nucleus and six electrons surrounding the nucleus.

In addition to neutral atoms, we will also encounter **charged ions**.

- A **cation** is positively charged and has fewer electrons than its neutral form.
- An **anion** is negatively charged and has more electrons than its neutral form.

The number of neutrons in the nucleus of a particular element can vary. **Isotopes** are two atoms of the same element having a different number of neutrons. The **mass number** of an atom is the total number of protons and neutrons in the nucleus. Isotopes have different mass numbers.

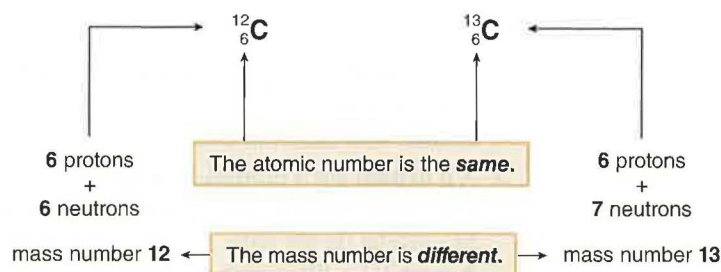
Isotopes of carbon and hydrogen are sometimes used in organic chemistry, as we will see in Chapter 14.

- The most common isotope of hydrogen has one proton and no neutrons in the nucleus, but 0.02% of hydrogen atoms have one proton and one neutron. This isotope of hydrogen is called **deuterium**, and is sometimes symbolized by the letter **D**.
- Most carbon atoms have six protons and six neutrons in the nucleus, but 1.1% have six protons and seven neutrons.

The **atomic weight** is the weighted average of the mass of all isotopes of a particular element, reported in atomic mass units (amu).

Figure 1.1

A comparison of two isotopes of the element carbon



Each atom is identified by a one- or two-letter abbreviation that is the characteristic symbol for that element. Carbon is identified by the single letter **C**. Sometimes the atomic number is indicated as a subscript to the left of the element symbol, and the mass number is indicated as a superscript, as shown in Figure 1.1.

A **row** in the periodic table is also called a **period**, and a **column** is also called a **group**. A periodic table is located on the inside front cover for your reference.

Long ago it was realized that groups of elements have similar properties, and that these atoms could be arranged in a schematic way called the **periodic table**. There are more than 100 known elements, arranged in the periodic table in order of increasing atomic number. The periodic table is composed of rows and columns.

- Elements in the same row are similar in *size*.
- Elements in the same column have similar *electronic and chemical properties*.

Each column in the periodic table is identified by a **group number**, an Arabic (1 to 8) or Roman (I to VIII) numeral followed by the letter A or B. For example, carbon is located in group **4A** in the periodic table in this text.

Carbon's entry in the periodic table:

group number	→ 4A
atomic number	→ 6
element symbol	→ C
element name	→ Carbon
atomic weight	→ 12.01

Although more than 100 elements exist, most are not common in organic compounds. Figure 1.2 contains a truncated periodic table, indicating the handful of elements that are routinely seen in this text. **Most of these elements are located in the first and second rows of the periodic table.**

Across each row of the periodic table, electrons are added to a particular shell of orbitals around the nucleus. The shells are numbered 1, 2, 3, and so on. Adding electrons to the first shell forms the first row. Adding electrons to the second shell forms the second row. **Electrons are first added to the shells closest to the nucleus.** These electrons are held most tightly.

Each shell contains a certain number of subshells called **orbitals**. An orbital is a region of space that is high in electron density. There are four different kinds of orbitals, called *s*, *p*, *d*, and *f*. The first shell has only one orbital, called an *s* orbital. The second shell has two kinds of orbitals, *s* and *p*, and so on. Each type of orbital occupies a certain space and has a particular shape.

Figure 1.2

A periodic table of the common elements seen in organic chemistry

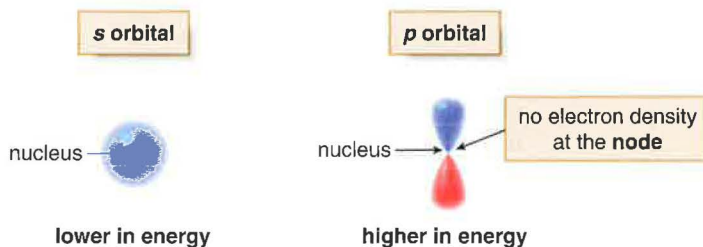
group number	1A	2A		3A	4A	5A	6A	7A	8A
first row	H								
second row	Li			B	C	N	O	F	
	Na	Mg		Si	P	S	Cl		
	K							Br	
								I	

↑ ↑
columns

- Note the location of carbon in the second row, group 4A.

For the first- and second-row elements, we must deal with only *s* orbitals and *p* orbitals.

- An *s* orbital has a **sphere of electron density**. It is **lower in energy** than other orbitals of the same shell, because electrons are kept close to the positively charged nucleus. An *s* orbital is filled with electrons before a *p* orbital in the same shell.
- A *p* orbital has a **dumbbell shape**. It contains a **node of electron density** at the nucleus. A node means there is no electron density in this region. A *p* orbital is **higher in energy** than an *s* orbital (in the same shell) because its electron density is farther away from the nucleus. A *p* orbital is filled with electrons only after an *s* orbital of the same shell is full.



Let's now look at the elements in the first and second rows of the periodic table.

1.1A The First Row

The first row of the periodic table is formed by adding electrons to the first shell of orbitals around the nucleus. There is only one orbital in the first shell, called the **1*s* orbital**.

- **Remember:** Each orbital can have a maximum of two electrons.

As a result, there are **two elements in the first row**, one having one electron added to the 1*s* orbital, and one having two. The element hydrogen (H) has what is called a 1*s*¹ configuration with one electron in the 1*s* orbital, and helium (He) has a 1*s*² configuration with two electrons in the 1*s* orbital.

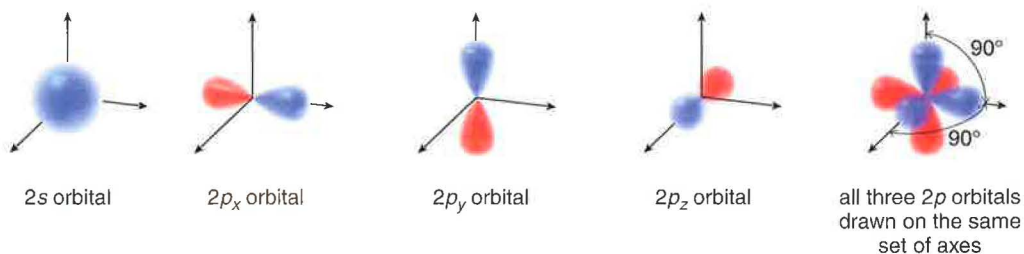


1.1B The Second Row

Every element in the second row has a filled first shell of electrons. Thus, all second-row elements have a 1*s*² configuration. These electrons in the inner shell of orbitals are called **core electrons**, and are not usually involved in the chemistry of a particular element.

Each element in the second row of the periodic table has four orbitals available to accept additional electrons:

- **one 2*s* orbital**, the *s* orbital in the second shell
- **three 2*p* orbitals**, all dumbbell-shaped and perpendicular to each other along the *x*, *y*, and *z* axes



Because each of the four orbitals in the second shell can hold two electrons, there is a **maximum capacity of eight electrons** for elements in the second row. The second row of the periodic table consists of eight elements, obtained by adding electrons to the $2s$ and three $2p$ orbitals.

group number	→ 1A	2A						
			Li	Be				
number of valence electrons	→ 1	2						

	3A	4A	5A	6A	7A	8A
	B	C	N	O	F	Ne
	3	4	5	6	7	8

The outermost electrons are called **valence electrons**. The valence electrons are more loosely held than the electrons closer to the nucleus, and as such, they participate in chemical reactions. **The group number of a second-row element reveals its number of valence electrons.** For example, carbon in group 4A has four valence electrons, and oxygen in group 6A has six.

Problem 1.1

While the most common isotope of nitrogen has a mass number of 14 (nitrogen-14), a radioactive isotope of nitrogen has a mass number of 13 (nitrogen-13). Nitrogen-13 is used in PET (positron emission tomography) scans by physicians to monitor brain activity and diagnose dementia. For each isotope, give the following information: (a) the number of protons; (b) the number of neutrons; (c) the number of electrons in the neutral atom; and (d) the group number.

1.2 Bonding

Until now our discussion has centered on individual atoms, but it is more common in nature to find two or more atoms joined together.

- **Bonding is the joining of two atoms in a stable arrangement.**

Bonding may occur between atoms of the same or different elements. Bonding is a favorable process because it always leads to **lowered energy and increased stability**. Joining two or more elements forms **compounds**. Although only about 100 elements exist, more than 50 million compounds are known. Examples of compounds include hydrogen gas (H_2), formed by joining two hydrogen atoms, and methane (CH_4), the simplest organic compound, formed by joining a carbon atom with four hydrogen atoms.

One general rule governs the bonding process.

- **Through bonding, atoms attain a complete outer shell of valence electrons.**

Alternatively, because the noble gases in group 8A of the periodic table are especially stable as atoms having a filled shell of valence electrons, the general rule can be restated.

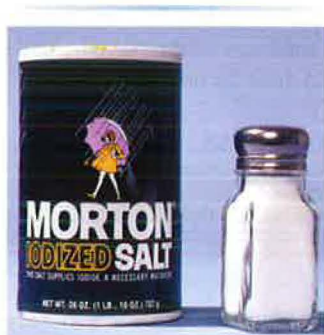
- **Through bonding, atoms attain a stable noble gas configuration of electrons.**

What does this mean for first- and second-row elements? **A first-row element like hydrogen can accommodate two electrons around it.** This would make it like the noble gas helium at the end of the same row. **A second-row element is most stable with eight valence electrons around it** like neon. Elements that behave in this manner are said to follow the **octet rule**.

There are two different kinds of bonding: **ionic bonding** and **covalent bonding**.

- **Ionic bonds result from the transfer of electrons from one element to another.**
- **Covalent bonds result from the sharing of electrons between two nuclei.**

The type of bonding is determined by the location of an element in the periodic table. An ionic bond generally occurs when elements on the **far left** side of the periodic table combine with elements on the **far right** side, ignoring the noble gases, which form bonds only rarely. **The resulting ions**

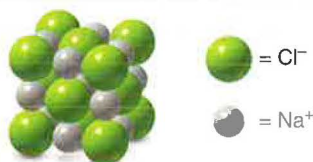


Atoms readily form ionic bonds when they can attain a noble gas configuration by gaining or losing just one or two electrons. NaCl and KI are ionic compounds.

are held together by extremely strong electrostatic interactions. A positively charged cation formed from the element on the left side attracts a negatively charged anion formed from the element on the right side. The resulting **salts** are seen in many of the inorganic compounds with which you are familiar. Sodium chloride (NaCl) is common table salt, and potassium iodide (KI) is an essential nutrient added to make iodized salt.

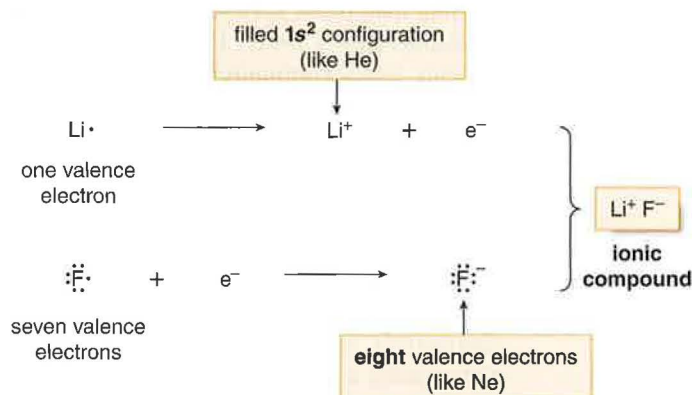
Ionic compounds form extended crystal lattices that maximize the positive and negative electrostatic interactions. In NaCl, each positively charged Na^+ ion is surrounded by six negatively charged Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions.

NaCl—An ionic crystalline lattice



Lithium fluoride, LiF, is an example of an ionic compound.

- The element **lithium**, located in group 1A of the periodic table, has just one valence electron in its second shell. If this electron is lost, lithium forms the cation Li^+ having no electrons in the second shell. However, it will have a stable electronic arrangement with two electrons in the first shell like helium.
- The element **fluorine**, located in group 7A of the periodic table, has seven valence electrons. By gaining one it forms the anion F^- , which has a filled valence shell (an octet of electrons), like neon.
- Thus, lithium fluoride is a stable ionic compound.



- The transfer of electrons forms stable salts composed of cations and anions.

The second type of bonding, **covalent bonding**, occurs with elements like carbon in the middle of the periodic table, which would otherwise have to gain or lose several electrons to form an ion with a complete valence shell. A **covalent bond is a two-electron bond**, and a compound with covalent bonds is called a **molecule**. Covalent bonds also form between two elements from the same side of the table, such as two hydrogen atoms or two chlorine atoms. H_2 , Cl_2 , and CH_4 are all examples of covalent molecules.

A **compound** may have either ionic or covalent bonds. A **molecule** has only covalent bonds.

Problem 1.2

Label each bond in the following compounds as ionic or covalent.

- a. F_2 b. LiBr c. CH_3CH_3 d. NaNH_2

How many covalent bonds will a particular atom typically form? As you might expect, it depends on the location of the atom in the periodic table. In the first row, **hydrogen forms one covalent bond** using its one valence electron. When two hydrogen atoms are joined in a bond, each has a filled valence shell of two electrons.



Second-row elements can have no more than eight valence electrons around them. For neutral molecules, two consequences result.

- **Atoms with one, two, three, or four valence electrons form one, two, three, or four bonds**, respectively, in neutral molecules.
- **Atoms with five or more valence electrons** form enough bonds to give an octet. This results in the following simple equation:

$$\boxed{\text{predicted number of bonds}} = 8 - \text{number of valence electrons}$$

For example, B has three valence electrons, so it forms three bonds, as in BF_3 . N has five valence electrons, so it also forms three bonds ($8 - 5 = 3$ bonds), as in NH_3 .

These guidelines are used in Figure 1.3 to summarize the usual number of bonds formed by the common atoms in organic compounds. Notice that when second-row elements form fewer than four bonds their octets consist of both **bonding (shared) electrons** and **nonbonding (unshared) electrons**. Unshared electrons are also called **lone pairs**.

Nonbonded pair of electrons = unshared pair of electrons = lone pair

Problem 1.3 How many covalent bonds are predicted for each atom?
 a. O b. Al c. Br d. Si

Figure 1.3

Summary: The usual number of bonds of common neutral atoms

	—H	$\begin{array}{c} \\ \text{—C—} \\ \end{array}$	$\begin{array}{c} \downarrow \\ \text{—}\ddot{\text{N}}\text{—} \\ \end{array}$	$\begin{array}{c} \downarrow \\ \text{—}\ddot{\text{O}}\text{—} \\ \downarrow \end{array}$	$\begin{array}{c} \downarrow \\ \text{—}\ddot{\text{X}}\text{:} \\ \downarrow \end{array}$	X = F, Cl, Br, I
number of bonds →	1	4	3	2	1	
number of nonbonded electron pairs →	0	0	1	2	3	

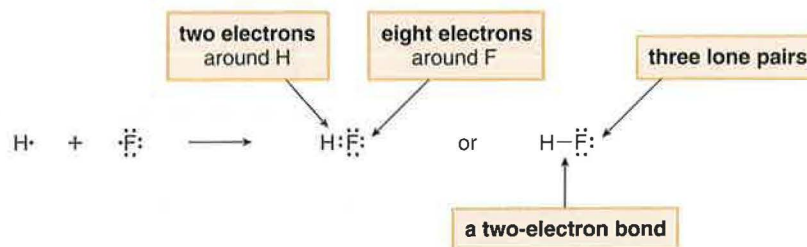
1.3 Lewis Structures

Lewis structures are electron dot representations for molecules. There are three general rules for drawing Lewis structures.

1. Draw only the valence electrons.
2. Give every second-row element no more than eight electrons.
3. Give each hydrogen two electrons.

The letter **X** is often used to represent one of the halogens in group 7A: F, Cl, Br, or I.

To draw a Lewis structure for a diatomic molecule like **HF**, recall that hydrogen has one valence electron and fluorine has seven. H and F each donate one electron to form a two-electron bond. The resulting molecule gives both H and F a filled valence shell.



In a Lewis structure, a **solid line** indicates a two-electron covalent bond.

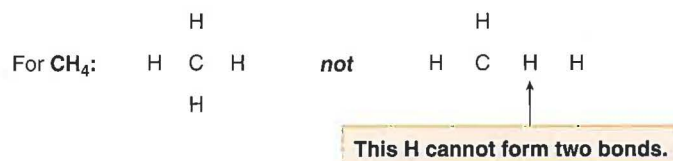
1.3A A Procedure for Drawing Lewis Structures

Drawing a Lewis structure for larger molecules is easier if you follow a stepwise procedure.

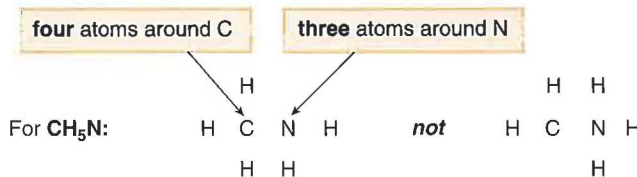
How To Draw a Lewis Structure

Step [1] Arrange atoms next to each other that you think are bonded together.

- Always place hydrogen atoms and halogen atoms on the periphery because H and X (X = F, Cl, Br, and I) form only one bond each.



- As a first approximation, place no more atoms around an atom than the number of bonds it usually forms.



- In truth, the proper arrangement of atoms may not be obvious, or more than one arrangement may be possible (Section 1.4). Even in many simple molecules, the connectivity between atoms must be determined experimentally.

Step [2] Count the electrons.

- Count the number of valence electrons from all atoms.
- Add one electron for each negative charge.
- Subtract one electron for each positive charge.
- This sum gives the total number of electrons that must be used in drawing the Lewis structure.

Step [3] Arrange the electrons around the atoms.

- Place a bond between every two atoms, giving two electrons to each H and no more than eight to any second-row atom.
- Use all remaining electrons to fill octets with lone pairs.
- If all valence electrons are used and an atom does not have an octet, form multiple bonds, as shown in Sample Problem 1.2.

Step [4] Assign formal charges to all atoms.

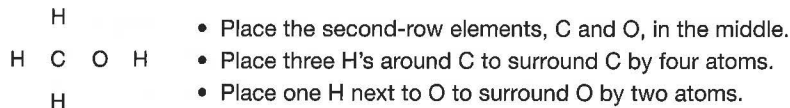
- Formal charges are discussed in Section 1.3C.

Sample Problem 1.1 illustrates how to draw a Lewis structure of a simple organic molecule.

Sample Problem 1.1 Draw a Lewis structure for methanol, a compound with molecular formula CH_4O .

Solution

Step [1] Arrange the atoms.

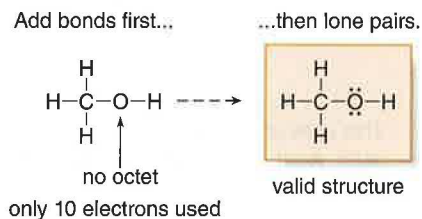


Step [2] Count the electrons.

$$\begin{array}{r} 1 \text{ C} \times 4 \text{ e}^- = 4 \text{ e}^- \\ 1 \text{ O} \times 6 \text{ e}^- = 6 \text{ e}^- \\ 4 \text{ H} \times 1 \text{ e}^- = 4 \text{ e}^- \\ \hline 14 \text{ e}^- \text{ total} \end{array}$$

Step [3] Add the bonds and lone pairs.

- Add five two-electron bonds to form the C–H, C–O, and O–H bonds, using 10 of the 14 electrons.
- Place two lone pairs on the O atom to use the remaining four electrons and give the O atom an octet.



To check if a Lewis structure is valid, we must answer YES to three questions.

- Have all the electrons been used?
- Is each H surrounded by two electrons?
- Is each second-row element surrounded by no more than eight electrons?

Since the answer to all three questions is YES, we have drawn a valid Lewis structure for CH_4O .

Problem 1.4 Draw a valid Lewis structure for each species:

- a. CH_3CH_3 b. CH_5N c. CH_3^- d. CH_3Cl

1.3B Multiple Bonds

Sample Problem 1.2 illustrates two examples of when multiple bonds are needed in Lewis structures.

Sample Problem 1.2 Draw a Lewis structure for each compound. Assume the atoms are arranged as follows:

- a. ethylene, C_2H_4 b. acetylene, C_2H_2



Solution

- a. **Ethylene, C_2H_4 :** Follow Steps [1] to [3] to draw a Lewis structure. After placing five bonds between the atoms and adding the two remaining electrons as a lone pair, one C still has no octet.

Step [2] Count the electrons.

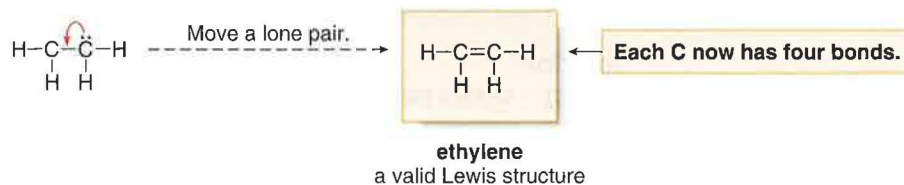
$$\begin{array}{r} 2 \text{ C} \times 4 \text{ e}^- = 8 \text{ e}^- \\ 4 \text{ H} \times 1 \text{ e}^- = 4 \text{ e}^- \\ \hline 12 \text{ e}^- \text{ total} \end{array}$$

Step [3] Add the bonds and lone pairs.

Add bonds first... ...then lone pairs.

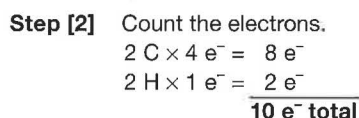
$\begin{array}{c} \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ <p>no octet</p>	\dashrightarrow	$\begin{array}{c} \text{H}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
----------------------------------------------------------------------------------------------------------------------------	-------------------	------------------------------------------------------------------------------------------------------------

To give both C's an octet, **change one lone pair into one bonding pair of electrons between the two C's, forming a double bond.**



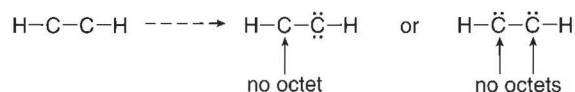
This uses all 12 electrons, each C has an octet, and each H has two electrons. The Lewis structure is valid. **Ethylene contains a carbon-carbon double bond.**

b. **Acetylene, C₂H₂:** A similar phenomenon occurs with acetylene. Placing the 10 valence electrons gives a Lewis structure in which one or both of the C's lack an octet.

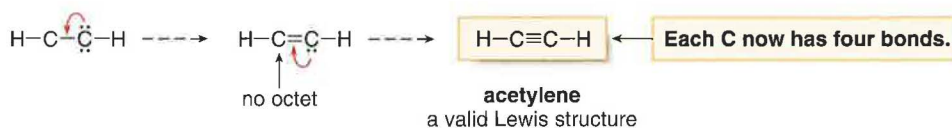


Step [3] Add the bonds and lone pairs.

Add bonds first... ..then lone pairs.



In this case, **change two lone pairs into two bonding pairs of electrons, forming a triple bond.**



This uses all 10 electrons, each C has an octet, and each H has two electrons. The Lewis structure is valid. **Acetylene contains a carbon-carbon triple bond.**

Carbon always forms four bonds in stable organic molecules. Carbon forms single, double, and triple bonds to itself and other elements.

For a second-row element in a stable molecule:

number of bonds

+ number of lone pairs

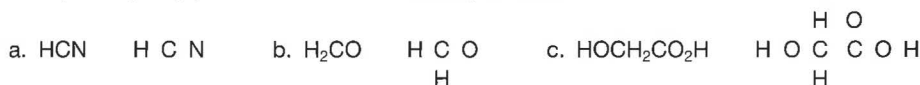
4

- After placing all electrons in bonds and lone pairs, use a lone pair to form a multiple bond if an atom does not have an octet.

You must change one lone pair into one new bond for each two electrons needed to complete an octet. In acetylene, for example, four electrons were needed to complete an octet, so two lone pairs were used to form two new bonds, forming a triple bond.

Problem 1.5

Draw an acceptable Lewis structure for each compound, assuming the atoms are connected as arranged. Hydrogen cyanide (HCN) is a poison, formaldehyde (H₂CO) is a preservative, and glycolic acid (HOCH₂CO₂H) is used to make dissolving sutures.



1.3C Formal Charge

To manage electron bookkeeping in a Lewis structure, organic chemists use **formal charge**.

- **Formal charge** is the charge assigned to individual atoms in a Lewis structure.

By calculating formal charge, we determine how the number of electrons around a particular atom compares to its number of valence electrons. Formal charge is calculated as follows:

$$\text{formal charge} = \text{number of valence electrons} - \text{number of electrons an atom "owns"}$$

The number of electrons “owned” by an atom is determined by its number of bonds and lone pairs.

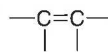
- An atom “owns” *all* of its unshared electrons and *half* of its shared electrons.

$$\boxed{\text{number of electrons owned}} = \boxed{\text{number of unshared electrons}} + \frac{1}{2} \boxed{\left[\text{number of shared electrons} \right]}$$

The number of electrons “owned” by different carbon atoms is indicated in the following examples:



- C shares eight electrons.
- C “owns” **four** electrons.



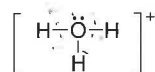
- Each C shares eight electrons.
- Each C “owns” **four** electrons.



- C shares six electrons.
- C has two unshared electrons.
- C “owns” **five** electrons.

Sample Problem 1.3 illustrates how formal charge is calculated on the atoms of a polyatomic ion. **The sum of the formal charges on the individual atoms equals the net charge on the molecule or ion.**

Sample Problem 1.3 Determine the formal charge on each atom in the ion H_3O^+ .



Solution

For each atom, two steps are needed:

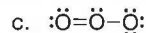
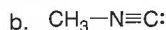
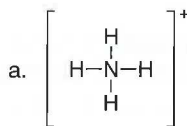
Step [1] Determine the number of electrons an atom “owns.”

Step [2] Subtract this sum from its number of valence electrons.

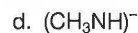
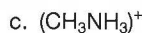
O atom	H atoms
[1] number of electrons “owned” by O $2 + \frac{1}{2}(6) = 5$	[1] number of electrons “owned” by each H $0 + \frac{1}{2}(2) = 1$
[2] formal charge on O $6 - 5 = \boxed{+1}$	[2] formal charge on each H $1 - 1 = \boxed{0}$

The formal charge on each H is 0. The formal charge on oxygen is +1. The overall charge on the ion is the sum of all of the formal charges; $0 + 0 + 0 + 1 = +1$.

Problem 1.6 Calculate the formal charge on each second-row atom:



Problem 1.7 Draw a Lewis structure for each ion:



Sometimes it is easier to count bonds, rather than shared electrons when determining formal charge.

$$\frac{1}{2}[\text{number of shared electrons}] = \text{number of bonds}$$

A shortcut method to determine the number of bonds in a Lewis structure is given in the *Student Study Guide/Solutions Manual* (page 1–4).

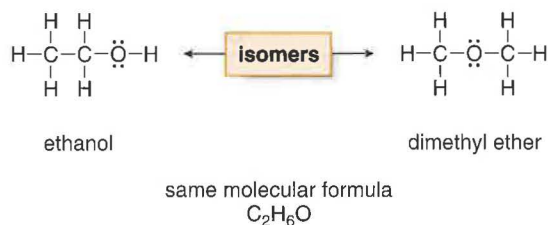
When you first add formal charges to Lewis structures, use the procedure in Sample Problem 1.3. With practice, you will notice that certain bonding patterns always result in the same formal charge. For example, any N atom with four bonds (and, thus no lone pairs) has a +1 formal charge. Table 1.1 lists the bonding patterns and resulting formal charges for carbon, nitrogen, and oxygen.

Table 1.1 Formal Charge Observed with Common Bonding Patterns for C, N, and O

Atom	Number of valence electrons	Formal charge		
		+1	0	-1
C	4			
N	5			
O	6			

1.4 Isomers

In drawing a Lewis structure for a molecule with several atoms, sometimes more than one arrangement of atoms is possible for a given molecular formula. For example, there are two acceptable arrangements of atoms for the molecular formula C_2H_6O .



Both are valid Lewis structures, and both molecules exist. One is called ethanol, and the other, dimethyl ether. These two compounds are called **isomers**.

- **Isomers** are different molecules having the same molecular formula.

Ethanol and dimethyl ether are **constitutional isomers** because they have the same molecular formula, but the **connectivity of their atoms is different**. For example, ethanol has one C–C bond and one O–H bond, whereas dimethyl ether has two C–O bonds. A second class of isomers, called **stereoisomers**, is introduced in Section 4.13B.

Problem 1.8

Draw Lewis structures for each molecular formula.

- a. $C_2H_4Cl_2$ (two isomers) b. C_3H_8O (three isomers) c. C_3H_6 (two isomers)

1.5 Exceptions to the Octet Rule

Most of the common elements in organic compounds—**C, N, O, and the halogens**—follow the octet rule. Hydrogen is a notable exception, because it accommodates only two electrons in bonding. Additional exceptions include boron and beryllium (second-row elements in groups 3A and 2A, respectively), and elements in the third row (particularly phosphorus and sulfur).



Alendronic acid, sold as a sodium salt under the trade name of **Fosamax**, is used to prevent osteoporosis in women. Osteoporosis decreases bone density, as shown by comparing normal bone (top) with brittle bone (bottom).

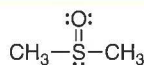
Elements in groups 2A and 3A of the periodic table, such as beryllium and boron, do not have enough valence electrons to form an octet in a neutral molecule. Lewis structures for BeH_2 and BF_3 show that these atoms have only four and six electrons, respectively, around the central atom. There is nothing we can do about this! There simply aren't enough electrons to form an octet.



Because the Be and B atoms each have less than an octet of electrons, these molecules are highly reactive.

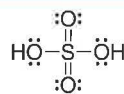
A second exception to the octet rule occurs with some elements located in the third row and later in the periodic table. These elements have empty *d* orbitals available to accept electrons, and thus they may have **more than eight electrons** around them. For organic chemists, the two most common elements in this category are **phosphorus** and **sulfur**, which can have 10 or even 12 electrons around them. Examples of these phosphorus and sulfur compounds include the following:

10 electrons around S



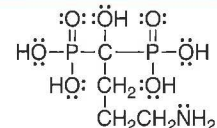
dimethyl sulfoxide
(abbreviated as DMSO)

12 electrons around S



sulfuric acid

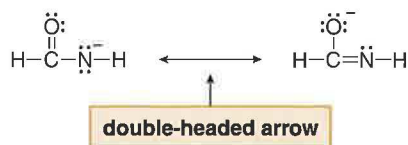
10 electrons around each P



alendronic acid

1.6 Resonance

Some molecules can't be adequately represented by a single Lewis structure. For example, two valid Lewis structures can be drawn for the anion $(\text{HCONH})^-$. One structure has a negatively charged N atom and a C–O double bond; the other has a negatively charged O atom and a C–N double bond. These structures are called **resonance structures** or **resonance forms**. A **double-headed arrow** is used to separate two resonance structures.



- **Resonance structures** are two Lewis structures having the *same* placement of atoms but a *different* arrangement of electrons.

Which resonance structure is an accurate representation for $(\text{HCONH})^-$? **The answer is neither of them.** The true structure is a composite of both resonance forms, and is called a **resonance hybrid**. The hybrid shows characteristics of **both** resonance structures.

Each resonance structure implies that electron pairs are localized in bonds or on atoms. In actuality, resonance allows certain electron pairs to be **delocalized** over two or more atoms, and this delocalization of electron density adds stability. **A molecule with two or more resonance structures is said to be resonance stabilized.** We will return to the resonance hybrid in Section 1.6C. First, however, we examine the general principles of resonance theory and learn how to interconvert two or more resonance structures.

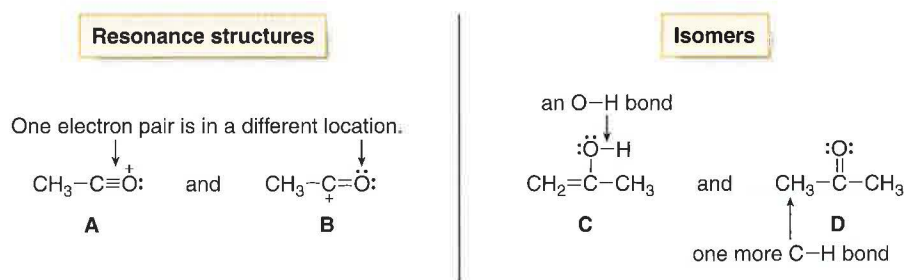
1.6A An Introduction to Resonance Theory

Keep in mind the following basic principles of resonance theory.

- Resonance structures are not real. An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.
- Resonance structures are *not* in equilibrium with each other. There is no movement of electrons from one form to another.
- Resonance structures are *not* isomers. Two isomers differ in the arrangement of *both* atoms and electrons, whereas resonance structures differ *only* in the *arrangement of electrons*.

Resonance structures are different ways of drawing the same compound. Two resonance structures are *not* different compounds.

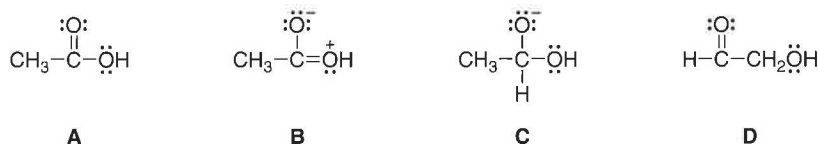
For example, ions **A** and **B** are resonance structures because the atom position is the same in both compounds, but the location of an electron pair is different. In contrast, compounds **C** and **D** are isomers since the atom placement is different; **C** has an O–H bond, and **D** has an additional C–H bond.



Problem 1.9 Classify each pair of compounds as isomers or resonance structures.



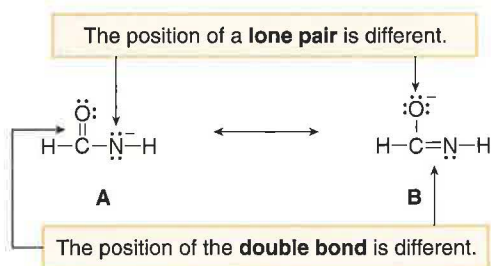
Problem 1.10 Considering structures **A–D**, classify each pair of compounds as isomers, resonance structures, or neither: (a) **A** and **B**; (b) **A** and **C**; (c) **A** and **D**; (d) **B** and **D**.



1.6B Drawing Resonance Structures

To draw resonance structures, use the three rules that follow:

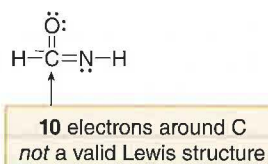
Rule [1] Two resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.



Rule [2] Two resonance structures must have the same number of unpaired electrons.



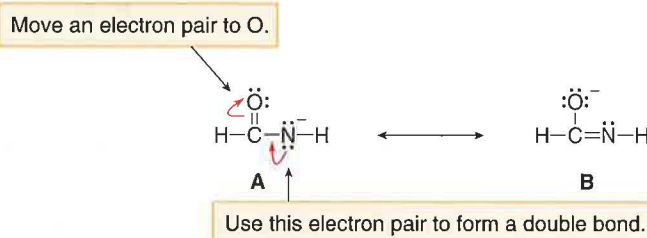
Rule [3] Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight electrons.



Curved arrow notation is a convention that shows how electron position differs between the two resonance forms.

- *Curved arrow notation shows the movement of an electron pair.* The tail of the arrow always begins at an electron pair, either in a bond or lone pair. The head points to where the electron pair “moves.”

A curved arrow always begins at an electron pair. It ends at an atom or a bond.



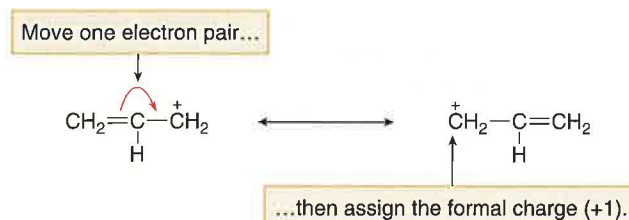
Resonance structures **A** and **B** differ in the location of two electron pairs, so two curved arrows are needed. To convert **A** to **B**, take the lone pair on N and form a double bond between C and N. Then, move an electron pair in the C–O double bond to form a lone pair on O. Curved arrows thus show how to reposition the electrons in converting one resonance form to another. **The electrons themselves do not actually move.** Sample Problem 1.4 illustrates the use of curved arrows to convert one resonance structure to another.

Sample Problem 1.4 Follow the curved arrows to draw a second resonance structure for each ion.



Solution

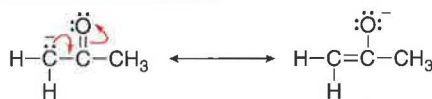
- a. The curved arrow tells us to move **one** electron pair in the double bond to the adjacent C–C bond. Then determine the formal charge on any atom whose bonding is different.



Positively charged carbon atoms are called **carbocations**. Carbocations are unstable intermediates because they contain a carbon atom that is lacking an octet of electrons.

- b. **Two** curved arrows tell us to move **two** electron pairs. The second resonance structure has a formal charge of (-1) on O.

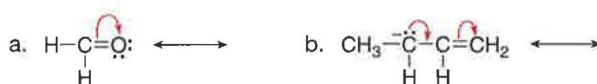
Move two electron pairs...



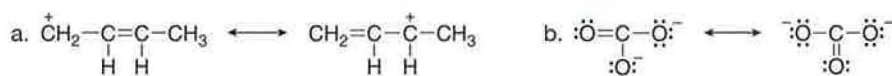
...then calculate formal charges.

This type of resonance-stabilized anion is called an **enolate anion**. Enolates are important intermediates in many organic reactions, and all of Chapters 23 and 24 is devoted to their preparation and reactions.

Problem 1.11 Follow the curved arrows to draw a second resonance structure for each species.

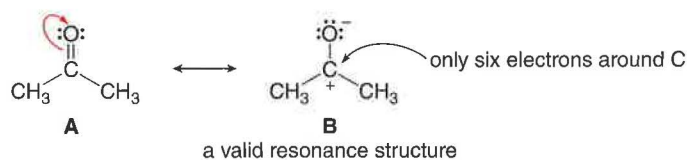


Problem 1.12 Use curved arrow notation to show how the first resonance structure can be converted to the second.

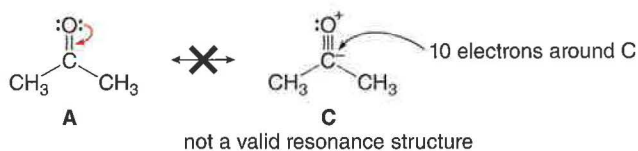


Two resonance structures can have exactly the same kinds of bonds, as they do in the carbocation in Sample Problem 1.4a, or they may have different types of bonds, as they do in the enolate in Sample Problem 1.4b. Either possibility is fine as long as the individual resonance structures are valid Lewis structures.

A resonance structure can have an atom with *fewer* than eight electrons around it. **B** is a resonance structure of **A** even though the carbon atom is surrounded by only six electrons.



In contrast, a resonance structure can *never* have a second-row element with more than eight electrons. **C** is *not* a resonance structure of **A** because the carbon atom is now surrounded by 10 electrons.

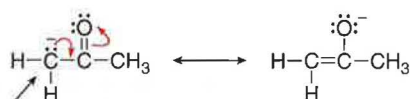
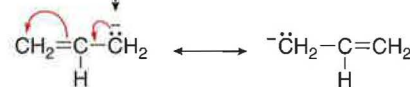


We will learn much more about resonance in Chapter 16.

The ability to draw and manipulate resonance structures is an important skill that will be needed throughout your study of organic chemistry. With practice, you will begin to recognize certain common bonding patterns for which more than one Lewis structure can be drawn. For now, notice that:

- A second resonance structure can be drawn when a lone pair is located on an atom directly bonded to a multiple bond.

lone pair adjacent to C=C



lone pair adjacent to C=O

- A second resonance structure can be drawn when an atom bearing a (+) charge is bonded to either a multiple bond or an atom with a lone pair.

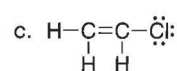
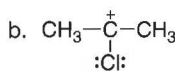
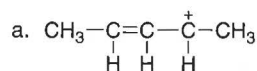
(+) charge adjacent to a double bond



(+) charge adjacent to an atom with a lone pair



Problem 1.13 Draw a second resonance structure for each species.



1.6C The Resonance Hybrid

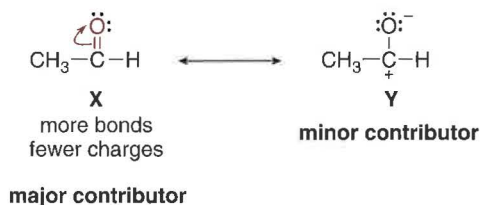
The **resonance hybrid** is the composite of all possible resonance structures. In the resonance hybrid, the electron pairs drawn in different locations in individual resonance structures are *delocalized*.

- The resonance hybrid is more stable than any resonance structure because it delocalizes electron density over a larger volume.

What does the hybrid look like? When all resonance forms are identical, as they were in the carbocation in Sample Problem 1.4a, each resonance form contributes **equally** to the hybrid.

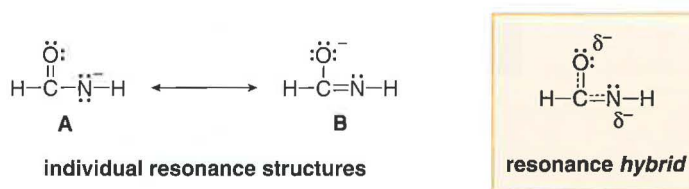
When two resonance structures are different, the hybrid looks more like the “better” resonance structure. The “better” resonance structure is called the **major contributor** to the hybrid, and all others are **minor contributors**. The hybrid is the weighted average of the contributing resonance structures. What makes one resonance structure “better” than another? There are many factors, but for now, we will learn just two.

- A “better” resonance structure is one that has *more bonds* and *fewer charges*.



Comparing resonance structures **X** and **Y**, **X** is the major contributor because it has more bonds and fewer charges. Thus, the hybrid looks more like **X** than **Y**.

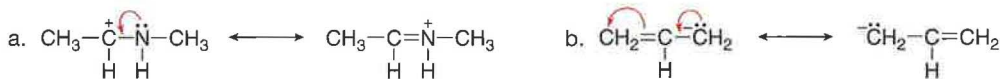
How can we draw a hybrid, which has delocalized electron density? First, we must determine what is different in the resonance structures. Two differences commonly seen are the **position of a multiple bond** and the **site of a charge**. The anion (HCONH^-) illustrates two conventions for drawing resonance hybrids.



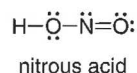
- **Double bond position.** Structure **A** has a C–O double bond, whereas structure **B** has a C–N double bond. A dashed line in the hybrid indicates partial double bond character between these atoms.
- **Location of the charge.** A negative charge resides on different atoms in **A** and **B**. The symbol δ^- (for a partial negative charge) indicates that the charge is delocalized on the N and O atoms in the hybrid.

This discussion of resonance is meant to serve as an introduction only. You will learn many more facets of resonance theory in later chapters. In Chapter 2, for example, the enormous effect of resonance on acidity is discussed.

Problem 1.14 Label the resonance structures in each pair as major, minor, or equal contributors to the hybrid. Then draw the hybrid.



Problem 1.15 Draw a second resonance structure for nitrous acid. Label each resonance structure as a major, minor, or equal contributor to the hybrid. Then draw the resonance hybrid.



1.7 Determining Molecular Shape

We can now use Lewis structures to determine the shape around a particular atom in a molecule. Consider the H_2O molecule. The Lewis structure tells us only which atoms are connected to each other, but it implies nothing about the geometry. What does the overall molecule look like? Is H_2O a bent or linear molecule? Two variables define a molecule's structure: **bond length** and **bond angle**.

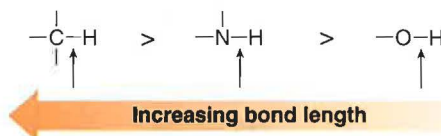
Common symbols and conventions used in organic chemistry are listed on the inside back cover.

1.7A Bond Length

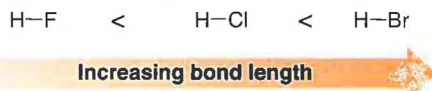
Although the SI unit for bond length is the picometer (pm), the angstrom (Å) is still widely used in the chemical literature; $1 \text{ Å} = 10^{-10} \text{ m}$. As a result, $1 \text{ pm} = 10^{-2} \text{ Å}$, and $95.8 \text{ pm} = 0.958 \text{ Å}$.

Bond length is the average distance between the centers of two bonded nuclei. Bond lengths are typically reported in picometers (pm), where $1 \text{ pm} = 10^{-12} \text{ m}$. For example, the O–H bond length in H_2O is 95.8 pm. Average bond lengths for common bonds are listed in Table 1.2.

- Bond length *decreases* across a row of the periodic table as the size of the atom *decreases*.



- Bond length *increases* down a column of the periodic table as the size of an atom *increases*.



Learn these general trends. Often, knowing such trends is more useful than learning a set of exact numbers, because we are usually interested in comparisons rather than absolute values.

Table 1.2 Average Bond Lengths

Bond	Length (pm)	Bond	Length (pm)	Bond	Length (pm)
H–H	74	H–F	92	C–F	133
C–H	109	H–Cl	127	C–Cl	177
N–H	101	H–Br	141	C–Br	194
O–H	96	H–I	161	C–I	213

1.7B Bond Angle

Bond angle determines the shape around any atom bonded to two other atoms. To determine the bond angle and shape around a given atom, we must first determine how many groups surround the atom. A **group is either an atom or a lone pair of electrons**. Then we use the **valence shell electron pair repulsion (VSEPR) theory** to determine the shape. VSEPR is based on the fact that electron pairs repel each other; thus:

- The most stable arrangement keeps these groups as far away from each other as possible.

A second-row element has only three possible arrangements, defined by the number of groups surrounding it.

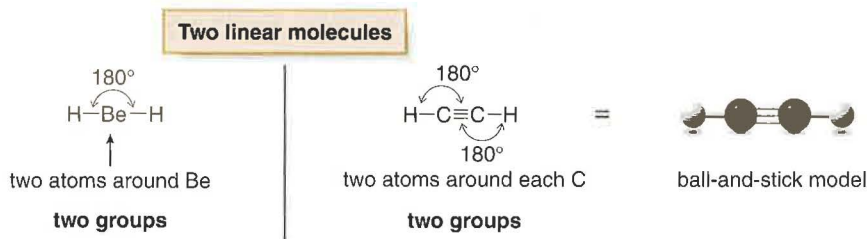
To determine geometry:
[1] Draw a valid Lewis structure; [2] count groups around a given atom.

Number of groups	Geometry	Bond angle
• two groups	linear	180°
• three groups	trigonal planar	120°
• four groups	tetrahedral	109.5°

Let's examine several molecules to illustrate this phenomenon. In each example, we first need a valid Lewis structure, and then we merely count groups around a given atom to predict its geometry.

Two Groups Around an Atom

Any atom surrounded by only two groups is linear and has a bond angle of 180° . Two examples illustrating this geometry are BeH_2 (beryllium hydride) and $\text{HC}\equiv\text{CH}$ (acetylene). We consider each carbon atom in acetylene *separately*. Because each C is surrounded by two atoms and no lone pairs, each H–C–C bond angle in acetylene is 180° , and therefore all four atoms are linear.



Most students in organic chemistry find that building models helps them visualize the shape of molecules. Invest in a set of models *now*.

Common element colors are also shown on the inside back cover.

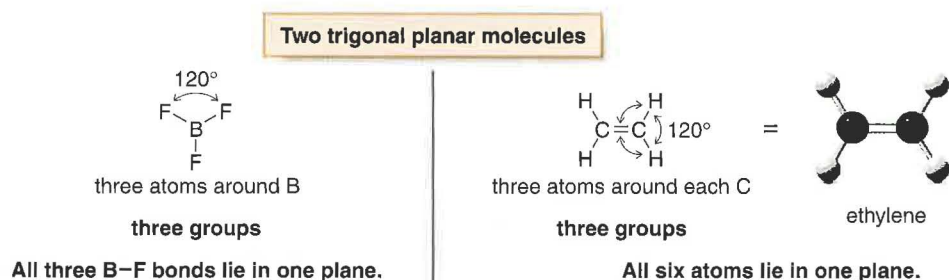
Acetylene illustrates another important feature: **ignore multiple bonds in predicting geometry. Count only atoms and lone pairs.**

We will begin to represent molecules with models having balls for atoms and sticks for bonds, as in the ball-and-stick model of acetylene just shown. These representations are analogous to a set of molecular models. Balls are color-coded using accepted conventions: carbon (black), hydrogen (white or gray), oxygen (red), and so forth, as shown.



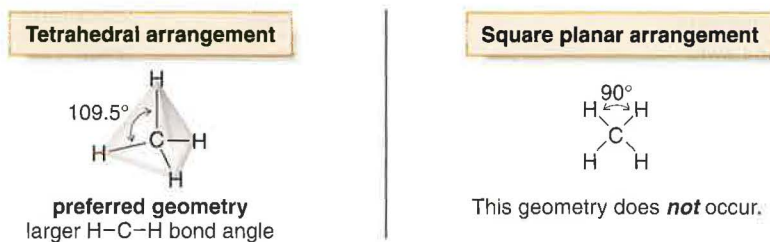
Three Groups Around an Atom

Any atom surrounded by three groups is trigonal planar and has bond angles of 120° . Two examples illustrating this geometry are BF_3 (boron trifluoride) and $\text{CH}_2=\text{CH}_2$ (ethylene). *Each* carbon atom of ethylene is surrounded by three atoms and no lone pairs, making *each* H–C–C bond angle 120° .



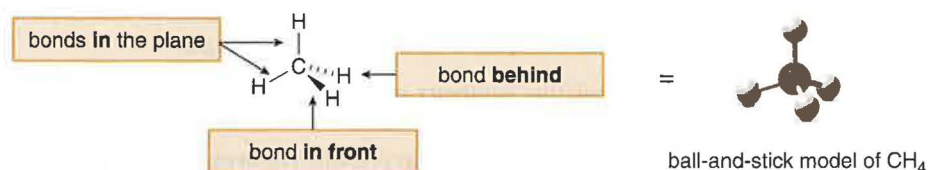
Four Groups Around an Atom

Any atom surrounded by four groups is tetrahedral and has bond angles of approximately 109.5° . For example, the simple organic compound methane, CH_4 , has a central carbon atom with bonds to four hydrogen atoms, each pointing to a corner of a tetrahedron. This arrangement keeps four groups farther apart than a square planar arrangement in which all bond angles would be only 90° .



How can we represent the three-dimensional geometry of a tetrahedron on a two-dimensional piece of paper? **Place two of the bonds in the plane of the paper, one bond in front and one bond behind**, using the following conventions:

- A *solid line* is used for a bond *in the plane*.
- A *wedge* is used for a bond *in front of the plane*.
- A *dashed line* is used for a bond *behind the plane*.

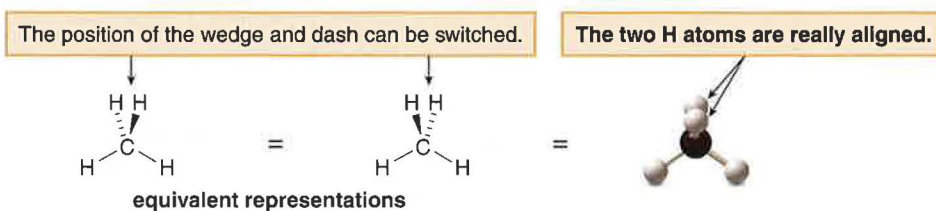


This is just one way to draw a tetrahedron for CH₄. We can turn the molecule in many different ways, generating many equivalent representations. For example, all of the following are acceptable drawings for CH₄.



Each drawing has two solid lines, one wedge, and one dashed line.

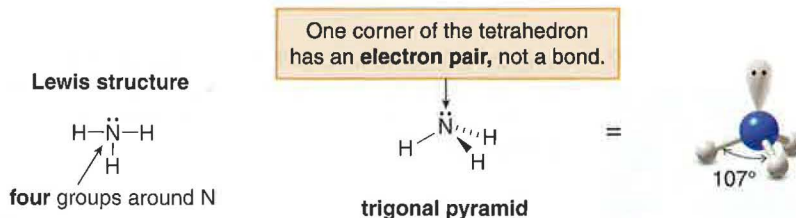
Finally, **wedges and dashes are used for groups that are really aligned one behind another**. It does not matter in the following two drawings whether the wedge or dash is skewed to the left or right, because the two H atoms are really aligned as shown in the three-dimensional model.



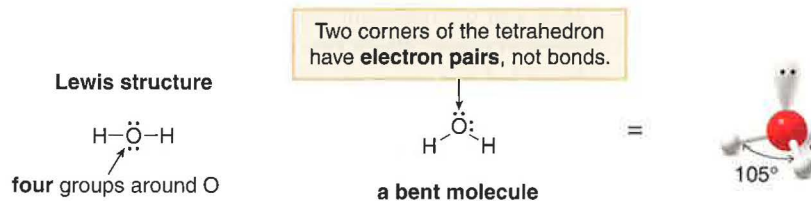
All carbons in stable molecules are **tetravalent**, but the geometry varies with the number of groups around the particular carbon.

Problem 1.16 Draw two different three-dimensional representations for CH₂Cl₂ (dichloromethane) using wedges and dashes.

Ammonia (NH₃) and water (H₂O) both have atoms surrounded by four groups, some of which are lone pairs. In **NH₃**, the three H atoms and one lone pair around N point to the corners of a tetrahedron. The H–N–H bond angle of 107° is close to the theoretical tetrahedral bond angle of 109.5°. This molecular shape is referred to as a **trigonal pyramid**, because one of the groups around the N is a nonbonded electron pair, not another atom.



In **H₂O**, the two H atoms and two lone pairs around O point to the corners of a tetrahedron. The H–O–H bond angle of 105° is close to the theoretical tetrahedral bond angle of 109.5°. Water has a **bent** molecular shape, because two of the groups around oxygen are lone pairs of electrons.



In both NH_3 and H_2O the bond angle is somewhat smaller than the theoretical tetrahedral bond angle because of repulsion of the lone pairs of electrons. The bonded atoms are compressed into a smaller space with a smaller bond angle.

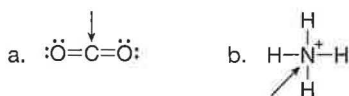
Predicting geometry based on counting groups is summarized in Table 1.3.

Table 1.3 Summary: Determining Geometry Based on the Number of Groups

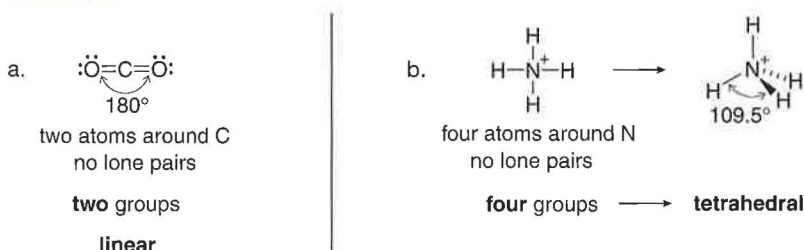
Number of groups around an atom	Geometry	Bond angle	Examples
2	linear	180°	BeH_2 , $\text{HC}\equiv\text{CH}$
3	trigonal planar	120°	BF_3 , $\text{CH}_2=\text{CH}_2$
4	tetrahedral	109.5°	CH_4 , NH_3 , H_2O

Sample Problem 1.5

Determine the geometry around the indicated atom in each species.

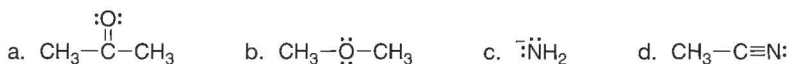


Solution



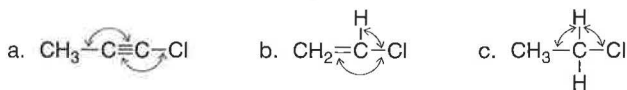
Problem 1.17

Determine the geometry around all second-row elements in each compound.



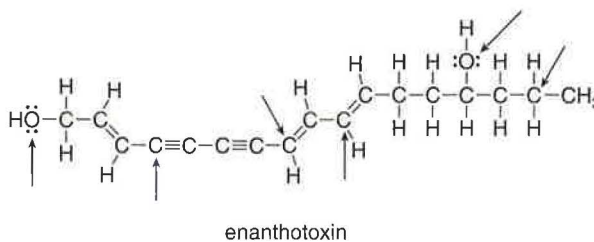
Problem 1.18

Predict the indicated bond angles in each compound.



Problem 1.19

Using the principles of VSEPR theory, you can predict the geometry around any atom in any molecule, no matter how complex. Enanthotoxin is a poisonous compound isolated from a common variety of hemlock grown in England. Predict the geometry around the indicated atoms in enanthotoxin.



The hemlock water dropwort is the source of the poison enanthotoxin.

1.8 Drawing Organic Structures

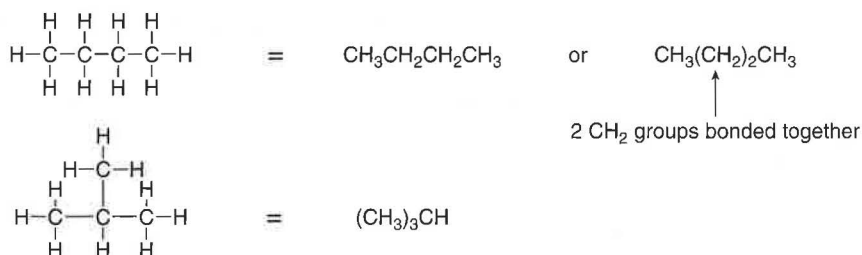
Drawing organic molecules presents a special challenge. Because they often contain many atoms, we need shorthand methods to simplify their structures. The two main types of shorthand representations used for organic compounds are **condensed structures** and **skeletal structures**.

1.8A Condensed Structures

Condensed structures are most often used for compounds having a chain of atoms bonded together, rather than a ring. The following conventions are used:

- All of the atoms are drawn in, but the two-electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.

To interpret a condensed formula, it is usually best to start at the **left side** of the molecule and remember that the **carbon atoms must be tetravalent**. A carbon bonded to three H atoms becomes CH₃; a carbon bonded to two H atoms becomes CH₂, and so forth. Two examples of condensed formulas for compounds having only carbon and hydrogen are given below.



Recall from the prologue:
A **heteroatom** is any atom that is not C or H.

Other examples of condensed structures with heteroatoms and carbon–carbon multiple bonds are given in Figure 1.4. You must learn how to convert a Lewis structure to a condensed structure, and vice versa.

Figure 1.4
Examples of condensed structures

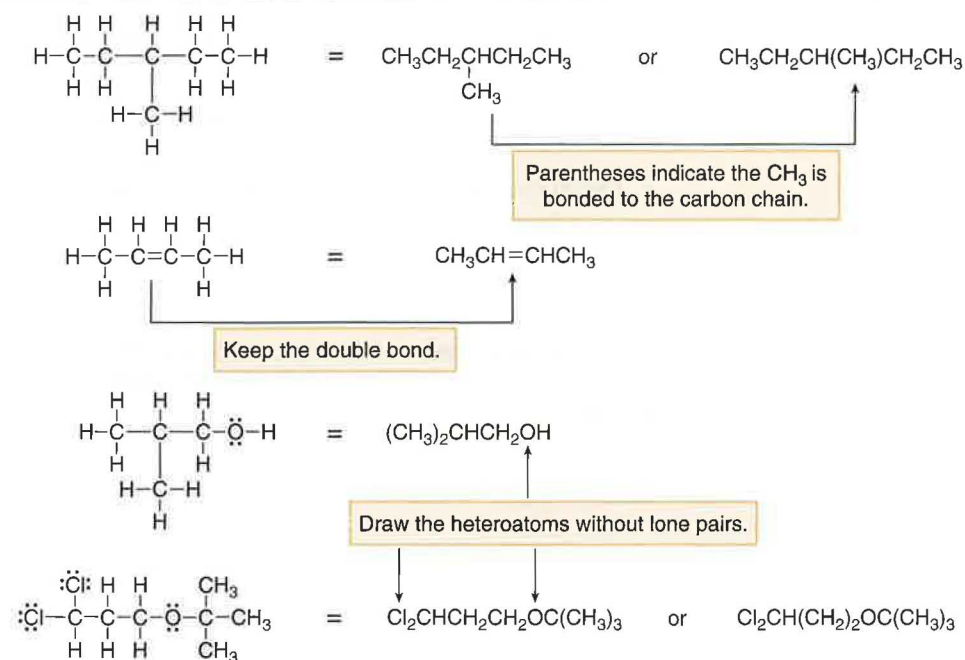


Figure 1.5

Condensed structures containing a C–O double bond



- Take special note of condensed structures with oxygen atoms. In these examples, the only way for all atoms to have an octet is by having a carbon–oxygen double bond.

Translating some condensed formulas is not obvious, and it will come only with practice. This is especially true for compounds containing a carbon–oxygen double bond. Some noteworthy examples in this category are given in Figure 1.5. While carbon–carbon double bonds are generally drawn in condensed structures, carbon–oxygen double bonds are usually omitted.

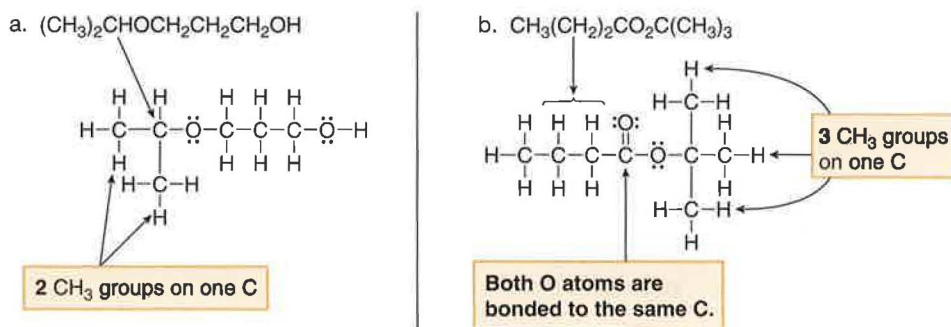
Sample Problem 1.6

Convert each condensed formula to a Lewis structure.

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

Solution

Start at the left and proceed to the right, making sure that each carbon has four bonds. Give any heteroatom enough lone pairs to have an octet.



Problem 1.20 Convert each condensed formula to a Lewis structure.

- a. $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{CH}_3)_2$ c. $(\text{CH}_3)_3\text{CCH}(\text{OH})\text{CH}_2\text{CH}_3$
 b. $(\text{CH}_3)_2\text{CHCH}(\text{CH}_2\text{CH}_3)_2$ d. $(\text{CH}_3)_2\text{CHCHO}$

Problem 1.21 Simplify each condensed structure by using parentheses around similar groups.

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ c. $\text{HOCH}_2\text{-}\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{C} \\ | \\ \text{H} \end{array}\text{-CH}_2\text{CH}_2\text{CH}_2\text{-}\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{array}\text{-CH}_2\text{-}\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{array}\text{-CH}_3$
- b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{-}\begin{array}{c} \text{CH}_2\text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{H} \end{array}\text{-CH}_2\text{CH}_3$

Problem 1.22 During periods of strenuous exercise, the buildup of lactic acid [$\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$] causes the aching feeling in sore muscles. Convert this condensed structure to a Lewis structure of lactic acid.