Introduction to Organic and Biological Chemistry

1 Chemical Bonding

Objectives

In this chapter we:

1. *Define organic chemistry and relate it to living systems.*
2. *Define covalent single, double, and triple bonds.*
3. *Draw Lewis structures of organic compounds.*
4. *Observe the angles between groups attached to carbon.*
5. *Consider the character of polar covalent bonds and their effect on the properties of a compound.*
6. *Learn about hydrogen bonds and their effect on the properties of a compound.*
7. *Discover what functional groups are.*

What is organic chemistry? As with any complex field, definitions are a bit tricky, but basically organic chemistry is the study of the covalent compounds of carbon. There are some exceptions to this generalization. For example, carbon dioxide (CO_2), carbon monoxide (CO), cyanide ion (CN^-), and carbonate ion (CO_3^{2-}) are structures we would generally term inorganic. However, more than 3 million carbon compounds are clearly organic; in fact, more than 90 percent of all the compounds chemists have made and identified are classed as organic compounds.[1]

1.1 How Does Organic Chemistry Relate to the Study of Living Systems?

As students, you are trying to understand how living systems function, particularly the living systems we call human beings. We can ask a series of questions:

1. ***What is the composition of a living system?*** Living systems are composed almost entirely of organic compounds. Some of these compounds belong to classes or groups of organic compounds that are as familiar as the evening paper—sugars or carbohydrates, proteins, fats or lipids. The sugar in our coffee is really an example of a carbohydrate; meat is protein; the bulge round our middles is a collection of fat molecules. Others seem more mysterious. What is the DNA that has made so many headlines recently? Knowing the structures of organic compounds is essential to understanding life processes.

2. ***How are these compounds produced?*** Living organisms are incredibly clever organic chemists. In the wink of an eye they

[1] See Appendix 1.

can convert one organic compound to another using basically the same reactions we would in the laboratory. In the laboratory, however, the same process might take hours or days. To understand life we need to understand the reactions of organic compounds.

3. How does all this chemistry result in a living being? As living beings, we are a bit like factories. Factories need raw materials that are readily available. Humans need food, and the substances we use for food are produced by other living organisms around us. We eat carbohydrates, such as wheat or potato starch; protein, such as animal, fish, or poultry muscle; fats, such as lard or corn oil.

Like a factory we need machinery, and our individual machines are a series of protein structures called *enzymes*. Enzymes cause the chemical changes that convert the raw materials into body parts. The food is not converted to the product in a single step; instead it moves along an assembly line of enzymes called a *metabolic pathway*, being changed a small amount by each enzyme. Because the raw material and the body parts are often chemically similar, we sometimes don't need to change the raw materials very much.

Like a factory we need energy, and we obtain this energy by burning a fuel, just as most factories do. This fuel in our case is the same as the raw material we make into new body parts. It is the carbohydrates, proteins, and fats in our diet. Again enzymes are the machinery for obtaining energy from the fuel. Just as burning coal or oil requires oxygen, so does the burning of fats, carbohydrates, and proteins. We stockpile fuel as body fat and as the carbohydrate glycogen in muscle and liver.

Our living factory can store energy, just as a car stores energy in its battery. Our energy storage takes the form of "high-energy" organic chemicals.

Our factory needs to maintain itself in good running order. Living organisms are capable of an impressive amount of self-repair, because we keep all the machinery for making parts in good working order even after we have made a complete set of parts.

No factory can operate long without a transportation system to move the products to storage, shipping, or other assembly lines. In humans the most important transportation system is the blood circulatory system. Many of the carriers in that system are proteins.

A factory needs a communication system. In humans the nervous system handles much of the communication function.

Our living factory needs management. There must be systems that sense how much is being produced by each assembly line and what the market looks like for each product. The factory needs to adapt to changes in the supply and kind of raw materials.

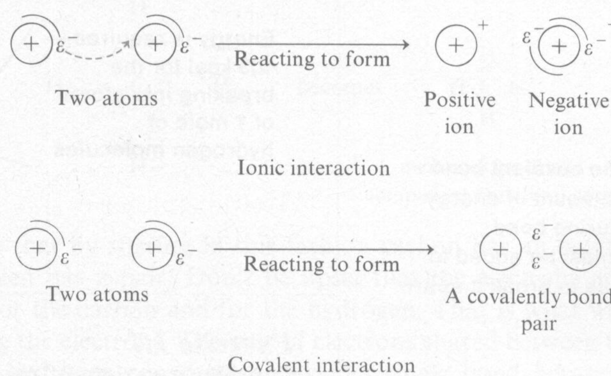
This management is very modern; it even has a computer. Learning about the machinery for this "coordination" or management is the object of much of the present research in biochemistry.

We must end the factory analogy at one point. Our living system can consult its blueprints, the DNA in the nucleus of the cells, and from those plans create a new organism. I have yet to see a factory that builds copies of itself—and I hope I won't.

In summary, it is not incorrect to view life as a collection of directed and controlled organic chemical reactions, with much of the direction and control also being provided by organic chemicals.

1.2 Covalent Compounds

Our definition of organic chemistry specified "covalent compounds." Recall that there are two extremes of chemical interaction between atoms, *ionic* and *covalent*. In ionic interactions, electrons are transferred completely from one atom to another; in covalent interactions, electrons are shared between two atoms.



Once formed, the ions can separate; that is, they are not bound together as a molecule. In fact, in solution they do move independently. In the solid state, however, the ions are fixed into a lattice arrangement. In covalent bonding, by contrast, the atoms must remain next to one another at all times to allow each atom to claim its share of the electrons. In fact, the distances between atoms (bond lengths) and the angles formed by these bonds are fairly rigidly fixed under usual circumstances.

In both ionic and covalent interaction the atoms are manipulating electrons to obtain a more desirable electron configuration, and if they succeed, a stable compound results. Saying "a stable compound results" is another way of saying "energy is released." How stable the compound is can be determined by measuring how much energy is released (Figure 1.1) or, conversely, by measuring how much energy must be added to break (reverse the formation of) the bond (Figure 1.2).

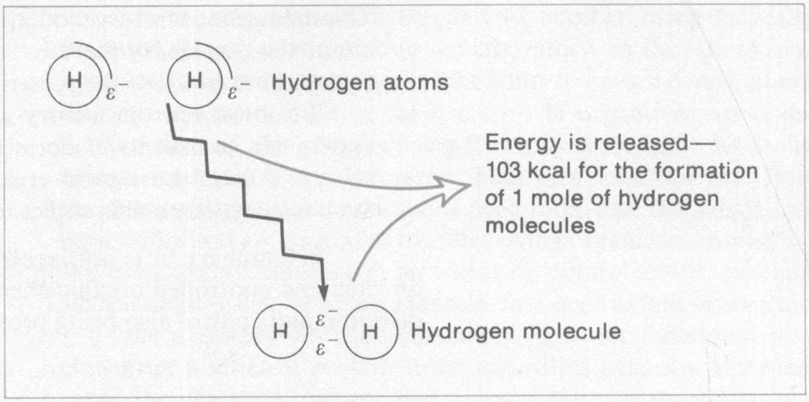


Figure 1.1
Energy and covalent bond formation
The formation of a covalent bond creates a more stable environment for the atoms. The increase in stability is measured by the amount of energy released.

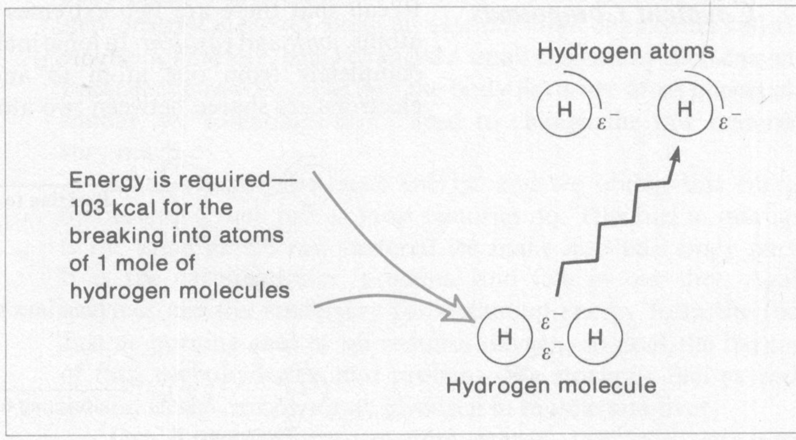


Figure 1.2
Breaking the covalent bond
The exact amount of energy released during bond formation must be added to the molecule to break it apart.

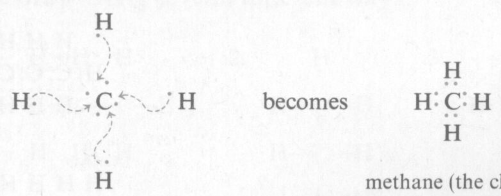
Exercise 1.1

Consider a variety of reactions where 2 moles of atoms combine to form 1 mole of covalently bonded molecules with the release of the indicated amounts of energy.

Atoms	*Molecule*	*Energy released*
2H	H_2	103 kcal
2F	F_2	38 kcal
2O	O_2	37 kcal
2N	N_2	118 kcal

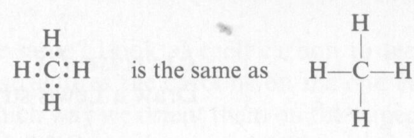
a) How much energy must be added to 1 mole of fluorine molecules to convert them to individual atoms?
b) Of the molecules listed above, which requires the greatest energy to break the covalent bonds?
c) Which of the molecules listed above has the weakest covalent bond? Which has the strongest?

Examine a periodic chart and notice that carbon is in group IVA, meaning that its outer electron shell has four electrons. As a fair generalization, atoms would like to gain, lose, or share electrons to have an outer shell of eight.[2] An important exception to this rule is hydrogen, which is content with two electrons. To interact in an ionic fashion, carbon would have to gain or lose four electrons. Gaining or losing that many electrons would require that a very large charge be carried by a very small atom. This is unlikely. Therefore, carbon is most likely to offer its four outer shell electrons to be matched by and shared with other atoms. This covalent sharing results in eight electrons (an octet) surrounding carbon: four carbon electrons and four from the atoms with which the carbon is sharing. We represent this on paper by *Lewis structures*, named for G. N. Lewis, an early student of bonding. In these structures, only outer-shell electrons are shown. These are indicated as dots around the symbol for the atom. Shared electrons are drawn between the bonded atoms. For example, consider the compound methane, which consists of one carbon and four hydrogens (CH_4). Hydrogen (H) has one outer shell electron ($H^{\cdot}$), and carbon (C) has four outer shell electrons ($\cdot\dot{\underset{\cdot}{C}}\cdot$).



methane (the chief component of natural gas)

Notice that by sharing in this fashion carbon has an octet and each hydrogen has a pair. Don't be upset that the electrons are counted both for the carbon and for the hydrogen. That is what we mean by sharing the electrons. The pair of electrons shared between the carbon and a hydrogen constitute a covalent single bond between the two atoms. In representing the structure, the pair of electrons is often replaced by a short straight line called a *bond*.



A single bond is a pair of electrons.

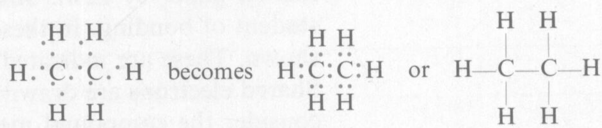
[2] Chemists commonly say that the atoms are creating the electron pattern of the inert gases at the right of the periodic chart (argon, neon, helium, etc.). However, this does not explain why those atoms are chemically inert (stable). There is a large body of theory and of experimental results that attempts to explain this stability. It is complex to understand, however, and a student can deal successfully with a surprising amount of organic chemistry just by creating outer shells of eight electrons.

Exercise 1.2

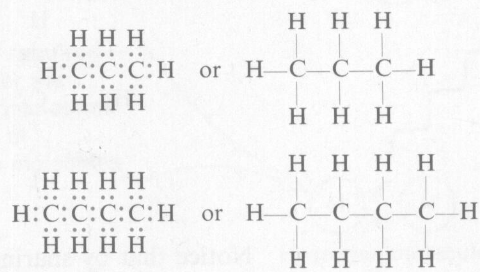
How many electrons does nitrogen have in its outer shell? How many additional electrons would it require by way of covalent sharing to be stable? Predict the structure that nitrogen forms with hydrogen by drawing the Lewis structure.

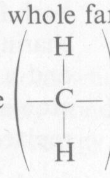
1.3 The Variety of Carbon Compounds

Why are there so many organic compounds? The answer lies in the ability of one carbon to share electrons with other carbons. Consider ethane (C_2H_6):



Similarly, we have propane (C_3H_8) and butane (C_4H_{10}):



Obviously, we can generate a whole family of compounds simply by inserting additional methylene  units into the chain.

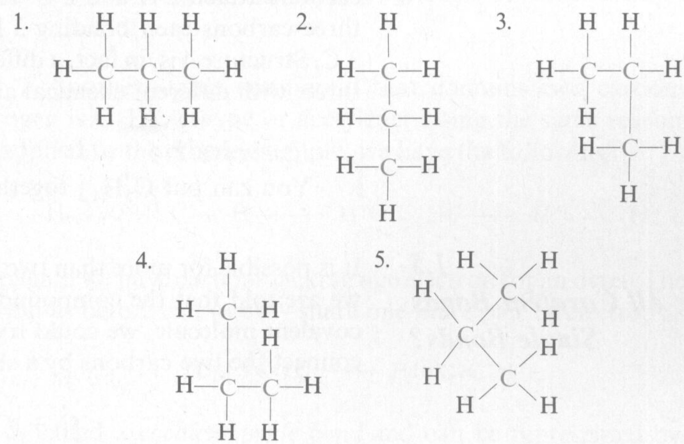
Exercise 1.3

Draw a Lewis structure for pentane (C_5H_{12}).

1.4 The Shape of Organic Molecules

At first thought it may seem that the shape of something as tiny as a molecule is unimportant. However, in biological systems, molecules very often interact in useful and predictable ways because they fit together like pieces in a jigsaw puzzle. Similarly, interactions that are not desirable don't occur if the shapes of two molecules are wrong for joining together. Our machinery for immunity from disease, the immunity provided by previous exposure to the disease or by vaccination, depends on our body's producing molecules that have the correct shape to fit onto the potentially harmful agent. With this in mind, let us develop a simple understanding of the shapes of organic molecules. We are not representing organic molecules properly by writing them flat on a piece of paper. First, molecules are three-dimensional, not flat. In the compounds considered so far, the atoms are actually attached to each carbon as if that carbon were at the center of a pyramid and the attached atoms were at the corners of the pyramid. Carbon surrounded by four groups in this fashion is referred to as *tetrahedral* (Figure 1.3). The angles between the atoms attached to the carbon are not 90°, as they seem to be on the flat drawing, but somewhat larger, 109.5°. Writing flat structures of organic compounds usually distorts the true shape of the structure, but it is much easier than trying to draw and interpret pictures that represent the three-dimensional shape. Therefore we will continue drawing them flat, but at the same time we will watch out for any misunderstandings.

A second type of confusion arises by representing structures with flat drawings. It is possible to arrange a structure several ways and become convinced that each is a different compound. For example, suppose we draw C_3H_8 several different ways:



Are these all the same? Look at each carbon to see what is attached to it. In all five structures the carbons on the end each have 3 H and 1 C no matter which way we orient them on the paper, while the middle carbon has 2 H and 2 C attachments. At this point we will say that this test is sufficient to indicate that all the drawings represent the same

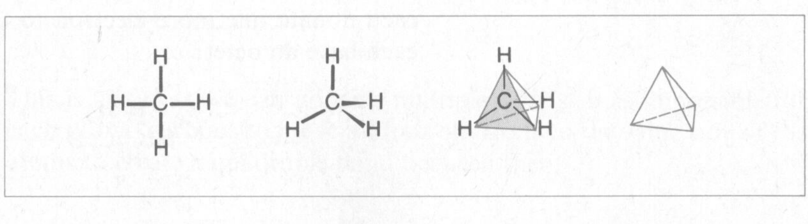
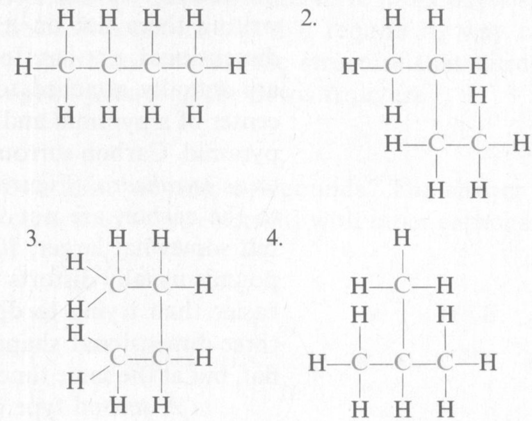


Figure 1.3
The tetrahedral carbon
Carbon with four covalent attachments is not flat with bond angles of 90° as shown on the left, but rather a pyramid, or tetrahedron, with bond angles of 109.5°.

structure. Now let us try the same thing with C_4H_{10}:

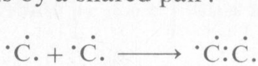


Notice that 1, 2, and 3 all meet the requirement for being the same; that is, the end carbons each attach 3 H and 1 C while the two middle carbons attach 2 H and 2 C. However, structure 4 is different; it has three carbons each bonding 3 H and 1 C, and one bonding 1 H and 3 C. Structure 4 is, in fact, a different organic compound from the other three, with different chemical and physical properties.

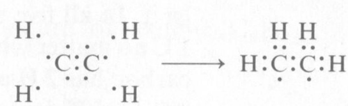
> ***Exercise 1.4***
> You can put C_5H_{12} together in three ways. Can you find them?

1.5 *Are All Covalent Bonds Single Bonds?*

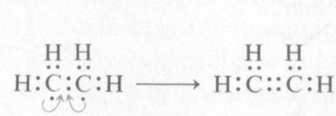
It is possible for more than two electrons to be shared. For example, if we are told that the compound C_2H_4, ethene or ethylene, is a stable covalent molecule, we could try to draw a Lewis structure of it. First connect the two carbons by a shared pair:



Then have each carbon share electrons with two of the four hydrogens:

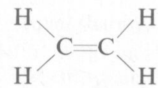


We see that the hydrogens have satisfied their need for a pair of electrons, but each carbon lacks one electron for an octet. If the carbons each donate one more electron to the bond between them, they will each have an octet:

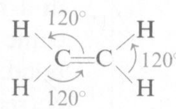


The sharing of four electrons between two atoms is called a *covalent double bond*, and such a bond can be represented by two parallel lines between the symbols for the atoms.

$$\mathrm{H{:}\overset{H}{\ddot{C}}{::}\overset{H}{\ddot{C}}{:}H} \quad \text{becomes}$$



This time our drawing of the molecule on paper is not a bad representation of its shape. A carbon with three groups attached to it (here two hydrogens and one carbon) *is* flat, and the angles between the atoms are not 109.5° but rather 120°.



Exercise 1.5

Can carbon be connected to hydrogen by a covalent double bond?

Another stable compound that contains two carbons with hydrogen is C_2H_2, ethyne or acetylene. Using the same reasoning as was applied to the ethene example, we have the following:

$$\mathrm{H\cdot + \cdot\dot{C}\cdot + \cdot\dot{C}\cdot + H \longrightarrow H{:}\dot{C}{:}\dot{C}{:}H \longrightarrow H{:}\dot{C}{::}\dot{C}{:}H}$$

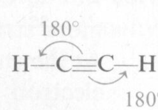
Once again we have carbons lacking one electron for an octet. The same solution as before can work—share one more pair of electrons.

$$\mathrm{H{:}\dot{C}{::}\dot{C}{:}H \longrightarrow H{:}C{:::}C{:}H}$$

This is called a *covalent triple bond* and can be represented by three parallel straight lines:

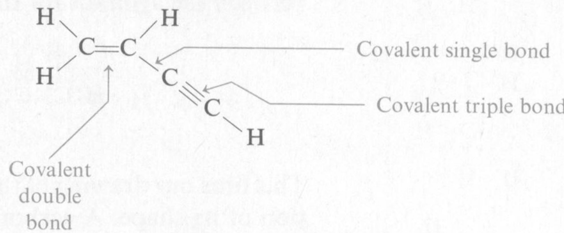
$$\mathrm{H{:}C{:::}C{:}H} \quad \text{becomes} \quad \mathrm{H{-}C{\equiv}C{-}H}$$

In a triple bond the atoms are arranged in a straight line; in other words, the angle between the atoms attached to the carbon is 180°.



This is as far as we can go with multiple bonds. It is impossible for each of two carbons to move all four electrons to the same side of the atoms to create a quadruple bond between them.

It is possible for one compound to contain more than one kind of covalent bond; for example,



Exercise 1.6

Draw the Lewis structures of two compounds with four carbons in a row. In one structure join the carbons by a single bond, a triple bond, and a single bond. In the other join them by a double bond, a single bond, and a double bond. Be careful to add the correct numbers of hydrogens to each. Look at the lines that represent the shared electrons. Each carbon always has how many lines leading to it? Does it make any difference whether the bonds are single, double, or triple? How does the number of bonds relate to the number of electrons in the outer shell of carbon?

1.6 Covalent Bonds with Unequal Electron Sharing

The examples we have used thus far involve atoms that share electrons equally. When two carbons share electrons, their ability to attract the electrons is equal, so there is no reason to imagine that one of them could pull the electrons extra close, leaving the other carbon with less than its share. Usually the bond between carbon and hydrogen involves approximately equal sharing of the electrons too. Bonds in which electrons are equally shared are called *nonpolar*.

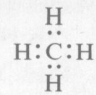
Water is a molecule in whose covalent bonds the electrons are not equally shared. With the exception of hydrogen, atoms can attract electrons more strongly (are more electronegative) the farther to the right or the nearer to the top row of the periodic chart they are placed. Oxygen is in the same row as carbon and is to the right of it; therefore we conclude that it is more electronegative.

Exercise 1.7

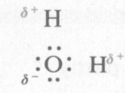
Which of the atoms in each of the following pairs is the more electronegative? C or F, Br or F, C or B

A more electronegative atom draws the electrons toward it more strongly, resulting in unequal sharing. We call this bond *polar*. At the end of the bond with the more electronegative atom, the higher electron concentration produces a weak negative charge, while the other end has an equal but positive weak charge.[3]

[3] It might help to think of polar bonds as intermediate cases between the totally covalent and totally ionic extremes presented on page 5. They are joined together tightly as covalent bonds are but have some of the ionic charge.



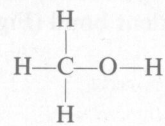
Approximately
equal sharing,
no charge

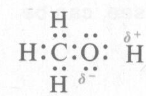


Unequal sharing,
small + charge on H,
small − charge on O

These charges are much smaller in magnitude than the charges on ions.

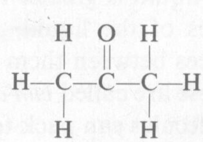
Organic molecules may contain polar bonds. For example, the —O—H bond shown above in water is also found attached to carbon:

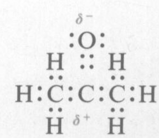




methanol (wood alcohol)

A polar double bond is also found:





propanone (acetone)

In compounds of carbon and hydrogen, all the outer-shell electrons become part of the pattern of covalent bonds. Notice in the case of oxygen, which starts out with six electrons in the outer shell, that an octet is obtained by sharing only two of the six electrons. The other two pairs of electrons remain unshared. Although not involved in the covalent bonding, these unshared electrons contribute to the chemical properties of the molecule.

Exercise 1.8

Consider a covalent compound between hydrogen and chlorine. Draw a Lewis structure. How many unshared electron pairs are on the chlorine?

1.7 *Hydrogen Bonds*

When the very small hydrogen atom is bonded to a very electronegative atom, such as oxygen, nitrogen, or fluorine, it is possible for a second electronegative atom with unshared electrons to approach the hydrogen and attract it strongly enough that the hydrogen actually becomes

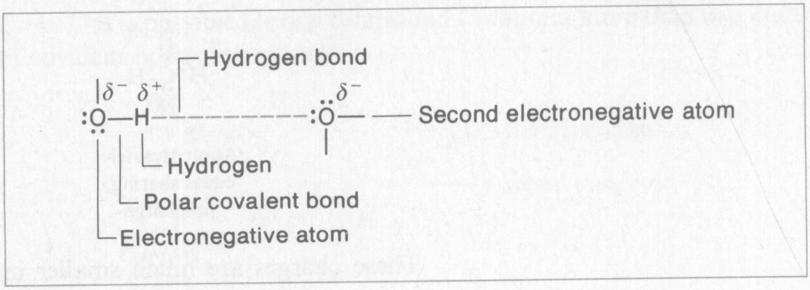


Figure 1.4
The hydrogen bond
The hydrogen bond is partly electrostatic and partly covalent. The electrostatic component is the attraction of the slightly positive hydrogen to a nearby somewhat negative O, N, or F. The covalent contribution represents the hydrogen sharing electrons most of the time with its assigned partner and the rest of the time with a convenient passerby. Hydrogen, we see, can be fickle.

weakly bonded to the second atom. The hydrogen becomes a sort of bridge between the two electronegative atoms. This bridge is called a *hydrogen bond*, and it is about one-twentieth as strong as a regular covalent bond (Figure 1.4).

1.8 Properties of Organic Molecules

First consider melting point and boiling point. A crystalline solid melts when the amount of heat energy added to the solid becomes greater than the forces holding the molecules next to each other in the crystal lattice. Similarly, a liquid boils when the heat energy added to the liquid is greater than the forces between the closely packed molecules of the liquid. All atoms and molecules have small attractive forces between them if they can approach each other closely enough. These are called *van der Waals forces*. The more closely the atoms and molecules can pack together, the greater the size of the van der Waals attractive forces. Small molecules do not have as many atoms as larger molecules to place very close to a neighboring molecule in either a crystal or a liquid, and as a result the total force for each molecule is smaller. Look at the melting points and boiling points of a small series of familiar carbon–hydrogen molecules (Table 1.1) to verify this fact. The shape of a molecule has an effect on the number of identical molecules that can approach it closely. For example, having a methyl[4] group protruding from an otherwise straight carbon chain makes it harder to pack molecules together tightly, just as it is harder to bundle branched sticks as compactly as straight sticks. This looser packing of the branched molecules reduces the van der Waals interactions, and the smaller attraction between the molecules means lower melting and boiling points (Table 1.2).

The presence of a polar covalent bond in a covalent compound has a dramatic effect on the melting and boiling points. The negative

[4] A methyl group is

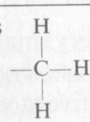


Table 1.1
Properties of Organic Molecules: Effect of Chain Length

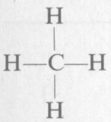
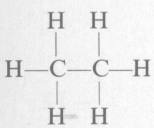
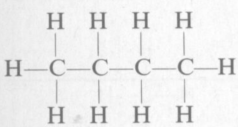
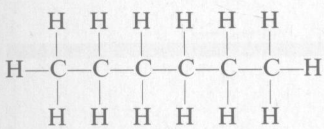
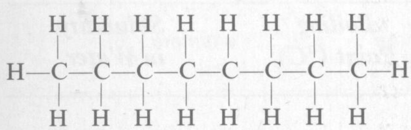
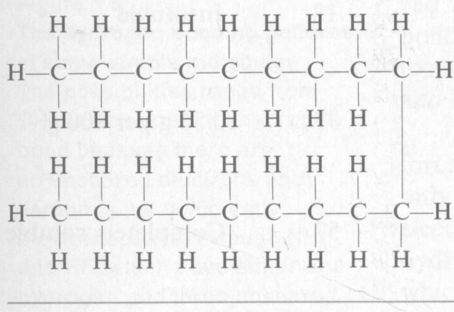
Structure	*Name*	*Melting Point (°C)*	*Boiling Point (°C)*
	Methane	−183	−162
	Ethane	−172	−89
	Butane	−138	0
	Hexane	−95	69
	Octane	−57	126
	Octadecane	28	316

Table 1.2
Properties of Organic Molecules: Effect of Branching

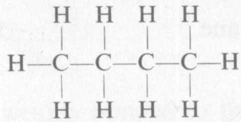
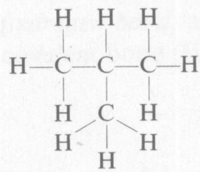
Structure	Name	Melting Point (°C)	Boiling Point (°C)
	Butane	−138	0
	Isobutane	−160	−12

Table 1.3
Properties of Organic Molecules: Effect of Polar Bonds

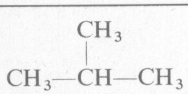
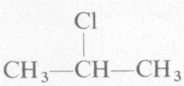
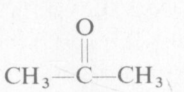
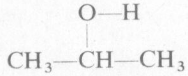
	Structure	Name	Melting Point (°C)	Boiling Point (°C)	Solubility in Water
Nonpolar Bond		Isobutane	−160	−12	Insoluble
Polar Bond		2-Chloropropane	−117	37	0.31 g per 100 g
Very Polar Bond		Acetone	−95	57	Completely soluble
Very Polar Bond and Hydrogen Bond		2-Propanol	−86	83	Completely soluble

Table 1.4
Properties of Organic Molecules: Effect of Hydrogen Bonding on Properties

Compound	*Molecular Weight*	*Melting Point (°C)*	*Boiling Point (°C)*
CH_4	16	−182.5	−161.5
NH_3	17	−77.7	−33.4
H_2O	18	0	100.0
HF	20	−83.1	19.5

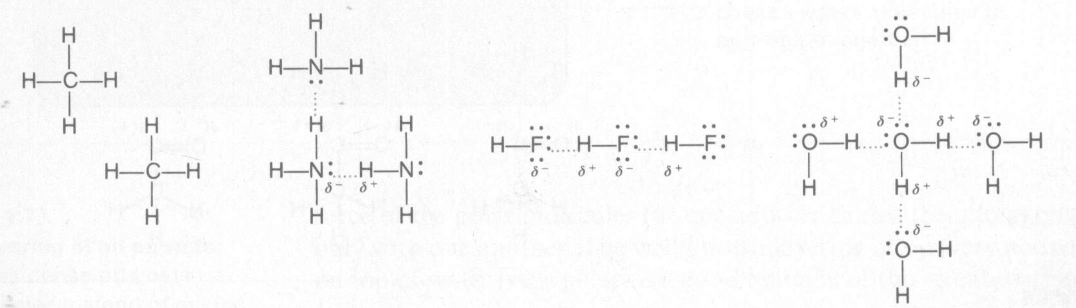


Figure 1.5
The hydrogen bonding patterns of some simple molecules
The possibilities range from CH_4, which does not hydrogen bond because there are no unshared electrons and carbon is not sufficiently electronegative, through NH_3 and HF, which have either one hydrogen and three unshared pairs of electrons or vice versa, to the optimum case of water, with two hydrogens and two unshared pairs of electrons per molecule.

end of the polar bond of one molecule and the positive end of the bond on a neighboring molecule attract one another, adding greatly to the heat energy required to separate them and raising the melting and boiling point sharply (Table 1.3).

The presence of hydrogen bonds provides even stronger forces between molecules. Compare the properties of CH_4, which has only nonpolar bonds, with those of NH_3 and HF. In HF and NH_3, the electronegative atoms have unshared electrons and are bonded to hydrogen, so they can form hydrogen bonds. Now consider water, which has an electronegative atom with two hydrogens and two unshared electron pairs, an optimum situation for forming the most hydrogen bonds (Table 1.4 and Figure 1.5). Forces between molecules are summarized in Figure 1.6.

If molecules associate only by van der Waals forces, there is no reason for them not to mix freely with one another. However, if we attempt to mix polar with nonpolar molecules, the strong attractive