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Section: Structure and Bonding in Organic Molecules

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Structure and Bonding in Organic Molecules

How do chemicals regulate your body? Why did your muscles ache this morning after last night's long jog? What is in the pill you took to get rid of that headache you got after studying all night? What happens to the gasoline you pour into the gas tank of your car? What is the molecular composition of the things you wear? What is the difference between a cotton shirt and one made of silk? What is the origin of the odor of garlic? You will find the answers to these questions, and many others that you may have asked yourself, in this book on organic chemistry.

Chemistry is the study of the structure of molecules and the rules that govern their interactions. As such, it interfaces closely with the fields of biology, physics, and mathematics. What, then, is organic chemistry? What distinguishes it from other chemical disciplines, such as physical, inorganic, or nuclear chemistry? A common definition provides a partial answer: *Organic chemistry is the chemistry of carbon and its compounds.* These compounds are called **organic molecules.**

Organic molecules constitute the chemical building blocks of life. Fats, sugars, proteins, and the nucleic acids are compounds in which the principal component is carbon. So are countless substances that we take for granted in everyday use. Virtually all the clothes that we wear are made of organic molecules—some of natural fibers, such as cotton and silk; others artificial, such as polyester. Toothbrushes, toothpaste, soaps, shampoos, deodorants, perfumes—all contain organic compounds, as do furniture, carpets, the plastic in light fixtures and cooking utensils, paintings, food, and countless other items. Consequently, organic chemical industries are among the largest in the world, including petroleum refining and processing, agrochemicals, plastics, pharmaceuticals, paints and coatings, and the food conglomerates.
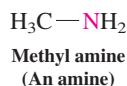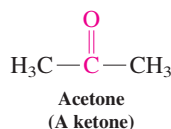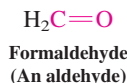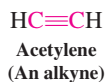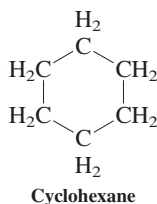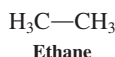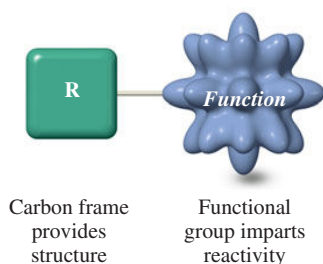
Organic substances such as gasoline, medicines, pesticides, and polymers have improved the quality of our lives. Yet the uncontrolled disposal of organic chemicals has polluted the environment, causing deterioration of animal and plant life as well as injury and disease to humans. If we are to create useful molecules—*and* learn to control their effects—we need a knowledge of their properties and an understanding of their behavior. We must be able to apply the principles of organic chemistry.
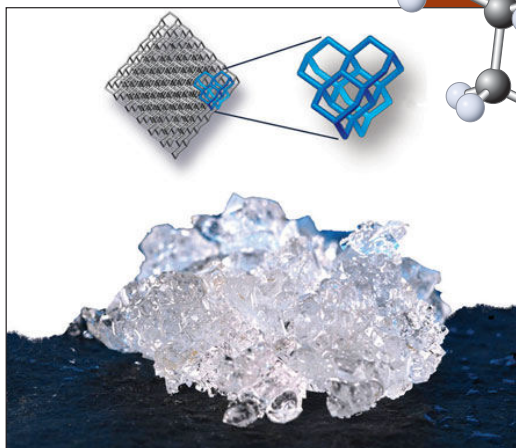
Tetrahedral carbon, the essence of organic chemistry, exists as a lattice of six-membered rings in diamonds. In 2003, a family of molecules called *diamandoids* was isolated from petroleum. Diamandoids are subunits of diamond in which the excised pieces are capped off with hydrogen atoms. An example is the beautifully crystalline pentamantane (molecular model on top right and picture on the left; © 2004 Chevron U.S.A. Inc. Courtesy of MolecularDiamond Technologies, ChevronTexaco Technology Ventures LLC), which consists of five "cages" of the diamond lattice. The top right of the picture shows the carbon frame of pentamantane stripped off its hydrogens and its superposition on the lattice of diamond.

Almost everything you see in this picture is made of organic chemicals.

Carbon frame provides structure

Functional group imparts reactivity

$$H_3C—CH_3$$
Ethane

Cyclohexane structure:
$$H_2C \quad \overset{\overset{H_2}{C}}{} \quad CH_2$$
Cyclohexane

$$HC≡CH$$
Acetylene
(An alkyne)

$$H_2C=O$$
Formaldehyde
(An aldehyde)

$$H_3C—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$
Acetone
(A ketone)

$$H_3C—NH_2$$
Methyl amine
(An amine)

This chapter explains how the basic ideas of chemical structure and bonding apply to organic molecules. Most of it is a review of topics that you covered in your general chemistry courses, including molecular bonds, Lewis structures and resonance, atomic and molecular orbitals, and the geometry around bonded atoms.

## 1-1 The Scope of Organic Chemistry: An Overview

A goal of organic chemistry is to relate the structure of a molecule to the reactions that it can undergo. We can then study the steps by which each type of reaction takes place, and we can learn to create new molecules by applying those processes.

Thus, it makes sense to classify organic molecules according to the subunits and bonds that determine their chemical reactivity: These determinants are groups of atoms called **functional groups.** The study of the various functional groups and their respective reactions provides the structure of this book.

Functional groups determine the reactivity of organic molecules

We begin with the **alkanes,** composed of only carbon and hydrogen atoms ("hydrocarbons") connected by single bonds. They lack any functional groups and as such constitute the basic scaffold of organic molecules. As with each class of compounds, we present the systematic rules for naming alkanes, describe their structures, and examine their physical properties (Chapter 2). An example of an alkane is ethane. Its structural mobility is the starting point for a review of thermodynamics and kinetics. This review is then followed by a discussion of the strength of alkane bonds, which can be broken by heat, light, or chemical reagents. We illustrate these processes with the chlorination of alkanes (Chapter 3).

A Chlorination Reaction

$$CH_4 \quad + \quad Cl_2 \quad \xrightarrow{\text{Energy}} \quad CH_3—Cl \quad + \quad HCl$$
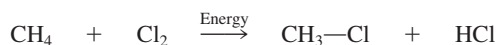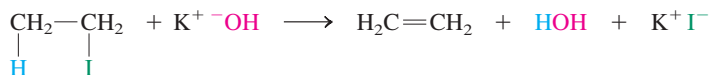
Next we look at cyclic alkanes (Chapter 4), which contain carbon atoms in a ring. This arrangement can lead to new properties and changes in reactivity. The recognition of a new type of isomerism in cycloalkanes bearing two or more substituents—either on the same side or on opposite sides of the ring plane—sets the stage for a general discussion of **stereoisomerism.** Stereoisomerism is exhibited by compounds with the same connectivity but differing in the relative positioning of their component atoms in space (Chapter 5).

We shall then study the haloalkanes, our first example of compounds containing a functional group—the carbon–halogen bond. The haloalkanes participate in two types of organic reactions: substitution and elimination (Chapters 6 and 7). In a **substitution** reaction, one halogen atom may be replaced by another; in an **elimination** process, adjacent atoms may be removed from a molecule to generate a double bond.

A Substitution Reaction

$$CH_3—Cl \quad + \quad K^+I^- \quad \longrightarrow \quad CH_3—I \quad + \quad K^+Cl^-$$

An Elimination Reaction

$$\underset{\underset{H \quad\quad I}{|\quad\quad\;\;|}}{CH_2—CH_2} \quad + \quad K^+\,{}^-OH \quad \longrightarrow \quad H_2C=CH_2 \quad + \quad HOH \quad + \quad K^+I^-$$

Like the haloalkanes, each of the major classes of organic compounds is characterized by a particular functional group. For example, the carbon–carbon triple bond is the functional group of alkynes (Chapter 13); the smallest alkyne, acetylene, is the chemical burned in a welder's torch. A carbon–oxygen double bond is characteristic of aldehydes and ketones (Chapter 17); formaldehyde and acetone are major industrial commodities. The amines (Chapter 21), which include drugs such as nasal decongestants and amphetamines, contain
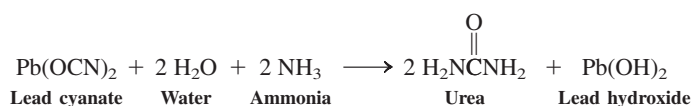
nitrogen in their functional group; methyl amine is a starting material in many syntheses of medicinal compounds. We shall study the tools for identifying these molecular subunits, especially the various forms of spectroscopy (Chapters 10, 11, and 14). Organic chemists rely on an array of spectroscopic methods to elucidate the structures of unknown compounds. All of these methods depend on the absorption of electromagnetic radiation at specific wavelengths and the correlation of this information with structural features.

Subsequently, we shall encounter organic molecules that are especially crucial in biology and industry. Many of these, such as the carbohydrates (Chapter 24) and amino acids (Chapter 26), contain multiple functional groups. However, in *every* class of organic compounds, the principle remains the same: *The structure of the molecule determines the reactions that it can undergo.*

Synthesis is the making of new molecules

Carbon compounds are called "organic" because it was originally thought that they could be produced only from living organisms. In 1828, Friedrich Wöhler* proved this idea to be false when he converted the inorganic salt lead cyanate into urea, an organic product of protein metabolism in mammals (Chemical Highlight 1-1).
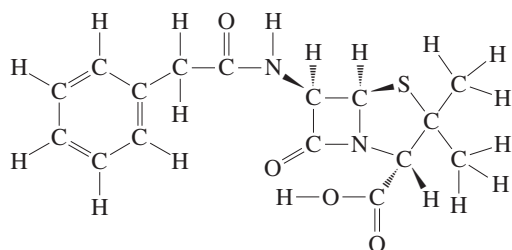
Wöhler's Synthesis of Urea

$$Pb(OCN)_2 \; + \; 2\,H_2O \; + \; 2\,NH_3 \; \longrightarrow \; 2\,H_2N\overset{\overset{\displaystyle O}{\|}}{C}NH_2 \; + \; Pb(OH)_2$$

Lead cyanate   Water   Ammonia   Urea   Lead hydroxide

Synthesis, or the making of molecules, is a very important part of organic chemistry (Chapter 8). Since Wöhler's time, many millions of organic substances have been synthesized from simpler materials, both organic and inorganic.[†] These substances include many that also occur in nature, such as the penicillin antibiotics, as well as entirely new compounds. Some, such as cubane, have given chemists the opportunity to study special kinds of bonding and reactivity. Others, such as the artificial sweetener saccharin, have become a part of everyday life.

Typically, the goal of synthesis is to construct complex organic chemicals from simpler, more readily available ones. To be able to convert one molecule into another, chemists must know organic reactions. They must also know the physical factors that govern such processes, such as temperature, pressure, solvent, and molecular structure. This knowledge is equally valuable in analyzing reactions in living systems.
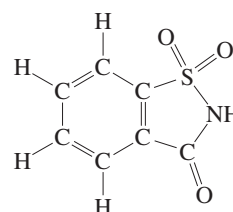
As we study the chemistry of each functional group, we shall develop the tools both for planning effective syntheses and for predicting the processes that take place in nature. But how? The answer lies in looking at reactions step by step.
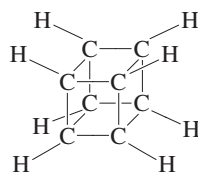
An organic molecular architect at work.

Benzylpenicillin   **Cubane**   **Saccharin**

*Professor Friedrich Wöhler (1800–1882), University of Göttingen, Germany. In this and subsequent biographical notes, only the scientist's last known location of activity will be mentioned, even though much of his or her career may have been spent elsewhere.

[†]As of September 2009, the Chemical Abstracts Service had registered over 50 million chemical substances and more than 61 million genetic sequences.

CHEMICAL HIGHLIGHT 1-1

Urea: From Urine to Wöhler's Synthesis to Industrial Fertilizer

Urination is the main process by which we excrete nitrogen from our bodies. Urine is produced by the kidneys and then stored in the bladder, which begins to contract when its volume exceeds about 200 mL. The average human excretes about 1.5 L of urine daily, and a major component is urea, about 20 g per liter. In an attempt to probe the origins of kidney stones, early (al)chemists, in the 18th century, attempted to isolate the components of urine by crystallization, but they were stymied by the cocrystallization with the also present sodium chloride. William Prout,* an English chemist and physician, is credited with the preparation of pure urea in 1817 and the determination of its accurate elemental analysis as CH_4N_2O. Prout was an avid proponent of the then revolutionary thinking that disease has a molecular basis and could be understood as such. This view clashed with that of the so-called vitalists, who believed that the functions of a living organism are controlled by a "vital principle" and cannot be explained by chemistry (or physics).

Into this argument entered Wöhler, an inorganic chemist, who attempted to make ammonium cyanate, $NH_4^+OCN^-$ (also CH_4N_2O), from lead cyanate and ammonia in 1828, but who obtained the same compound that Prout had characterized as urea. To one of his mentors, Wöhler wrote, "I can make urea without a kidney, or even a living creature." In his landmark paper, "On the Artificial Formation of Urea," he commented on his synthesis as a "remarkable fact, as it is an example of the artificial generation of an organic material from inorganic materials." He also alluded to the significance of the finding that a compound with an identical elemental composition as ammonium cyanate can have such completely different chemical properties, a forerunner to the recognition of isomeric compounds. Wöhler's synthesis of

urea forced his contemporary vitalists to accept the notion that simple organic compounds could be made in the laboratory. As you shall see in this book, over the ensuing decades, synthesis has yielded much more complex molecules than urea, some of them endowed with self-replicating and other "lifelike" properties, such that the boundaries between what is lifeless and what is alive are dwindling.

Apart from its function in the body, urea's high nitrogen content makes it an ideal fertilizer. It is also a raw material in the manufacture of plastics and glues, an ingredient of some toiletry products and fire extinguishers, and an alternative to rock salt for deicing roads. It is produced industrially from ammonia and carbon dioxide to the tune of 100 million tons per year.

The effect of nitrogen fertilizer on wheat growth: treated on the left; untreated on the right.

*Dr. William Prout (1785–1850), Royal College of Physicians, London.

Reactions are the vocabulary and mechanisms are the grammar of organic chemistry

When we introduce a chemical reaction, we will first show just the starting compounds, or **reactants** (also called **substrates**), and the **products.** In the chlorination process mentioned earlier, the substrates—methane, CH_4, and chlorine, Cl_2—may undergo a reaction to give chloromethane, CH_3Cl, and hydrogen chloride, HCl. We described the overall transformation as $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$. However, even a simple reaction such as this one may proceed through a complex sequence of steps. The reactants could have first formed one or more *unobserved* substances—call these X—that rapidly changed into the observed products. These underlying details of the reaction constitute the **reaction mechanism.** In our example, the mechanism consists of two major parts: $CH_4 + Cl_2 \rightarrow X$ followed by $X \rightarrow CH_3Cl + HCl$. Each part is crucial in determining whether the overall reaction will proceed.

Substances X in our chlorination reaction are examples of **reaction intermediates,** species formed on the pathway between reactants and products. We shall learn the mechanism of this chlorination process and the nature of the reaction intermediates in Chapter 3.

How can we determine reaction mechanisms? The strict answer to this question is, we cannot. All we can do is amass circumstantial evidence that is consistent with (or points to) a certain sequence of molecular events that connect starting materials and products ("the postulated mechanism"). To do so, we exploit the fact that organic molecules are no more than collections of bonded atoms. We can, therefore, study how, when, and how fast bonds break and form, in which way they do so in three dimensions, and how changes in substrate structure affect the outcome of reactions. Thus, although we cannot strictly prove a mechanism, we can certainly rule out many (or even all) reasonable alternatives and propose a most likely pathway.

In a way, the "learning" and "using" of organic chemistry is much like learning and using a language. You need the vocabulary (i.e., the reactions) to be able to use the right words, but also need the grammar (i.e., the mechanisms) to be able to converse intelligently. Neither one on its own gives complete knowledge and understanding, but together they form a powerful means of communication, rationalization, and predictive analysis. To highlight the interplay between reaction and mechanism, icons are displayed in the margin at appropriate places throughout the text.

Before we begin our study of the principles of organic chemistry, let us review some of the elementary principles of bonding. We shall find these concepts useful in understanding and predicting the chemical reactivity and the physical properties of organic molecules.

REACTION

MECHANISM

1-2 Coulomb Forces: A Simplified View of Bonding

The bonds between atoms hold a molecule together. But what causes bonding? Two atoms form a bond only if their interaction is energetically favorable, that is, if energy—heat, for example—is released when the bond is formed. Conversely, breaking that bond requires the input of the same amount of energy.

The two main causes of the energy release associated with bonding are based on Coulomb's law of electric charge:

1. Opposite charges attract each other (electrons are attracted to protons).
2. Like charges repel each other (electrons spread out in space).

Bonds are made by simultaneous coulombic attraction and electron exchange

Each atom consists of a nucleus, containing electrically neutral particles, or neutrons, and positively charged protons. Surrounding the nucleus are negatively charged electrons, equal in number to the protons so that the net charge is zero. As two atoms approach each other, the positively charged nucleus of the first atom attracts the electrons of the second atom; similarly, the nucleus of the second atom attracts the electrons of the first atom. As a result, the nuclei are held together by the electrons located between them. This sort of bonding is described by **Coulomb's* law:** Opposite charges attract each other with a force inversely proportional to the square of the distance between the centers of the charges.

Charge separation is rectified by Coulomb's law, appropriately in the heart of Paris.
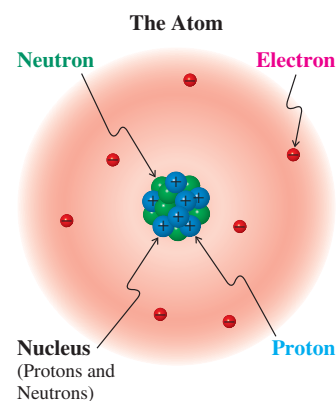
Coulomb's Law

$$\text{Attracting force} = \text{constant} \times \frac{(+)\text{ charge} \times (-)\text{ charge}}{\text{distance}^2}$$

This attractive force causes energy to be released as the neutral atoms are brought together. This energy is called the **bond strength.**

The Atom

Neutron   Electron

Nucleus
(Protons and Neutrons)   Proton

*Lieutenant-Colonel Charles Augustin de Coulomb (1736–1806), Inspecteur Général of the University of Paris, France.

Notes

Reference Note

Licensing Note

Preservation Notices

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