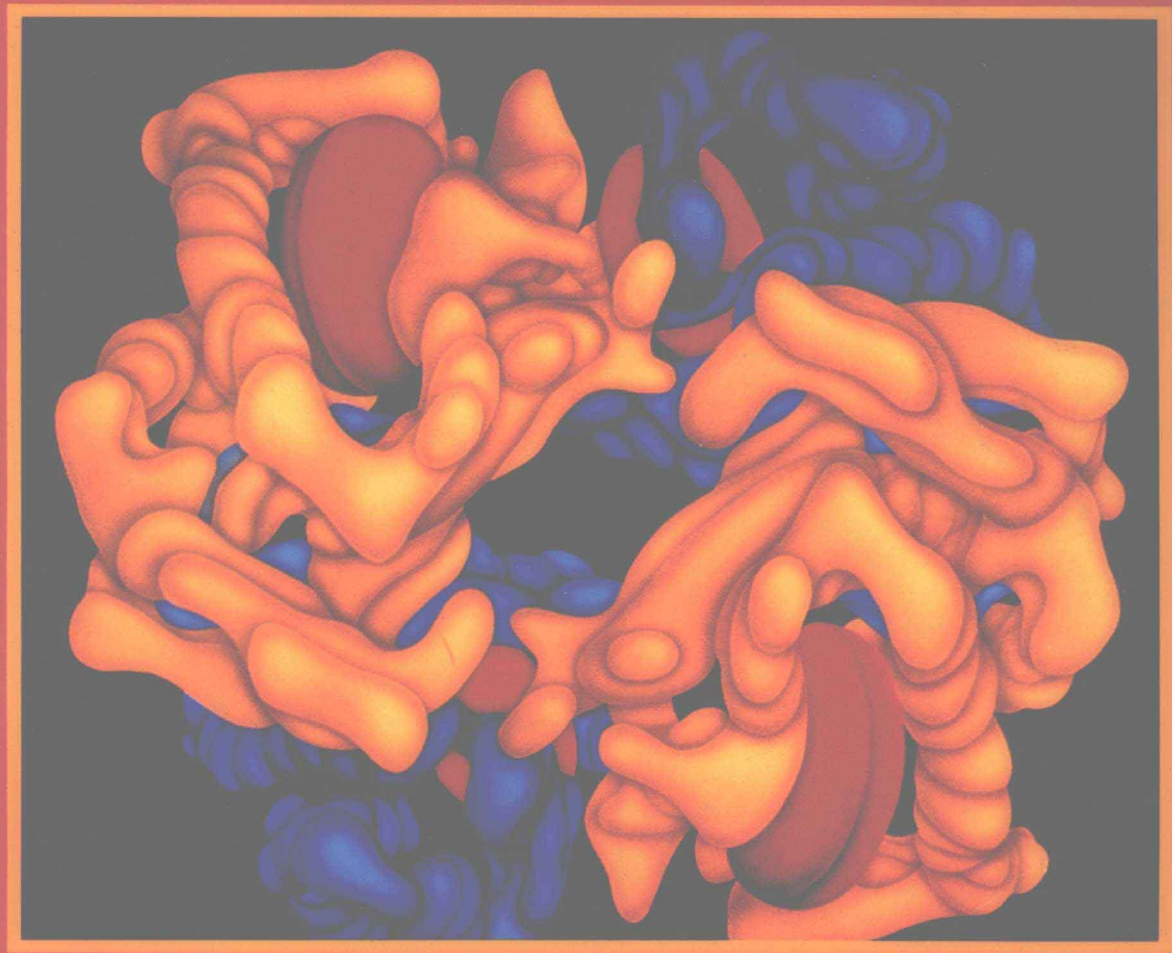

INTRODUCTION TO ORGANIC AND BIOLOGICAL CHEMISTRY



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Introduction to ORGANIC AND BIOLOGICAL CHEMISTRY

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PREFACE

There are two major approaches to the teaching of a chemistry course for students majoring in the health-related sciences. Most colleges offer a one-year course in general, organic, and biological chemistry. We have revised the text *Chemistry and Life* to meet the needs of students in this type of course.

Some colleges split the subject matter into two separate courses. The first semester is devoted to the principles of chemistry, and this is followed in the second semester by a course that combines organic chemistry and biochemistry. This text, which is written for such a course, had its genesis in the earlier four editions of *Introduction to Organic and Biological Chemistry*. We have combined the prominent features of that text with the style and pedagogical techniques of *Chemistry and Life* to produce a new text that best serves the interests of instructors and their students.

Again, students are assumed to have had at least one prior course in general chemistry. The text is designed to assist the student in acquiring a sound background in the subject without presenting an overwhelming amount of factual material. It is intended for those who are mainly interested in applying the principles of organic chemistry and biochemistry to related areas of science such as genetics, microbiology, pharmacology, physiology, and nutrition.

Features of This Text

- Chapter 2 contains sections on the alkanes, alkenes, aromatic hydrocarbons, and alkyl halides. Much of the material has been revised to enhance student understanding.
- Amides are included within Chapter 5, "Carboxylic Acids and Derivatives."
- Carbohydrate metabolism is treated in two chapters (13 and 14) to differentiate the anaerobic and aerobic pathways.
- Chapter 17, "Body Fluids," presents the chemistry of blood and a study of lymph, urine, sweat, and tears.
- There are frequent boxed features dealing with topics of current interest that illustrate the chemistry presented in the chapters. Examples include ozone depletion, anesthetics, Halcion, environmental effects, DNA fingerprinting, and muscle building.
- Special Topics follow some chapters to relate chemical concepts to societal concerns. These Topics include petroleum, drugs, sight and odor, hormones, vitamins, and viruses and cancer.
- Visual material is especially important for learning chemistry. Color is used to enhance the learning process, as well as the attractiveness of the design, and to maintain student interest. Special color photographs show descriptive chemistry at its best, and many illustrations are made more meaningful by the judicious use of color.
- Comments and definitions appear in the margins to emphasize important points or add interesting asides.
- The number of exercises at the ends of the chapters offers instructors a variety of choices.
- A Glossary follows the text.

Supplements

Study Guide/Solutions Manual by Marvin Hackert and Roger Sandwick contains a key word list, chapter summary, study hints, additional worked-out examples with practice problems, and a self-test for each chapter. It also includes solutions to all end-of-chapter exercises in the text.

A laboratory manual, *Laboratory Exercises in Organic and Biological Chemistry* by Baum, Bowen, Poulter, and Baumgarten, also published by Macmillan, complements the text.

A set of full color transparencies of illustrations and tables from the text is available from the publisher.

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Once again, as in our previous editions, production supervisor Elisabeth Belfer has converted a bundle of words, tables, and figures into a book that we are proud of. Thanks Liz for all your efforts on our behalf.

S. J. B.

J. W. H.

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Chapter 1

INTRODUCTION TO ORGANIC CHEMISTRY



The word organic has different meanings. Organic fertilizer is organic in the original sense that it is derived from a living organism. There is no legal definition of organic foods, but the term generally means foods grown without pesticides or synthetic fertilizers. Organic chemistry is the chemistry of compounds of carbon.

Scientists of the eighteenth and nineteenth centuries studied compounds isolated from rocks and ores and from the atmosphere and oceans, and they labeled them **inorganic compounds** because they were obtained from nonliving systems. Compounds obtained from plants and animals were called **organic compounds** because they were isolated from organized (living) systems. The early chemists believed that only living organisms, within their tissues, could synthesize organic compounds, that some **vital force** was required for such syntheses. By the middle of the nineteenth century, however, a number of "organic" compounds had been prepared using ordinary laboratory techniques. The vital-force theory had to be discarded, but the labels *organic* and *inorganic* remained.

Today, **organic chemistry** is defined simply as the chemistry of the compounds of carbon.¹ It may seem strange that we divide chemistry into two branches, one of which

Definitions from the 18th and 19th centuries:

Inorganic—from a nonliving source

Organic—from a living system

Modern definition: Organic chemistry is the chemistry of the compounds of carbon.

¹ This definition is not adhered to strictly; several of the following compounds of carbon properly belong to the domain of inorganic chemistry.

Carbon monoxide (CO)
Carbon dioxide (CO₂)
Carbon disulfide (CS₂)

Carbonates (e.g., Na₂CO₃)
Bicarbonates (e.g., NaHCO₃)
Cyanides (e.g., KCN)

Thiocyanates (e.g., NaSCN)
Cyanates (e.g., KOCN)
Carbides (e.g., CaC₂)

In January 1990 the Chemical Abstract Service of the American Chemical Society recorded the 10 millionth known chemical compound. Over 600,000 new compounds are added to the list each year. About 95% of all the compounds are organic substances.

considers the chemistry of one element while the other handles the chemistry of the more than 100 remaining elements. This division seems more reasonable when one discovers that, of the millions of compounds that have been characterized, the overwhelming majority contain carbon. Carbon has a unique ability to form stable, covalent bonds with itself and with other elements in infinite variations. The molecules thus produced may contain only one or over a million carbon atoms. So complex is the chemistry of carbon that we shall approach its study by dividing its millions of compounds into families. We will study one family at a time and begin by concentrating on the simpler members of each family. Eventually we will move to a consideration of those molecules that deserve to be called organic in the old sense—complex, carbon-containing molecules that determine the form and function of living systems. We might pause to ponder how far science has come since the eighteenth century, when scientists believed it was impossible to synthesize even the simplest organic molecule. In 1980, the Supreme Court ruled that a new form of life, developed in a laboratory, could be patented.

1.1

A COMPARISON OF ORGANIC AND INORGANIC COMPOUNDS

Organic compounds, like inorganic ones, obey all the natural laws. Often there is no clear distinction in chemical or physical properties between organic and inorganic molecules. Nevertheless, it may be useful to compare and contrast typical members of each class. Table 1.1 lists a variety of properties of the organic compound benzene (C_6H_6 , a solvent once widely used to strip furniture for refinishing) and the inorganic compound sodium chloride (NaCl , common table salt).

Most organic compounds have relatively low melting points. Many, like benzene, are liquids at room temperature. The typical inorganic substance, like sodium chloride, is a crystalline solid with a high melting point.

The typical organic compound is insoluble in water and less dense than water. An attempt to mix an organic liquid with water usually produces two layers, with the organic layer on top. The typical inorganic compound is readily soluble in water.

The typical organic compound is highly flammable, an important point to remember when one is working with organic compounds. Both the anesthetic ether and gasoline are flammable organic substances that form explosive mixtures with air. Typical inorganic compounds are nonflammable. Some inorganic compounds, such as water, baking soda (sodium bicarbonate, NaHCO_3), and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), are used in fighting fires.

Table 1.1
Comparison of an Organic
and an Inorganic
Compound

	Benzene	Sodium Chloride
Formula	C_6H_6	NaCl
Solubility in H_2O	Insoluble	Soluble
Solubility in gasoline	Soluble	Insoluble
Flammable?	Yes	No
Melting point	5.5°C	801°C
Boiling point	80°C	1413°C
Density	0.88 g/cm^3	2.7 g/cm^3 (crystal)
Bonding	Covalent	Ionic

The typical organic compound is covalently bonded, and the properties of organic compounds reflect this fact. The typical inorganic compound is ionic and exhibits the properties characteristic of ionic bonding. Do not forget, though, that there are covalent inorganic compounds (water, for example) and organic ions (acetate ion, for example).

1.2 COVALENT BONDS

A **covalent bond** arises from the attraction between two atoms as a result of the sharing of one or more pairs of electrons by the two atoms. A single covalent bond results when two atoms are held together by the sharing of a pair of electrons to which each atom normally contributes one electron.

The hydrogen molecule is the simplest case involving a covalent bond.



The shared electron pair forming the covalent bond is shown as two dots (or as a line) *between* the two H atoms.

The covalent bond in the diatomic H_2 molecule has specific properties. It is a *single* bond because the two H atoms share *one* electron pair. Its *bond length* is the center-to-center distance between the two nuclei. Its *bond energy* is the energy required to break a gaseous H_2 molecule apart into two gaseous H atoms (104 kcal/mole, about enough energy to raise the temperature of 1 L of water from 0 to 100 °C). It is a *nonpolar* covalent bond because both atoms are identical, both have the same attraction for the electron pair, and both share the electron pair equally. There is no separation of positive and negative charge between the two H atoms.

1.3 MULTIPLE COVALENT BONDS

Multiple covalent bonds occur when more than one electron pair is shared between two atoms. When *two* electron pairs are shared between two atoms, a **double bond** is formed. It is stronger than a single bond, but not twice as strong because the two electron pairs repel each other and cannot become fully concentrated between the two atoms. Its bond length is shorter than that of a single bond. When *three* electron pairs are shared between two atoms, a **triple bond** is formed. It is stronger than a single bond and a double bond, but not three times as strong as a single bond. Its bond length is shorter than that of a double bond. *Saturated* molecules possess only single bonds; *unsaturated* molecules possess one or more double or triple bonds. Table 1.2 gives examples of some carbon compounds that illustrate the increase in bond energy and decrease in bond distance with the formation of multiple bonds.

Multiple bonds are formed commonly by carbon, nitrogen, and oxygen atoms and occasionally by phosphorus, sulfur, and other atoms. Multiple bonds arise whenever there are too few outer-shell electrons to provide each atom with a stable noble gas electron configuration using a completely single-bonded structure. Lewis structures can be used to predict whether or not multiple bonds exist in simple molecules (see Exercise 1.5). Each

Table 1.2
Compounds Illustrating
Single and Multiple
Carbon–Carbon Bonds

Name	Formula	Bond Energy (kcal/mol)	Bond Distance (Å)
Ethane	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	88 ^a	1.54
Ethylene	$\begin{array}{c} \text{H} \quad \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array}$	172	1.33
Acetylene	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	230	1.20

^aThe carbon–carbon single bond is stronger than any other single bonds between identical atoms, with the exception of H–H.

carbon atom in the molecules in Table 1.2 forms four bonds—by means of four single bonds in ethane, two single bonds and one double bond in ethylene, and one single bond and one triple bond in acetylene.

1.4 STRUCTURE OF CARBON COMPOUNDS

Lewis structures provide useful representations of the nature of bonding in atoms but provide little direct information about the distribution of electron density within molecules or the geometry of atoms within molecules.

A number of bonding theories can be used for predicting shapes of simple molecules.

We shall use the *valence shell electron pair repulsion* (VSEPR) theory. This model has the advantages of being relatively simple and nonmathematical while still providing accurate qualitative shapes for most of the compounds that we encounter in this text.

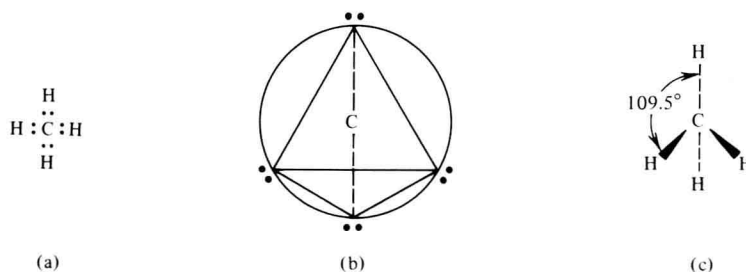
The basic premise of VSEPR theory is that *electron pairs, having like charge, repel each other*. Other factors being equal, outer-shell or valence-shell electron pairs around an atom will try to spread as far apart as possible. Furthermore, interactions between electron clouds of atoms bonded to a central atom are assumed to be negligible. Therefore, orientation of several atoms around a given central atom is dependent only upon interactions between electron pairs around the central atom. A corollary to the basic premise of VSEPR theory is that unshared electron pairs require more space (that is, exhibit greater repulsions) than shared electron pairs.

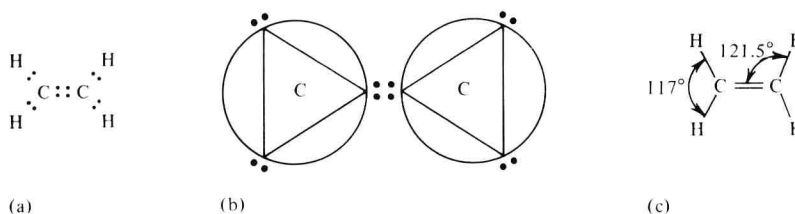
Many other texts invoke the concept of hybridization of *s* and *p* atomic orbitals to describe the bonding and the shapes of organic molecules.

Figure 1.1

Various representations of the methane molecule.

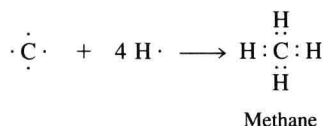
- (a) Lewis structure;
(b) structure showing electron pair distributions;
(c) structure showing bond angle.



**Figure 1.2**

(a) Lewis structure, (b) structure showing electron pair distribution, and (c) structure showing bond angles for ethylene. All six atoms of ethylene lie in the same plane.

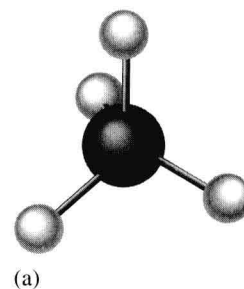
The simplest organic molecule, methane, contains one carbon atom and four hydrogen atoms. Its formation may be represented as follows.



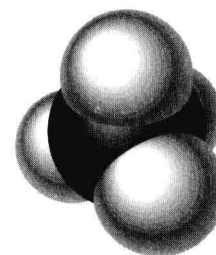
There are four shared electron pairs around carbon. They can be kept as far apart as possible by placing them at the corners of a tetrahedron with the carbon atom at the center of the tetrahedron. The **bond angle**, which is the angle formed by two covalent bonds, is 109.5° (Figure 1.1). This is the approximate configuration around all carbon atoms that are bonded to four other atoms, as in alkanes (Chapter 2), alcohols and ethers (Chapter 3), and amines (Chapter 6).

Double or triple bonds involving two or three shared electron pairs can be considered as just another region of electron density and do not affect the gross shape of a molecule. However, they have larger electron clouds than a single shared electron pair. Therefore, like unshared electron pairs, double and triple shared electron pairs cause greater repulsion and occupy more space than single shared electron pairs.

The Lewis structure for C_2H_4 shows three regions of electron density around each carbon atom (Figure 1.2). They can be kept as far apart as possible by placing them at the corners of an equilateral triangle with a carbon atom in the center of, and thus in the plane of, the equilateral triangle. However, the double shared electron pair occupies more space than the single shared electron pairs, thus opening the $\text{H}-\text{C}-\text{C}$ bond angles and closing the $\text{H}-\text{C}-\text{H}$ bond angle. These predictions are verified by the experimentally determined bond angles. Similar bond angles around a doubly bonded carbon atom are typical for all alkenes (Chapter 2), as well as for aldehydes and ketones (Chapter 4) and for acids, esters, and amides (Chapter 5).



(a)



(b)

1.5

MOLECULAR MODELS AND CHEMICAL FORMULAS

Molecular models are often employed to illustrate organic molecules. Two widely used methods of representation are

1. The ball-and-stick model in which different colored balls represent the different atoms, and sticks connecting them are used to represent the covalent bonds (Figure 1.3a).
2. The space-filling model, which shows the shape of the molecule and the relative sizes of the atoms (Figure 1.3b).

Figure 1.3

Molecular models of methane. (a) Ball-and-stick model; (b) space-filling model.