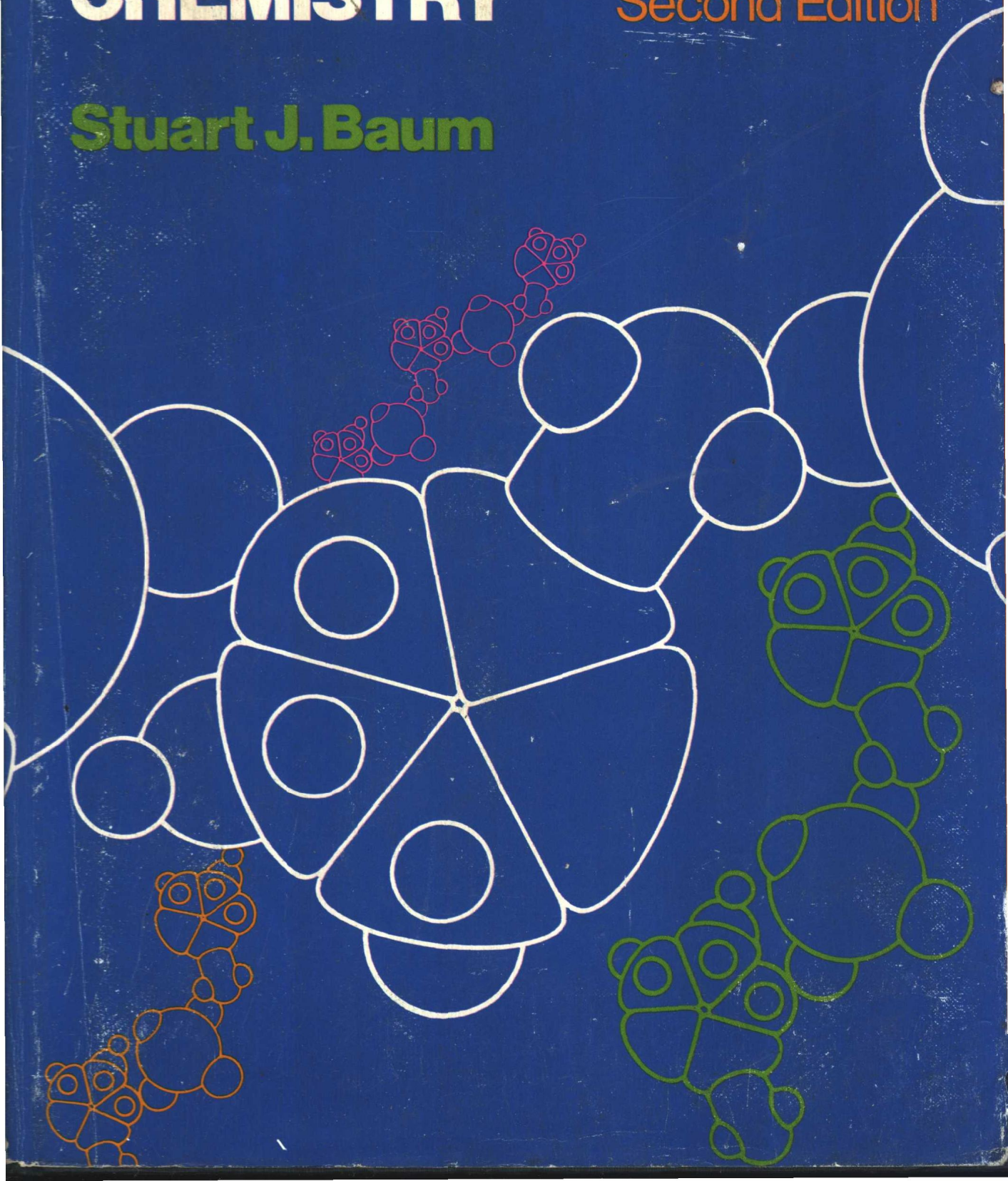


INTRODUCTION TO ORGANIC & BIOLOGICAL CHEMISTRY

Second Edition

Stuart J. Baum



Organic and Biological Chemistry

Macmillan Publishing Co., Inc.

N E W Y O R K

Collier Macmillan Publishers
L O N D O N

COPYRIGHT © 1978, STUART J. BAUM

PRINTED IN THE UNITED STATES OF AMERICA

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the Publisher.

Earlier edition copyright © 1970 by Stuart J. Baum.

MACMILLAN PUBLISHING Co., INC.
866 Third Avenue, New York, New York 10022

COLLIER MACMILLAN CANADA, LTD.

Library of Congress Cataloging in Publication Data

Baum, Stuart J

Introduction to organic and biological chemistry.

Includes index.

1. Biological chemistry. 2. Chemistry, Organic.

I. Title.

QP514.2.B37 1978 574.1'92 77-618

ISBN 0-02-306570-2

Printing: 1 2 3 4 5 6 7 8

Year: 8 9 0 1 2 3 4

Preface

Within the past decade, the teaching of chemistry to nonchemistry majors has undergone a considerable change. Students in biology, nursing, medical technology, agriculture, and veterinary science view chemistry as a tool, and not as an end in itself. Their interest lies in the chemistry of biological systems rather than industrial chemistry or theoretical chemistry. Many colleges now offer an organic chemistry course with heavy emphasis on biological applications.

The second edition of this text maintains the purpose of the first edition, namely, to present an introduction to organic chemistry and biochemistry. 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 the application of the principles of organic chemistry and biochemistry to related areas of science (e.g., genetics, microbiology, pharmacology, physiology, nutrition).

Many chapters in this edition have been extensively revised; one chapter has been deleted, and one chapter has been added. The general organization remains the same, but the treatment of organic chemistry has been expanded to satisfy those teachers who use the book in a short organic chemistry course. Additions to this text include: a chapter on the compounds of phosphorus and sulfur, some use of reaction mechanisms, sections on aging, taste, smell, pesticides, drugs, viruses, recombinant DNA, and birth control.

The book is divided into two main sections. The first part is devoted to

establishing the fundamental principles of organic chemistry. Because of the time limit imposed by a one-semester course, much of the material normally covered in an introductory organic chemistry text has been condensed, and some of the interesting peripheral aspects of the field have been omitted. The first ten chapters deal with the structure and properties of the different classes of organic compounds, with emphasis on the characteristic reactions of the various functional groups. Chapter 11 deals with stereoisomerism, and its importance to an understanding of enzyme specificity is stressed. Systematic names for the organic compounds are used repeatedly. I have found that students enjoy learning organic nomenclature. They derive much the same satisfaction to be gained from learning a foreign language, and are well disposed to practice this language.

Chapters 12 through 20 present the fundamental concepts of biochemistry in a form that will be understandable to students having only a limited background in organic chemistry. The major emphasis is placed on the dynamic nature of biochemistry and the interrelationships of the various metabolic pathways. Nothing of importance is consciously omitted. Chapters 12 through 14 discuss the chemistry of the three major classes of food-stuffs—carbohydrates, lipids, and proteins. Enzymes (Chapter 15) are presented in a separate chapter as a special class of proteins. Because of the limited mathematics background of most of the students using this text, statements have to be qualitative rather than mathematical. Thus, for example, no extensive treatment of enzyme kinetics is attempted. In Chapter 16, the molecular basis of life is sketched by a clear and concise discussion of nucleic acid structure and replication, and by the role of nucleic acids in protein synthesis. This particular chapter should be of major interest to all students since this area of biochemistry has received so much publicity in the past few years. Chapters 17 through 19 present the basic metabolic reaction sequences that occur within the cells from the point of view of their interrelationships and integration into a fundamental whole. Metabolism is concerned with the production and utilization of energy, and it is here that the student is able to tie together the chemical principles learned in general chemistry with organic chemistry and biochemistry. The human body is viewed as an intricate machine which utilizes the energy of foods to run chemical reactions so as to meet its own needs. The final chapter on blood is especially well suited to those students who are majoring in one of the health sciences.

At the end of each chapter, I have included a selection of study questions. It is my contention that a student learns chemistry only through repeated practice. The more questions a student is able to answer, the more confident he will be about his understanding of the subject. Too often the student of organic chemistry and biochemistry has the mistaken idea that he does not need any of the subject matter learned in general chemistry. Therefore, a few simple numerical problems have been included where appropriate. (Other worthwhile reviews are the sections dealing with acidity, pH and buffer solutions, and the balancing of oxidation-reduction equations

using half-reactions.) In response to repeated requests, I have provided an answer manual to accompany the text.

In the preparation of this second edition, I have had the opportunity to redraw structures, and to correct the factual and typographical errors that appeared in the first edition. I have been aided considerably by the many comments received from users and reviewers of the previous edition. I am especially grateful to Macmillan editors Elisabeth Belfer and James Smith, to reviewers James O. Schreck, Neil R. Coley, and George W. Gokel, and to all of the students who have enrolled in Chemistry 271 at Plattsburgh. The constant feedback and encouragement that I received from them has nurtured my love of teaching and has, I hope, greatly strengthened this text.

S. J. B.

Contents

1	Introduction to Organic Chemistry	1
1.1	The Nature of Organic Compounds	2
1.2	The Structure of Carbon Compounds	3
1.3	Chemical Formulas	5
1.4	Isomers	7
1.5	Homologous Series and Functional Groups	7
2	The Saturated Hydrocarbons	10
2.1	Nomenclature of Alkanes	10
2.2	Application of the IUPAC Rules	14
2.3	Physical Properties of Alkanes	18
2.4	Chemical Properties of Alkanes	20
2.5	Free Radical Theory of Aging	22
2.6	Sources and Uses of Alkanes	24
2.7	Octane Rating	25
2.8	Cycloalkanes	26
3	The Unsaturated Hydrocarbons	32
	ALKENES	
3.1	Nomenclature of Alkenes	33
3.2	Preparation of Alkenes	35
3.3	Physical Properties of Alkenes	37
3.4	Chemical Properties of Alkenes	37
3.5	The Isoprene Unit	44
	ALKYNES	
3.6	Nomenclature of Alkynes	47
3.7	Preparation of Alkynes	48
3.8	Physical Properties of Acetylene	48
3.9	Chemical Properties of Alkynes	48

4	The Aromatic Hydrocarbons	53
4.1	Structure of the Aromatic Ring	53
4.2	Nomenclature	56
4.3	Reactions of Aromatic Hydrocarbons	60
4.4	Mechanism of Aromatic Substitution	61
4.5	Directive Influence of Substituents	63
4.6	Uses of Benzene and Benzene Derivatives	64
5	Halogen Derivatives of Hydrocarbons	68
5.1	Nomenclature of Alkyl Halides	68
5.2	Preparation of Organic Halides	70
5.3	Physical Properties of Alkyl Halides	72
5.4	Chemical Properties of Organic Halides	73
5.5	Uses of Halogenated Hydrocarbons	76
5.6	The Polychlorinated Pesticides	80
6	Alcohols and Ethers	88
	ALCOHOLS	
6.1	Classification and Nomenclature of Alcohols	88
6.2	Preparation of Alcohols	91
6.3	Physical Properties of Alcohols	93
6.4	Chemical Properties of Alcohols	97
6.5	Important Alcohols	103
	ETHERS	
6.6	Nomenclature of Ethers	108
6.7	Preparation of Ethyl Ether	109
6.8	Williamson Synthesis of Ethers	109
6.9	Physical Properties of Ethers	110
6.10	Chemical Properties of Ethers	111
6.11	Uses and Hazards of Ethyl Ether	112
6.12	Cyclic Ethers	113
7	Aldehydes and Ketones	117
7.1	Nomenclature of Aldehydes and Ketones	118
7.2	Preparation of Aldehydes and Ketones	120
7.3	Physical Properties of Aldehydes and Ketones	123
7.4	The Carbonyl Group	124
7.5	Chemical Properties of Aldehydes and Ketones	125
7.6	Important Aldehydes and Ketones	139
8	Acids and Esters	143
	ACIDS	
8.1	Nomenclature of Carboxylic Acids	144
8.2	Preparation of Carboxylic Acids	145
8.3	Physical Properties of Carboxylic Acids	149
8.4	Acidity, Hydrogen Ion Concentration, and pH	150
8.5	Buffers	154

- 8.6 Effect of Structure upon Acidity 157
- 8.7 Chemical Properties of Carboxylic Acids 159
- 8.8 Important Carboxylic Acids 165

ESTERS

- 8.9 Nomenclature of Esters 169
- 8.10 Preparation of Esters 170
- 8.11 Physical Properties of Esters 173
- 8.12 Chemical Properties of Esters 174
- 8.13 Esters of Salicylic Acid 177

9 Amides and Amines

182

AMIDES

- 9.1 Nomenclature of Amides 183
- 9.2 Preparation of Amides 184
- 9.3 Physical Properties of Amides 185
- 9.4 Chemical Properties of Amides 186
- 9.5 Urea 188

AMINES

- 9.6 Classification and Nomenclature of Amines 189
- 9.7 Preparation of Primary Amines 191
- 9.8 Physical Properties of Amines 193
- 9.9 Basicity of Amines 195
- 9.10 Chemical Properties of Amines 198
- 9.11 Diazonium Salts 202
- 9.12 Nitrogen Heterocycles 205
- 9.13 Drugs 210

10 Organic Compounds of Phosphorus and Sulfur

224

PHOSPHORUS COMPOUNDS

- 10.1 Phosphines 225
- 10.2 Esters of Phosphorous Acid 225
- 10.3 Esters of Phosphoric Acid 226

SULFUR COMPOUNDS

- 10.4 Derivatives of Hydrogen Sulfide 234
- 10.5 The Sulfonic Acids and Derivatives 239

11 Stereoisomerism

244

- 11.1 Optical Isomerism 245
- 11.2 Structure and Optical Activity 248
- 11.3 Diastereomers 254
- 11.4 Racemic Mixtures and Meso Compounds 256
- 11.5 The R-S Convention for Absolute Configuration 258
- 11.6 Geometric Isomerism (*Cis-Trans* Isomerism) 259
- 11.7 Biochemical Significance 264
- 11.8 Molecules to See and to Smell 265

12	Carbohydrates	272
12.1	Classification of Carbohydrates	273
12.2	Monosaccharides—General Terminology	274
12.3	Stereochemistry	274
12.4	Cyclic Forms of Sugars	279
12.5	Mutarotation	282
12.6	Important Monosaccharides	284
12.7	The Disaccharides	285
12.8	The Polysaccharides	290
12.9	Tests for Carbohydrates	294
13	Lipids	301
13.1	Classification of Lipids	301
13.2	Simple Lipids	302
13.3	Fatty Acids	303
13.4	Physical Properties of Lipids	306
13.5	Chemical Properties of Lipids	306
13.6	Special Features of Lipids	310
13.7	Waxes	311
13.8	Soaps and Synthetic Detergents	311
13.9	Compound Lipids	316
13.10	Steroids	320
13.11	The Pill	324
14	Proteins	330
14.1	Classification of Proteins	331
14.2	Amino Acids	333
14.3	General Properties of Amino Acids	338
14.4	Primary Structure of Proteins—Peptides	342
14.5	Secondary Structure of Proteins	349
14.6	Tertiary Structure of Proteins	351
14.7	Quaternary Structure of Proteins	355
14.8	Electrochemical Properties of Proteins	358
14.9	Denaturation of Proteins	359
14.10	Color Tests for Proteins	363
15	Enzymes	367
15.1	Discovery of Enzymes	368
15.2	Nomenclature and Classification of Enzymes	368
15.3	Characteristics of Enzymes	369
15.4	Coenzymes and Vitamins	371
15.5	Mode of Enzyme Action	371
15.6	Specificity of Enzymes	376
15.7	Factors Influencing Enzyme Activity	379
15.8	Enzyme Inhibition	382
15.9	Chemotherapy	386

16 The Nucleic Acids	391
16.1 Structure of Nucleic Acids	391
16.2 Deoxyribonucleic Acid (DNA)	398
16.3 DNA as the Hereditary Material	403
16.4 Ribonucleic Acid (RNA)	408
16.5 The Genetic Code	413
16.6 Genetic Diseases	421
16.7 The Nature of Viruses	423
16.8 Recombinant DNA	427
17 Carbohydrate Metabolism	432
17.1 Digestion and Absorption of Carbohydrates	433
17.2 Blood Glucose	436
17.3 Embden-Meyerhof Pathway / Anaerobic Glycolysis	437
17.4 Reversal of Glycolysis and Fermentation	447
17.5 Energetics of Glycolysis and Fermentation	447
17.6 Storage of Chemical Energy	448
17.7 Aerobic Metabolism	449
17.8 Respiratory Chain (Electron Transport System)	455
17.9 Oxidative Phosphorylation	459
17.10 Energy Yield of Carbohydrate Metabolism	460
18 Lipid Metabolism	466
18.1 Digestion and Absorption of Lipids	467
18.2 Fatty Acid Oxidation	468
18.3 Bioenergetics of Fatty Acid Oxidation	472
18.4 Ketosis	473
18.5 Glycerol Metabolism	474
18.6 Synthesis of Fatty Acids	475
18.7 Biosynthesis of Triacylglycerols	478
19 Protein Metabolism	480
19.1 Digestion and Absorption of Proteins	480
19.2 Nitrogen Balance	482
19.3 Metabolism of Amino Acids	484
19.4 Storage of Nitrogen	489
19.5 Excretion of Nitrogen—The Urea Cycle	490
19.6 Relationships Among the Metabolic Pathways	494
20 The Blood	497
20.1 General Characteristics of Mammalian Blood	497
20.2 Osmotic Pressure	500
20.3 Clotting of Blood	501
20.4 Hemoglobin	503
20.5 Respiratory Functions of the Blood	504
20.6 Blood Buffers	506
Index	509

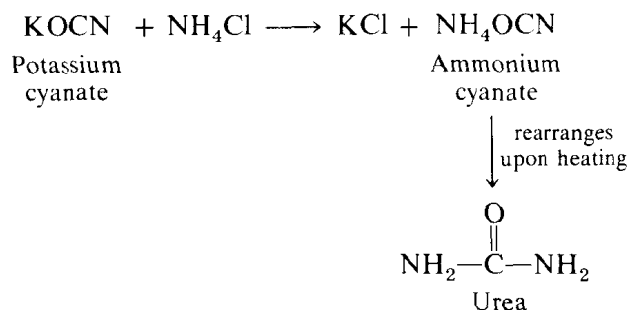
1

Introduction to Organic Chemistry

In 1685 Nicolas Lémery, a French chemist, published a book entitled *Cours de Chyme* in which he classified substances as animal, vegetable, or mineral on the basis of their origin. This was probably the first attempt made to distinguish substances derived from plant or animal sources from those obtained from mineral constituents. The term **organic** was later applied to those compounds derived from living matter; substances that originated from nonliving sources were accordingly referred to as **inorganic**. Furthermore, it was universally believed that living organisms contained some mysterious vital force necessary to the formation of organic substances. Throughout the ensuing century, scientists were thwarted in all their attempts to synthesize organic substances from inorganic materials. Their failures served to entrench more firmly the vital force theory, which eventually achieved a status akin to religious dogma.

In 1814, a Swedish chemist, J. J. Berzelius, dealt the vital force theory a serious blow when he proved that the basic laws of chemical change (the law of definite composition and the law of multiple proportions) applied both to organic and inorganic compounds. Fourteen years later, the erroneous theory suffered a crippling blow by a stroke of chemical serendipity.

The birth of modern organic chemistry is generally placed in the year 1828. It was in that year that Friedrich Wöhler, a professor of chemistry at Germany's University of Göttingen, attempted to prepare ammonium cyanate by heating a mixture of two inorganic salts, potassium cyanate and ammonium chloride. To his surprise, instead of ammonium cyanate he obtained crystals of the well-known organic compound urea. (Urea is a



substance excreted in the urine of mammals.) Wöhler correctly concluded that ammonium cyanate is first formed, but then rearranges under the influence of heat to yield urea. Urea contains the same number and kind of atoms as ammonium cyanate, but these atoms are arranged differently.

The next several decades witnessed a renewed effort on the part of chemists to synthesize organic compounds from inorganic starting materials. As a result of the enlightenment of Wöhler's discovery, many other organic compounds were synthesized in chemical laboratories. Moreover, while many of these compounds were identical to compounds found in nature, many others were entirely new, having no known counterpart in nature.

1.1 The Nature of Organic Compounds

By 1850 the vital force theory was essentially dead, and the relationship between the two branches of chemistry was clearly recognized. Table 1.1 contrasts the general properties of organic and inorganic compounds. It must be understood, however, that there are exceptions to every entry in this table.

The one constituent common to all organic compounds is the element carbon. Today, the term organic chemistry, although no longer descriptive, implies the study of carbon-containing compounds.¹ There are approximately 90,000 known inorganic compounds and this number is not rapidly increasing. On the other hand, there are over one million known organic compounds (isolated from nature or synthesized in the laboratory) and several thousand new compounds are synthesized and described each year.

What is so unique about carbon that differentiates it from all of the other elements in the periodic table? Carbon has the ability to bond successively to other carbon atoms to form chains and rings of varying sizes. As the number of carbon atoms in a chain increases, the number of ways that these atoms may arrange themselves increases, yielding compounds with the same chemical composition but with different structures. Finally, carbon can form

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

Carbon monoxide, CO	Carbonates, e.g., Na ₂ CO ₃	Thiocyanates, e.g., NaSCN
Carbon dioxide, CO ₂	Bicarbonates, e.g., NaHCO ₃	Cyanates, e.g., KOCN
Carbon disulfide, CS ₂	Cyanides, e.g., KCN	Carbides, e.g., CaC ₂

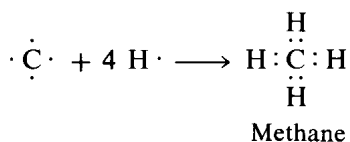
Table 1.1 Contrasting Properties of Organic and Inorganic Compounds

<i>Organic</i>	<i>Inorganic</i>
1. Low melting points	1. High melting points
2. Low boiling points	2. High boiling points
3. Low solubility in water; high solubility in nonpolar solvents	3. High solubility in water; low solubility in nonpolar solvents
4. Flammable	4. Nonflammable
5. Solutions are nonconductors of electricity	5. Solutions are conductors of electricity
6. Chemical reactions are usually slow	6. Chemical reactions are rapid
7. Exhibit isomerism	7. Isomers are limited to a few exceptions
8. Exhibit covalent bonding	8. Exhibit ionic bonding
9. Exist as gases, liquids, and solids at room temperature	9. Exist predominantly as solids at room temperature

equally strong bonds with a number of different elements. Those elements most frequently encountered in organic compounds are hydrogen, oxygen, nitrogen, sulfur, phosphorus, and the halogens.

Carbon has an atomic mass of 12 and an atomic number of 6. Two of carbon's six electrons reside in the first shell outside the nucleus. The remaining four electrons occupy the second shell, called the **valence-electron shell**. Since this shell can accommodate eight electrons, a carbon atom can acquire four additional electrons to complete its outer shell by the sharing of electrons with other atoms. When two atoms share a pair of electrons, they are joined by a **covalent bond**. In practically all cases, carbon forms four covalent bonds, and thus is said to be tetravalent.²

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



This formula for methane is an **electron-dot formula** and shows only the valence electrons involved in covalent bond formation. Such a representation gives no indication of the spatial orientation of atoms within a molecule. There is a great deal of evidence that the four bonds of carbon are equivalent

²The term *tetravalent* refers only to the number of bonds formed by carbon atoms in organic compounds. It implies nothing about the charge of the carbon atom or its oxidation state.

1.2 The Structure of Carbon Compounds

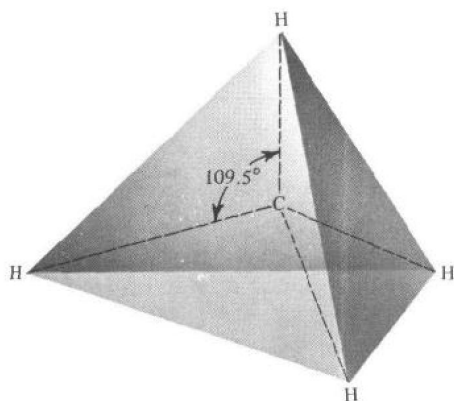


Figure 1.1 The four covalent bonds of carbon are directed toward the corners of a tetrahedron.

and that they are directed toward the corners of a **tetrahedron** (Figure 1.1).

The best representation of the methane molecule is achieved by picturing the carbon atom in the center of a tetrahedron, with the four hydrogen atoms located at the corners. All four hydrogen atoms are equivalent; that is, they are equidistant from the central carbon atom and from each other. The angle between any two carbon–hydrogen bonds is 109.5° .

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 1.2a).
2. The space-filling model, which attempts to show the shape of the molecule and the relative sizes of the atoms (Figure 1.2b).

Most organic compounds contain more than one carbon atom and thus are considerably more complex than methane. The simplest compound that illustrates the covalent bonding of one carbon atom to another is ethane.

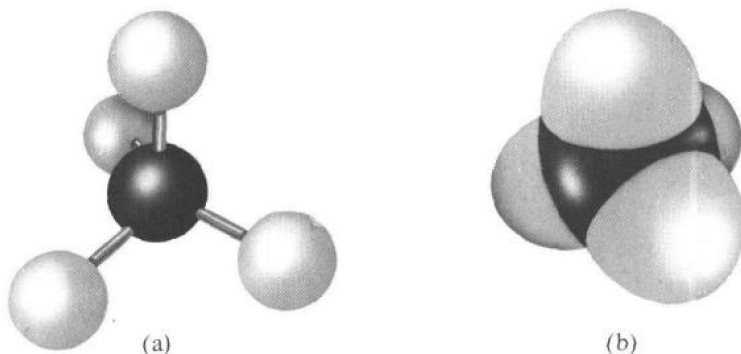


Figure 1.2 Molecular models of methane. (a) Ball-and-stick model; (b) space-filling model.

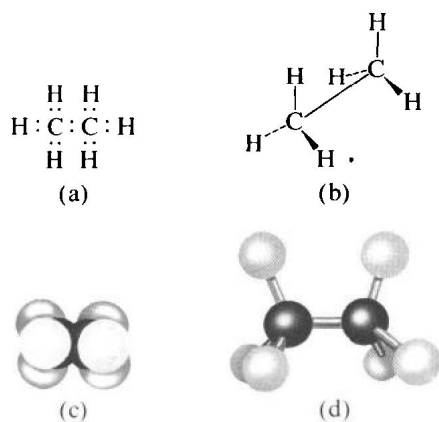
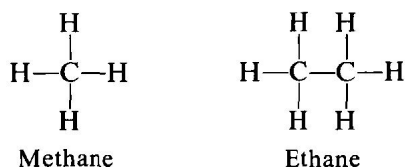


Figure 1.3 Representations of the ethane molecule. (a) Electron-dot formula; (b) perspective formula; (c) space-filling model; (d) ball-and-stick model.

Ethane is represented by any of the various models given in Figure 1.3. However, it is extremely difficult and very inconvenient to draw three-dimensional diagrams each time we wish to discuss a particular compound. Therefore chemists have chosen to project the three-dimensional ball-and-stick model of a compound onto a two-dimensional surface. The resultant formulas for methane and for ethane are called **structural formulas**.

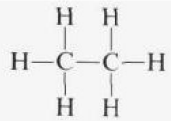
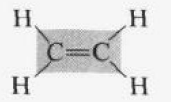
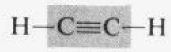
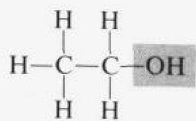
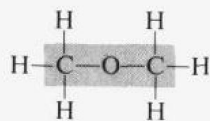
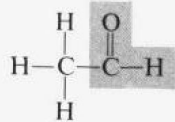
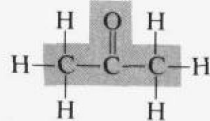
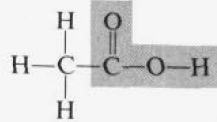
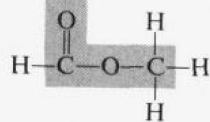
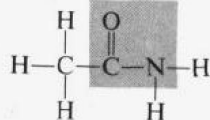
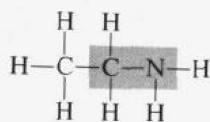


They are identical to the electron dot formulas, but a dash now represents the shared pair of electrons. It should be reemphasized that organic compounds are three dimensional, and we write flat two-dimensional formulas solely for our own convenience. In no way is it implied that such a formula accurately represents the three-dimensional structure of the molecule.

The student is probably already familiar with the terms **empirical formula** and **molecular formula**. The empirical formula (simplest formula) gives a minimum of information since it expresses only the relative number of atoms in a molecule. The molecular formula gives more information since it expresses the actual number of atoms in a molecule. In some cases, the molecular formula and the empirical formula are identical. The structural formula, as we have seen, is even more informative. It clearly shows the arrangement of constituent atoms in a molecule. A fourth formula, the **condensed structural formula**, is perhaps the most widely employed by organic chemists. As the name implies, it is a shorthand (and less descriptive) method of representing the structural formula. The convention is to omit the bonds between each carbon and the hydrogens attached to it. Very often,

1.3 Chemical Formulas

Table 1.2 Chemical Formulas of Some Organic Compounds

Name of Compound	Class of Compound	Empirical Formula	Molecular Formula	Structural Formula	Condensed Structural Formula
Ethane	Alkane	CH ₃	C ₂ H ₆		CH ₃ CH ₃
Ethylene	Alkene	CH ₂	C ₂ H ₄		H ₂ C=CH ₂
Acetylene	Alkyne	CH	C ₂ H ₂		HC≡CH
Ethyl alcohol	Alcohol	C ₂ H ₆ O	C ₂ H ₆ O		CH ₃ CH ₂ OH
Dimethyl ether	Ether	C ₂ H ₆ O	C ₂ H ₆ O		CH ₃ OCH ₃
Acetaldehyde	Aldehyde	C ₂ H ₄ O	C ₂ H ₄ O		CH ₃ CHO
Acetone	Ketone	C ₃ H ₆ O	C ₃ H ₆ O		CH ₃ COCH ₃
Acetic acid	Carboxylic acid	CH ₂ O	C ₂ H ₄ O ₂		CH ₃ COOH
Methyl formate	Ester	CH ₂ O	C ₂ H ₄ O ₂		HCOOCH ₃
Acetamide	Amide	C ₂ H ₅ ON	C ₂ H ₅ ON		CH ₃ CONH ₂
Ethylamine	Amine	C ₂ H ₇ N	C ₂ H ₇ N		CH ₃ CH ₂ NH ₂