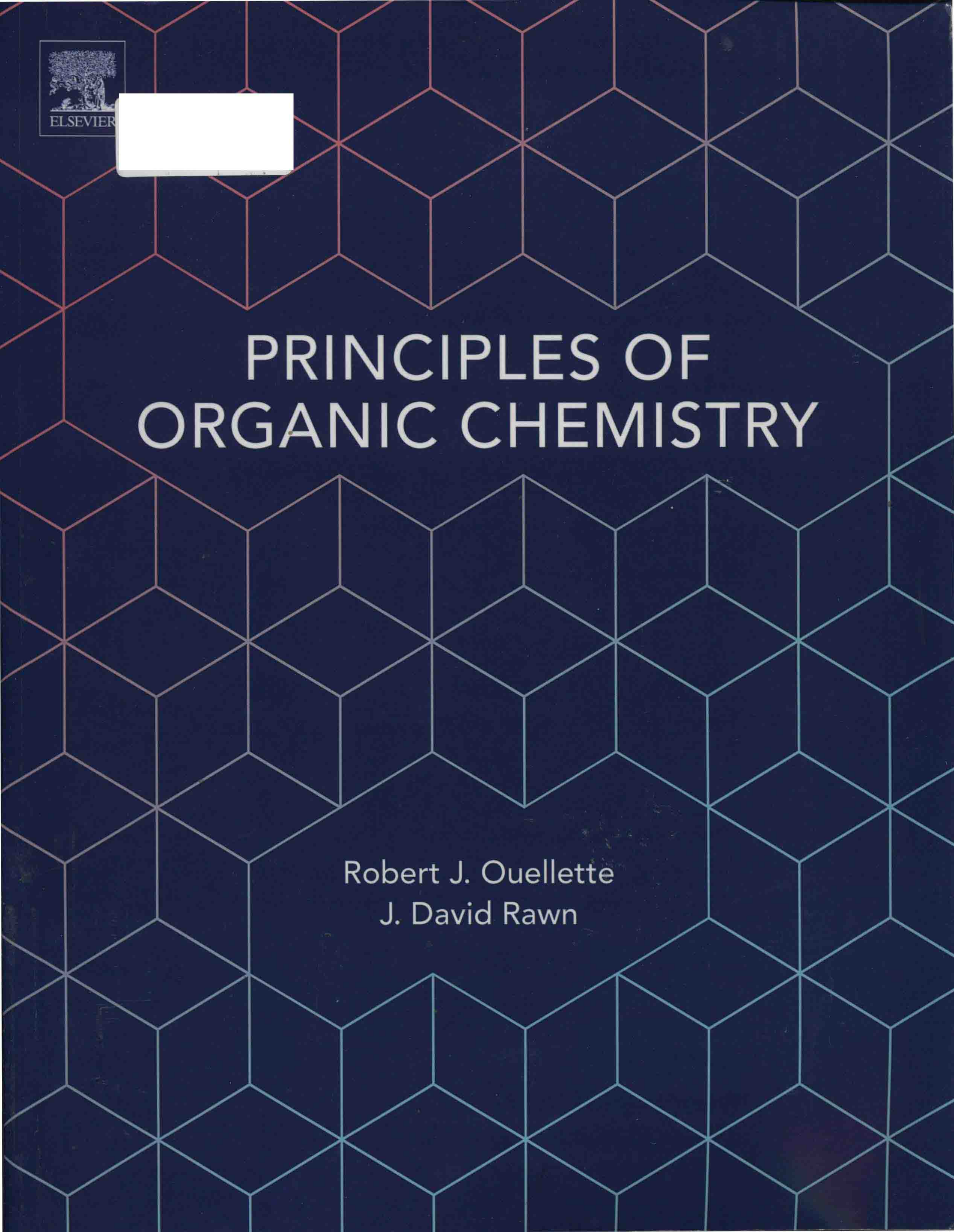

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Robert J. Ouellette
J. David Rawn

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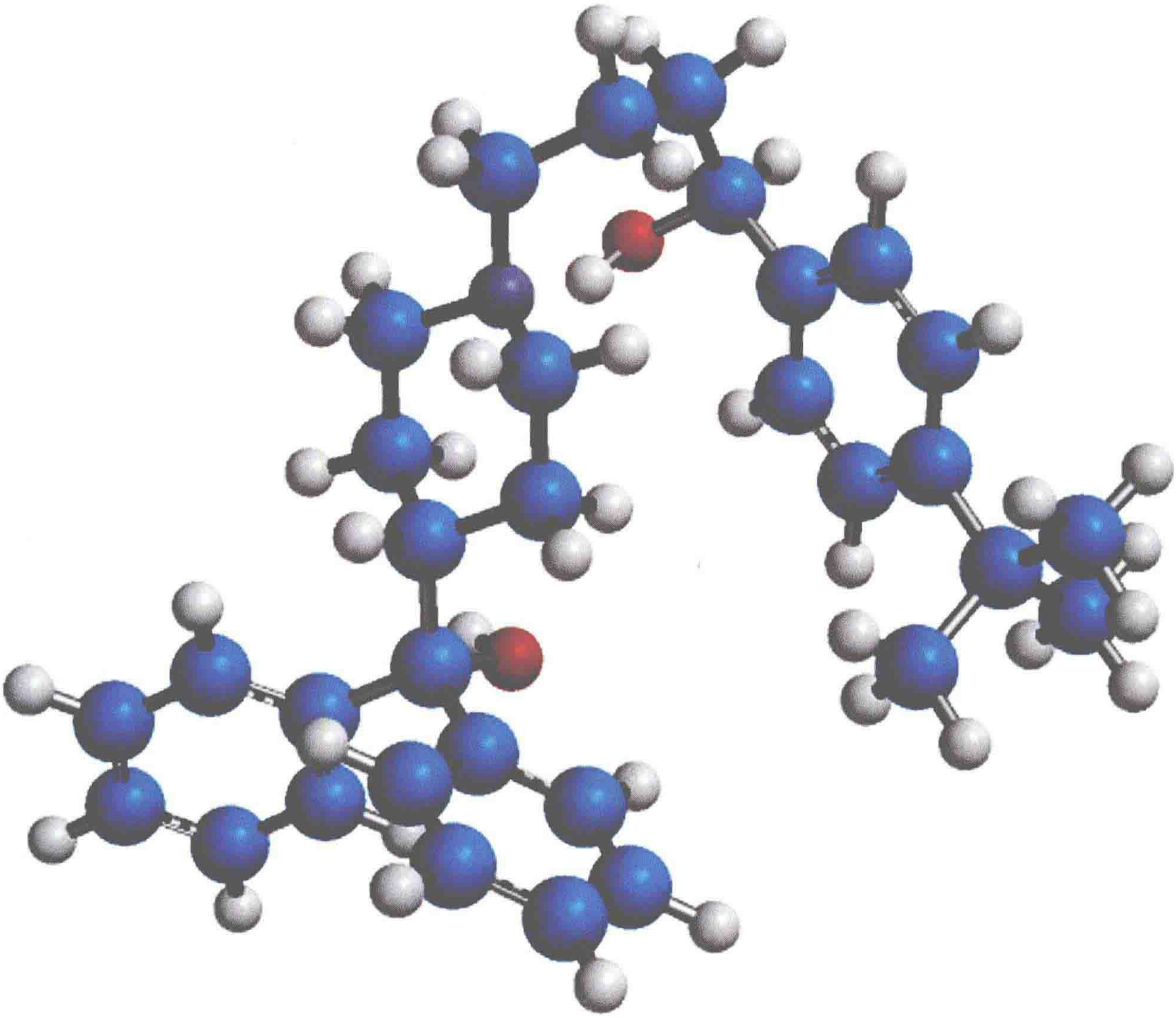

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TABLE OF CONTENTS

CHAPTER 1 STRUCTURE OF ORGANIC COMPOUNDS 1
1.1 ORGANIC AND INORGANIC COMPOUNDS 1
1.2 ATOMIC STRUCTURE 1
1.3 TYPES OF BONDS 4
1.4 FORMAL CHARGE 7
1.5 RESONANCE STRUCTURES 8
1.6 PREDICTING THE SHAPES OF SIMPLE MOLECULES 10
1.7 ORBITALS AND MOLECULAR SHAPES 11
1.8 FUNCTIONAL GROUPS 15
1.9 STRUCTURAL FORMULAS 18
1.10 ISOMERS 23
1.11 NOMENCLATURE 25
EXERCISES 27

CHAPTER 2 PROPERTIES OF ORGANIC COMPOUNDS 33
2.1 STRUCTURE AND PHYSICAL PROPERTIES 33
2.2 CHEMICAL REACTIONS 38
2.3 ACID-BASE REACTIONS 39
2.4 OXIDATION-REDUCTION REACTIONS 41
2.5 CLASSIFICATION OF ORGANIC REACTIONS 44
2.6 CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANTS 45
2.7 EQUILIBRIA IN ACID-BASE REACTIONS 47
2.8 EFFECT OF STRUCTURE ON ACIDITY 49
2.9 INTRODUCTION TO REACTION MECHANISMS 51
2.10 REACTION RATES 54
EXERCISES 58

CHAPTER 3 ALKANES AND CYCLOALKANES 65
3.1 CLASSES OF HYDROCARBONS 65
3.2 ALKANES 65
3.3 NOMENCLATURE OF ALKANES 68
3.4 CONFORMATIONS OF ALKANES 72
3.5 CYCLOALKANES 75
3.6 CONFORMATIONS OF CYCLOALKANES 78
3.7 PHYSICAL PROPERTIES OF ALKANES 81
3.8 OXIDATION OF ALKANES AND CYCLOALKANES 83
3.9 HALOGENATION OF SATURATED ALKANES 84

3.10 NOMENCLATURE OF HALOALKANES 87
SUMMARY OF REACTIONS 89
EXERCISES 90

CHAPTER 4 ALKENES AND ALKYNES 95
4.1 UNSATURATED HYDROCARBONS 95
4.2 GEOMETRIC ISOMERISM 99
4.3 E,Z NOMENCLATURE OF GEOMETRICAL ISOMERS 101
4.4 NOMENCLATURE OF ALKENES AND ALKYNES 103
4.5 ACIDITY OF ALKENES AND ALKYNES 106
4.6 HYDROGENATION OF ALKENES AND ALKYNES 107
4.7 OXIDATION OF ALKENES AND ALKYNES 110
4.8 ADDITION REACTIONS OF ALKENES AND ALKYNES 111
4.9 MECHANISM OF ADDITION REACTIONS 113
4.10 HYDRATION OF ALKENES AND ALKYNES 115
4.11 PREPARATION OF ALKENES AND ALKYNES 116
4.12 ALKADIENES (DIENES) 119
4.13 TERPENES 120
SUMMARY OF REACTIONS 124
EXERCISES 126

CHAPTER 5 AROMATIC COMPOUNDS 133
5.1 AROMATIC COMPOUNDS 133
5.2 AROMATICITY 134
5.3 NOMENCLATURE OF AROMATIC COMPOUNDS 137
5.4 ELECTROPHILIC AROMATIC SUBSTITUTION 139
5.5 STRUCTURAL EFFECTS IN ELECTROPHILIC AROMATIC SUBSTITUTION 143
5.6 INTERPRETATION OF RATE EFFECTS 145
5.7 INTERPRETATION OF DIRECTING EFFECTS 148
5.8 REACTIONS OF SIDE CHAINS 150
5.9 FUNCTIONAL GROUP MODIFICATION 152
5.10 SYNTHESIS OF SUBSTITUTED AROMATIC COMPOUNDS 154
SUMMARY OF REACTIONS 156
EXERCISES 158

CHAPTER 6 STEREOCHEMISTRY 163
6.1 CONFIGURATION OF MOLECULES 163
6.2 MIRROR IMAGES AND CHIRALITY 163
6.3 OPTICAL ACTIVITY 167

6.4 FISCHER PROJECTION FORMULAS 168
6.5 ABSOLUTE CONFIGURATION 170
6.6 MOLECULES WITH MULTIPLE STEREOGENIC CENTERS 173
6.7 SYNTHESIS OF STEREOISOMERS 178
6.8 REACTIONS THAT PRODUCE STEREOGENIC CENTERS 179
6.9 REACTIONS THAT FORM DIASTEREOMERS 182
EXERCISES 184

CHAPTER 7 NUCLEOPHILIC SUBSTITUTION AND ELIMINATION REACTIONS 189
7.1 REACTION MECHANISMS AND HALOALKANES 189
7.2 NUCLEOPHILIC SUBSTITUTION REACTIONS 192
7.3 NUCLEOPHILICITY VERSUS BASICITY 194
7.4 MECHANISMS OF SUBSTITUTION REACTIONS 197
7.5 S_N2 VERSUS S_N1 REACTIONS 200
7.6 MECHANISMS OF ELIMINATION REACTIONS 201
7.7 EFFECT OF STRUCTURE ON COMPETING REACTIONS 203
SUMMARY OF REACTIONS 206
EXERCISES 206

CHAPTER 8 ALCOHOLS AND PHENOLS 209
8.1 THE HYDROXYL GROUP 209
8.2 PHYSICAL PROPERTIES OF ALCOHOLS 212
8.3 ACID-BASE REACTIONS OF ALCOHOLS 214
8.4 SUBSTITUTION REACTIONS OF ALCOHOLS 215
8.5 DEHYDRATION OF ALCOHOLS 216
8.6 OXIDATION OF ALCOHOLS 218
8.7 SYNTHESIS OF ALCOHOLS 221
8.8 PHENOLS 226
8.9 SULFUR COMPOUNDS: THIOLS AND THIOETHERS 229
SUMMARY OF REACTIONS 231
EXERCISES 232

CHAPTER 9 ETHERS AND EPOXIDES 239
9.1 STRUCTURE OF ETHERS 239
9.2 NOMENCLATURE OF ETHERS 240
9.3 PHYSICAL PROPERTIES OF ETHERS 241
9.4 THE GRIGNARD REAGENT AND ETHERS 242
9.5 SYNTHESIS OF ETHERS 244

9.6 REACTIONS OF ETHERS 245
9.7 SYNTHESIS OF EPOXIDES 246
9.8 REACTIONS OF EPOXIDES 246
SUMMARY OF REACTIONS 254
EXERCISES 255

CHAPTER 10 ALDEHYDES AND KETONES 259
10.1 THE CARBONYL GROUP 259
10.2 NOMENCLATURE OF ALDEHYDES AND KETONES 261
10.3 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES 263
10.4 OXIDATION-REDUCTION REACTIONS OF CARBONYL COMPOUNDS 265
10.5 ADDITION REACTIONS OF CARBONYL COMPOUNDS 267
10.6 SYNTHESIS OF ALCOHOLS FROM CARBONYL COMPOUNDS 269
10.7 ADDITION REACTIONS OF OXYGEN COMPOUNDS 272
10.8 FORMATION OF ACETALS AND KETALS 274
10.9 ADDITION OF NITROGEN COMPOUNDS 275
10.10 REACTIVITY OF THE α-CARBON ATOM 278
10.11 THE ALDOL CONDENSATION 279
SUMMARY OF REACTIONS 282
EXERCISES 284

CHAPTER 11 CARBOXYLIC ACIDS AND ESTERS 287
11.1 CARBOXYLIC ACIDS AND ACYL GROUPS 287
11.2 NOMENCLATURE OF CARBOXYLIC ACIDS 289
11.3 PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS 292
11.4 ACIDITY OF CARBOXYLIC ACIDS 294
11.5 SYNTHESIS OF CARBOXYLIC ACIDS 297
11.6 NUCLEOPHILIC ACYL SUBSTITUTION 300
11.7 REDUCTION OF ACYL DERIVATIVES 304
11.8 ESTERS AND ANHYDRIDES OF PHOSPHORIC ACID 305
11.9 THE CLAISEN CONDENSATION 308
SUMMARY OF REACTIONS 309
EXERCISES 311

CHAPTER 12 AMINES AND AMIDES 315
12.1 ORGANIC NITROGEN COMPOUNDS 315
12.2 BONDING AND STRUCTURE OF AMINES 316
12.3 STRUCTURE AND CLASSIFICATION OF AMINES AND AMIDES 317
12.4 NOMENCLATURE OF AMINES AND AMIDES 319

12.5 PHYSICAL PROPERTIES OF AMINES 322
12.6 BASICITY OF NITROGEN COMPOUNDS 325
12.7 SOLUBILITY OF AMMONIUM SALTS 328
12.8 NUCLEOPHILIC REACTIONS OF AMINES 328
12.9 SYNTHESIS OF AMINES 331
12.10 HYDROLYSIS OF AMIDES 333
12.11 SYNTHESIS OF AMIDES 334
SUMMARY OF REACTIONS 334
EXERCISES 336

CHAPTER 13 CARBOHYDRATES 343
13.1 CLASSIFICATION OF CARBOHYDRATES 343
13.2 CHIRALITY OF CARBOHYDRATES 344
13.3 HEMIACETALS AND HEMIKETALS 349
13.4 CONFORMATIONS OF MONOSACCHARIDES 353
13.5 REDUCTION OF MONOSACCHARIDES 354
13.6 OXIDATION OF MONOSACCHARIDES 354
13.7 GLYCOSIDES 356
13.8 DISACCHARIDES 358
13.9 POLYSACCHARIDES 362
SUMMARY OF REACTIONS 365
EXERCISES 366

CHAPTER 14 AMINO ACIDS, PEPTIDES, AND PROTEINS 371
14.1 PROTEINS AND POLYPEPTIDES 371
14.2 AMINO ACIDS 371
14.3 ACID-BASE PROPERTIES OF α-AMINO ACIDS 372
14.4 ISOIONIC POINT 376
14.5 PEPTIDES 377
14.6 PEPTIDE SYNTHESIS 380
14.7 DETERMINATION OF PROTEIN STRUCTURE 382
14.8 PROTEIN STRUCTURE 386
EXERCISES 393

CHAPTER 15 SYNTHETIC POLYMERS 397
15.1 NATURAL AND SYNTHETIC MACROMOLECULES 397
15.2 STRUCTURE AND PROPERTIES OF POLYMERS 397
15.3 CLASSIFICATION OF POLYMERS 399
15.4 METHODS OF POLYMERIZATION 401

15.5 ADDITION POLYMERIZATION 404
15.6 COPOLYMERIZATION OF ALKENES 405
15.7 CROSS-LINKED POLYMERS 406
15.8 STEREOCHEMISTRY OF ADDITION POLYMERIZATION 408
15.9 CONDENSATION POLYMERS 410
15.10 POLYESTERS 411
15.11 POLYCARBONATES 413
15.12 POLYAMIDES 414
15.13 POLYURETHANES 415
EXERCISES 416

CHAPTER 16 SPECTROSCOPY 421
16.1 SPECTROSCOPIC STRUCTURE DETERMINATION 421
16.2 SPECTROSCOPIC PRINCIPLES 422
16.3 ULTRAVIOLET SPECTROSCOPY 424
16.4 INFRARED SPECTROSCOPY 425
16.5 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY 431
16.6 SPIN-SPIN SPLITTING 435
16.7 ^{13}C NMR SPECTROSCOPY 439
EXERCISES 442

Solutions to In-Chapter Problems 447
Index 477

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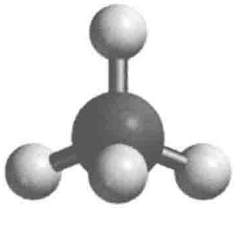
STRUCTURE OF ORGANIC COMPOUNDS



1.1 ORGANIC AND INORGANIC COMPOUNDS

Organic chemistry began to emerge as a science about 200 years ago. By the late eighteenth century, substances were divided into two classes called inorganic and organic compounds. Inorganic compounds were derived from mineral sources, whereas organic compounds were obtained only from plants or animals. Organic compounds were more difficult to work with in the laboratory, and decomposed more easily, than inorganic compounds. The differences between inorganic and organic compounds were attributed to a "vital force" associated with organic compounds. This unusual attribute was thought to exist only in living matter. It was believed that without the vital force, organic compounds could not be synthesized in the laboratory. However, by the mid-nineteenth century, chemists had learned both how to work with organic compounds and how to synthesize them.

Organic compounds always contain carbon and a limited number of other elements, such as hydrogen, oxygen, and nitrogen. Compounds containing sulfur, phosphorus, and halogens are known but are less prevalent. Most organic compounds contain many more atoms per structural unit than inorganic compounds and have more complex structures. Common examples of organic compounds include the sugar sucrose ($C_{12}H_{22}O_{11}$), vitamin B2 ($C_{117}H_{120}N_4O_6$), cholesterol ($C_{27}H_{46}O$), and the fat glycerol tripalmitate ($C_{51}H_{98}O_6$). Some organic molecules are gigantic. DNA, which stores genetic information, has molecular weights that range from 3 million in *Escherichia coli* to 2 billion for mammals.

Based on the physical characteristics of compounds, such as solubility, melting point, and boiling point, chemists have proposed that the atoms of the elements are bonded in compounds in two principal ways—ionic bonds and covalent bonds. Both types of bonds result from a change in the electronic structure of atoms as they associate with each other. Thus, the number and type of bonds formed and the resultant shape of the molecule depend on the electron configuration of the atoms. Therefore, we will review some of the electronic features of atoms and the periodic properties of the elements before describing the structures of organic compounds.

1.2 ATOMIC STRUCTURE

Each atom has a central, small, dense nucleus that contains protons and neutrons; electrons are located outside the nucleus. Protons have a +1 charge; electrons have a −1 charge. The number of protons, which determines the identity of an atom, is given as its **atomic number**. Since atoms have an equal number of protons and electrons and are electrically neutral, the atomic number also indicates the number of electrons in the atom. The number of electrons in the hydrogen, carbon, nitrogen, and oxygen atoms are one, six, seven, and eight, respectively.

The periodic table of the elements is arranged by atomic number. The elements are arrayed in horizontal rows called **periods** and vertical columns called **groups**. In this text, we will emphasize hydrogen in the first period and the elements carbon, nitrogen, and oxygen in the second period. The electronic structure of these atoms is the basis for their chemical reactivity.

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Atomic Orbitals

Electrons around the nucleus of an atom are found in **atomic orbitals**. Each orbital can contain a maximum of two electrons. The orbitals, designated by the letters s, p, d, and f, differ in energy, shape, and orientation. We need to consider only the s and p orbitals for elements such as carbon, oxygen, and nitrogen.

Orbitals are grouped in shells of increasing energy designated by the integers $n = 1, 2, 3, 4, \cdots, n$. These integers are called **principal quantum numbers**. With few exceptions, we need consider only the orbitals of the first three shells for the common elements found in organic compounds.

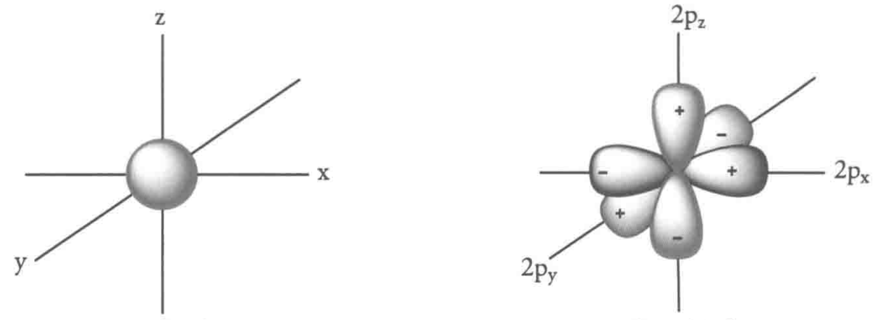
Each shell contains a unique number and type of orbitals. The first shell contains only one orbital—the s orbital. It is designated 1s. The second shell contains two types of orbitals—one s orbital and three p orbitals.

An s orbital is a spherical region of space centered around the nucleus (Figure 1.1). The electrons in a 2s orbital are higher in energy than those in a 1s orbital. The 2s orbital is larger than the 1s orbital, and its electrons on average are farther from the nucleus. The three p orbitals in a shell are shaped like "dumbbells." However, they have different orientations with respect to the nucleus (Figure 1.1). The orbitals are often designated p_x, p_y, and p_z to emphasize that they are mutually perpendicular to one another. Although the orientations of the p orbitals are different, the electrons in each p orbital have equal energies.

Orbitals of the same type within a shell are often considered as a group called a **subshell**. There is only one orbital in an s subshell. An s subshell can contain only two electrons, but a p subshell can contain a total of six electrons within its p_x, p_y, and p_z orbitals. Electrons are located in subshells of successively higher energies so that the total energy of all electrons is as low as possible. The order of increasing energy of subshells is 1s< 2s < 2p < 3s < 3p for elements of low atomic number. If there is more than one orbital in a subshell, one electron occupies each with parallel spins until all are half full. A single electron within an orbital is unpaired; two electrons with opposite spins within an orbital are paired and constitute an electron pair. The number and location of electrons for the first 18 elements are given in Table 1.1. The location of electrons in atomic orbitals is the **electron configuration** of an atom.

Figure 1.1
Shapes of 2s and 2p Orbitals

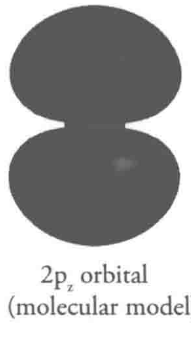
Electrons are pictured within a volume called an orbital. A "cloud" of negative charge surrounds the nucleus, which is located at the origin of the intersecting axes. (a) The s orbital is pictured as a sphere. (b) The three orbitals of the p subshell are arranged perpendicular to one another. Each orbital may contain two electrons. (c) Molecular model of a $2p_z$ orbital.



s orbital
(a)

2p orbitals
(b)

(c)



$2p_z$ orbital
(molecular model)

Table 1.1
Electron Configurations of First and Second Period Elements

Element	*Atomic Number*	*1s*	*2s*	$2p_x$	$2p_y$	$2p_z$	*Electron Configuration*
H	1	1					$1s^1$
He	2	2					$1s^2$
Li	3	2	1				$1s^2 2s^1$
Be	4	2	2				$1s^2 2s^2$
B	5	2	2	1(↑)			$1s^2 2s^2 2p^1$
C	6	2	2	1 (↑)	1 (↑)		$1s^2 2s^2 2p^2$
N	7	2	2	1 (↑)	1 (↑)	1 (↑)	$1s^2 2s^2 2p^3$
O	8	2	2	2(↑↓)	1 (↑)	1 (↑)	$1s^2 2s^2 2p^4$
F	9	2	2	2 (↑↓)	2 (↑↓)	1 (↑)	$1s^2 2s^2 2p^5$
Ne	10	2	2	2 (↑↓)	2 (↑↓)	2 (↑↓)	$1s^2 2s^2 2p^6$

Valence Shell Electrons

Electrons in filled, lower energy shells of atoms have no role in determining the structure of molecules, nor do they participate in chemical reactions. Only the higher energy electrons located in the outermost shell, the **valence shell**, participate in chemical reactions. Electrons in the valence shell are valence electrons. For example, the single electron of the hydrogen atom is a **valence electron**. The number of valence electrons for the common atoms contained in organic molecules is given by their group number in the periodic table. Thus carbon, nitrogen, and oxygen atoms have four, five, and six valence electrons, respectively. With this information we can understand how these elements combine to form the structure of organic compounds.

The physical and chemical properties of an element may be estimated from its position in the periodic table. Two principles that help us to explain the properties of organic compounds are atomic radius and electronegativity. The overall shape of an isolated atom is spherical, and the volume of the atom depends on the number of electrons and the energies of the electrons in occupied orbitals. The sizes of some atoms expressed as the **atomic radius**, in picometers, are given in Figure 1.2. The atomic radius for an atom does not vary significantly from one compound to another. Atomic radii increase from top to bottom in a group of the periodic table. Each successive member of a group has one additional energy level containing electrons located at larger distances from the nucleus. Thus, the atomic radius of sulfur is greater than that of oxygen, and the radii of the halogens increase in the order F < Cl < Br.

The atomic radius decreases from left to right across a period. Although electrons are located in the same energy level within the s and p orbitals of the elements, the nuclear charge increases from left to right within a period. As a result, the nucleus draws the electrons inward and the radius decreases. The radii of the common elements in organic compounds are in the order C > N > 0.

Figure 1.2
Atomic radii in picometers, pm (10^{-12} m)

H						
37						
Li	**Be**	**B**	**C**	**N**	**O**	**F**
152	111	88	77	70	66	64
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
186	160	143	117	110	104	99
						Br
						114
						I
						133

Electronegativity

Electronegativity is a measure of the attraction of an atom for bonding electrons in molecules compared to that of other atoms. The electronegativity values devised by Linus Pauling, an American chemist, are dimensionless quantities that range from slightly less than one for the alkali metals to a maximum of four for fluorine. Large electronegativity values indicate a stronger attraction for electrons than small electronegativity values.

Electronegativities increase from left to right across the periodic table (Figure 1.3). Elements on the left of the periodic table have low electronegativities and are often called electropositive elements. The order of electronegativities F > O > N > C is an important property that we will use to explain the chemical properties of organic compounds. Electronegativities decrease from top to bottom within a group of elements. The order of decreasing electronegativities F > Cl > Br > I is another sequence that we will use to interpret the chemical and physical properties of organic compounds.

Figure 1.3
Electronegativity

H						
2.1						
Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.9	1.2	1.5	1.8	2.1	2.5	3.0
						Br
						2.8
						I
						2.5

1.3 TYPES OF BONDS

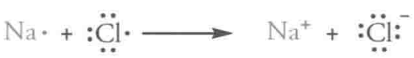
In 1916, the American chemist G.N. Lewis proposed that second period elements tend to react to obtain an electron configuration of eight electrons so that they electronically resemble the inert gases. This hypothesis is summarized in the **Lewis octet rule**: Second period atoms tend to combine and form bonds by transferring or sharing electrons until each atom is surrounded by eight electrons in its highest energy shell. Note that hydrogen requires only two electrons to complete its valence shell.

Ionic Bonds

Ionic bonds form between two or more atoms by the transfer of one or more electrons between atoms. Electron transfer produces negative ions called **anions** and positive ions called **cations**. These ions attract each other.

Let's examine the ionic bond in sodium chloride. A sodium atom, which has 11 protons and 11 electrons, has a single valence electron in its 3s subshell. A chlorine atom, which has 17 protons and 17 electrons, has seven valence electrons in its third shell, represented as $3s^23p^5$. In forming an ionic bond, the sodium atom, which is electropositive, loses its valence electron to chlorine. The resulting sodium ion has the same electron configuration as neon ($\mathrm{ls^22s^22p^6}$) and has a +1 charge, because there are 11 protons in the nucleus, but only 10 electrons about the nucleus of the ion.

The chlorine atom, which has a high electronegativity, gains an electron and is converted into a chloride ion that has the same electron configuration as argon ($\mathrm{ls^22s^22p^63s^23p^6}$). The chloride ion has a –1 charge because there are 17 protons in the nucleus, but there are 18 electrons about the nucleus of the ion. The formation of sodium chloride from the sodium and chlorine atoms can be shown by Lewis structures. Lewis structures represent only the valence electrons; electron pairs are shown as pairs of dots.



$$\mathrm{Na\cdot} + \mathrm{:\ddot{\underset{..}{Cl}}\cdot} \longrightarrow \mathrm{Na^+} + \mathrm{:\ddot{\underset{..}{Cl}}:^-}$$

Note that by convention, the complete octet is shown for anions formed from electronegative elements. However, the filled outer shell of cations that results from loss of electrons by electropositive elements is not shown.

Metals are electropositive and tend to lose electrons, whereas nonmetals are electronegative and tend to gain electrons. A metal atom loses one or more electrons to form a cation with an octet. The same number of electrons are accepted by the appropriate number of atoms of a nonmetal to form an octet in the anion, producing an ionic compound. In general, ionic compounds result from combinations of metallic elements, located on the left side of the periodic table, with nonmetals, located on the upper right side of the periodic table.

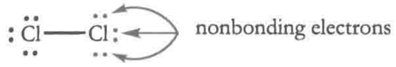
Covalent Bonds

A **covalent bond** consists of the mutual sharing of one or more pairs of electrons between two atoms. These electrons are simultaneously attracted by the two atomic nuclei. A covalent bond forms when the difference between the electronegativities of two atoms is too small for an electron transfer to occur to form ions. Shared electrons located in the space between the two nuclei are called **bonding electrons.** The bonded pair is the "glue" that holds the atoms together in molecular units.

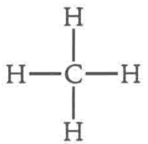
The hydrogen molecule is the simplest substance having a covalent bond. It forms from two hydrogen atoms, each with one electron in a 1s orbital. Both hydrogen atoms share the two electrons in the covalent bond, and each acquires a helium-like electron configuration.

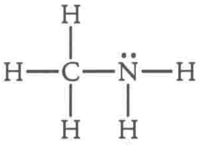
$$\mathrm{H}\bullet + \mathrm{H}\bullet \longrightarrow \mathrm{H{-}H}$$

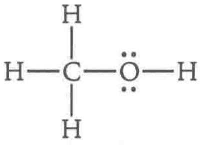
A similar bond forms in Cl_2. The two chlorine atoms in the chlorine molecule are joined by a shared pair of electrons. Each chlorine atom has seven valence electrons in the third energy level and requires one more electron to form an argon-like electron configuration. Each chlorine atom contributes one electron to the bonding pair shared by the two atoms. The remaining six valence electrons of each chlorine atom are not involved in bonding and are concentrated around their respective atoms. These valence electrons, customarily shown as pairs of electrons, are variously called **nonbonding electrons**, **lone pair electrons**, or **unshared electron pairs**.

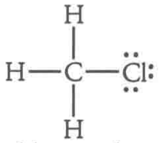


The covalent bond is drawn as a dash in a **Lewis structure** to distinguish the bonding pair from the lone pair electrons. Lewis structures show the nonbonding electrons as pairs of dots located about the atomic symbols for the atoms. The Lewis structures of four simple organic compounds—methane, methylamine, methanol, and chloromethane—are drawn here to show both bonding and nonbonding electrons. In these compounds carbon, nitrogen, oxygen, and chlorine atoms have four, three, two, and one bonds, respectively.


methane


aminomethane

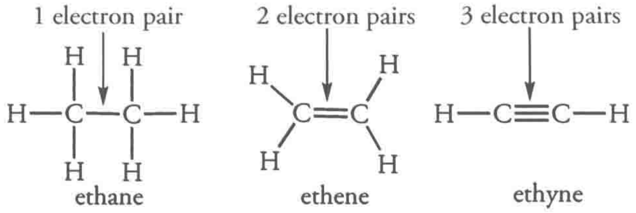

methanol


chloromethane

The hydrogen atom and the halogen atoms form only one covalent bond to other atoms in most stable neutral compounds. However, the carbon, oxygen, and nitrogen atoms can simultaneously bond to more than one atom. The number of such bonds is the **valence** of the atom. The valences of carbon, nitrogen, and oxygen are four, three, and two, respectively.

Multiple Covalent Bonds

In some molecules more than one pair of electrons is shared between pairs of atom. If four electrons (two pairs) or six electrons (three pairs) are shared, the bonds are called **double** and **triple bonds**, respectively. A carbon atom can form single, double, or triple bonds with other carbon atoms as well as with atoms of some other elements. Single, double, and triple covalent bonds link two carbon atoms in ethane, ethylene, and acetylene, respectively. Each carbon atom in these compounds shares one, two, and three electrons, respectively, with the other. The remaining valence electrons of the carbon atoms are contained in the single bonds with hydrogen atoms.



Polar Covalent Bonds

A polar covalent bond exists when atoms with different electronegativities share electrons in a covalent bond. Consider the hydrogen chloride (HCl) molecule. Each atom in HCl requires one more electron to form an inert gas electron configuration. Chlorine has a higher electronegativity than hydrogen, but the chlorine atom's attraction for electrons is not sufficient to remove an electron from hydrogen. Consequently, the bonding electrons in hydrogen chloride are shared unequally in a polar covalent bond. The molecule is represented by the conventional Lewis structure, even though the shared electron pair is associated to a larger extent with chlorine than with hydrogen. The unequal sharing of the bonding pair results in a partial negative charge on the chlorine atom and a partial positive charge on the hydrogen atom. The symbol δ (Greek lowercase delta) denotes these fractional charges.

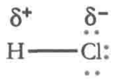
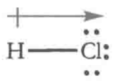


Table 1.2
Average Dipole Moments (D)

Structural Unit[1]	*Bond Moments (D)*
H—C	0.4
H—N	1.3
H—O	1.5
H—F	1.7
H—S	0.7
H—Cl	1.1
H—Br	0.8
H—I	0.4
C—C	0.0
C—N	0.2
C—O	0.7
C—F	1.4
C—Cl	1.5
C—Br	1.4
C—I	1.2
C=O	2.3
C≡N	3.5

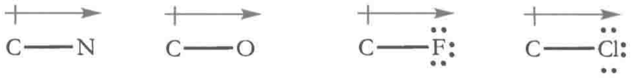
[1] The more negative element is on the right.

The hydrogen chloride molecule has a **dipole** (two poles), which consists of a pair of opposite charges separated from each other. The dipole is shown by an arrow with a cross at one end. The cross is near the end of the molecule that is partially positive, and the arrowhead is near the partially negative end of the molecule.



Single or multiple bonds between carbon atoms are nonpolar. Hydrogen and carbon have similar electronegativity values, so the C—H bond is not normally considered a polar covalent bond. Thus ethane, ethylene, and acetylene have nonpolar covalent bonds, and the compounds are nonpolar.

Bonds between carbon and other elements such as oxygen and nitrogen are polar. The polarity of a bond depends on the electronegativities of the bonded atoms. Large differences between the electronegativities of the bonded atoms increase the polarity of bonds. The direction of the polarity of common bonds found in organic molecules is easily predicted. The common nonmetals are more electronegative than carbon. Therefore, when a carbon atom is bonded to common nonmetal atoms, it has a partial positive charge.



Hydrogen is also less electronegative than the common nonmetals. Therefore, when a hydrogen atom is bonded to common nonmetals, the resulting polar bond has a partial positive charge on the hydrogen atom.

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