CHAPTER 2

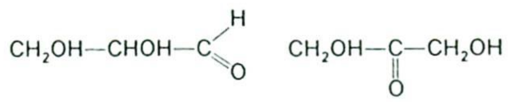
CARBOHYDRATES

In the next few chapters of this text, we shall describe the more important building blocks of the biosphere — the simple sugars, fatty acids, amino acids, and mononucleotides — that are assembled into the biopolymers of the cell — the polysaccharides, lipids, proteins, and nucleic acids. In the present chapter, we shall examine the simple sugars, the storage carbohydrates, and the structural polysaccharides. The subject of stereochemistry will be reviewed and the various ways of representing carbohydrates with different structural formulas will be presented. Physical and chemical properties of simple sugars will be described, and the structures of some of the more complex storage and structural polysaccharides will be given. Complex carbohydrates play not only a structural role in the cell but may serve as a reservoir of chemical energy to be enlarged and decreased as fits the needs of the organism. Two examples of structural carbohydrates are cellulose, the major structural component of plant cell walls, and the peptidoglycans of bacterial cell walls. The storage carbohydrates include starch and glycogen, polysaccharides that may be produced and consumed in line with the energy needs of the cell.

Carbohydrates may be defined as polyhydroxy aldehydes or ketones, or as substances that yield one of these compounds on hydrolysis. Many carbohydrates have the empirical formula $(CH_2O)_n$ where n is 3 or larger. This formula obviously contributed to the original belief that this group of compounds could be represented as **hydrates of carbon.** It became clear that this definition was not suitable when other compounds were encountered that had the general properties of carbohydrates but contained nitrogen, phosphorus, or sulfur in addition to carbon, hydrogen, and oxygen. Moreover, the important simple sugar deoxyribose, found in every cell as a component of deoxyribonucleic acid, has the molecular formula $C_5H_{10}O_4$ rather than $C_5H_{10}O_5$.

2.1 CLASSIFICATION OF CARBOHYDRATES

Carbohydrates can be classified into three groups based on the number of sugar units they contain: monosaccharides, oligosaccharides, and polysaccharides. Monosaccharides are simple sugars that cannot be hydrolyzed into smaller units under reasonably mild conditions. The simplest monosaccharides fitting our definition and empirical formula are the **aldose** glyceraldehyde and its isomer, the **ketose** dihydroxy acetone. Both of these sugars are trioses because they contain three



Glyceraldehyde — Dihydroxy acetone

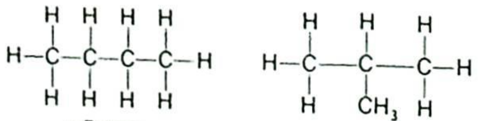
carbon atoms. In addition to the functional groups (aldehyde and ketone) that are used in describing these two sugars, note that they contain alcoholic hydroxyls and, in the case of glyceraldehyde, an asymmetric carbon atom.

Oligosaccharides are hydrolyzable polymers of monosaccharides that contain from two to six molecules of simple sugars. The disaccharides, which have two monosaccharide units, are the most abundant; trisaccharides also occur free in nature. Oligosaccharides with more than three subunits are usually found bound as side chains in glycoproteins.

Polysaccharides are polymers, frequently insoluble, consisting of hundreds or thousands of monosaccharide units; they may be either linear or branched in structure. If the polymer is made up from a single monosaccharide, the polysaccharide is called a *homo*polysaccharide. If two or more different monosaccharides are found in the polymer, it is called a *hetero*polysaccharide. Some of the monosaccharides that are bound together by glycosidic bonds to form polysaccharides are glucose, xylose, and arabinose.

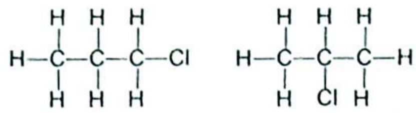
2.2 STEREOISOMERISM

The study of carbohydrates requires an understanding of isomerism, especially stereoisomerism. The subject of isomerism may be divided into **structural isomerism** and **stereoisomerism.** Structural isomers have the same molecular formula but differ from each other by having different structures; that is, they differ in the order in which their atoms are bonded together. Stereoisomers have the same molecular formula and the same structure, but they differ in **configuration,** that is, in the arrangement of their atoms in space. Structural isomers, in turn, can be of three types. One type is the **chain isomers,** in which the isomers have different arrangements of the carbon atoms. As an example, *n*-butane is a chain isomer of



n-Butane — Isobutane

isobutane. Other examples of structural isomers are the **positional isomers,** *n*-propyl chloride and isopropyl chloride, in which the two compounds involved have the same carbon chain but differ in the position of a substituent group. The third type of



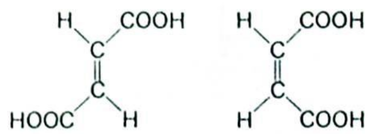
n-Propyl chloride   Isopropyl chloride

structural isomers is the **functional group isomers,** in which the compounds have different functional groups. Examples are *n*-propanol and methylethyl ether.

$H_3C—CH_2—CH_2OH$ $H_3C—CH_2—O—CH_3$

n-Propanol   Methylethyl ether

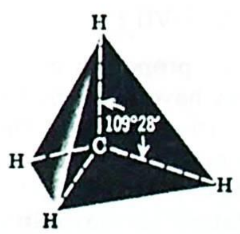
The subject of stereoisomerism can be divided into the smaller areas of **optical** isomerism and **geometrical** (or *cis-trans*) isomerism. The latter type of isomerism is illustrated by the *cis-trans* pair, fumaric and maleic acids.



Fumaric acid (*trans*)   Maleic acid (*cis*)

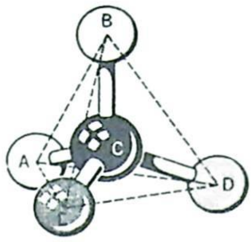
2.2.1 OPTICAL ISOMERISM

This is the type of isomerism commonly found in carbohydrates; it is usually encountered when a molecule contains one or more **chiral** (Greek cheir = hand) or asymmetric carbon atoms. The subject of stereoisomerism was extensively developed after van't Hoff and LeBel introduced the concept of the **tetrahedral carbon atom.** This atomic structure has four covalent bonds or bond axes that extend out from the central carbon nucleus to the corners of a tetrahedron (Structure 2.1).



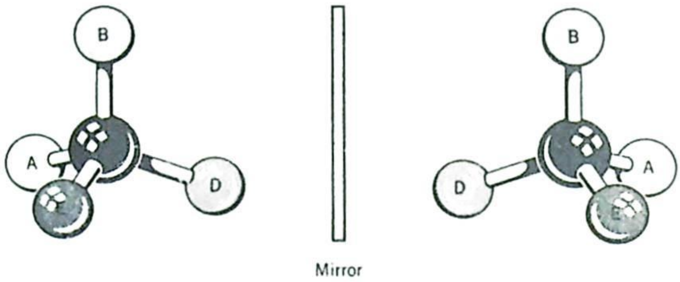
STRUCTURE 2.1

When four different groups are attached to those bonds, the carbon atom in the center of the molecule is said to be a chiral center (or a chiral **carbon atom).** This is indicated in Structure 2.2 in which the compound C(ABDE), containing a single chiral carbon atom, is represented as having the four groups A, B, D, and E attached. These groups may be arranged in space in two different ways so that two different compounds are formed. These compounds are obviously different; that is, they cannot be superimposed on each other. Instead, one compound is related to the other as a right hand is related to a left hand. Such



STRUCTURE 2.2

chiral molecules are said to possess "handedness" and are therefore mirror images of each other; if one molecule is held before a mirror, the image in the mirror corresponds to the other molecule (Structure 2.3).



STRUCTURE 2.3

These mirror image isomers constitute an **enantiomeric pair;** one member of the pair is said to be the **enantiomer** of the other.

In molecules that contain more than one chiral carbon atom, more than two stereoisomers can exist. Any two that are mirror image isomers, and therefore constitute an enantiomeric pair, will be related to the remaining stereoisomers as **diastereomers.** They are stereoisomeric with, but are not mirror image isomers of, the remaining compounds.

2.2.2 OPTICAL ACTIVITY

Almost all the properties of the two members of an enantiomeric pair are identical: they have the same boiling point, the same melting point, the same solubility in various solvents. They also exhibit optical activity; in this property, they differ in one important manner. One member of the enantiomeric pair will rotate a plane of polarized light in a clockwise direction and is therefore said to be *dextro*rotatory. Its mirror image isomer or enantiomer will rotate the plane of polarized light to the same extent, but in the opposite or counterclockwise direction. This isomer is said to be *levo*rotatory. It must be noted, however, that not all compounds possessing a chiral center are chiral or exhibit optical activity. On the other hand, a molecule may possess chirality, exhibit optical activity, and not contain a chiral center.

2.2.3 PROJECTION AND PERSPECTIVE FORMULAS

In the study of carbohydrates, many examples of optical isomerism are encountered, and it is necessary to have a means for representing the different