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主 编：蒋本固

副主编：赵小青 金黎明

主 审：范全弟

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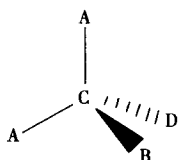
Chapter 1 Introduction

Organic chemistry is most commonly and simply defined as the chemistry of carbon compounds. Compared with hydrogen and helium, carbon is not an abundant element in the universe, nor in the solar system; but it is an essential element of life. Indeed, four elements: carbon, hydrogen, nitrogen and oxygen make up most of the matter found in living organisms. Trace elements such as sulfur, phosphorous, sodium, potassium and iron, to name a few, also play an important role in the chemistry of life; but it is the unique properties of carbon that permits the immense diversity of compounds associated with life. From simple single-carbon compounds such as methane and carbon dioxide to the more complex structures found in vitamins, hormones and enzymes, and ultimately to very large macromolecules like DNA, carbon is the underlying essential structural component.

Since the birth of organic chemistry over two hundred years ago, chemists have worked to unravel the structural complexities of these compounds. Today, all the facts and principles they have learned are consolidated in our texts and journals. Industrial applications have led to the manufacture of medicinal agents (drugs), synthetic fibers, plastics, dyes, pesticides and a host of other useful materials. Clearly, organic chemistry has touched all our lives. The study of organic chemistry is both fascinating and relevant, due in large part to the widespread distribution of both natural and synthetic organic chemicals.

1.1 The Shape of Molecules

The three dimensional shape or configuration of a molecule is an important characteristic. This shape is dependent on the preferred spatial orientation of covalent bonds to atoms having two or more bonding partners. Three dimensional configurations are best viewed with the aid of models.

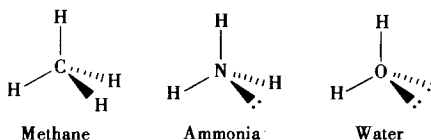


In order to represent such configurations on a two-dimensional surface (paper, blackboard or screen), we often use perspective drawings in which the direction of a bond is specified by the line connecting the bonded atoms. In most cases the focus of configuration is a carbon atom so the lines specifying bond directions will originate there. As defined in the diagram on the right, a simple straight line represents a bond lying approximately in the surface plane. The two bonds to substituents A in the structure on the left are of this kind. A wedge shaped bond is

	normal bond
	wedge bond
	hatched bond
	dashed bond

directed in front of this plane (thick end toward the viewer), as shown by the bond to substituent B; and a hatched bond is directed in back of the plane (away from the viewer), as shown by the bond to substituent D. Some texts and other sources may use a dashed bond in the same manner as we have defined the hatched bond, but this can be confusing because the dashed bond is often used to represent a partial bond (i.e. a covalent bond that is partially formed or partially broken). The following examples make use of this notation, and also illustrate the importance of including

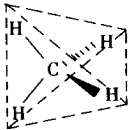
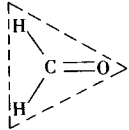
non-bonding valence shell electron pairs when viewing such configurations.



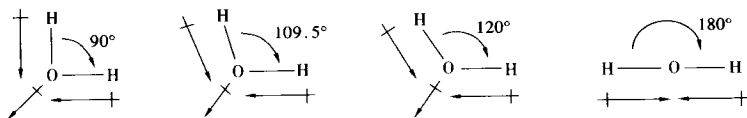
Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as VSEPR in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories. In the three examples shown above, the central atom (carbon) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. For molecules of water and ammonia, however, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds (H_2O 104.5° & NH_3 107.3°) show that they are closer to being tetrahedral than trigonal or linear. Of course, it is the configuration of atoms (not electrons) that defines the shape of a molecule, and in this sense ammonia is said to be pyramidal (not tetrahedral). The compound boron trifluoride, BF_3 , does not have non-bonding valence electrons and the configuration of its atoms is trigonal.

The best way to study the three-dimensional shapes of molecules is by using molecular models. Many kinds of model kits are available to

students and professional chemists. Some of the useful features of physical models can be approximated by the model viewing plugin Chime.

Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5°	
Trigonal	3	120°	
Linear	2	180°	$--O\equiv C\equiv O--$

One way in which the shapes of molecules manifest themselves experimentally is through molecular dipole moments. A molecule which has one or more polar covalent bonds may have a dipole moment as a result of the accumulated bond dipoles. In the case of water, we know that the O-H covalent bond is polar, due to the different electronegativities of hydrogen and oxygen. Since there are two O-H bonds in water, their bond dipoles will interact and may result in a molecular dipole which can be measured. The following diagram shows four possible orientations of the O-H bonds.



In the linear configuration (bond angle 180°) the bond dipoles

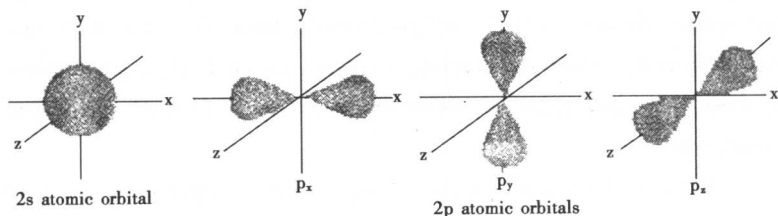
cancel, and the molecular dipole is zero. For other bond angles (120 to 90°) the molecular dipole would vary in size, being largest for the 90° configuration. In a similar manner the configurations of methane (CH_4) and carbon dioxide (CO_2) may be deduced from their zero molecular dipole moments. Since the bond dipoles have canceled, the configurations of these molecules must be tetrahedral (or square-planar) and linear respectively.

The case of methane provides insight to other arguments that have been used to confirm its tetrahedral configuration. For purposes of discussion we shall consider three other configurations for CH_4 , square-planar, square-pyramidal and triangular-pyramidal. Substitution of one hydrogen by a chlorine atom gives a CH_3Cl compound. Since the tetrahedral, square-planar and square-pyramidal configurations have structurally equivalent hydrogen atoms, they would each give a single substitution product. However, in the trigonal-pyramidal configuration one hydrogen (the apex) is structurally different from the other three (the pyramid base). Substitution in this case should give two different CH_3Cl compounds if all the hydrogens react. In the case of disubstitution, the tetrahedral configuration of methane would lead to a single CH_2Cl_2 product, but the other configurations would give two different CH_2Cl_2 compounds. These substitution possibilities are shown in the above Chime insert.

1.2 Atomic and Molecular Orbitals

A more detailed model of covalent bonding requires a consideration of valence shell atomic orbitals. For second period elements such as

carbon, nitrogen and oxygen, these orbitals have been designated $2s$, $2p_x$, $2p_y$ & $2p_z$. The spatial distribution of electrons occupying each of these orbitals is shown in the diagram below.



The valence shell electron configuration of carbon is $2s^2$, $2p_x^1$, $2p_y^1$ & $2p_z^0$. If this were the configuration used in covalent bonding, carbon would only be able to form two bonds.

Hybrid Orbitals

In order to explain the structure of methane (CH_4), the $2s$ and three $2p$ orbitals must be converted to four equivalent hybrid atomic orbitals, each having 25% s and 75% p character, and designated sp^3 . These hybrid orbitals have a specific orientation, and the four are naturally oriented in a tetrahedral fashion.

