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# I

## ▪ STRUCTURE AND SYMMETRY

### 1-1 Introduction

MOLECULAR *structure* is a description of the arrangement or distribution of particles in a molecule. We shall elaborate this definition by explaining our use of the terms *description* and *particles*.

A description may take many forms. It may be verbal, or it may be visual—as, for example, through the use of molecular models. The most accurate descriptions are also the most complex: These are the equations which describe the motion of the particles as a function of time and spatial position.

There are two kinds of submolecular particles which are of interest to the organic chemist: the electrons and the nuclei. Wave-mechanical arguments lead to a description of electronic structure as a probability distribution of negative charge, i.e., as a smeared-out charge density cloud. In contrast, the distribution of nuclei in space may be discussed more nearly in classical terms, i.e., we may think of nuclei as particles which vibrate with a very small amplitude around well-defined average positions in space. These vibrations are completely analogous to the quivers executed by two weights connected by a spring: the coulombic and exchange

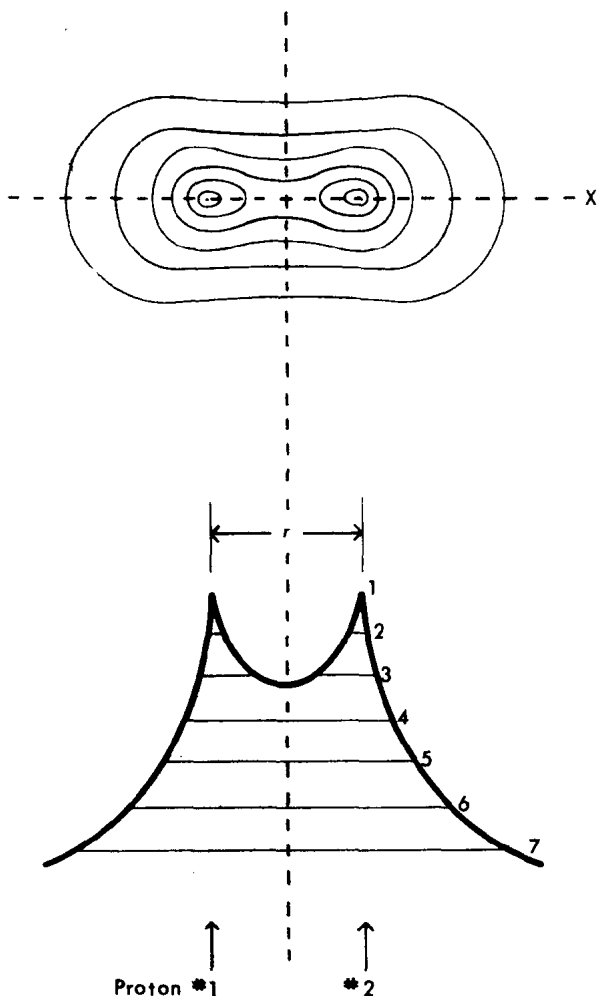


FIGURE 1-1

*Schematic representation of electron probability contours in the hydrogen molecule. Electronic charge density decreases in the order  $1 > 2 \dots > 7$ . Bond length =  $r$ . Internuclear axis =  $x$ . Above: plane of symmetry through molecule = cross section. Below: plot of electron density against distance along  $x$ .*

forces in the molecule simply take the place of the mechanical restoring force in the spring.

Compared to organic molecules, the hydrogen molecule is an extraordinarily simple one (in fact, except for its positive ion  $[H_2^+]$ ,

it is the simplest polyatomic molecule conceivable). It might therefore be appropriate to begin our discussion of structure and symmetry by analyzing the case of the hydrogen molecule. In the formation of that molecule, two protons and two electrons have been brought together. The electrons distribute themselves so that the position of the protons assumes an equilibrium value. This distribution of protons and electrons is indicated in Figure 1-1, which shows a cross section of the molecule made by a plane which contains the nuclei. This plane shows contour lines of equal electronic charge density, and the three-dimensional contour surfaces may be developed by rotation around the internuclear line  $x$ . Note that well-defined positions are assigned to the protons, whereas the electrons can only be described in terms of the over-all charge density. The molecule may be pictured as a roughly cigar-shaped region of electron density within which the two protons are buried. As shown by the contour lines, the density is highest at points on the  $x$ -axis corresponding to the positions of the nuclei, falls off at all distances, but remains high in the region between the nuclei. This region of electron localization between the nuclei coincides in direction with the internuclear line. The outermost contour line shown in diagrams such as these is conventionally chosen to enclose in the neighborhood of 95% of the electron cloud, that is: the probability of finding the electron or electrons within the outermost contour is about 95%.

This description of the distribution of two electrons in the field of the two protons corresponds to the bonding molecular orbital (MO) of hydrogen molecule.

The protons jiggle about but maintain an equilibrium distance  $r$ , the *bond length*. The bond length (10.74 Å in this case) refers to the molecular configuration of the vibrating system at a potential energy minimum. The potential energy of the molecule is raised whenever the bond is stretched (say to 10.75 Å) or compressed (say to 10.73 Å), very much as in the analogous case of the two vibrating weights connected by a spring.

We shall now consider symmetry in simple molecules. Every molecule may be classified according to its symmetry, and each particular symmetry class is characterized by the number and type of *symmetry elements* present in such a molecule. For our immediate purposes, the most important such elements are *planes of symmetry*, symbolized by  $\sigma$ , and *simple (or proper) axes of rotation of order  $n$*  ( *$n$ -fold axes of symmetry*), symbolized by  $C_n$ .

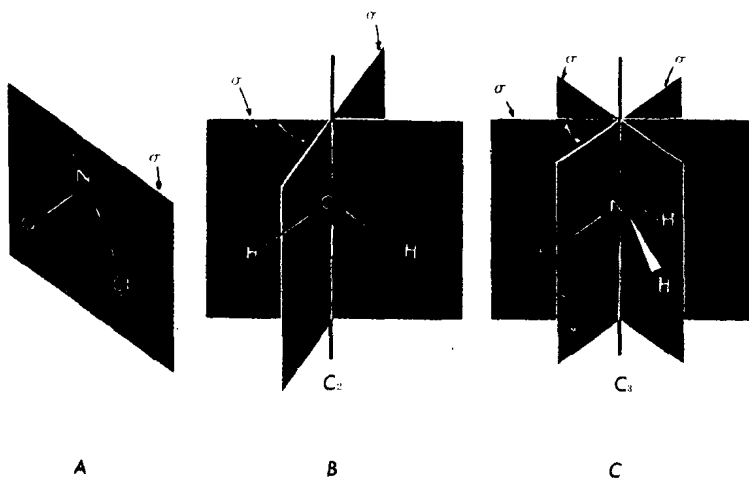


FIGURE 1-2

*A molecule with a single plane of symmetry: nitrosyl chloride (A). Two molecules with single axes of symmetry: water (B) and ammonia (C). One of the dihedral angles is shown.*

A  $\sigma$  plane is defined as a mirror plane which bisects a geometric figure so that the half of the figure on one side of the plane is exactly mirrored by the half on the other side. Objects like idealized forks, spoons, hammers, and cups have just one plane of symmetry, and so do molecules like nitrosyl chloride (Figure 1-2), bromocyclopropane and vinyl chloride. A  $C_n$  axis is defined as an axis which passes through the molecule so that, by a rotation of  $360^\circ/n$  around this axis, a three-dimensional arrangement is obtained which is indistinguishable from the original. For example, water has a twofold axis of symmetry and ammonia a threefold axis, as indicated in Figure 1-2. It is important to note that planes and axes of symmetry are often both encountered in the same molecule. For example, while nitrosyl chloride does not have an axis of symmetry (the trivial one-fold axis  $C_1$  is never considered), water and ammonia have, respectively, two and three planes of symmetry (Figure 1-2) which intersect at the  $C_n$  axis. The angles between the planes, the *dihedral angles*, have the values  $90^\circ$  and  $60^\circ$  for water and ammonia, respectively.

Let us now apply a similar analysis to the case of the hydrogen molecule. It is readily seen (Figure 1-3A) that there exists an

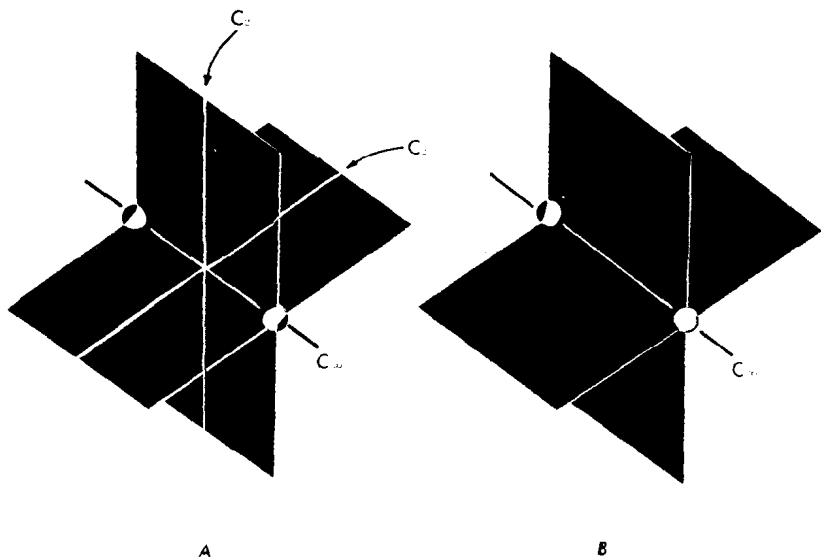


FIGURE 1-3

*Some symmetry elements in diatomic molecules. Molecules with cylindrical symmetry have an infinite number of planes of symmetry  $\sigma$  (two are shown) which intersect at the internuclear axis  $C_\infty$  (A), and the same is true of molecules with conical symmetry (B). Cylindrically symmetrical molecules also have a plane of symmetry perpendicular to  $C_\infty$  which contains an infinite number of twofold axes  $C_2$ , two of which are shown in A.*

infinite number of  $\sigma$  planes which are identical with the cross section shown in Figure 1-1 and which intersect at the internuclear axis. This axis, which is called the *cylindrical axis*, is also  $C_\infty$  because an infinitesimal rotation suffices to transform the new position into one indistinguishable from the original. In addition to the above-mentioned planes there also exists a  $\sigma$  plane which is perpendicular to the internuclear axis, which bisects the molecule, and which contains an infinite number of  $C_2$  axes. Molecules such as oxygen and carbon dioxide have that kind of symmetry which is called *cylindrical symmetry*. Objects such as idealized hourglasses, footballs (American), and doughnuts also have cylindrical symmetry. *Conical symmetry* is a closely related kind of axial symmetry. In molecules possessing conical symmetry, e.g., hydrogen chloride, there also exists an infinite number of  $\sigma$  planes which inter-

sect at the internuclear axis  $C_\infty$ . However, we now have no  $\sigma$  plane and no  $C_2$  axes which are perpendicular to the  $C_\infty$  axis (Figure 1-3B). Objects like idealized funnels, saucers, soda bottles, pins, and eggs have conical symmetry.

Cylindrically and conically symmetrical objects have *one*  $C_\infty$  axis. The only object possessing more than one such axis is the sphere, which has an infinite number of  $C_\infty$  axes intersecting at the center (*spherical symmetry*).

We shall elaborate on the subject of symmetry elements in Section 1-4.

### 1-2 Bonding Geometries in Carbon Compounds

Although molecules containing carbon are far more complex than the hydrogen molecule, a description of bonding in organic molecules may be approached in fundamentally the same manner. A carbon nucleus, one or more other nuclei, and the appropriate number of electrons are brought together, and the electrons are allowed to distribute themselves in a fashion which stabilizes the equilibrium configuration of all the nuclei. As in hydrogen molecules, there exist regions of high electron density between the nuclei which generally coincide in direction with the internuclear lines. The atoms thus bonded to the central carbon atom are called *ligand atoms*. The nonbonding electrons, e.g., the three pairs of nonbonding electrons in chloromethane or the lone pair in trimethylamine, give rise to additional regions of high electron density in the molecule.

The number of ligand atoms defines the *coordination number*. Carbon in its various stable combinations may exhibit coordination numbers varying from one to four. We shall discuss the geometry of bonding separately for each coordination number.

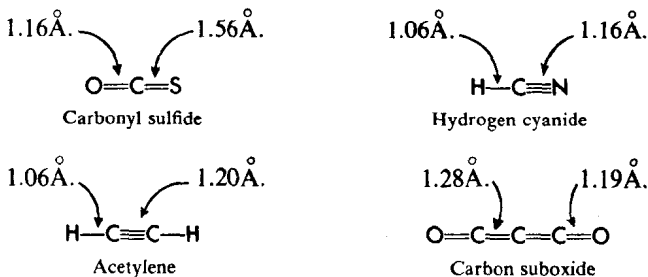
**COORDINATION NUMBER ONE** This coordination number is exhibited by cyanide ion and carbon monoxide. These molecules have conical symmetry and in that respect resemble hydrogen chloride.

**COORDINATION NUMBER TWO** In triatomic molecules—and carbon with a coordination number of two implies a minimum of three atoms in the molecule—our description of bonding geometry



must take into account two factors. First, the ligand atoms may be equivalent or they may be nonequivalent. Second, the molecular array may be linear or nonlinear. As it happens, the latter question rarely arises in practice, for stable compounds of carbon in which carbon exhibits a coordination number of two are linear. The angle between the bonds is  $180^\circ$ .

Carbon dioxide is a linear molecule in which the ligand atoms are equivalent and in which the bond lengths are equal ( $1.16\text{\AA}$ ). Carbonyl sulfide, hydrogen cyanide, and acetylene are linear molecules in which the ligand atoms are not equivalent and in which the two bond lengths of carbon must therefore be different. Carbon suboxide contains one carbon atom with two equivalent ligands and two carbon atoms with different ligands (see Formula I).



I

It may be noted that carbon dioxide, carbon suboxide, and acetylene have the cylindrical symmetry of hydrogen molecule, while hydrogen cyanide and carbonyl sulfide have the conical symmetry of hydrogen chloride.

**COORDINATION NUMBER THREE** Since four atoms need not lie in one plane, combinations of carbon with three ligand atoms raises for the first time the question of *nonplanarity*. However, with the exception of carbanions (and possibly radicals), in which the *unshared electrons* may be regarded as occupying an additional position on the coordination sphere, the most stable groupings containing carbon bonded to three atoms are planar, and our discussion is therefore considerably simplified.

Groupings of this type in which carbon is attached to three identical ligands (as in graphite) are quite exceptional. Other than carbonate ion, the only common members in this group of compounds are the carbonium ions  $R_3C^+$ , of which the methyl

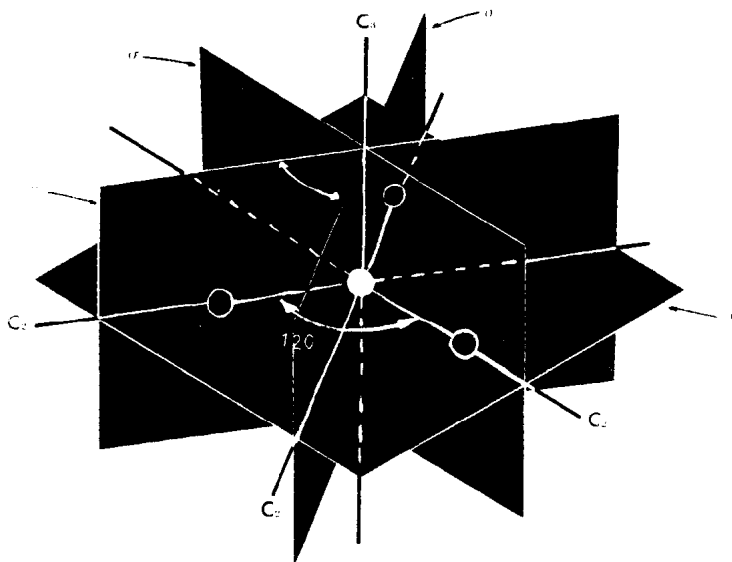


FIGURE 1-4

*Trigonal symmetry illustrated by methyl cation, showing the four  $\sigma$ -planes, the three  $C_2$  axes, the  $C_3$  axis, one of the three trigonal bond angles (heavy arrow), and one of the dihedral angles (light arrow). Black circle = carbon atom; open circle = hydrogen atom.*

cation ( $\text{CH}_3^+$ ) is the simplest representative. Methyl cation has *trigonal symmetry*, the chief attributes of which are summarized in Figure 1-4. The three ligands are completely equivalent in space and it is easily seen that the bond angles of such arrays must be  $120^\circ$ . However, in the vast majority of compounds containing tricoordinate carbon, the carbon atom is attached to nonequivalent ligands. Hence, the totality of the interactions of the three ligands (including nuclei, bonding, and nonbonding electrons) with each other no longer has regular trigonal symmetry (Figure 1-5). Because the distribution of electrons around the central carbon atom now does not have regular trigonal symmetry, the three bond angles cannot be  $120^\circ$ . In other words, even if the bond angles in such cases were experimentally found to be  $120^\circ$ , such an observation would merely indicate that the differences in the interactions of the three ligands are very slight, and therefore that the differences

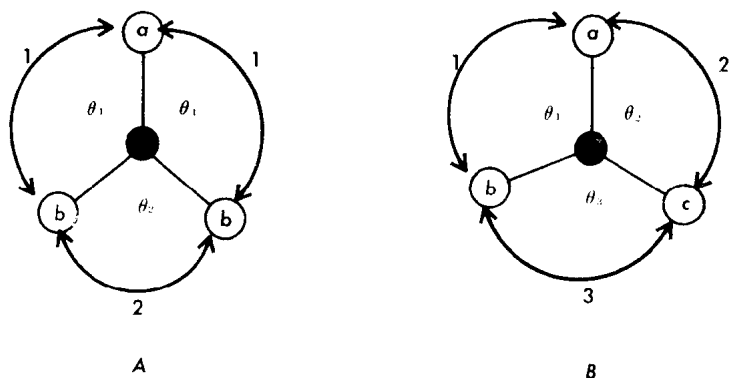
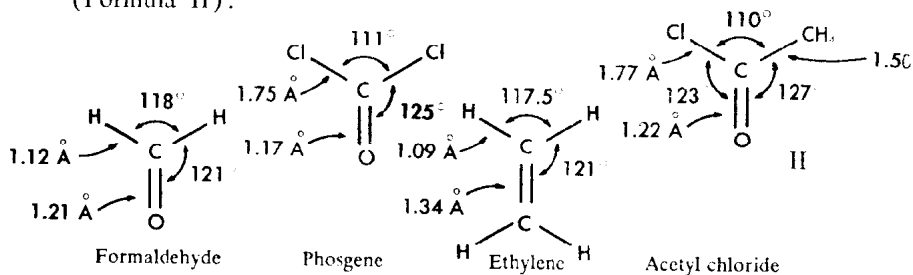


FIGURE 1-5

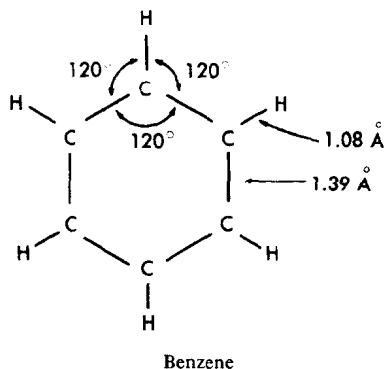
*Illustration of a symmetry argument. Numbered arrows indicate interaction of ligands a, b, and c attached to carbon (black circle). In A, two ligands (b) are equivalent and two of the interactions (labeled 1) and bond angles ( $\theta_1$ ) are therefore identical and different from the third (except in cases of  $D_{3h}$  symmetry). In B the three ligands are all non-equivalent and the three interactions and bond angles must therefore be different. All four atoms are in one plane.*

in the bond angles are extremely small. It cannot be doubted that such differences, though they might perhaps be too small to be observable with currently available measuring techniques, would nevertheless be finite and could in principle be detected by more sensitive devices.

Actually the differences in the bond angles are usually large enough to be detected, and a few examples can be adduced (Formula II):

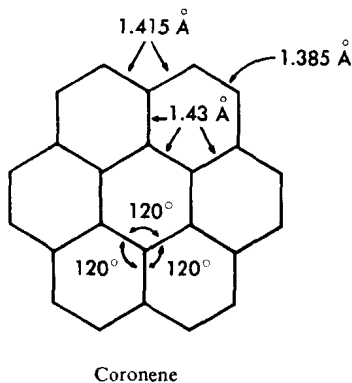


One exception to the generalization implicit in Figure 1-5A is the case of a molecule having  $D_{6h}$  symmetry (section 1-4), such as benzene (Formula III):



III

This planar array of twelve atoms has perfect hexagonal symmetry (i.e., it contains a  $C_6$  axis perpendicular to the plane of the paper which is also a  $\sigma$  plane) and *all* the bond angles are precisely  $120^\circ$ . Another example is the inner ring in coronene (Formula IV):

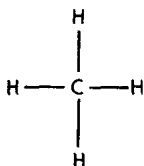


IV

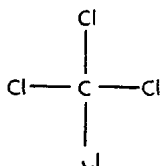
Symmetry arguments such as these are extremely useful in stereochemical discussions. It must be re-emphasized that the nature and magnitude of the electronic interactions are completely immaterial to the validity of such arguments and become important only when we attempt to predict or justify the direction and magnitude of the observed effects.

**COORDINATION NUMBER FOUR** Groupings of this type, in which carbon is attached to four ligands, are the ones most

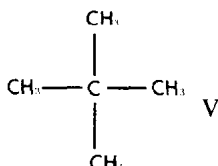
commonly encountered in organic chemistry. In diamond these ligands are identical. As shown by a great variety of physical measurements, the atoms attached to carbon in compounds of type  $CX_4$  are completely equivalent. Examples of such compounds are (Formula V):



Methane



Carbon tetrachloride



Neopentane (central carbon only)

Equivalence in three dimensions means that a molecule of the type  $CX_4$  has only one  $X-C-X$  angle and only one  $X-X$  internuclear distance. A square planar array of four  $X$  groups with a carbon atom at the center does not meet these specifications. It may be shown that equivalence in three dimensions signifies *regular tetrahedral symmetry*, an analysis of which is given in Figure 1-6. This figure shows a carbon atom, called the *tetrahedral carbon atom*, attached to four hydrogen atoms numbered 1 through 4. Inspection of the figure shows that there are four  $C_3$  axes, one for each of the  $C-H$  bonds. In this respect we are reminded of the case of ammonia (Figure 1-2C). Each of the four  $C_3$  axes in methane is the locus of intersection of three  $\sigma$  planes, so that one might expect a total of twelve planes: However, each of the  $\sigma$  planes contains two  $C_3$  axes, so that there are actually only six  $\sigma$  planes. These six planes may be ordered into the three pairs shown in Figure 1-6. In each pair the two planes are perpendicular to each other and they intersect to form a  $C_2$  axis. The three resulting  $C_2$  axes are mutually perpendicular, and they bisect the six tetrahedral angles.

The value of the regular tetrahedral angle is  $\arccos -\frac{1}{3}$ . Expressed in degrees, this is approximately  $109.5^\circ$ .

As soon as the ligands are no longer equivalent, the regular tetrahedral symmetry vanishes since the various interactions of the ligands around the central carbon are no longer identical. It follows that the bond angles can also no longer be  $109.5^\circ$ . The conclusion of this symmetry argument is borne out by numerous

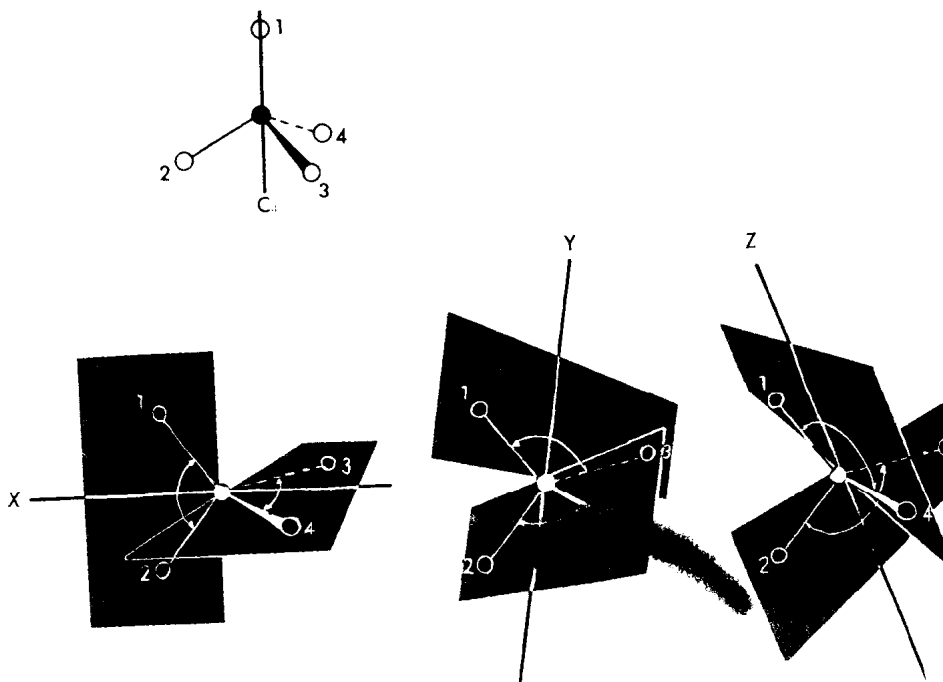
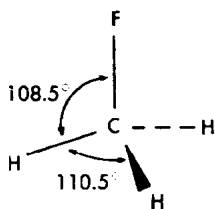


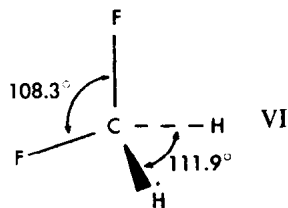
FIGURE 1-6

*Tetrahedral symmetry illustrated by methane, showing one of the four  $C_3$  axes, the six  $\sigma$  planes, the three mutually perpendicular  $C_2$  axes ( $x$ ,  $y$  and  $z$ ), and the six tetrahedral angles. Black circle = carbon atom; open circle = hydrogen atom.*

experimental observations. Two examples are given below (Formula VI):



Methyl fluoride



Methylene fluoride

Even in acyclic hydrocarbons, such as propane and *n*-butane, the C—C—C bond angle is approximately  $112^\circ$ , not  $109.5^\circ$ . *The*

*regular tetrahedral angle is therefore the exception rather than the rule in organic chemistry.*

### 1-3 Bonding Orbitals in Carbon Compounds

When atoms are brought together to form a molecule, the electrons and nuclei interact. The electronic distributions in the atoms (i.e., the atomic orbitals or AO's) are perturbed. We say that the AO's *overlap*. The charge density distribution in the localized bonding MO bears a relationship to the charge density distribution in the original AO's, and it is therefore customary to discuss the localized bonding MO with reference to the AO's which would result at infinite separation of the nuclei. For example, in the case of hydrogen molecule the bonding MO may be mathematically described in terms of the component hydrogen AO's.

A discussion of localized bonding orbitals in carbon compounds is rendered far more complex by the fact that carbon has four low-lying AO's which are available for bonding, whereas hydrogen has only one (i.e.,  $1s$ ). These four orbitals are the  $2s$  and the three  $2p$  orbitals. In its lowest energy state, the carbon atom has two electrons in the  $2s$  orbital and two electrons in the  $2p$  orbitals, so that the description of the electron configuration is  $1s^2 2s^2 p^2$ . A slightly higher energy state is described by  $1s^2 2sp^3$ , where one electron occupies each of the four AO's. Like all  $s$ -orbitals, the  $2s$ -orbital is spherically symmetrical and has its highest charge density at the nucleus. Each  $p$ -orbital, however, is cylindrically symmetrical, and the charge density at the nucleus is zero. The three  $p$ -orbitals differ only in direction in space and the three cylindrical axes define a Cartesian coordinate system ( $x$ ,  $y$ , and  $z$ ). The  $\sigma$  planes which are perpendicular to the cylindrical axes (i.e.,  $yz$ ,  $xz$ , and  $xy$ , respectively) define the regions of zero electron density and are the *nodal surfaces*. Figure 1-7A shows projected contour lines of equal electronic charge density for the  $2p_z$  AO. The three-dimensional contour surfaces may be developed by rotation around the  $C_x$  axis  $z$ . It is seen that the charge density is concentrated in the *lobes*, two separated distorted ellipsoids which float above and below the nodal  $xy$ -plane.

If these AO's were directly developed into bonding orbitals, tetra-coordinate carbon would have three equivalent bonds at right angles to each other, and a fourth nonequivalent bond. This does not correspond to any experimentally observed geometry of carbon

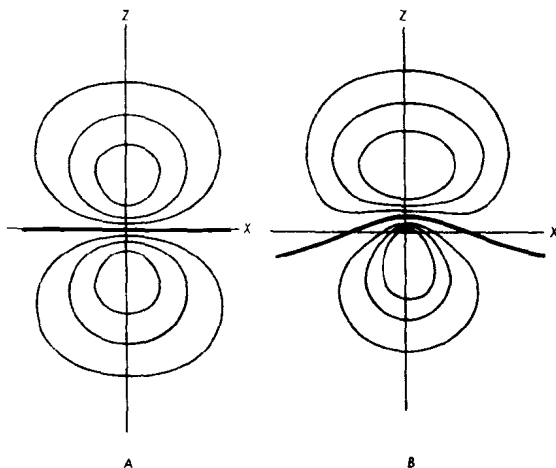


FIGURE 1-7

A, schematic representation of contours for the  $2p_z$  atomic orbital in the  $xz$  plane. The  $xy$  plane is the nodal surface (heavy line) and the nucleus is at the origin of the coordinate system. B, schematic representation of contours for a  $2(s + \lambda p)$  atomic orbital in the  $xz$  plane. The nodal surface (heavy line) is seen edgewise, and the nucleus is at the origin of the coordinate system.

bonding orbitals. It follows, therefore, that the wave function (i.e., the mathematical description of the motion and distribution of an electron in the field of the nucleus) of the bonding AO's must be different from the wave functions of the AO's of unbonded carbon.

This difficulty is overcome by a mathematical description of the bonding AO's as various linear combinations of the  $2s$  and  $2p$  AO's in carbon  $1s^2 2s^2 2p^2$ . The bonding orbital is now called a *hybrid orbital* and the process of linear combination is called "hybridization" or "mixing" of "contributing" AO's (LCAO). The AO's included in the LCAO are the  $2s$ -orbital, plus one, two, or three  $2p$ -orbitals. Each bonding AO may therefore be represented by  $s + \lambda_i p$ , where  $\lambda_i$  is the *mixing coefficient* or *hybridization parameter* for the  $i$ th bonding AO and is a measure of the extent to which the  $2p$  AO contributes to the hybrid AO. The condition which is imposed on  $\lambda_i$  is that (Eq. 1-1)

$$\sum_i \frac{1}{1 + \lambda_i^2} = 1 \quad (1-1)$$



The fraction  $1/(1 + \lambda_i^2)$  is the *s*-character of the *i*th bonding AO and the above equation simply states that the sum total of the fractional *s*-contributions of the individual hybrid AO's must add up to one *2s* AO. Similarly, the sum total of the fractional *p*-contributions of the individual hybrid AO's must add up to the number of *p*-orbitals mixed in (Eq. 1-2)

$$\sum_i \frac{\lambda_i^2}{1 + \lambda_i^2} = 1, 2, \text{ or } 3 \quad (1-2)$$

where  $\lambda_i^2/(1 + \lambda_i^2)$  is the *p*-character of the *i*th bonding AO.

Figure 1-7B shows projected contour lines of equal electronic charge density for a hybrid  $2(s + \lambda p)$  AO, where  $\lambda$  has generally some value between 1 and  $\sqrt{3}$ , though the value may fall outside these limits. The three-dimensional contour surfaces may be developed by rotation around the  $C_\infty$  axis *z*. The orbital has conical symmetry. It may be noted that the hybrid orbital betrays its parentage: Like the *2s* and unlike the *2p* orbital it has a finite charge density at the nucleus, but unlike the *2s* and like the *2p* orbital it has an open nodal surface. The nodal surface, however, is no longer planar and does not pass through the nucleus; instead it is roughly bell-shaped, and the charge density is concentrated in unequal lobes on either side of the nodal surface as schematically shown in cross section of Figure 1-7B. Again like the *2p* AO's, the  $2(s + \lambda p)$  AO's have directionality: This affords better overlap and makes for stronger bonds.

Since the *2s* orbital has its highest electron density at the nucleus whereas the *2p* orbital has zero electron density at the nucleus, it follows that the greater the *s*-character of the bonding AO, the greater will be the polarization of electrons toward the nucleus. This theoretical concept permits a number of correlations of physical properties, but to the student of stereochemistry the most important consequence of hybridization is the change of bond angle with *s*- or *p*-character. In the following highly simplified treatment, the approximation is made that the bonding orbitals are directed along the internuclear lines, i.e., are not bent away from them, and that each hybrid orbital is localized so that we may neglect interactions between adjacent bonds and bonded atoms. This approximation is in fact not always satisfactory. Nevertheless, for the present purposes we shall adhere to this simplification ex-