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Bent Chemical Bonds

Present theories and experimental results concerning electrons in some specific molecules are discussed.

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A scientist who claims to have evidence that a chemical bond is bent or straight has been dealing with one of the most elusive properties of a molecule, namely the location of electrons. This account of various ways of determining the electronic distribution in a molecule is accompanied by a critical look at the quoted results (*1*).

One commonly thinks of chemical bonds as being formed by bringing atoms sufficiently close together so that the individual atomic electron distributions rearrange and distribute themselves in a fashion that stabilizes an equilibrium configuration of the atomic nuclei. The determination of molecular structure, or the distances between these equilibrium configurations of nuclei, has comprised one of the major efforts in science during this century. The experimental techniques for determining molecular structure, a few of which are electron, x-ray, and neutron diffraction, infrared, Raman, and microwave spectroscopy, and others, are quite familiar and need not be elaborated on here. The important point is that very accurate molecular structures are generally determined by experimental methods, not by a priori calculations in molecular quantum mechanics.

On the other hand, the distribution of electrons in molecules is not so well known. There are very few experiments that can be done to obtain direct information on the electronic distribution. Some of these experiments will be described after a short description of the theoretical approach to electronic structure. This order of presentation is necessary in order to give an objective definition of the distribution of electrons in molecules and finally the definition of a bent bond. Theoretical approaches may be tentatively divided into the delocalized molecular orbital and the localized valence-bond methods. Both methods are equivalent if carried to completion (*2*) and yield the total description of the system in the form of the molecular eigenfunction Ψ. We are concerned here only with the ground molecular state.

Molecular Orbital Theory

One of the most promising treatments of molecular electronic structure is the Hartree-Fock self-consistent field method. In the Hartree-Fock treatment the total electronic wave function for an equilibrium distribution of nuclei is approximated as the antisymmetrized product of one-electron electronic orbitals, ψ_i. The antisymmetrized Hartree-Fock approximation to the true function, Ψ_{T}, can be written in the form of a determinant as

$$\Psi_{\mathrm{HF}} = \sqrt{\frac{1}{N!}} \left| \psi_1 (1)\, \bar{\psi}_1 (2)\, \psi_2 (3) \times \bar{\psi}_2 (4) \ldots \right| \qquad (1)$$

N is the number of electrons and the barred functions include the complex conjugate spin functions in correspondence to those included in the unbarred functions. The total Hamiltonian for the system is the usual sum of terms including the electronic kinetic energy, the potential energy of electrons in the field produced by the nuclei, and the interelectronic potential. If the Hamiltonian (H) describes an atom, ψ_i is an atomic orbital; and if the Hamiltonian describes a molecule, ψ_i is a molecular orbital. The total Hartree-Fock energy (E) is given by the solution to the Schrödinger equation.

$$H\, \Psi_{\mathrm{HF}} = E\, \Psi_{\mathrm{HF}} \qquad (2)$$

By application of the variation theorem (*3, 4*), however, Eq. 2 can be solved by solving a set of one-electron self-consistent field equations.

$$H_i\, \psi_i = \epsilon_i\, \psi_i \qquad (3)$$

Where H_i and ϵ_i are the one-electron self-consistent field Hamiltonian and energy, respectively, and ψ_i is the one-electron orbital that appears in the antisymmetrized Hartree-Fock product in Eq. 1. The one-electron self-consistent field Hamiltonian is a sum of three terms: (i) the kinetic energy of the i^{th} electron, (ii) the potential energy of the i^{th} electron in the field caused by the equilibrium configuration of nuclei (the internuclear separations can be obtained from molecular structure studies), and (iii) the potential energy of the i^{th} electron in the field caused by the average distribution of all the rest of the electrons (including the exchange potential). This third term in the Hamiltonian is the self-consistent field term and can be calculated if the eigenfunctions of all the other electrons are known. As the positions of the other electrons are not initially known their eigenfunctions are guessed and the average electronic field on the i^{th} electron can be calculated and substituted into the Hamiltonian in Eq. 3. The equation is then solved and ψ_i is obtained. Using ψ_i we can now compute the potential seen by the k^{th} electron due to the i^{th} electron. The remaining guessed functions are then used to compute the remaining potential, and Eq. 3 is solved for the k^{th} electron. The ψ_k from Eq. 3 will be different from that guessed in solving for ψ_i. Next ψ_i, ψ_k, and the other guessed functions are used to compute the third term in the Hamiltonian for the g^{th} electron and Eq. 3 is again solved for ψ_g. This process is obviously iterative and is continued until the func-

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tions $\psi_1, \psi_2, \ldots \psi_n$ remain unchanged or become self-consistent. The resulting functions are the Hartree-Fock self-consistent field functions which are the best nonrelativistic electronic functions which do not take direct account of the instantaneous electron-electron interactions. The difference between the Hartree-Fock energy in Eq. 2 and the true energy is called the correlation error and is due to the neglect of instantaneous electron-electron interactions. As the Hartree-Fock calculation does not yield the true energy there is some question concerning the accuracy of other observable quantities (such as dipole moment, electron density, and so forth) calculated from the Hartree-Fock functions. Presumably the Hartree-Fock value for the electron density is reliable (*4*) and that is the quantity of interest here. The true molecular wave function, ψ_T, could be obtained from the Hartree-Fock basis by adding corrections for electronic correlation such as configuration interaction (mixing of excited electronic states with the ground-state function) or alternatively direct interelectronic dependence could be included in the wave function.

The self-consistent field solution to Eq. 3 has been given for many atoms in either numerical or analytical form (*5*). Solution of Eq. 3 in the case of molecules is orders of magnitude more difficult because of the lack of spherical symmetry and it is necessary to express the molecular orbitals, ψ_j, as linear combinations of functions, ϕ_k, which form a complete set.

$$\psi_j = \sum_k a_{kj}\, \phi_k \tag{4}$$

Roothaan (*6*) has given a method of determining the coefficients, a_{kj}, in Eq. 4 to minimize the energy. In practice it is convenient to use a truncated set of one-electron molecular orbitals defined as

$$\psi'_j = \sum_m a_{mj}\, \phi_m \tag{5}$$

By using the truncated set ψ'_j, the total molecular function may be written in a manner similar to Eq. 1 with ψ'_j in place of the more accurate ψ_j; it is called the Roothaan function, Ψ_R. Thus the molecular function and the total molecular energy can be ranked in ascending order of truth as follows:

$$\left.\begin{array}{l} \Psi_R \rightarrow \Psi_{HF} \rightarrow \Psi_T \\ E_R \rightarrow E_{HF} \rightarrow E_T \end{array}\right\} \tag{6}$$

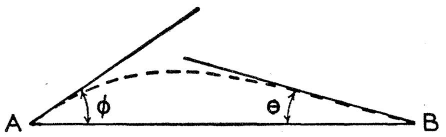

Fig. 1. Definition of a bent bond. The dotted line represents the line passing through the maximum electron density in the plane of the paper. The electron density function is given in Eq. 7. ϕ is the amount of bending observed from nucleus A, and θ is the amount of bending observed from nucleus B.

The important choice of a minimal basis set, ϕ_m in Eq. 5, such that ψ'_j is as nearly equal to ψ_j as possible has been discussed by Mulliken (*7*). The usual form of the ϕ_m are various forms of hydrogen-like (Slater-type) atomic orbitals at the various centers in the molecule. Thus the Hartree-Fock one-electron function, ψ_j, has been approximated by a linear combination of atomic orbitals at the different nuclear centers in the molecule with the coefficients in the expansion being determined by the Roothaan method (*6*). This choice of atomic orbitals as basis functions is quite natural as one would expect a considerable amount of atomic character remaining in molecules, at least for the inner-shell electrons. The outer-shell atomic electrons participate in the bonding and will occupy the region of space described by ψ'_j. The total electron density in the molecule is given in terms of Roothaan functions as

$$\rho_R = \int\int \ldots \int \left| \psi'_1(1)\, \bar{\psi}'_1(2)\, \psi'_2(3) \times \bar{\psi}'_2(4) \ldots \right|^2 d\tau_2 d\tau_3 \ldots d\tau_N \tag{7}$$

As ψ'_j approaches ψ_j the Roothaan density function will approach the true Hartree-Fock density function ρ_{HF}.

Similarly, if the true molecular wave function were available, the true electron density, ρ_T, could be obtained. The electron densities, or any other operator averaged over these molecular functions, can also be arranged in ascending order of truth as were the functions and energies in Eq. 6.

$$\rho_R \rightarrow \rho_{HF} \rightarrow \rho_T \tag{8}$$

The charge density in a molecule can now be used to define a straight and bent bond.

A bond line is defined, in a plane containing two nuclei, as the line connecting the two nuclei that passes through the maximum electron density. If the bond line traverses directly between the nuclei the bond is defined as straight. If the bond line deviates from the internuclear line the bond is bent with the angle of bending being that between the internuclear line and the tangent of the bond line at the nucleus (see Fig. 1). If the bond is cylindrically symmetric, as it must be for any linear molecule, any plane will define the bending. If the bond is not cylindrically symmetric the bond bending must be investigated three dimensionally.

Batoz, Daudel, Roux, and Allavena (*8*) have given plots of ρ for three diatomic molecules. The bond line calculated for H_2 lies on the internuclear line. The James-Coolidge (*9*) function, which includes direct interelectronic correlation and is undoubtedly the best molecular function available, was used for this calculation. ρ for N_2 was calculated with a Roothaan function. The electron distribution in N_2 shows that the maximum electron density does not lie along the internuclear line but surrounds the internuclear line in a cylindrical fashion. Hence, by the definition given above it appears that the N_2 bond is bent but completely symmetric about the internuclear line. The results for O_2 (*8*) calculated by a Roothaan function are similar to those of N_2. It is significant to note that in these three cases the ρ_R is just what would have been predicted by the classical Lewis (*10*) electronic structures. It is evident that the approximate Roothaan type molecular functions will lead to situations in which the maximum electron density will not lie along the internuclear line. A Roothaan function indicates that a molecule is made up of atoms which retain, to a large degree, their atomic shapes even in the near presence of each other. Whether the true molecular function would still reflect the atomic character of the atoms in molecules is a question which has not been answered because of the paucity of molecular wave functions.

Another interesting series of systems is the planar triatomic fragments included in molecules such as H_2O, H_2S, the halosubstituted methanes, silanes, and the small-ring carbon and carbon-oxygen molecules. These molecules have no necessary requirement of cylindrical symmetry along the bond axis. Again, true electron distributions of these molecules and fragments are not available at present. For nonlinear molecules the concept of a bent bond is difficult to define. If all bonds were completely localized a bent bond could be defined as the deviation from cylindrical bond symmetry which appears to be the common definition. This definition is consistent with that given in Fig. 1. Therefore, no change is necessary.

Valence Bond Theory

The observation that the Roothaan charge density, ρ_R, predicts that atoms remain as atoms in molecules is similar to what would be concluded from a description of chemical bonding with special reference to the localized valence bond method. In this scheme a molecule is formed from a combination of atoms in definite states. A definite state of an atom might be a hybridized (linear combination of atomic orbitals on the same center) state depending on the angular location of the bonding atoms.

Hybridization is usually defined by the angular dependence of the bonding atoms. Mulliken (*7*) has defined hybridization in terms of the perturbations arising from the bonding atoms, or more precisely as valence and coulomb polarization arising from the bonding atoms. The combination of atoms in definite states gives a perfect-pairing approximation of a molecule which assumes that each bonding atomic or hybrid orbital is localized and there is no interaction between the adjacent bonding atoms or bonds. This approximation is fairly accurate for symmetric molecules such as homonuclear diatomics but will be quite inaccurate for unsymmetrical molecules. The divergence of the perfect pairing of electrons can be accounted for by configuration interaction which essentially acknowledges bonding and nonbonding interactions between adjacent bonds and atoms. Eventually the valence-bond method will approach the true molecular wave function but the difficulties in achieving a valence-bond function with the same order of truth as a Hartree-Fock function are very great as shown in a calculation on the OH radical by Freeman (*11*). On the other hand a single-configuration valence-bond function (perfect-pairing approximation) can be written down relatively easily and results are obtained without the detailed programming and use of a digital computer, so essential to the Roothaan or Hartree-Fock schemes. For these reasons the single-configuration perfect-pairing valence bond approximation has been used quite extensively, and with considerable success in chemistry, to interpret experimental data such as bond lengths, bond angles, force constants, and others.

In assessing the order of truth in the perfect pairing approximation the calculated energies from the valence bond and self-consistent field methods in H_2 can be compared as shown by Coulson (*12*). The results show the importance of a proper choice in the set of atomic orbitals on each of the hydrogen atoms. In some cases the calculated valence bond perfect-pairing functions give an energy better than the self-consistent field calculation. Karplus and Anderson (*13*) have shown that the deviations from perfect pairing in the highly symmetric methane molecule are very small. As the complexity of a molecule increases and symmetry is lost, however, there is apt to be considerable deviation from the perfect-pairing approximation and the reliability of the electronic function will decrease. In general the perfect-pairing function will lie even with or to the left of Ψ_{HF} in order of truth (see Eq. 6).

Evidence for and against

Coulson and Moffitt (*14*) have used the perfect-pairing approximation to describe the bonding in highly strained small-ring hydrocarbons. The perfect-pairing functions are constructed from sp^3 hybrid functions on the carbon atoms and s functions on the hydrogen atoms. It is well known that certain angular constraints are imposed on sp^3 hybrids if the requirement that each hybrid is orthonormal (localized) is adhered to. The following pairs of equivalent orthonormal hybrid sp^3 orbitals (f) are constructed from Fig. 2.

$$\left.\begin{array}{ll}
\begin{array}{l} xy \\ \text{plane} \end{array} & \left\{\begin{array}{l} f_1 = as + bp_x + cp_y \\ f_2 = as + bp_x - cp_y \end{array}\right. \\
\begin{array}{l} xz \\ \text{plane} \end{array} & \left\{\begin{array}{ll} f_3 = a's - b'p_x & + dp_z \\ f_4 = a's - b'p_x & - dp_z \end{array}\right. \\
\cos\theta_{12} & = \dfrac{a^2}{a^2 - 1} \\
\cos\theta_{34} & = \dfrac{-(a')^2}{1-(a')^2} = \dfrac{a^2 - \frac{1}{2}}{\frac{1}{2} + a^2}
\end{array}\right\} \quad (9)$$

The angles θ_{12} and θ_{34} between the hybrid pairs f_1–f_2 and f_3–f_4 are obtained from the orthonormal character of the hybrids. It is clear from Eq. 9 that both angles between the equivalent orbitals in Fig. 2 are determined by assigning the s character (the s character is the square of the coefficients a or a') in any *one* of the bonds. The results

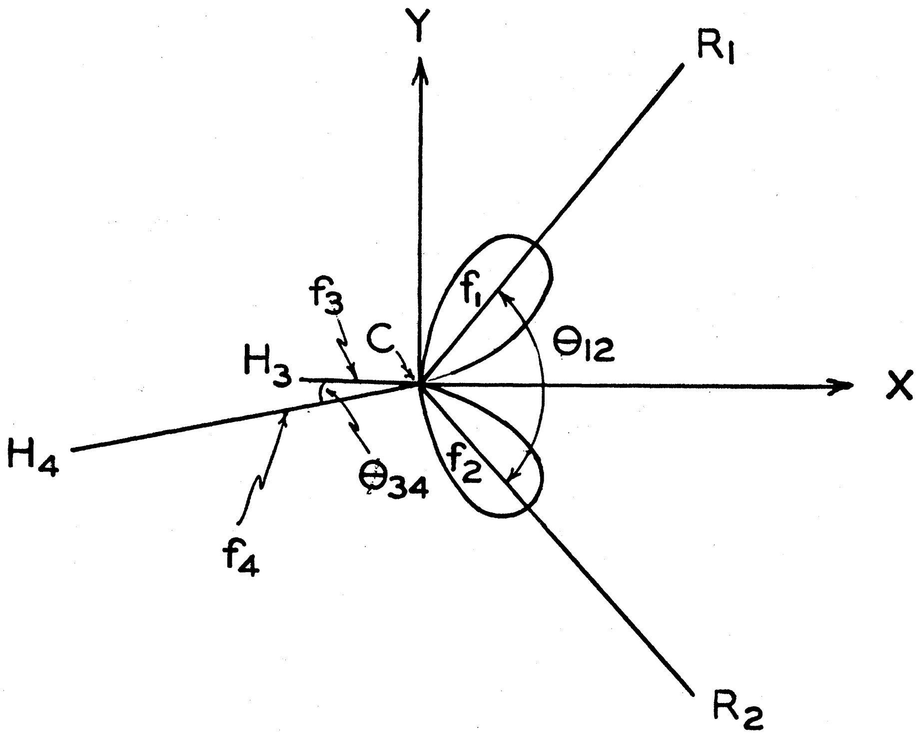

Fig. 2. sp^3 orthonormal hybrid orbitals. R_1, C, and R_2 are in the xy plane and H_1, H_2, and C are in the zx plane. The sp^3 hybrid orbitals are given in the text. The hybrid orbitals are directed toward the bonding atoms.

Table 1. Values of the angles θ_{12} and θ_{34} in Fig. 1 for various values of *s* character in the sp^3 hybrids (see Eq. 9); a = 0.500 in the case of tetrahedral hybrids.

a	θ_{12}	θ_{34}
0.300	95°40′	134°1′
.400	101°1′	121°0′
.500	109°28′	109°28′
.600	124°16′	99°23′
.700	163°44′	90°35′

for various values of a (Table 1) show that as the *s* character in a hybrid increases, the angle between its equivalent-partner orbital increases with a resultant decrease in the angle between the other two equivalent orbitals. Coulson and Moffitt determined the coefficients in Eq. 9 for the carbon hybrid orbitals in strained hydrocarbon rings by minimizing the energy in the valence bonds formed from the four hybrids. If the carbon-hydrogen (C-H) bonds are not bent, their results indicate that the carbon-carbon hybrid bonds are bent away from the internuclear line. In cyclopropane for instance the angle of bending (Fig. 1) is 22°. Recognizing that a perfect-pairing approximation in molecules like cyclopropane is not justified, Coulson and Moffitt then attempted to calculate the energy contributions from the remaining combinations of valence states. In other words their model is essentially a forced localized sigma-bonding skeleton of bent bonds with a delocalized segment of electrons not associated with any single atom in the molecule. Coulson and Moffitt then show that the energy loss in a bent carbon-carbon (C-C) bond compared to a straight C-C bond cannot be made up by the remaining delocalization and hence conclude that the strain energy is attributable to bent bonds (*15*).

Walsh (*16*) has explained the bonding in cyclopropane by bringing together three ethylenic ($H_2C=$) links to form the molecule. This model is completely delocalized and explains a reasonable amount of experimental data. In comparing their work on cyclopropane with that of Walsh, Coulson and Moffitt say, ". . . that the description of the molecule's C-C bonds as 'bent' is much more simple and richer intuitively than is Walsh's more complicated symbolism; and much less liable to lead to misunderstandings."

More recently Handler and Anderson (*17*) have discussed cyclopropane and have suggested nonorthogonal carbon hybrids which are directed toward each other. This acknowledges at the onset the delocalized character of the bonding but no quantitative calculations were made.

Table 2. Bond angles for the halogen-substituted methanes. Figures in parentheses in column 1 are reference citations.

Molecule	Angle		
	HCH	XCH	XCX
CH_4	109°28′		
CH_3F (*38*)	110°26′	108°27′	
CH_2F_2 (*39*)	111°52′		108°17′
CHF_3 (*39*)		110°7′	108°48′
CF_4 (*39*)	109°28′		
CH_3Cl (*38*)	110°51′	108°00′	
CH_2Cl_2 (*39*)	112°58′		111°47′
$CHCl_3$ (*39*)		108°33′	110°24′
CCl_4 (*39*)	109°28′		
CH_3Br (*38*)	111°36′	107°14′	
CH_2Br_2 (*39*)			112 ± 2°
$CHBr_3$ (*39*)		108°12′	110°48′
CBr_4 (*39*)	109°28′		
CH_3I (*38*)	111°47′	106°58′	
CH_2I_2 (*39*)			114 ± 2°
CHI_3 (*39*)			(113°)
CI_4 (*39*)	109°28′		

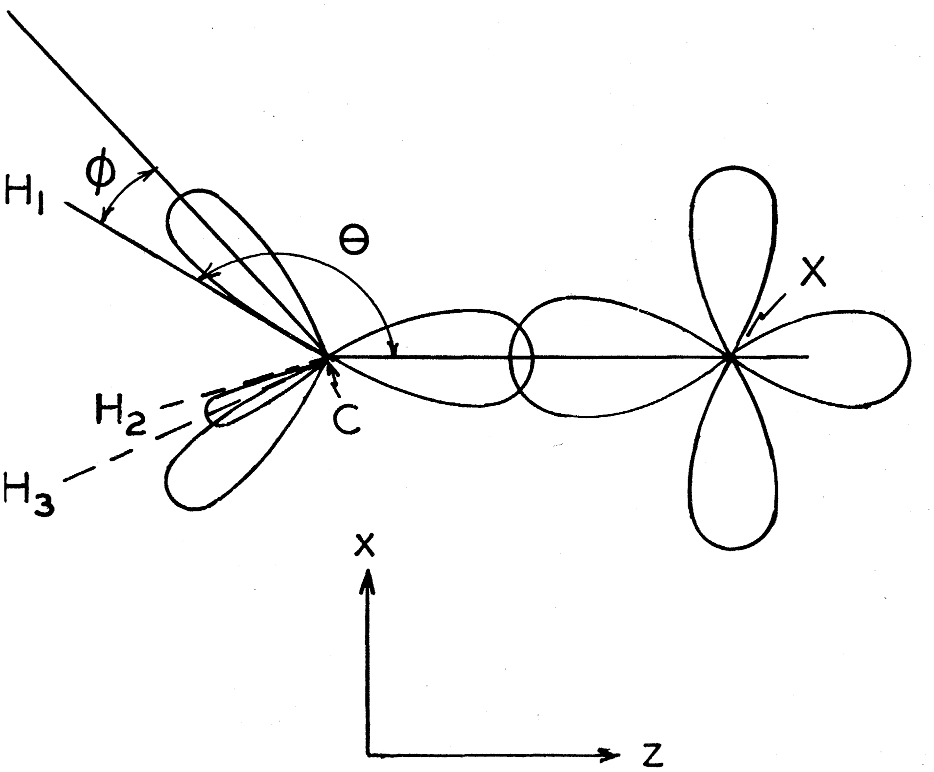

Fig. 3. Muller and Pritchard's view of bent bonds in CH_3X where X is a halogen atom. X and H_1 are in the zx plane and y is out of the plane of the paper. θ is given in Table 2 and ϕ is the angle of bending calculated to be 4 or 5 degrees. The hybrids directed near the three hydrogens are equivalent.

The concept of bent bonds was employed by Moffitt (*18*) in a discussion of the strain energy in the tetrahedral P_4 molecule. Only the orthonormal *p* atomic orbitals in phosphorus were used in the bonding. Pauling and Simonetta (*19*) have also discussed the bonding in P_4 postulating bent bonds formed from promoted *spd* hybrid orbitals. The strain energy was reduced by postulating the *spd* hybrids which require less bond bending.

Another interesting molecule whose bonding has been discussed at great length is H_2O. One connected series of works, from different laboratories, begins with a Roothaan calculation on H_2O by Ellison and Shull (*20*). Burnelle and Coulson (*21*) transform the molecular orbitals of Ellison and Shull to localized equivalent orthogonal bond orbitals (*22*) and they conclude that the oxygen 2*s* and 2*p* hybrid orbitals are bent away from the O-H internuclear line. The requirements of orthogonality in the two O-H bonds seem rather stringent here. McWeeny and Ohno (*23*) have also used the integrals of Ellison and Shull to study the bonding in H_2O by both the Roothaan method and a localized bond-orbital method. In their localized bond-orbital method they have attempted to analyze the 2*s* and 2*p* hybrids. They indicate the bond might be bent but in the absence of more elaborate configuration interaction calculations, which they were unable to do, they say that ". . . it is impossible to give any convincing analysis of the angular reorganization of the electron distribution." Even if they would have found a bent bond, recent discussion by Slater (*24*) indicates that the integrals of Ellison and Shull (*22*) were in error and the results, therefore, have only qualitative significance. The recent work of Merrifield (*25*) on the water molecule may ultimately decide the question.

Another series of molecules for which claims of bent bonds have been made are the halogen-substituted methanes. Table 2 lists the known bond angles in the substituted methanes (*26*). The major body of knowledge of the electronic structure of the substituted methanes centers about the interpretation of nuclear-spin coupling constants as determined by high resolution nuclear magnetic resonance and the interpretation of nuclear quadrupole coupling constants as observed in high-resolution microwave spectroscopy and pure nuclear quadrupole spectroscopy. Only molecules having zero electron spin are considered here.

Nuclear Spin Coupling Constants

The energy levels of a magnetic nucleus in an external magnetic field may be perturbed because of the magnetic field of another magnetic nucleus. The perturbation will be a function of the magnetic moments and spins of the two nuclei and the electronic distribution between them. The perturbations are observed as splittings in nuclear magnetic resonance spectroscopy and if the nuclear properties are known the electronic distribution can be inferred. Shoolery (*27*) and Muller and Pritchard (*28*) have obtained empirical evidence that the carbon-13-proton coupling constant, J_{CH}, is dependent on the s character of the carbon-hybrid orbital and is relatively independent of the polarity of the bond. On the basis of J_{CH}, and resultant hybrid-s character, in the substituted methanes, Muller and Pritchard have suggested that the C-H bonds in the CH_3X (where X is halogen) molecules are bent away from the internuclear line by 4 or 5 degrees as shown in Fig. 3. Their conclusion is based upon the approximation of perfect-pairing and the orthonormal character of the carbon hybrid orbitals as in Eq. 9.

A quantitative valence-bond calculation exhibiting the limited independence of J_{CH} on the bond polarity and its definite dependence on the s character of the hybrid has been given by Juan and Gutowsky (*29*). Continuing, Juan and Gutowsky have assumed that Eq. 9 is valid and present a self-consistent theory of obtaining the amount of s character in the carbon hybrid directed toward various bonding atoms, including the halogens. From their values for the s character an alternate view of the bonding in the CH_3X molecules can be presented. Consider the three equivalent orthonormal carbon hybrids that are bonding with the hydrogen atoms. The values given by Juan and Gutowsky for the s character of these orbitals gives for CH_3Cl ($a^2 = 0.300$):

$$\left.\begin{aligned} f_1 &= 0.548s - 0.279p_z + 0.790p_x \\ f_2 &= 0.548s - 0.279p_z - 0.395p_x \\ &\qquad - 0.683p_y \\ f_3 &= 0.548s - 0.279p_z - 0.395p_x \\ &\qquad + 0.683p_y \end{aligned}\right\} \quad (10)$$

The angle between these equivalent orbitals for CH_3Cl is 112°13′ and the angle between any of the C-H hybrids and the C-Cl internuclear line is 106°28′. The experimental values given in Table 2 are 110°51′ and 108°0′, respectively. Similar calculations were performed for X = F, Br, and I and the results are summarized in Table 3. The results indicate that the differences between the hybrid orbital angles and the observed bond angles are less than 2 degrees. The use of Juan and Gutowsky's value of the s character of the C-Cl hybrid in CH_3Cl gives (the hybrid must lie on the symmetry axis pointed toward the Cl atom)

$$f_{Cl} = 0.317s + 0.949p_z \qquad (11)$$

As the C-H hybrids in Eq. 10 are orthonormal the integrated product of any function with itself is unity and the integrated product of any function with any of its equivalent partners is zero. The integrated product of f_{Cl} with any of the C-H hybrids is not zero, however, yielding a number equal to 0.090 which is called the overlap between the two functions. The overlap gives some indication of the nonlocalized character of the bonding. The only way of decreasing the overlap between the C-Cl and the C-H sp^3 hybrids is to force the CH hybrids away from the C-H internuclear line as in Fig. 3. This is the same result as obtained with H_2O where the bond-bending phenomenon appeared to result from the forced localization of electrons into orthogonal hybrids. Pauling (*30*) has suggested that it might be appropriate to add a reasonable amount of d_z character into Eq. 11. A reasonable amount of d_z character for a C-Cl hybrid along a z-axis was determined to be 3 percent which decreases slightly the overlap between the C-H hybrids in Eq. 10. Indeed, 51 percent d character was necessary to decrease the overlap to zero which seems, in view of the high promotional energy, to be unreasonable (*31*). Similar considerations on the other substituted methanes will be deferred until the next section.

Quadrupole Coupling Constants

A nucleus having a permanent electric quadrupole moment (a few of which are N, Cl, Br, I, and deuterium but not carbon) may interact with the molecular electronic charge distribution resulting in a small perturbation of nuclear energy levels. The magnitude of the perturbation will depend upon the spin and quadrupole moment of the nucleus and the molecular-charge distribution. The spacings between the perturbed nuclear-energy levels are either observed directly by pure nuclear quadrupole resonance spectroscopy or indirectly as a perturbation on rotational energy levels by high resolution microwave spectroscopy. Thus, if the nuclear properties are known the electronic distribution can be inferred. The electronic contribution to the coupling constant is proportional to the second derivative of the electric potential, at

Table 3. Calculated angles between the CH hybrid orbitals in CH_3X where X equals F, Cl, Br, and I; and the calculated angles between the CH hybrids and the threefold axis of symmetry in the molecule. Also given are the experimental bond angles.

Molecule	a^2 (*29*)	Angle			
		Between C-H hybrids (calcd)	HCH exptl.	Between C-H hybrid and axis of symmetry (calcd)	HCX exptl.
CH_3F	0.298	112°5′	110°26′	106°40′	108°27′
CH_3Cl	.300	112°13′	110°51′	106°28′	108°0′
CH_3Br	.304	112°24′	111°36′	106°15′	107°14′
CH_3I	.302	112°20′	111°47′	106°13′	106°58′

the nucleus, resulting from all the electrons in the molecule. In analyzing the value of the second derivative of the electric potential, Townes and Dailey (*32*) find it to be mainly dependent on the valence *p* electrons of the atom with the quadrupolar nucleus. In addition, when an atom having a quadrupolar nucleus bonds with another atom the coupling constant is dependent on the bond polarity and the hybridization of the atomic orbitals (*32*). If the bond polarity is known the hybridization can be obtained. Attempts have been made to use semiempirical schemes of ionic character and electronegativities to adjust the relative bond polarities and hybridization ratios in molecules; the most notable, other than that of Townes and Dailey, is the work of Gordy (*33*). This dilemma of not being able to adjust all the parameters directly from experimental measurements might be compared to the analysis of J_{CH} in nuclear magnetic resonance in which the coupling constant was insensitive to the bond polarity. In conclusion, it appears that an analysis of the hybrids projecting from the nitrogen atom in NH_3, for example, from the quadrupole coupling constant data would be unreliable because of the uncertainty in the polarity of the N-H bond.

On the other hand the orientation of the valence-bond structure of an atom in a molecule, with respect to some molecular axis, can be determined quite accurately from quadrupole coupling constants. The orientation is independent of the degree of polarity and hybridization. In the case of symmetric top molecules such as CH_3Cl in Fig. 3 the half filled $3p_z$ orbital in Cl will be directed toward the central carbon atom. A small amount of *s* character on Cl has been included in Fig. 3 which increases the valence structure on the bonding side. The filled $3p_x$ and $3p_y$ Cl orbitals are in a plane perpendicular to the C-Cl bond and would preserve axial symmetry along the C-Cl bond in the absence of interaction with the CH_3 group. In the presence of $Cl\text{-}CH_3$ interactions the Cl electrons in a plane perpendicular to the *z*-axis must be symmetric to rotations of 120° about the *z*-axis. If the coupling constants at X are calculated in the *xyz*-axis system in Fig. 3, three nonzero components are found and are called χ_{zz}, χ_{xx}, and χ_{yy}. The three nonzero terms are not independent, however, and are related by

$$\chi_{zz} = -2\,\chi_{xx} = -2\,\chi_{yy} \qquad (12)$$

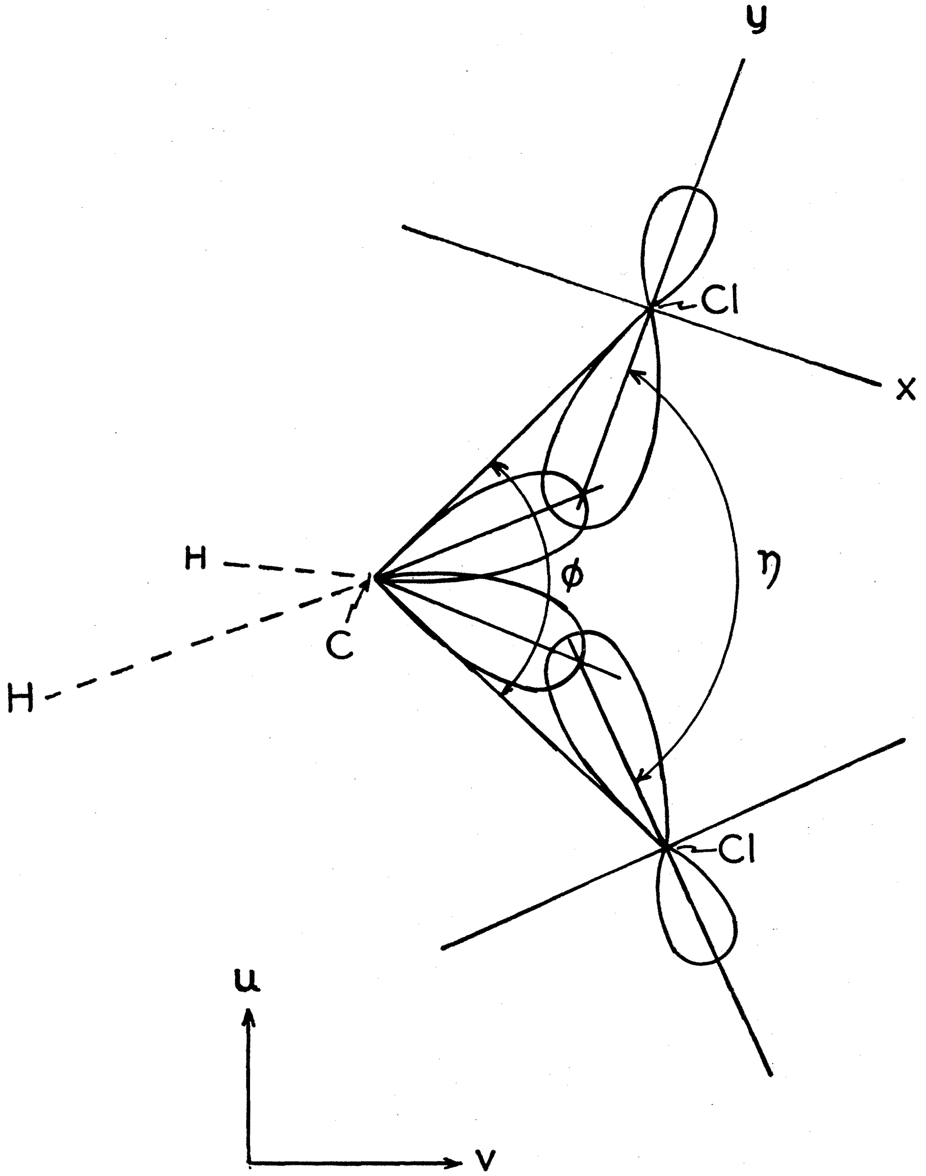

Fig. 4. Possible bent bond structure of methylene chloride if the C-H bonds are not bent. ϕ is the observed internuclear angle equal to 111°47′. η is the angle between the valence bond projections of the chlorine atoms. Experimentally η was identical to ϕ within an experimental error of one degree. The molecular principal axis system is labeled by *uv* and the quadruple principal axis system by *xy*. The Cl and C atoms are in the plane of the paper.

If a new axis system *uvw* were chosen in which no new axis were parallel to any of the original *xyz*-axes the quadrupole coupling constants could also be calculated in the *uvw*-axis system. The results show that in the new axis system the cross terms (χ_{uv}, χ_{uw}, and so forth) are not zero as in the *xyz*-axis system. These new χ components are conveniently written in matrix form as

$$\begin{pmatrix} \chi_{uu} & \chi_{uv} & \chi_{uw} \\ \chi_{vu} & \chi_{vv} & \chi_{vw} \\ \chi_{wu} & \chi_{wv} & \chi_{ww} \end{pmatrix} \qquad (13)$$

The coupling constant elements calculated in the *uvw*-axis system are related to those in the *xyz*-axis system by a mere rotation of coordinates *uvw* into *xyz*. This transformation is written as

$$T^{-1}\begin{pmatrix} \chi_{uu} & \chi_{uv} & \chi_{uw} \\ \chi_{vu} & \chi_{vv} & \chi_{vw} \\ \chi_{wu} & \chi_{wv} & \chi_{ww} \end{pmatrix} T = \begin{pmatrix} \chi_{xx} & 0 & 0 \\ 0 & \chi_{yy} & 0 \\ 0 & 0 & \chi_{zz} \end{pmatrix} (14)$$

where T^{-1} and T are matrices effecting the transformation. It is clear from these considerations that the coupling-constant matrix is diagonal in the axis system used to describe the valence state of the atom, called the quadrupole principal axis system, and is not necessarily diagonal in any other axis system. Measurements made in pure rotational spectroscopy are referred to an axis system embedded in the molecular

Table 4. Molecules where the orientation of the valence orbital in Cl was found to lie on the internuclear line. Only data where direct measurements were made are included. This excludes data where axial bond symmetry was an assumption.

Molecule	References	Experimental error (degrees)
CH_2CHCl	(*40*)	5.00
$C_3H_4Cl_2$	(*41*)	.25
$CHClCHF$	(*42*)	.33
CH_2Cl_2	(*36*)	1.00

geometry called the molecular principal-axis system. In the case of CH_3X the molecular principal axes coincide with the quadrupole principal axes so that any measurement of the quadrupole coupling in rotational spectroscopy gives the diagonal elements χ_{xx}, χ_{yy}, and χ_{zz} directly in Eq. 14.

In less symmetric molecules, however, the two axis systems do not coincide and any measurement of quadrupole coupling constants from rotational perturbations will give χ elements in the molecular principal axis system. Consider CH_2Cl_2, in Fig. 4. As both the H-C-H and Cl-C-Cl angles in Table 2 are larger than tetrahedral there is a good possibility that there are bent bonds in this molecule (see Eq. 9). It seems reasonable to start by assuming the C-H bonds are not bent; this requires the C-Cl bonds to be bent as shown in Fig. 4. Mulliken (*34*) has discussed the apparent small H-H interactions in H_2O and NH_3-type molecules as well as the halogen substituted methanes where Simanouti (*35*) studied the normal vibrations and found very little H-H repulsion but quite strong H-R and R-R repulsions. Flygare and Gwinn (*36*) have studied the nuclear quadrupole interaction in CH_2Cl_2 and have obtained all nonzero quadrupole coupling constants in the molecular principal-axis system (*uvw* in Eq. 13). The simple geometric transformation, in Eq. 14, to the quadrupole principal axis system gives the angle η in Fig. 4 between the Cl valence orbitals. The angle between the Cl valence orbitals and the measured Cl-C-Cl angle were identical within an experimental error of one degree. Thus, if the C hybrid orbital is directed toward the Cl valence orbital the C-Cl bond is not bent. There have been no molecules where the valence structure of a bonding atom deviated from the internuclear line as deduced from quadrupole coupling constants. Other molecules for which the orientation of the valence structure of bonding atoms is known are listed in Table 4. This gives strong evidence that the C-Cl bonds in these molecules are not bent. If the C-Cl bond in CH_2Cl_2 is not bent the C-H orthonormal hybrids must be bent such that the C-H interhybrid angle is less than tetrahedral. This conclusion is just the opposite of that obtained from the nuclear magnetic resonance data.

No consistent set of reasonable carbon orthonormal hybrids can be constructed to explain the above data in CH_2Cl_2. Attempts to force localization into the bonds by including H-H, H-Cl, and Cl-Cl interactions have also failed.

Conclusion

The obvious and not original conclusion is that the results obtained from considerations of sp^3 hybridization in the substituted methanes breaks down as soon as all of the bonding atoms are not equivalent. Indeed, the concept of sp^3 localized carbon hybrids may be invalid even for tetrahedral molecules like CCl_4 where the result of tetrahedral angles may be inferred from a naive hard sphere model. In other words the electrons in CCl_4 have a more delocalized molecular quality than the apparently more localized atomic quality in CH_4. This result implies that perhaps a Hartree-Fock treatment of the outer valence electrons in the substituted methanes (frozen inner atomic shells) might give a fairly good description of the electron distribution. On the other hand, the valence bond method would have to be carried well past the convenient approximation of perfect pairing. McWeeny and Ohno (*23*) were quite optimistic about the frozen inner atomic shell approximation in their treatment of H_2O. As far as the strained small-ring compounds it appears the bending of a bond is a function of where one decides to draw the line between localized and delocalized character. Finally, no more appropriate ending could be contrived than a classic quote by Professor R. S. Mulliken (*37*), "I believe the chemical bond is not so simple as some people seem to think."

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