AN APPRAISAL OF VALENCE-BOND STRUCTURES AND HYBRIDIZATION IN COMPOUNDS OF THE FIRST-ROW ELEMENTS

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I. INTRODUCTION: SCOPE, METHODS, AND LIMITATIONS

Orbital hybridization is well known to have a marked effect on bond angles. One may ask, Is this the only molecular property affected by hybridization? *A priori*, should not one expect changes in orbital hybridization ratios to affect also such properties as bond moments, bond force constants, bond dissociation energies, and bond lengths? The purpose of this review is twofold: to consider the experimental evidence bearing on this question, and to review recent attempts to correlate properties of covalent molecules with Lewis octet structures.

Mathematical theories of molecular structure (317), excited states, metals (6), ionic compounds, sterically hindered compounds, and compounds in which *d* orbitals play a prominent role, are not considered, other than incidentally, in this review.

The discussion in this review is by turns descriptive, empirical, inductive, deductive, and analytic. The terminology of *s–p* hybridization and the shapes of molecules that satisfy the octet rule are introduced descriptively in Sections II and III. A catalogue of electronic structures is developed in Sections III and IV. The effects of (*i*) hybridization on molecular properties (Sections III, IV, and V) and of (*ii*) electronegative substituents on molecular properties (Section VI,A) are reviewed next from a purely empirical point of view. From the combination of (*i*) with (*ii*), a rule is formulated to describe the effect of electronegative substituents on atom hybridization (Section VI,B), and for the rule, a model (Section VI,C). In Section VII, this model is applied to several problems of current chemical interest. The octet rule and electron deficiency are discussed analytically in Section VIII.

This review attempts to cover the literature through March, 1960.

II. HYBRID ORBITALS ($\sigma-\pi$ DESCRIPTION)

A. TERMINOLOGY

Frequent use will be made of the phase "*s* character" or "*s* content." By this will be meant the following (59, 62, 205, 217, 236): For atoms that satisfy the octet rule, and it is with such atoms (e.g., carbon, nitrogen, oxygen, fluorine) that this review is primarily concerned, the four valence-shell orbitals of an atom may be thought of as compounded from one spherically symmetrical 2*s* atomic orbital and three mutually perpendicular dumbbell-shaped 2*p* orbitals, designated $2p_x$, $2p_y$, $2p_z$ (*x*, *y*, *z* indicate mutually orthogonal axes). The 2*s* orbital is lower in energy than the 2*p* orbital; hence the ground state of a carbon atom, for example, is written $1s^22s^22p^2$ (not $1s^2, 2s\,2p^3$). However, in a molecule such as methane, which is known to have the shape of a regular tetrahedron, the 2*s* orbital of carbon may be considered to mix (or "hybridize") with the three 2*p* orbitals to form four equivalent orbitals that point to the corners of a regular tetrahedron and make angles with each other of 109°28′. These are called hybrid orbitals. Each contains one-quarter *s* character and three-quarters *p* character, abbreviated $s^{1/4}p^{3/4}$, or sp^3, or *te* (for tetrahedral) (223). In ethylene, on the other hand, the 2*s* orbital of carbon may be considered to mix with but two of the three 2*p* orbitals to form three equivalent hybrid orbitals that lie in a plane and make angles with each other of 120°; these three hybrids, which contain 33 per cent *s* character, are abbreviated $s^{1/3}p^{2/3}$, or sp^2, or *tr* (for trigonal); perpendicular to the plane of these three orbitals is the axis of cylindrical symmetry of the remaining pure 2*p* orbital. The geometry of acetylene is often explained by assuming that the carbon 2*s* orbital mixes with but one of the three 2*p* orbitals, forming two *di* (for digonal) hybrids that point in diametrically opposed directions; these are abbreviated $s^{1/2}p^{1/2}$ or *sp*. This manner of discussing orbital hybridization is summarized in table 1.

TABLE 1

σ–π description of s–p hybridization

Orbital Designation	Number of Hybrid Orbitals	Abbreviations	Per Cent *s* Character in Hybrid Orbitals	Inter-orbital Angle	Number of Pure 2*p* Orbitals Remaining
Tetrahedral . .	4	*te* $s^{1/4}p^{3/4}$ sp^3	25	109°28′	0
Trigonal.	3	*tr* $s^{1/3}p^{2/3}$ sp^2	33	120°	1
Digonal.	2	*di* $s^{1/2}p^{1/2}$ sp	50	180°	2

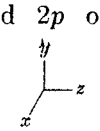
The term σ orbital refers to a hybrid orbital. The unhybridized 2*p* orbitals (in number 0, 1, and 2 for tetrahedral, trigonal, and digonal hybridization, respectively) are termed π orbitals.

Examination of table 1 reveals a useful fact. As the *s* character in two equivalent hybrid orbitals increases (*te* to *tr* to *di*), the interorbital angle increases. Conversely, a relatively large (small) angle between equivalent hybrid orbitals implies that the *s* content of the orbitals is relatively large (small). If the two orbitals in question overlap orbitals from adjacent atoms, forming thereby chemical bonds, and if these bonds are not highly strained, as are those in cyclopropane (since the smallest possible interorbital angle for *s–p* hybrids is 90°), it is probably reasonable to assume as a first approximation that the orbitals point toward the bonded atoms. Molecular geometry provides then a direct clue to interorbital angles and (table 1) the distribution of *s* character. For example, from the bond angles in ammonia (106°46′) (284) and water (104°27′) (134, 284), it is inferred that the nitrogen atom of NH_3 devotes slightly more *s* character to its bonding orbitals than does the oxygen atom of H_2O.

B. VALENCE-BOND NOTATION

The traditional notation of valence-bond theory provides a concise summary of the main features of the distribution of atomic *s* character in molecules. For atoms that satisfy the octet rule, four major structural types may be distinguished. The atom may be chemically bound by (*1*) single bonds only, (*2*) a double bond, (*3*) two double bonds, or (*4*) a triple bond. These four possibilities are shown in figure 1.

In figure 1, X represents an atom that satisfies the octet rule (e.g., carbon, nitrogen, oxygen, fluorine) and dots represent electrons unshared *or* in single bonds. The abbreviation *te* after a pair of electrons (structure 1) indicates that the orbital occupied by the pair is, to a first approximation, a tetrahedral hybrid (25 per cent *s* character); *tr* (structure 2) indicates an approximately trigonal hybrid (33 per cent *s* character); *di* (structures 3 and 4) indicates an approximately digonal hybrid (50 per cent *s* character) (223). The *te* hybrid orbitals of structure 1 point to the corners of a regular tetrahedron. The *tr* hybrid orbitals in structure 2 lie on a plane. If it is chosen to call this plane, the plane of the paper, the *yz*-plane, with, say, the *z*-axis horizontal and the *y*-axis vertical, and the axis perpendicular to this plane is called the *x*-axis, the lone, unhybridized 2*p* orbital in structure 2,



indicated $2p_x$, points along the *x*-axis. In structures 3 and 4 the colinear *di* hybrids have been hybridized from the 2*s* and $2p_z$ orbitals; the remaining, unhybridized 2*p* orbitals then point along the *x*- and *y*-axes.

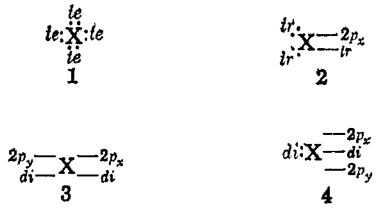


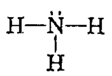
FIG. 1. Octet structures and orbital hybridization.

To summarize, it may be conjectured that a useful first approximation to the state of hybridization of an atom in a molecule can be obtained from the valence-bond structure for the molecule according to the following prescription. The state of hybridization is sp^3 when the atom is bound by only single bonds; sp^2 when it is adjacent to a double bond; *sp* when it is adjacent to two double bonds or a triple bond. The corresponding σ-orbital angles are, respectively, 109° 28′, 120°, and 180°. This rule places the unshared electrons in ethers, alcohols, and amines in sp^3 hybrids, those of the carbonyl group in sp^2 hybrids, and those of a cyanide group in an *sp* orbital. These conjectures may be tested against observed bond angles (Section III).

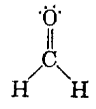
III. ISOELECTRONIC FAMILIES

A. LOCALIZED MOLECULAR ORBITALS

In the previous section, the valence electrons about an atom in a molecule were pictured in localized orbitals. The advantages of partitioning the electron cloud of a molecule into localized, nonoverlapping parts, called in molecular orbital theory equivalent orbitals, have been discussed by several authors (48, 112, 120, 161, 163, 178, 247, 271). Two types of localized orbitals are frequently encountered: orbitals occupied by unshared, nonbonding electrons, and orbitals occupied by bonding or shared electrons. These may be termed, respectively, one-centered and two-centered molecular orbitals.



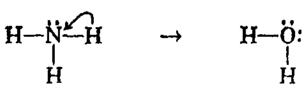
$\mathrm{H{-}\underset{\underset{\displaystyle H}{|}}{\ddot{N}}{-}H}$



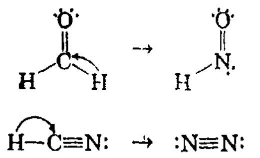
H—C≡N:

A one-centered orbital consists of a single hybrid atomic orbital (to a first approximation, an N_{sp^3} orbital in NH_3, an O_{sp^2} orbital in H_2CO, an N_{sp} orbital in HCN). Two-centered orbitals are formed by the overlap of two hybrid atomic orbitals (H_{1s} with N_{sp^3} in NH_3, H_{1s} with C_{sp^2} for the carbon–hydrogen bonds in H_2CO, H_{1s} with C_{sp} for the carbon–hydrogen bond in HCN).

A surprising feature of molecular structure and a feature that greatly simplifies the classification of molecular shapes by their Lewis structures may be illustrated with the molecule ammonia. Imagine that by some means the proton of one of the bound hydrogen atoms in NH_3 were removed from its normal position on the edge of the molecule and squeezed into the nucleus of the heavy atom. By this process, one additional pair among the four pairs of valence electrons about the heavy atom would be left unshared—two pairs would remain shared with hydrogen atoms—and the atomic number of the heavy atom would increase from 7 (nitrogen) to 8 (oxygen). The hydrogen—(heavy atom)—hydrogen angle would change, albeit only slightly, from the value that makes the energy of NH_3 a minimum (106°46′) to the value that minimizes the energy of H_2O (104°27′). By a similar mechanism, formaldehyde may be converted to nitroxyl and hydrogen cyanide to nitrogen. Molecules related to each other in this manner will be termed isoelectronic molecules. Though differing from each other in the number and/or distribution of their extranuclear protons, isoelectronic molecules have often remarkably similar electronic structures.



$H-\underset{H}{\overset{..}{N}}-H \rightarrow H-\underset{H}{\overset{..}{O}}:$



$H-C\equiv N: \rightarrow :N\equiv N:$

B. METHANE–NEON FAMILY (FIGURE 1, STRUCTURE 1)

The simplest family of isoelectronic structures that satisfy the octet rule is well known (61, 166, 180, 247, 269); it includes methane, ammonia, water, hydrogen fluoride, neon, and such important ions as NH_4^+, H_3O^+, CH_3^-, OH^-, and F^-. This family is illustrated in figure 2. In figure 2, the atomic number of the heavy atom is plotted vertically and the number of extranuclear protons horizontally. The eight valence-shell electrons are pictured tetrahedrally disposed in four pairs about the heavy atom, as though their angular dependence were the same whether they were shared or not (269). While tetrahedral hybridization is probably an accurate description of the valence orbitals in the first column, and also the last column (see below), departures from sp^3 hybridization are known to occur in the second and third columns. As mentioned earlier, the valence angle decreases steadily in the series methane, ammonia, water. Presumably a further change in hybridization occurs in going from water to hydrogen fluoride, although this supposition cannot be checked against a bond angle. Fortunately, other methods exist for probing the spatial distribution of electrons about these atoms. Nuclear magnetic resonance studies show that fluorine retains some s character in its bonding orbital, and the fluoride ion in ammonium fluoride is found to be surrounded tetrahedrally by hydrogen bonds (112). X-ray studies of hydrogen-bonded organic crystals (26, 77, 107) and infrared studies of the zigzag, hydrogen-bonded polymeric chains in crystalline hydrogen halides (141) indicate directional bonding in these substances appropriate to the structures pictured in figure 2. BH_4^- has been found to be tetrahedral (226), and H_3O^+ is approximately so (96). The spatial distribution of the valence electrons in neon has been discussed theoretically (161) and, again, in connection with the crystal structures of the noble gases (71). If the binding energy of these crystal lattices were solely the sum of two-body, nondirectional interactions of the van der Waals type, the solid noble gases would be expected to be hexagonal close-packed. In fact, only helium crystallizes in this manner. The other noble gases adopt the face-centered cubic close-packing of methane. Semiquantitative calculations suggest that this structure may be more suitable than hexagonal close-packing for atoms of tetrahedral symmetry (71).

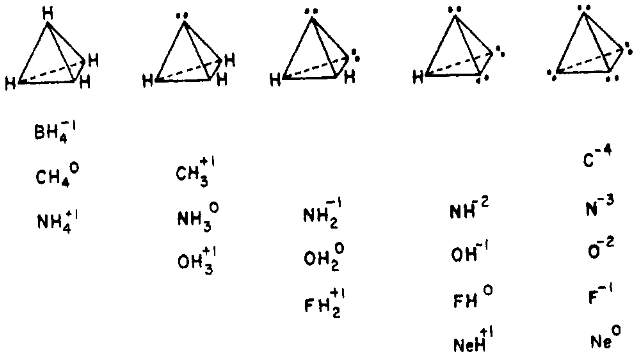


FIG. 2. Methane–neon family.

The structure of the water molecule has been discussed theoretically by several authors (48, 84, 89, 122, 128, 163, 246).

These examples support the hypothesis that lone pairs on atoms not involved in multiple bonds may be viewed as residing in approximately tetrahedral hybrid orbitals (84, 110, 111, 163, 246, 261). Departures from perfect sp^3 hybridization that occur are in a direction that concentrates s character in the lone-pair orbitals, this effect being greater, so far as the bonding orbitals are concerned, the greater the number of unshared pairs about the heavy atom. In the species NH^{2-}, OH^-, HF, and NeH^+, the shift of *s* character to the lone-pair orbitals may be nearly complete.

A figure similar to figure 2 may be drawn up for the hydrides of the second-row elements. In these compounds, species with lone pairs show larger departures from tetrahedral hybridization than do their counterparts from the first row. This effect is discussed in Section VII,I.

C. ETHYLENE–(OXYGEN) FAMILY (FIGURE 1, STRUCTURE 2)

From ethylene, $H_2C{=}CH_2$, one may derive in the afore-described manner the isoelectronic species $H_2C{=}NH$, $H_2C{=}O$, $HN{=}O$ (42, 73, 257), $HN{=}NH$ (101), and $O{=}O$. With the exception of the last molecule (O_2), whose electron cloud is cylindrically symmetrical about the internuclear axis, the six pairs of valence electrons in these molecules may be represented in the following manner (247) (dots indicate electrons unshared or in single bonds):

The electronic spectra of nitroso compounds, azo compounds, and nitrites have been treated as perturbations of the oxygen spectrum (228).

D. ALLENE–CARBON DIOXIDE FAMILY (FIGURE 2, STRUCTURE 3)

To allene, $H_2C{=}C{=}CH_2$, the parent hydrocarbon of this family, are related such species as $H_2C{=}C{=}O$ (ketene), $HN{=}C{=}O$ (hydrogen isocyanate), $O{=}C{=}O$ (carbon dioxide), $N{=}N{=}O$ (nitrous oxide), $N{=}N{=}NH$ (hydrazoic acid), $N{=}N{=}N^-$ (azide ion), and $O{=}N{=}O^+$ (nitronium ion). In the infrared the colors of these species are remarkably alike (10, 131, 132, 292). This is a stringent test of these valence-bond structures and of the rules used in their formulation, for color in the infrared is sharply dependent on the distribution of charge and mass in a molecule. The bond-bending, symmetric stretching, and asymmetric stretching frequencies of the heavy-atom skeleton of five members of this family are listed in table 2. These frequencies provide an unusual picture of the striking similarity of the five structures to one another. In those structures with no extranuclear protons (CO_2, N_2O, NO_2^+, N_3^-), resonance among alternate methods of pairing the π orbitals adds to the stability of the structures (244) and renders the electron cloud cylindrically symmetrical about the internuclear axis (161, 215). The infrared spectrum of NCO^- supports the structure $:N{\equiv}C{-}O^-$ (195).

TABLE 2

Infrared spectrum of structures isoelectronic with carbon dioxide

Structure	Bond-bending Frequency	Symmetric Stretching Frequency	Asymmetric Stretching Frequency
	cm.$^{-1}$	*cm.*$^{-1}$	*cm.*$^{-1}$
$O{=}C{=}O$	667	1388	2349
$N{=}N{=}O$	589	1285	2223
$N{=}N{=}N^-$	630	1348	2080
$O{=}N{=}O^+$	538	1400	2375
$H_2C{=}C{=}O$	588	1120	2150

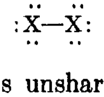
E. ACETYLENE–NITROGEN FAMILY (FIGURE 2, STRUCTURE 4)

To the hydrocarbon $H{-}C{\equiv}C{-}H$ are related $H{-}C{\equiv}N{:}$, $H{-}N{\equiv}C{:}$, $:N{\equiv}N{:}$, $:C{\equiv}O{:}$, and such ions as $:C{\equiv}N{:}^-$, $:C{\equiv}C{:}^{2-}$ (CaC_2), and $:N{\equiv}O{:}^+$ ($NO\cdot ClO_4$). Both chemical and physical evidence exists for $H{-}C{\equiv}O{:}^+$ (9, 282) and $H{-}N{\equiv}N{:}^+$ (123, 282). (The related ions RCO^+ and RN_2^+ have been compared recently (139).)

The electronic structure of CO has been examined theoretically (186, 203), and it suggested that the σ bonding hybrid from carbon is approximately a tetrahedral hybrid (203); this estimate places 75 per cent *s* character in the orbital occupied by the lone pair on carbon. The electronic structure of N_2 has been compared with those of CO (219, 222) and C_2H_2 (178). A close similarity is observed in the computed molecular orbitals for N_2 and CO (260) and in the derived electron overlap populations (219, 221). From experimental measurements (117) (on molecular quadrupole moments), and from theoretical calculations (203, 220, 260), it has been estimated that there is 20–26 per cent *s–p* hybridization in N_2. These examples support the implications of figure 1 and provide additional evidence for the rule that unshared electrons tend to preëmpt *s* character. A recent study of the electron distribution in nitrogen emphasizes the remarkable similarity between the equivalent orbitals for this molecule (obtained from Slater-based (276) molecular orbitals (260)) and the usual chemical description of a triple bond and two lone pairs (271).

F. OTHER FAMILIES

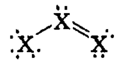
The family of molecules summarized by the structure



$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}{-}\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:$$

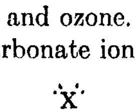
(dots indicate electrons unshared or in single bonds) includes such well-known molecules as $H_3C{-}CH_3$, $H_3C{-}NH_2$, $H_3C{-}OH$, $H_3C{-}F$, $H_2N{-}NH_2$, $H_2N{-}OH$, $H_2N{-}F$, $HO{-}OH$, ($HO{-}F$), $F{-}F$, $H_3B{-}NH_3$, ($H_3C{-}BH_3^+$) (31), and ions formed by the addition or removal of one or more protons from these species. Broadly speaking, the heavy atoms in these structures may be taken as tetrahedrally hybridized, with the refinement, as in the methane–neon family, that an increase in the number of lone pairs decreases the s content of the bonding orbitals, a minimum being reached presumably at F_2 or O_2^{2-}. Applications of this isoelectronic family have been made in the interpretation of the infrared spectrum of NH_3OH^+ (105) and in a discussion of the standard enthalpy and free energy of formation of diimide (277). For the saturated hydrocarbons beyond methane and ethane, some useful analogies have been found between the frequencies of vibration of the paraffin and its polar analog in which CH_3 groups have been replaced by NH_2, OH, or F (267).

The family of molecules represented by the structure



includes $H_3C—CH{=}CH_2$, $H_3C—CH{=}O$, $H_3C—N{=}O$, $H_2N—CH{=}O$, $HO—CH{=}O$, $HO—N{=}O$, $F—N{=}O$, $H_2N—N{=}NH$ (102), and ozone.

The isobutylene–carbonate ion family contains some



sixty-odd members; included are acetamide, urea, guanidine, boric acid, nitromethane, 1,1-difluoroethylene, nitric acid, acetic acid, and nitryl fluoride. The infrared spectrum of guanidine (150) has been compared with those of other members of the family, and the skeletal frequencies of guanidinium ion, $C(NH_2)_3^+$, $B(OH)_3$, BF_3, CO_3^{--}, and NO_3^- have been compared with one another (7).

Other applications of the isoelectronic principle have been made (32, 40, 61, 65). When attempting to construct a valence-bond representation for a molecule whose structure is not known, it is sometimes helpful to develop isoelectronic sequences for each trial structure. Often the best valence-bond representation is found to be a member of the longest sequence, or that sequence which contains the greatest diversity of known structures. Application of this prescription to the problem of the structure of gaseous B_2O_3 (79, 291, 314), for example, yields the prediction that the most stable structure satisfying the octet rule is probably $:O{\equiv}B—O—B{\equiv}O:$, which is isoelectronic with $HC{\equiv}C—CH_2—C{\equiv}CH$ and malononitrile.

G. CLASSIFICATION OF MOLECULAR SHAPES

The shape of a molecule is largely determined by the hybridization of its heavy atoms. A study of the structures discussed above reveals that, in the main, the hybridization of the heavy atoms is determined by one parameter: the number of bonds (double bonds count as two, triple bonds as three) between the heavy atoms. This number is independent of the number of hydrogen atoms in the molecule. For structures that satisfy the octet rule, the number of bonds between the heavy atoms depends only on the number of valence electrons, V, and the number of heavy atoms, N, and is equal to $4N - (1/2)V$ (Section VIII). In some problems, it is helpful to classify molecules according to their values of V, N, and $4N - (1/2)V$.

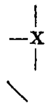
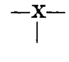
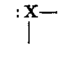
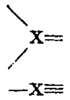
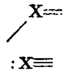
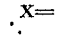
Inspection of the structures above reveals also that when the octet rule is satisfied, the number of lone pairs plus the number of hydrogen atoms cannot total less than 2 if N is even [acetylene, hydrogen cyanide, nitrogen, . . .; diacetylene ($H—C{\equiv}C—C{\equiv}C—H$), cyanogen, ($:N{\equiv}C—C{\equiv}N:$), . . .] and 4 if N is odd [methane, ammonia, water, hydrogen fluoride, neon, . . .; carbon dioxide, ketene, allene, . . .; carbon suboxide ($O{=}C{=}C{=}C{=}O$), . . .]. Use will be made of this fact in Section VIII,C.

IV. LEWIS STRUCTURES FOR COMBINED ATOMS

In the σ–π description of s–p hybridization, the distribution of valence electrons about chemically combined first-row atoms may be classified into one of four categories (figure 1, table 1) according as the four valence-shell atomic orbitals of the atom in question are hybridized into (*i*) four σ hybrid orbitals (to a first approximation, each sp^3), with no $2p$ π orbitals, as in methane, ammonia, and water; (*ii*) three σ hybrid orbitals (each approximately sp^2), with one $2p$ π orbital, as in ethylene, nitroxyl, and diimide; or two σ hybrid orbitals (each approximately sp), with $2p$ π bonds, as in (*iii*) allene and carbon dioxide or (*iv*) acetylene and nitrogen. If all pairs of shared electrons are indicated by lines and all unshared pairs in the valence shell by dots, the usual practice in drawing valence-bond structures, these four categories may be elaborated to the eleven structures tabulated in table 3. In each column of this table the number of unshared pairs is the same, and similarly in each row the basic hybridization is the same. Typically, carbon atoms carry no unshared pairs, nitrogen atoms one, oxygen atoms two, fluorine atoms three, and neon atoms four. In this way, formal charges (166) vanish. However, other structures do exist. Nitrogen atoms,

TABLE 3

Table of Lewis structures for combined atoms

	0	1	2	3	4
sp^3.				$:\overset{..}{\underset{..}{X}}—$	$:\overset{..}{\underset{..}{X}}:$
sp^2.					
sp.	$—X{\equiv}$	$:X{\equiv}$			
sp.	$=X=$				

for example, may occur in each of the eleven different environments; e.g.,

NH_4^+ NH_3 NH_2^- NH^{2-} N^{3-}

$(HO)_2NO_2^+$ FNO CN_2^{2-}

RNC RCN

NO_2^+

V. CORRELATION OF LEWIS STRUCTURES WITH MOLECULAR PROPERTIES. ROLE OF ATOM HYBRIDIZATION

A. EFFECT OF HYBRIDIZATION ON ELECTRONEGATIVITY

It has been mentioned that a 2*s* orbital lies lower in energy than a 2*p* orbital. This implies that the electronegativity of an atomic valency should increase as the *s* character in that valency increases (205, 216, 303). A carbon *sp* valency, for example, should be more electronegative than a carbon sp^2 valency, which, in turn, should be more electronegative than a carbon sp^3 valency.

1. Chemical evidence

Extensive evidence from organic chemistry as to the effect of hybridization on electronegativity has been summarized in the statement that compared with a methyl group, vinyl, phenyl, and ethynyl groups act as attractors of electrons, the attraction of vinyl and phenyl groups being of the same order of intensity, while that of the ethynyl group is considerably stronger (146). This is illustrated by the data in table 4, which show the effect of orbital hybridization on the acidity of a proton three atoms removed from the inductive center. For comparison later with data on bond moments, attention is directed to the fact that the change in acidity in going from $C(sp^3)—CH_2COOH$ to $C(sp^2)—CH_2COOH$ (case c to d) is less than the change in acidity that occurs in going from $C(sp^2)—CH_2COOH$ to $C(sp)—CH_2COOH$ (case d to e). The order of electronegativities determined by the data in table 4 is

TABLE 4

Effect of unsaturation on acidity

Acid	$K_a \times 10^5$ (75)	Acid	$K_a \times 10^5$ (75)
a. $HCOOH$	17.12	d. $CH_2{=}CHCH_2COOH$	4.62
b. CH_3COOH	1.75	e. $N{\equiv}C—CH_2COOH$	<360.
c. CH_3CH_2COOH	1.33	f. $Cl—CH_2COOH$	137.8

$$C(sp\text{, in cyanide}) > Cl > C(sp^2\text{, in vinyl}) > H > C(sp^3\text{, in methyl})$$

Further evidence in support of the first inequality comes from the ionization constants of the following acids: $N{\equiv}C—(CH_2)_2COOH$ and $Cl—(CH_2)_2COOH$, $N{\equiv}C—(CH_2)_3COOH$ and $Cl—(CH_2)_3COOH$, whose pK_a's are, respectively, 3.99, 4.08, 4.44, and 4.52 (41).

Recently Taft has surveyed the vast literature relating to the evaluation of inductive constants from kinetic data (288). Some of his σ^* values are shown in table 5. A positive value indicates that the group is electron withdrawing, compared to methyl; a negative value, that it is electron releasing. The effect of atom hybridization is clearly indicated (289), and the order of electronegativities cited above is confirmed.

TABLE 5

Effects of orbital hybridization on inductive constants

Group	Carbon Hybrid (approx.)	Inductive Constant (289) (σ^*)
$NC—$	*sp*	+3.64
Cl		+2.94
$CH_3\overset{\overset{O}{\Vert}}{C}—$	sp^2	+1.65
$C_6H_5—$	sp^2	+0.60
H		+0.49
$H_3C—$	sp^3	0.00
$(CH_3)_3C—$	sp^3	−0.30

2. Physical evidence

Dipole moments provide additional evidence of the effect of hybridization on electronegativity. For many years it has been known that unsaturated compounds have dipole moments different from those of their aliphatic analogs (75). In each of the examples cited in table 6, the unsaturated compound has the smaller dipole moment. Similar effects have been observed for acetylenic compounds. More striking is the case of toluene and methylacetylene. If all carbon–carbon bonds were nonpolar and all carbon–hydrogen bond moments were equal, these molecules would have no dipole moment. Yet they do. It has been suggested that the difficulty with the vector model may arise from the assumption of zero bond moments for carbon–carbon $(sp^3—sp^2)$-, $(sp^2—sp)$-, and $(sp^3—sp)$-type single bonds and/or the assumption that all carbon–hydrogen bond moments are the same (241). Postulating that single bonds between carbon atoms of different

TABLE 6

Effect of atom hybridization on dipole moments

Molecule	Dipole Moment (75)
	debyes
Vinyl bromide	1.48
Ethyl bromide	2.09
Allyl bromide	1.93
n-Propyl bromide	2.15
Allyl chloride	1.97
n-Propyl chloride	2.11

hybridization have nonzero moments, and using for carbon–hydrogen bonds variable bond moments derived from infrared dispersion data on methane, ethylene, and acetylene (the precise values adopted for the carbon–hydrogen moments are not too important), Petro has obtained from a vector model calculation on a limited number of compounds the carbon–carbon bond moments listed in table 7. Also, it is found that chlorine constitutes the positive end of the carbon–chlorine bond moment in HC≡CCl. These results agree well with the conclusions of the previous section, and with group electronegativities based on the cyanide stretching frequency in substituted aliphatic compounds (91), and assignments of bond polarities in dimethylacetylene (201) and cyanogen chloride (142) based on infrared intensities. Both chemical and physical evidence appear to support the view that a change in hybridization ratio may have a powerful effect on the electronegativity of an atomic valency (216).

TABLE 7

Effect of atom hybridization on bond moments

Carbon–Carbon Bond (and Polarity)	Bond Moment (241)
	debyes
$C(sp^3)^+$—$C(sp^2)^-$	0.68
$C(sp^2)^+$—$C(sp)^-$	1.15
$C(sp^3)^+$—$C(sp)^-$	1.48

B. EFFECT OF HYBRIDIZATION ON ACID–BASE STRENGTH

Hydrogen cyanide and acetylene are stronger (Brönsted) acids (better proton donors) than ethylene, which is a stronger acid than methane; i.e., in terms of base strength (ability to accept protons), the acetylide ion, HC≡C:⁻, and the cyanide ion, :C≡N:⁻, are weaker bases than the vinyl carbanion, $H_2C{=}\dot{C}H^-$, which is a weaker base than the methyl carbanion $H_3C{:}^-$ (199). The orbitals in which reside the electron pairs responsible for the basic properties of these ions are, respectively, digonal-, trigonal-, and tetrahedral-type hybrid orbitals. This example suggests that the more *s* character an atom devotes to an orbital occupied by an unshared pair, and the better, thereby, the provision by the atom of low-potential-energy space for the lone pair, the poorer the electron-donor properties of the system. Aldehydes and ketones, for example, are less basic than ethers and alcohols (108). In these pairs of compounds, the lone-pair electrons reside, respectively, in $O(sp^2)$- and $O(sp^3)$-type hybrid orbitals. Similarly, nitrogen is less basic than pyridine, which in turn is less basic than ammonia. Also, amines form stronger complexes (116) with boron trifluoride than do nitriles (118). In each case, as the *s* character in the orbital occupied by the unshared electrons increases, the base strength decreases. Nitrite ion is an interesting case in point. Despite the negative charge carried by this ion, NO_2^- is a weaker base than ammonia. Indeed, when the ion does add a proton, it does so at one of the approximately tetrahedrally hybridized oxygen atoms, rather than at the trigonally hybridized nitrogen atom, although this must diminish carboxyl-type resonance in the molecule. On the other hand, phosphorous acid, in which the phosphorus is tetrahedrally hybridized, is most stable in the zwitter-ion form $HP^+(OH)_2O^-$.

C. EFFECT OF HYBRIDIZATION ON GEOMETRY

1. Bond angles

The effect of hybridization on bond angles has been described in Sections II and III, table 1, and figures 1 and 2, and summarized in the structure table in Section IV.

2. Bond lengths

(a) Nonaromatic compounds

Experimental evidence that all carbon–carbon single bonds are not of the same length seems first to have been obtained by Lonsdale in 1929 in a study by x-ray diffraction of the crystal and molecular structure of hexamethylbenzene (189). This result was questioned in 1937 by Pauling and Brockway, who examined by electron diffraction (237) the structures of thirteen hydrocarbons and concluded that the carbon–carbon single-bond distance has the constant value of 1.54 ± 0.02 A., being unaffected by the presence of an adjacent double bond (provided that it does not form part of a conjugated system); it was concluded, also, that the carbon–carbon double bonds in allene and ethylene are of the same length (238). This conclusion leads to the view that the normal covalent radius of carbon in single bonds to other elements is 0.77 A. In 1939, however, Pauling, Springall, and Palmer confirmed the fact, which had been obtained spectroscopically (136), that the carbon–carbon single-bond distance in methylacetylene is only 1.46 A. At the same time, they proposed for this shortening two explanations (239). One explanation developed subsequently into the theory of hyperconjugation (15, 224). The other explanation, which is considered here, directed attention to the possibility that bond lengths might be affected by changes in hybridization ratios of the σ bonds.

The effect of hybridization on bond lengths was reconsidered nearly a decade later by Coulson, who has listed three factors that affect bond lengths: bond order, hybridization type, and distribution of formal charge (63, 70). Following in part proposals made by Walsh (302) and others (216, 239), Coulson concluded that differences in hybridization ratio between the different types of single σ-type bonds cause changes in the single-bond radius of carbon that are not less than 0.035 A. (60). Moffitt has pointed out that the use of Slater functions (276), which have the same radial distribution for both *s* and *p* electrons, may have led Coulson to underestimate the effect of hybridization on covalent radius (203). Recent experimental data suggest that the variation with hybridization of the atomic radius of carbon may, in fact, be significantly greater than the lower limit set by Coulson. This conclusion is based primarily on a study of carbon–carbon interatomic distances.

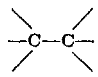
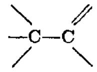
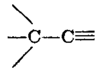
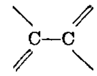
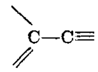
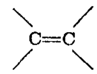
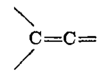
There exist several reasons for singling out carbon–carbon distances for special consideration. Coulson's study was based on the carbon–hydrogen distances in methane, ethylene, and acetylene because, as had been noted by others (239), any variation in the carbon–hydrogen distance could reasonably be attributed to the carbon atom, the hydrogen atom being constrained to the use of a 1*s* orbital. Usually it is left unexplained, however, why the radius of hydrogen should be 0.30 A., or 0.322 A., instead of 0.37 A. (263). Further, the experimental uncertainty in carbon–hydrogen distances is generally much greater than that for distances between heavy atoms. Classical structure methods depend on the mass or scattering power of an atom. On either account, hydrogen atoms are difficult to locate (34, 50, 212). Also, owing to its small mass, hydrogen has an unusually large zero-point energy, making corrections for anharmonicity larger for hydrogen than for any other atom (20); moreover, the anharmonicity corrections are not the same in molecules isotopically substituted with deuterium, which adds to the difficulty of determining carbon–hydrogen distances accurately (200, 294). Thus, it is not surprising to find that in the past the positions of hydrogen atoms have been assumed perhaps more often than they have been determined. The carbon–hydrogen distances used in Coulson's study (60) for methane (and ethane), ethylene, and acetylene, respectively, were 1.093, 1.071, and 1.057 A. More recent values are 1.11–1.12 (21, 34, 35, 130), 1.086 (1, 26), and 1.055 (209) A., respectively.

Another reason for singling out carbon–carbon bonds for special consideration is that in addition to the carbon–carbon triple bond, there exist three types of carbon–carbon double bonds (not counting aromatic systems) and six types of carbon–carbon single bonds, compared to three types of carbon–hydrogen bonds.

Data on interatomic distances reported prior to December 31, 1955, have been summarized in a recent publication by The Chemical Society (284). A critical list of carbon–carbon and carbon–hydrogen distances has been given by Costain and Stoicheff (55). While the present review was in preparation, carbon–carbon, carbon–hydrogen, and carbon–halogen distances for a large number of compounds were reviewed by Brown (43) (see, also, Somayajulu (280)). Costain and Stoicheff in their classification make use of valence-bond structures, while Brown uses the σ–π description of *s–p* hybridization. In the summary presented in table 8, both designations are given.

TABLE 8

Effect of atom hybridization on bond lengths of carbon–carbon bonds

Class	Description	Structure	Characteristic Bond Length	References
			A.	
1.....	sp^3—sp^3		1.54	(2, 130)
2.....	sp^3—sp^2		1.50	(169)
3.....	sp^3—sp		1.46	(164, 266)
4.....	sp^2—sp^2		1.46	(25)
5.....	sp^2—sp		1.42	(55)
6.....	sp—sp	≡C—C≡	1.38	(126, 147, 311)
7.....	sp^2—sp^2 + π		1.34	(1, 26)
8.....	sp^2—sp + π		1.31	(55)
9.....	sp—sp + π	=C=C=	1.28	(283)
10.....	sp—sp + 2π	—C≡C—	1.20_6	(230)

In table 8, bond distances cited as representative of each class of carbon–carbon bonds represent the reported interatomic distances for essentially all representatives of that class to within 0.02 A., and for most members the values lie within 0.01 A. of the listed value. This summary shows that Lewis structures are useful in classifying bonds and in predicting bond lengths. The separation between classes is generally several times greater than the variation in bond lengths within any one class. A useful rule of thumb is that the carbon–carbon single-bond distance decreases by 0.04 A. when one of the participating carbon atoms changes hybridization type from sp^3 to sp^2, or from sp^2 to sp. When a π bond exists superimposed on the σ bond, the figure 0.03 A. is a better one to use.

Changes in bond lengths with hybridization appear to be somewhat greater for carbon–carbon bonds than for carbon–hydrogen bonds. When the hybridization of carbon changes from sp^3 to sp, the carbon–hydrogen distance decreases by about 0.06 A., while the corresponding change in carbon–carbon distance when the adjacent carbon atom is hybridized either sp^3 (cases 1 and 3) or sp^2 (cases 2 and 5) or sp (cases 3 and 6) is about 0.08 A. The change is still greater for C—X bonds (X = Cl, Br, I), amounting to about 0.14–0.15 A. (29, 54, 140, 268, 299, 300, 310). A plausible explanation for this variation has not been offered. The effect of hybridization on bond length is generally greater the larger the attached atom and, hence, the larger the internuclear distance; in these cases, this also is the order in which the p character of the bonding orbital of the attached atom increases. It has been suggested that the observed trends may follow the electronegativities of the substituents (43). However, it was seen above (Section V,A) that whereas a carbon sp^3 valency is less electronegative than chlorine, a carbon sp valency is more electronegative than chlorine, yet neither carbon valency shows a substituent effect as large as that of chlorine. This fact might be explained by observing that in a carbon–carbon bond, as opposed to a carbon–halogen bond, a change in hybridization of one carbon atom induces a change in hybridization of the adjacent carbon atom, this induced rehybridization always being in a direction to oppose the effect on the bond length of the initial change in hybridization. If the initial change were for the first carbon atom to change from sp^3-type to sp^2-type hybridization, thereby increasing the s content of the single bond to the second carbon atom, the second carbon atom would withdraw some s character from the bond. This effect is discussed in more detail in Sections VI and VII. Halogen atoms, when singly bonded, bond by more nearly pure p orbitals than do carbon atoms and would have less s character to withdraw from the bond. However, this explanation depends on a number of unstated assumptions; moreover, it fails to explain the position of hydrogen. Possibly hydrogen is peculiar (46). Another possibility is that empty d orbitals on chlorine, bromine, and iodine participate in some π bonding with multiple bonds adjacent to a carbon–halogen bond, this effect becoming larger as the carbon–halogen bond becomes shorter. Against this explanation is the statement that quadrupole coupling constants appear to provide little evidence of double-bond character in carbon–halogen bonds (72). Supporting it is the fact that the implication that fluorine should behave differently from the other halogens does not seem to be openly contradicted by existing data on bond lengths. The length of the carbon–fluorine bond is considered in more detail in Sections VII,C and VII,D.

Implicit throughout the present discussion is the assumption that changes in hybridization ratios in σ bonds provide a natural explanation for variations in bond lengths that in molecular orbital theory would normally be attributed to effects of conjugation and hyperconjugation (in table 8, cases 4, 5, 6, 9 and 2, 3, 8, 10, respectively) (15, 28, 164). Questions concerning hyperconjugation have been raised by several authors (43, 47, 74, 160, 210, 241, 245, 295). Especially noteworthy is the fact that carbon–carbon bonds from any one of the ten classes catalogued in table 8 are to a first approximation independent of the chemical nature of the attached groups. Noteworthy, also, is the fact that the bond lengths in 1,3,5,7-cycloöctatetraene (25) are very close to those predicted from table 8. This is difficult to explain in terms of conventional molecular orbital theory; so, too, are the alternations in bond lengths that have been observed in extended polyenes, such as 1,8-diphenyl-1,3,5,7-octatetraene (80) (however, see references 157 and 188). It has been suggested, also, that conjugation and hyperconjugation are not necessary, nor indeed sufficient, to explain certain aspects of ultraviolet spectra (45, 47). In a recent careful analysis, Sutton has concluded that bond lengths neither prove nor disprove hyperconjugation (285). It is suggested here that current data may support a less guarded conclusion. The two contending accounts of bond lengths may be compared by considering the overlap integrals to which each directs attention. The view adopted in this review directs attention to the overlap of σ hybrid orbitals, in the supposition that the larger the overlap between two atomic orbitals, and the lower the energy of these orbitals, the greater the effect on bond properties. Molecular orbital theory supposes that variations in bond lengths arise from variations in the often smaller overlap of more highly energetic π orbitals. Present data require of the latter view that the effect of the relatively small overlap of often dissimilar bonds be essentially constant, while of the former view the requirement is simply that the effect on bond lengths of these auxiliary π-orbital overlaps be small compared to the effect of the overlap of adjacent σ orbitals.

To summarize, the important overlap integrals to consider in predicting interatomic distances in covalent compounds of the first-row elements are believed to be those that receive explicit recognition in the conventional valence-bond structures of these compounds (47, 313).

(b) Aromatic compounds

The data in table 8 clearly show that the superposition of a π bond on a σ bond compresses the latter, and, further, that this compression is less the greater the s character of the σ bond. This is seen by the comparison of 4 with 7, 5 with 8, 6 and 9, and these with each other. The changes are: sp^2—sp^2 to sp^2—sp^2 + π, 0.12 A.; sp^2—sp to sp^2—sp + π, 0.11 A.; and sp—sp to sp—sp + π, 0.10 A. Superposition of a second π bond causes a further, but smaller, decrease in bond length (6, 9, and 10).

Superposition of less than a full π bond appears to compress the σ bond proportionately less. Benzene and graphite provide two particularly good examples. Following the prescriptions of valence-bond theory, the carbon skeletons of these compounds are taken to be sp^2 hybridized with π-bond orders of exactly $^1/_2$ and $^1/_3$, respectively. Linear interpolation between classes 4 and 7 (table 8) yields the values in table 9. Linear interpolation between classes 1 and 7 would yield rather different values.

TABLE 9

Bond lengths in benzene and graphite

Molecule	Bond Type	Predicted Bond Length	Observed Bond Length (284)
		A.	*A.*
Benzene..........	$sp^2—sp^2 + (1/2)\pi$	1.40	1.397
Graphite.........	$sp^2—sp^2 + (1/3)\pi$	1.42	1.421

From table 8 it is predicted that carbon–carbon bond lengths in aromatic systems should lie between 1.46 A. (class 4) and 1.34 A. (class 7). This appears to be the case. In table 10 are listed observed carbon–carbon interatomic distances in benzene, graphite, naphthalene, and anthracene, together with values predicted for these distances based on per cent double-bond character calculated from a simple averaging of Kekulé structures (two for benzene, three for graphite and naphthalene, four for anthracene), figure 3, and linear interpolation between the numbers 1.34 and 1.46. Broadly speaking, the agreement between the two sets of values is good. In over half the cases, the average discrepancy is only slightly over 0.003 A. In the other cases, the discrepancies are larger. In molecular orbital theory, this is attributed to variations in electron density in the π orbitals. Another factor is the following.

TABLE 10

Bond orders and bond lengths

Double-bond Character*	Predicted Bond Length†	Observed Bond Length	References
per cent	*A.*	*A.*	
0	1.46	1.462 (cycloöctatetraene)	(25)
		1.48 (butadiene)	(55)
25	1.43	1.436 (anthracene, D)	(254)
		1.423 (anthracene, B)	(254)
		1.408 (anthracene, E)	(254)
33	1.42	1.425 (naphthalene, B)	(254)
		1.404 (naphthalene, D)	(254)
		1.393 (naphthalene, C)	(254)
50	1.40	1.396 (anthracene, C)	(254)
		1.397 (benzene)	(69, 284)
66	1.38	1.365 (naphthalene, A)	(254)
75	1.37	1.370 (anthracene, A)	(254)
100	1.34	1.33_8 (ethylene)	(1, 26)

* See figure 3.

† Linear interpolation, table 8.

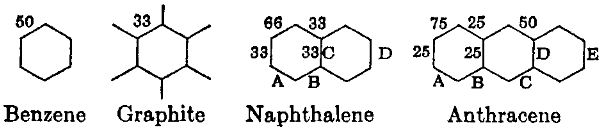


FIG. 3. Per cent donble-bond character in benzene, graphite, naphthalene, and anthracene based on equal weighting of Kekulé structures.

The carbon atoms in benzene are in identical environments; so are the carbon atoms in graphite. It is different for the carbon atoms in naphthalene or anthracene. The three σ orbitals of a bridgehead carbon atom in naphthalene, for example, participate in carbon–carbon bonds that are nominally 33 per cent double bonds (figure 3); however, the σ orbitals of an α-carbon atom participate in (*i*) a 66 per cent double bond, (*ii*) a 33 per cent double bond, and (*iii*) a carbon–hydrogen bond. While the bridgehead carbon atom should to a first approximation distribute its *s* character equally among its three σ orbitals, the α-carbon atom should devote more *s* character to the 66 per cent double bond than to the 33 per cent double bond, and more to the latter than to the carbon–hydrogen bond (the seeking character of multiple bonds in the σ–π approximation is discussed in Section VII,H). Subject to the geometrical limitations imposed by the ring, this unequal distribution of *s* character about an α-carbon atom should be revealed both by interbond angles about the atom and by its distance from adjacent atoms. When the hybridization of adjacent atoms is considered, the situation becomes more complex. It is to be expected, however, that bond lengths in naphthalene and anthracene are influenced to some extent by the number of adjacent hydrogen atoms.

In the assignment of bond orders for naphthalene and anthracene (figure 3), it was assumed that the Kekulé structures of each molecule contribute equally. It has been stated that better agreement is obtained with experiment if those structures that show the greatest number of double bonds in exposed positions are given the greatest weight (255). This statement corresponds closely to the statement that bonds with the greatest number of adjacent hydrogen atoms tend to be shorter than one would otherwise expect. This effect should be greater the greater the electronegativity of the substituent off carbon. It would be interesting to compare the bond lengths in naphthalene and anthracene with the corresponding bond lengths in the completely fluorinated derivatives.

At the other extreme lie the azines. The unusual substituent off the aromatic ring is here an unshared pair. Typically, the nitrogen atoms with their *s*-seeking unshared pairs lie at the apices of angles smaller than 120° (11, 26, 30, 121).

D. EFFECT OF HYBRIDIZATION ON BOND STRENGTH

Hybridization, it has been seen, affects bond angles, bond polarities, and bond lengths. Since bond strength is often associated with bond length, it is not surprising to find the former affected by hybridization also. Two measures of bond strength will be discussed: bond-stretching force constants and bond dissociation energies.

1. *Force constants*

The data in table 11 show that bond-stretching force constants may be classified in a manner very similar to bond lengths. The carbon–carbon single-bond stretching force constants of methyl cyanide and methylacetylene (b and c), for example, bear a closer resemblance to each other than they do to the force constant of either ethane (a) or cyanogen (d). Similarly, the carbon–oxygen stretching force constant in carbon dioxide (g) resembles the stretching force constant of the carbon–oxygen bond in carbon suboxide (f) more closely than it does the stretching force constant of the carbon–oxygen bond in either formaldehyde (e) or carbon monoxide (h). Throughout table 11 there is illustrated the same trend: an increase in bond-stretching force constant with increasing *s* content of the bond. Now bond lengths decrease with increasing *s* content. Hence, the trends in table 11 are consistent with the statement, known as Badger's rule, that bond force constants increase as bond lengths decrease. Since *s* orbitals are nondirectional, bond-bending force constants tend to decrease with increasing *s* content.

TABLE 11

Effect of atom hybridization on bond-stretching force constants

Molecule	Bond Type	$k \times 10^{-5}$ (174)
		dynes/cm.
(a) $CH_3—CH_3$..........	$sp^3—sp^3$	4.5
(b) $CH_3—CN$..........	$sp^3—sp$	5.3
(c) $CH_3—CCH$.........	$sp^3—sp$	5.5
(d) NC—CN...........	$sp—sp$	6.7
(e) $H_2C{=}O$............	$C(sp^2)—O(sp^2) + \pi$	12.3
(f) $O{=}C{=}C{=}C{=}O$....	$C(sp)—O(sp^2) + \pi$	14.2
(g) $O{=}C{=}O$...........	$C(sp)—O(sp^2) + \pi$	15.5
(h) $C{\equiv}O$..............	$C(sp)—O(sp) + 2\pi$	18.9
(i) $CH_3—Cl$ (Br, I, H)..	$C(sp^3)—Cl$ (Br, I, H)	3.4 (2.9, 2.3, 5.0)
(j) NC—Cl (Br, I, H)...	$C(sp)—Cl$ (Br, I, H)	5.3 (4.2, 2.9, 5.9)

For nitrogen–oxygen single bonds, the state of hybridization of the nitrogen atom affects the nitrogen–oxygen stretching frequency in the following manner: $N_{sp^3}—O$, 900 cm.$^{-1}$; $N_{sp^2}—O$, 1240 cm.$^{-1}$; $N_{sp}—O$, 1340 cm.$^{-1}$ (49).

2. *Bond dissociation energies*

Broadly speaking, a large force constant implies a strong bond. Thus, the difficulty of scission of a carbon–carbon bond increases in the order ethane, methyl cyanide, cyanogen, and the carbon–hydrogen bond dissociation energy is greater in acetylene, or ethylene (98), than in methane or ethane (58). Some trends in bond lengths, stretching force constants, and dissociation energies with hybridization are illustrated in table 12. Generally speaking, the more *s* character in a bonding orbital, the shorter the bond (Section V,C), the larger the bond-stretching force constant (Section V,D,1), the more acidic an attached proton (Section V,B), the larger the inductive constant of that valency (Section V,A,1), and the larger the bond dissociation energy (table 12). For carbon–chlorine bonds, Bersohn has pointed out a correlation, also, between *s* character and quadrupole coupling constant (29).

TABLE 12

Effect of atom hybridization on bond dissociation energies and other molecular properties

Molecule	Carbon–Carbon Bond Type	Bond Length	Force Constant $k \times 10^{-5}$	Bond Dissociation Energy, *E*	Reference (for *E*)
		A.	*dynes/cm.*	*kcal./mole*	
$CH_3—CH_3$......	$sp^3—sp^3$	1.54	4.5	83	(58)
$CH_3—C_2H_3$......	$sp^3—sp^2$	1.49		92.5	(127)
$CH_3—CN$.......	$sp^3—sp$	1.46	5.4	103	(58)
$C_2H_3—C_2H_3$	$sp^2—sp^2$	1.4_8		104	(127)
NC—CN.......	$sp—sp$	1.38	6.7	112	(58)

It is interesting that acetylene is a stronger acid than methane, for the strength of the carbon–hydrogen bond in acetylene is greater than that in methane. Apparently an increase in *s* content of a carbon–hydrogen bond increases the difficulty of removal of the hydrogen atom but decreases the difficulty of removal of the proton. On reflection, this seems reasonable. Removal of a proton from a bond leaves behind both bonding electrons, while removal of a hydrogen atom amounts from the point of view of the carbon atom to partial ionization of the bonding pair (176). The more *s* character in the bond at the carbon end, the easier the former process (Section V,B) but the more difficult the latter; this is discussed in more detail in Section VI,C.

E. STRUCTURE OF CARBON DIOXIDE

Reasoning from bond lengths in carbon dioxide and ketones, Pauling introduced the notion that the structures $^{+}O{\equiv}C—O^{-}$ and $^{-}O—C{\equiv}O^{+}$ contribute importantly to the ground state of carbon dioxide (235).

In selecting a valence-bond structure, or set of structures, for carbon dioxide, it is instructive to compare the carbon–oxygen distance in this molecule with the carbon–oxygen distances in the isoelectronic molecules ketene ($H_2C{=}C{=}O$) and hydrogen isocyanate ($HN{=}C{=}O$). In each of these molecules the σ component in the bond to oxygen is a carbon *sp*-type hybrid, instead of the usual sp^2-type hybrid of a carbonyl group. A similar situation occurs in carbon suboxide ($O=C=C=C=O$). Interestingly, the carbon–oxygen distances in these four molecules are remarkably alike (table 13). The variation in interatomic distance in table 13 is analogous to the effects described in greater detail for carbon–carbon bonds (Section V,C,2) and repeats the pattern of the carbon–oxygen stretching force constants listed in table 11 (e through h). It may be noted, also, that the characteristic ultraviolet absorption bands of aldehydes and ketones are missing in ketene, the isocyanates, and carbon dioxide (316).

TABLE 13

Effect of atom hybridization on the length of the carbon–oxygen double bond

Molecule	Carbon–Oxygen Distance	Reference
Carbon trigonally hybridized		
	A.	
$H_2C=O$	1.225	(284)
Carbon digonally hybridized		
$O=C=O$	1.162	(284)
$H_2C=C=O$	1.16	(39)
$HN=C=O$	1.171	(148)
$O=C=C=C=O$	1.16	(185)
$C\equiv O$	1.128	(284)

On these grounds it would appear that the ground state of carbon dioxide is well represented by the classical structure $O=C=O$.

F. EFFECT OF HYBRIDIZATION ON PROTON–C^{13} COUPLING CONSTANTS

The C^{13} nucleus has a magnetic moment. This can couple with the magnetic moment of a bound proton via magnetic interactions with the intervening bonding electrons. Theory predicts that the magnitude of the magnetic interaction constant, J_{CH}, between a C^{13} nucleus and an adjacent proton should depend on the probability of finding the bonding electrons at the two nuclei in question. Since an electron in a pure *p* orbital of carbon has zero probability of being found at the nucleus of the carbon atom, whereas this probability is finite for an electron in an *s* orbital (143), it seems plausible that the coupling between a proton and the C^{13} nucleus should depend on the state of hybridization of the carbon atom. The data in table 14 show that the greater the *s* character in a carbon valency toward hydrogen, and hence the greater the probability of finding the bonding electrons at the C^{13} nucleus, the greater the coupling constant J_{CH}.

TABLE 14

Effect of atom hybridization on proton–C^{13} coupling constants

Molecule	J_{CH} (211)
	sec.$^{-1}$
Methane	125
Benzene	159
Methylacetylene	248

G. SUMMARY

In this section data have been cited concerning the effect of atom hybridization on the following molecular properties:

- * bond angles
- * bond lengths in nonaromatic systems
- bond lengths in aromatic systems
- acid strength
- base strength
- * inductive constants
- dipole moments
- bond polarity
- bond-stretching force constants
- bond-bending force constants
- bond length of carbon–oxygen double bonds
- quadrupole coupling constants of chlorine
- * proton–C^{13} coupling constants

Since the hybridization of a combined atom is determined to a first approximation by the unsaturation about that atom, i.e., by the distribution of multiple bonds in the molecule, and since the latter is immediately evident from the Lewis structure of the molecule, Lewis structures may be viewed as useful summaries of the data reviewed in this section.

The effect of electronegative substituents on the starred properties in the list above is discussed in the following section.

VI. ATOM HYBRIDIZATION AND ELECTRONEGATIVE SUBSTITUENTS

It was found in Section III that the hybridization of an atom, one not involved in multiple bonds, deviates from perfect tetrahedral hybridization when there is present on the atom one or more pairs of unshared electrons. Often it is suggestive to regard unshared electrons as electrons in a bond to an atom of very low (zero) electronegativity. This view leads one to suppose that electronegative groups affect atom hybridization and, by inference (Section V), such molecular properties as bond angles, bond lengths, proton–C^{13} coupling constants, and inductive constants. Evidence for this is examined in the present section (Section VI,A). It is found that a simple rule may be formulated to describe the effect of electronegative substituents on atom hybridization (Section VI,B). For this rule a model is formulated (Section VI,C). In Section VII this model is applied to several problems of current chemical interest.

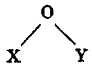
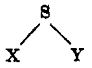
A. EFFECT OF ELECTRONEGATIVE SUBSTITUENTS ON MOLECULAR PROPERTIES

1. Bond angles

In compounds of the type AX_2 and AX_3, the valence angle X—A—X appears to be correlated with the electronegativity of X. In the absence of obvious steric effects, the valence angle generally decreases as the electronegativity of the substituent X increases. Illustrative examples are given in table 15. Additional examples have been cited by Mellish and Linnett (197). These data suggest that as the electronegativity of the substituent increases, the central atom (atom A) diverts increasing amounts of *s* character to the orbital, or orbitals, occupied by the lone-pair electrons.

TABLE 15

Effect of electronegative groups on bond angles

			∠XOY	References
1a........	CH_3	CH_3	111°	(153, 237)
1b........	CH_3	H	107–109°	(286, 298)
1c........	H	H	105°	(134)
1d........	F	F	103.8°	(145)
			∠XSY	
2a........	CH_3	H	100°	(279)
2b........	H	H	92°	(197)
	AX_3 Compound		∠XAX	
3a........	$N(CH_3)_3$		109°	(312)
3b........	NH_3		106°46′	(312)
3c........	NF_3		102°30′	(262)
3d........	$P(CH_3)_3$		98°36′	(19)
3e........	PH_3		93°18′	(312)
3f........	$As(CH_3)_3$		96°	(312)
3g........	AsH_3		91°30′	(312)
	X, Y in $CF_2{=}CXY$		∠FCF	
4a........	H, H		110°	(151)
4b........	F, F		114°	(151)

It is an interesting fact that these changes in interbond angles are sometimes in the reverse direction from what one would expect were repulsions between nonbonded atoms the most important effect operating (18). One explanation for this directs attention to the electrostatic interactions that exist between substituents and the lone-pair electrons (262). The latter would attract protons but repel fluorine atoms. However, this explanation appears to leave unanswered (see below) the effect of electronegative substituents on bond lengths.

Several compounds containing second- and third-row elements have been included in table 15. The data on these compounds suggest that unshared electrons capture an increasing share of the *s* character of the central atom as the electronegativity of this atom decreases (1b and 2a; 1c and 2b; 3a, 3d, and 3f; 3b, 3e, and 3g). This observation is considered again in Section VII,I.

2. Bond lengths

In the absence of marked steric effects, replacement in the structure X—A—Y of X by an atom more electronegative than X causes the adjacent A—Y bond to become shorter. This effect is particularly noticeable when fluorine is introduced into a molecule (the carbon-fluorine distances in H_3C—F and F_3C—F, for example, are 1.391 A. and 1.323 A., respectively) (38), but occurs, also, on further substitution of halogen in chloroform (27) and the chlorinated and brominated silanes (57), in the methyltin chlorides, bromides, and iodides, and in the methylarsenic chlorides (57, 275). Additional data are summarized in table 16. The evidence points to a definite phenomenon (275).

TABLE 16

Effects of electronegative groups on bond lengths

Single bonds

Molecule	Bond Length	References
1. Bond C—F. Substitution of F for H		
	A.	
CH_3F........................	1.391	(38)
	1.385	(115)
CH_2F_2........................	1.358	(168)
CHF_3........................	1.332	(109)
	1.326	(168)
CF_4........................	1.323	(38)
2. Bond C—Cl. Substitution of Cl for H		
CH_3Cl........................	1.784	(284)
	1.781	(200)
CH_2Cl_2........................	1.772	(168)
$CHCl_3$........................	1.767	(109)
	1.761	(297)
CCl_4........................	1.766	(23)
3. Bond C—Br. Substitution of Br for H		
CH_3Br........................	1.939	(294)
$CHBr_3$........................	1.930	(294)
4. Bond C—Cl. Substitution of F for H		
CH_3Cl........................	1.784	(284)
CF_3Cl........................	1.751	(22)
5. Bond C—Cl. Substitution of F for Cl		
CCl_2F_2........................	1.77_6	(184)
CF_3Cl........................	1.751	(22)
6. Bond C—C. Substitution of F for H		
C_2H_6........................	1.536	(2, 130)
C_2F_6........................	1.51	(36)
7. Bond N—Cl. Substitution of Cl for CH_3		
$N(CH_3)_2Cl$..................	1.77	(263)
$N(CH_3)Cl_2$..................	1.74	(263)

8. Bond Si—C. Substitution of F for H

CH_3SiH_3	1.867	(287)
CH_3SiH_2F	1.848	(287)
CH_3SiHF_2	1.833	(287)

9. Bond Si—C. Substitution of H for CH_3

$Si(CH_3)_4$	1.888	(265)
$Si(CH_3)_3H$	1.873	(33)
$Si(CH_3)_2H_2$	1.860	(33)
$Si(CH_3)H_3$	1.857	(33)

10. Bond Si—F. Substitution of F for CH_3

CH_3SiH_2F	1.600	(287)
SiH_2F_2	1.576	(287)

11. Bond Si—F. Substitution of F for H

CH_3SiH_2F	1.600	(287)
CH_3SiHF_2	1.583	(287)

Double bonds

Molecule	Bond Length	Reference
12. Bond C═C. Substitution of F for H		
	A.	
C_2H_4	1.337	(2)
C_2F_4	1.313	(151)

13. Bond C═O in XCY

$X\overset{\overset{O}{\|}}{C}Y$

X	Y	C═O Distance	Reference
		A.	
H	CH_3	1.226	(171)
H	H	1.225	(284)
H	C≡CH	1.216	(209)
H	F	1.192	(149)
F	F	1.17	(39)

Again, it is an interesting fact that these changes in geometry are sometimes in the reverse direction from what one would expect were repulsions between nonbonded atoms the most important effect operating (18). This problem has been reviewed by Pritchard and Skinner (249). Explanations that invoke participation of double-bonded structures (37) have been criticized by Skinner and Sutton (275), Wells (309), and Burawoy (45, 46). Explanations in terms of ionic-covalent resonance (306) and inner-orbital repulsions (243) have been criticized by Duchesne, who focuses attention on changes in hybridization of the substituent halogen atoms, but encounters difficulty in accounting for the bond angles in the hydrides of elements of Group V (82). The problem appears to merit further consideration.

As an illustrative example, consider the carbon–fluorine bond in CH_3F and CH_2F_2. The length of this bond in these two structures is 1.39 A. and 1.36 A., respectively (table 16). It is the bond labeled *b* in figure 4.

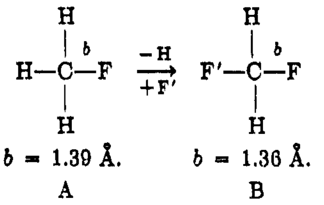


Fig. 4. The carbon–fluorine bond in CH_3F and CH_2F_2.

Suppose one asks, What are the perturbations on the carbon and fluorine atoms of the carbon–fluorine bond in going from structure A to structure B? The perturbation on carbon is clearly an important perturbation; it is the perturbation caused by the replacement of one of the three hydrogen atoms about carbon by fluorine (F′ in figure 4). To a first approximation, there is no perturbation of the fluorine atom (of the original carbon–fluorine bond), since the atom attached to fluorine has not been changed; it is still a carbon atom. To a second approximation, the perturbation on fluorine is only the perturbation caused by changing from the *group* CH_3— to the *group* CH_2F'—; at best it is a second-order perturbation compared to the perturbation on the carbon atom. The effect on carbon can be inferred from the change in bond length (Section V,C,2). It appears that the *s* character in the carbon–fluorine bond increases in going from CH_3F to CH_2F_2.

The effects described here are next-nearest-neighbor effects; i.e., they involve the effect of an atom on a bond one atom removed. In this respect, the effect of electronegative substituents on bond lengths is similar to the inductive effect of organic chemistry. The inductive effect is considered below in this section in part 4 and again in Section VII.

It may be noted, also, that the variations in bond length in table 16 are not those predicted by the Schomaker–Stevenson rule (263); they are, in fact, opposite in direction from what one would expect from a logical extension of that rule. The Schomaker–Stevenson rule is considered in more detail in Section VII,C.

3. Proton–C^{13} coupling constants

Replacement in the structure X—C—H of X by an atom, or group, more electronegative than X increases the coupling constant J_{CH} of the carbon–hydrogen bond. The coupling constant in the series CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, for example, increases in the order 125, 150, 178, 209 $sec.^{-1}$; concomitantly, the carbon–hydrogen distance decreases in the order 1.11, 1.0959, 1.082, 1.07 A. (212). Additional examples of the effect of electronegative groups on proton–C^{13} coupling constants are cited in table 17. These are taken from the work of Muller and Pritchard, who have discussed in detail the correlation of J_{CH} with r(C—H) (212). Recalling that J_{CH} increases with increasing *s* content of the carbon–hydrogen bond (Section V,F), one infers from these data that replacement in the

TABLE 17

Effect of electronegative groups on proton–C^{13} coupling constants

X in CH_3X	J_{CH} (212)
	sec.$^{-1}$
H	125
CHO	127
CO_2H	130
C≡CH	132
CCl_3	134
OH	141
NO_2	147
F	149

structure X—C—H of X by an atom, or group, more electronegative than X causes the carbon atom to rehybridize in such a manner as to increase the *s* character of the carbon–hydrogen bond. An analogous conclusion was reached above from the effect of electronegative groups on bond lengths: namely, replacement in the structure X—C—Y of X by a group more electronegative than X causes the carbon atom to rehybridize in such a manner as to increase the *s* character in the C—Y bond. The effect of electronegative groups on inductive constants supports a similar conclusion.

The effect of Cl, Br, and I on J_{CH} (212), as well as on k_{CH} (bond-bending and bond-stretching force constants) (81), D_{CH} (the bond dissociation energy) (58), and σ^* (polar substituent constants) (289), is, at first sight, anomalous. Participation of halogen *d* orbitals appears to be indicated (*cf.* Section V,C,2,(a); also reference 289).

4. *Inductive constants*

The data in table 18 illustrate the well-known fact that replacement in the structure X—A—Y of X by an atom, or group, more electronegative than X increases the effective electronegativity of atom A toward Y. Recalling that the electronegativity of an atomic orbital increases with increasing *s* content (Section V,A,1), one infers from this that replacement in the structure X—A—Y of X by an atom, or group, more electronegative than X causes atom A to rehybridize in a manner such as to increase the *s* content in its orbital toward Y.

TABLE 18

Effect of electronegative groups on inductive constants

Group	Inductive Constant (289)
$C(CH_3)_3$	−0.30
CH_3	0.00
CH_2Cl	+1.05
$CHCl_2$	+1.94
CCl_3	+2.65

B. A RULE

The effect of atom hybridization and electronegative substituents on bond angles, bond lengths, proton–C^{13} coupling constants, and inductive constants, suggests this rule: *Atomic s character concentrates in orbitals directed toward electropositive substituents.*[1] Lone-pair electrons are regarded as electrons in bonds to very electropositive atoms. Experimental evidence for this rule, which describes the direction of second-order (205) or isovalent hybridization (218), is summarized in these tables: table 15 (with table 1), table 16 (with table 8), table 17 (with table 14), and table 18 (with table 5). A model for this rule is described below in part C.

Walsh has stated this rule in these terms: If a group X attached to carbon is replaced by a more electronegative group Y, then the carbon valency toward Y has more *p* character than it had toward X (303).

C. A MODEL

The model described in this section has three ingredients. First, use is made of the generally accepted facts regarding electronegativity. Second, use is made of the fact that *s* electrons are bound more tightly than *p* electrons (57). Third, use is made of the result from perturbation theory that to a first approximation the change in energy, W', of a system whose potential energy is perturbed by an amount H' and whose wave function is initially ψ_0 is simply the weighted average of H' over the unperturbed state (240). The larger the overlap of the perturbation with the wave function of

$$W' = \int \psi_0^* H' \psi_0 \, d\tau$$

the system, the larger the effect of the perturbation on the energy of the system.

Consider, for example, a particle such as an electron bound by the potential depicted in figure 5 by the curve labeled V. The wave function for the lowest bound state will look like ψ_0. This is drawn to show that the particle tends to spend most of its time in the region of space where V is small (most negative). Thus, a perturbation such as H_2' that occurs where V is most highly negative has a greater effect on the energy of

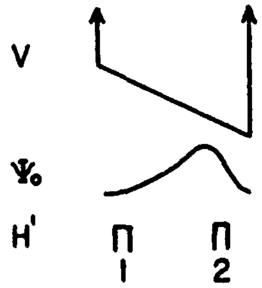


FIG. 5. Wave function ψ_0 for the ground state for the potential V and sample perturbations H'.

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[1] Or, atomic *p* character concentrates in orbitals directed toward electronegative substituents.

the particle than a differently placed but otherwise equal perturbation H_1'.

Consider, now, an electron in a bond between two atoms X and Y that differ in electronegativity, with Y more electronegative than X. In such a bond, the potential energy and the ground-state wave function vary from point to point along the internuclear axis in the manner illustrated in figure 6.

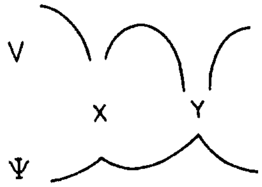


FIG. 6. One-dimensional model of a polar bond.

The general tilt of these curves is the feature of particular interest here. As long as Y is more electronegative than X, the potential-energy curve slants down toward Y and the camel-humped curve, ψ, has its maximum value at that point. With the exception of the extremum that occurs near the center of each curve (51), the general features of these curves may be summarized schematically by figures of the type labeled above (V and ψ_0 in figure 5). (One-dimensional square-well-type models of this type have been discussed by Barrow (16, 17); for additional references, see Platt (245).) This convention provides a convenient, visual representation of a polar bond in potential-energy space. Bonds between groups that differ in electronegativity are visualized as tilting downward toward the more electronegative group.

As an illustration, consider again two atoms or groups X and Y that differ in electronegativity, Y more electronegative than X, and suppose that these are bonded to an atom A of intermediate electronegativity, A being more electronegative than X but less electronegative than Y. The system X—A—Y might, for example, represent the array CH_3—N—Cl in $N(CH_3)_2Cl$, or the sequence unshared pair—oxygen atom—fluorine atom in OF_2. Figuratively, such a system may be represented in potential-energy space by orbitals directed downward from X to A and from A to Y. Considering the electrons in each bond separately, the usual procedure of valence-bond theory, one obtains the representation of V and ψ for the system X—A—Y shown in figure 7.

As shown by the curve for ψ, the energy-minimization procedure of quantum mechanics tends to concentrate electrons about regions of low potential energy. Consequently, owing to the tilt to the localized molecular orbital between X and A, the electrons in that orbital are polarized in the direction of the ionic structure X^+A^-. Similarly, because of the assumed difference in electronegativity between A and Y, the electrons in the A—Y bond tend to concentrate at the Y end of that bond. If either of these polar bonds were to dissociate homolytically, it is apparent that while one electron would remain in a region of relatively low potential energy associated with the atom on the right, one of the bonding electrons would have to receive some extra energy to promote it to full occupancy in the atomic orbital of the less electronegative atom on the left. This extra energy should contribute to the stability of the bond. The greater the tilt to the molecular orbital, presumably the greater this contribution to bond stabilization. This manner of thinking may be turned about. Pauling has found that the excess in A—X bond energy over the arithmetic (or geometric) mean of the A—A and X—X bond energies provides a useful, quantitative measure of the difference in electronegativity of A and X. One may consider that the model is in this way able to provide its own electronegativity scale.

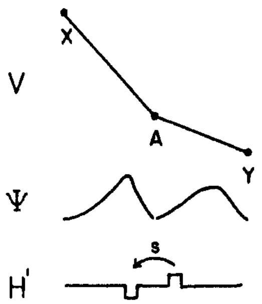


FIG. 7. One-dimensional model of the structure X—A—Y when χ_Y (the electronegativity of Y) > χ_A > χ_X.

In the potential-energy curve for X—A—Y (figure 7) the two bonds are shown as meeting at A, in accordance with the convention of beginning the analysis of the distribution of *s* character in molecules with the approximation that the *s* character of each atom is distributed equally among *sp*, sp^2, or sp^3 hybrids, as the case may be. However, it is known that when the attached groups differ among themselves in electronegativity, the central atom does not distribute its *s* character uniformly among its hybrid σ orbitals. The line beneath V and ψ labeled H' in figure 7 illustrates schematically an explanation for this dependence of atom hybridization on the electronegativities of the adjacent groups. The figure depicts the transfer by A of some *s* character from the orbital directed toward Y to the orbital directed toward X. This lowers the low end of the A—X bond and heightens the high end of the A—Y bond. (Data on quadrupole coupling constants appear to confirm this effect.) Because the electrons are more in the lower end of the A—X bond than they are in the upper end of the A—Y bond, this perturbation decreases the energy of the A—X pair more than it increases the energy of the A—Y pair. The net effect is a decrease in the energy of the molecule. Were the electronegativity of A assumed to be less than that of

X, or greater than that of Y, the conclusion would still be reached that the *s* character of A tends to concentrate in the bond to X, the more electropositive substituent.

To summarize, atoms tend to concentrate their *s* character in orbitals that slope inward most steeply or outward least sharply; that is to say, in orbitals directed toward the most electropositive of the attached groups. This effect increases as the spread in electronegativity of the attached groups increases, reaching an extreme for atoms that coördinate simultaneously both fluorine atoms and unshared electrons in their valence shell: for example, oxygen in OF_2 and nitrogen in NF_3 (table 15).

The effect of the electronegativity of the central atom on the distribution of its own *s* character is considered in Section VII,I,1.

VII. APPLICATIONS

A. A MECHANISM FOR THE INDUCTIVE EFFECT

If the effect of electronegative substituents on atom hybridization is combined with the effect of atom hybridization on electronegativity, there is obtained forthwith a concrete mechanism for the inductive effect.

To illustrate, consider again the system of bonded atoms X—A—Y, and suppose that the electronegativity of Y increases, i.e., that the orbital between A and Y becomes tilted more steeply downward toward Y. This change will cause atom A to rehybridize slightly, so as to shift *s* character from the bond to Y to the bond to X, where the low-potential-energy space characteristic of an *s* orbital will be used to greater advantage. This increase in *s* character at A's end of the A—X bond represents an increase in electronegativity of A with respect to X. In turn, by an identical, though smaller, operation of the same mechanism, the electronegativity of X toward attached groups (other than A) increases. In this manner, the original perturbation is relayed in an attenuated manner throughout the bonded system. It may be added that at each atomic center that engages in a significant redistribution of *s* character there should exist coupled to the inductive effect definite, albeit perhaps small, changes in bond angles and bond lengths.

B. APPLICATIONS OF THE INDUCTIVE EFFECT

1. Correlation of bond angles, base strength, and rates of inversion

The work required to deform an elastic spring increases as the square of the displacement from equilibrium. In pyramidal molecules the barrier to inversion is therefore strongly dependent on the equilibrium bond angle. Were deformation force constants constant over large deformations, deformation from 90° to planarity would be eight to nine times more difficult than deformation to planarity from 109°. Thus, while the force constant near equilibrium for the umbrella deformation of ammonia is nearly twice that of phosphine, the barrier to inversion in phosphine is three to five times greater than that in ammonia, and greater still in arsine (56, 312), owing to the difference in equilibrium configurations of these molecules (table 15).

Among pyramidal molecules, small valence angles and relatively large barriers to inversion are to be found in molecules that contain electronegative substituents attached to an electropositive atom, since both conditions favor withdrawal of *s* character from the bonding orbitals by the unshared electrons on the central (electropositive) atom (table 15).

Diminished basicity is another property correlated with lone-pair orbitals rich in *s* character (Section V,B). H_2S, for example, is a weaker base than $(CH_3)_2S$; PH_3 is a weaker base than $P(CH_3)_3$ (110) (also, fluoroalkylphosphines are weaker bases than the corresponding alkylphosphines). Too, phosphine is a weaker base than ammonia.

These facts suggest that in unconjugated pyramidal molecules of the type AB_3, base strength and valence angle ought to decrease and the barrier to inversion ought to increase as the electronegativity of A decreases and the electronegativity of B increases.

2. Ionization potentials

Removal of an electron from a free radical or from a molecule with lone pairs, or a double bond, may be compared to the formation of a coördinate link by a base. The two processes differ in the number of electrons involved and in the magnitude of the electronic displacement, but are nonetheless similar in character. The analogy leads to the prediction that the ionization potential of a molecule or radical should decrease as the *s* character in the orbital from which the electron is removed decreases. For simple molecules a decrease in ionization potential should be accompanied by an increase in intrinsic base strength. The data in table 19 support this view. Substitution of hydrogen by methyl, a process that draws *s* character from neighboring orbitals into the orbital where substitution occurred and thereby generally enhances intrinsic base strength, decreases the difficulty of removing an unshared electron from carbon (a to f), nitrogen (g to p), oxygen (q to u), or a shared electron from a carbon–carbon double bond (v to z). (Other examples may be found in references 93 and 103.) Alkyl groups have a similar effect on bond dissociation energies (97) and carbon–hydrogen stretching force constants (270).

3. Stability of classical carbonium ions

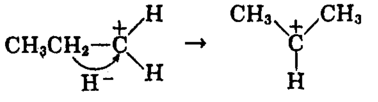
The structure of carbonium ions has been reviewed

TABLE 19

Ionization potentials of some molecules and radicals

Species	Ionization Potential (103)
	e.v.
Alkyl radicals (192):	
a. CH_3	9.95
b. CH_3CH_2	8.8
c. $CH_3CH_2CH_2$	8.69
d. $(CH_3)_2CHCH_2$	8.35
e. $(CH_3)_2CH$	7.90
f. $(CH_3)_3C$	7.42
Amines (308):	
g. NH_3	10.154
h. CH_3NH_2	8.97
i. $C_2H_5NH_2$	8.86
j. $C_3H_7NH_2$	8.78
k. $(CH_3)_2NH$	8.24
l. $(C_2H_5)_2NH$	8.01
m. $(C_3H_7)_2NH$	7.84
n. $(CH_3)_3N$	7.82
o. $(C_2H_5)_3N$	7.50
p. $(C_3H_7)_3N$	7.23
XOY compounds (248, 307):	
q. H_2O	12.59
r. CH_3OH	10.85
s. C_2H_5OH	10.50
t. $(CH_3)_2O$	10.00
u. $(C_2H_5)_2O$	9.53
Ethylenes (248):	
v. $H_2C{=}CH_2$	10.50
w. $CH_3HC{=}CH_2$	9.70
x. $CH_3HC{=}CHCH_3$	9.24
y. $(CH_3)_2C{=}CHCH_3$	8.80
z. $(CH_3)_2C{=}C(CH_3)_2$	8.30

by Bethell and Gold (31). Relatively low energies of activation are usually associated with the formation of the *tert*-butyl carbonium ion (124), and it is known that an isopropyl group dissociates as a carbonium ion far more readily than does a methyl group from the same position (5). Spontaneous hydride shifts of the type shown below



A B

have been observed for carbonium ions in solution (125) and in the gas phase (99, 100). Hammett has summarized these rearrangements in the following statement: The new carbonium ion generally carries a greater number of alkyl groups than the old one (125). It has been suggested that these facts concerning the behavior of carbonium ions may be examples of the rule that, where possible, atomic *s* character concentrates in bonds to electropositive groups; i.e., *s* character tends to be used where it contributes most effectively to the minimization of the energy of the molecule.

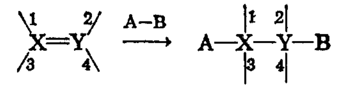
Efficient utilization of *s* character requires, first, that all *s* character be removed from the empty orbital of the carbonium ion; i.e., that the configuration about the atom with the open sextet, the carbonium carbon, be planar. Should this be prevented by steric effects, as, for example, at a bridgehead, formation is difficult (104) and the carbonium ion ceases to be an important reaction intermediate (8). Secondly, efficient utilization of *s* character requires, where possible, that the rich-in-*s*-character and electronegative sp^2 hybrids of the carbonium carbon be used to best advantage in the molecule: namely, to bonds to weakly electronegative groups. Thus, in structure A, the carbonium carbon is bonded to one weakly electronegative alkyl group and two hydrogen atoms, whereas in the more stable structure B, it is bonded to but one hydrogen atom and to two alkyl groups.

The *s*-seeking character of unshared electrons makes *carbanion* formation easier the *fewer* the number of adjacent alkyl groups. The ease of ionization of the benzyl hydrogen, for example, falls off in the order $C_6H_5CH_3 > C_6H_5CH_2CH_3 > C_6H_5CH(CH_3)_2$ (165). A similar effect appears to operate in certain aromatic nucleophilic displacement reactions (44).

4. Heats of addition to multiple bonds

Trends in the heats of hydrogenation of olefins have been discussed in molecular orbital language by Mulliken, Rieke, and Brown (224). A special postulate was introduced—that of hyperconjugation. Recently, it has been suggested that calorimetric data alone can neither prove nor disprove this postulate (295). Attention here is directed to the possibility that atom hybridization may play some part in determining heats of addition to multiple bonds.

When a reagent A—B, such as hydrogen, a halogen, or hydrogen bromide, adds to a double bond X=Y, a significant change occurs in the hybridization of the two atoms X and Y. In particular, the four orbitals labeled 1, 2, 3, 4 below change from approximately sp^2 hybrids to sp^3 hybrids, i.e., the *s* content of these orbitals decreases. Destruction of the double bond must, therefore, entail some promotion in energy of the electrons in these localized orbitals.



How important this promotion is to the net heat of the reaction will depend on how important the potential-energy space in the immediate vicinity of X and Y is to the electrons in bonds 1, 2, 3, and 4. The more electropositive the substituents attached through these four bonds, and, therefore, the greater the use made by the bonding electrons of the *s* character of atoms X and Y, the more will the loss in *s* character be felt, and the less the observed evolution of energy. Heats of hydrogenation of olefins, for example, are well known to decrease with increasing methyl substitution on the double bond. This is analogous to the situation encountered with carbonium ions. To paraphrase Hammett, the double bond of the more stable isomer of two isomeric olefins carries a greater number of alkyl groups than does the double bond of the less stable isomer. Algebraically, for the heat of hydrogenation of propene, for example, one may write, following Dewar and Schmeising (74), that E(hydrogenation of propene) = E(hydrogenation of ethylene) − $[E(C_{sp^3}—C_{sp^2}) - E(C_{sp^3}—C_{sp^3})] + [E(H_{1s}—C_{sp^2}) - E(H_{1s}—C_{sp^3})]$, where, for example, $E(C_{sp^3}—C_{sp^2})$ represents the energy of a pair of electrons in a single bond formed by the overlap of a carbon sp^3 hybrid orbital with a carbon sp^2 hybrid orbital. The statement above concerning the effect of the tilt in potential-energy space of the single bonds adjacent to the multiple bond on the energetics of the addition reaction provides a means for deciding when the first bracketed term in such an expression is greater than the second.

This model may be extended to other reactions. In the previous paragraph attention was focused on the addition of hydrogen to double bonds between carbon atoms holding alkyl groups. The data in table 20 show that in the same manner that substitution of hydrogen by the less electronegative methyl group causes a monotonic decrease in the heats of hydrogenation of a carbon–carbon double bond (b to f), substitution of hydrogen by a more electronegative group, such as chlorine, increases the heat of hydrogenation (a and b). Likewise, the effect of changing substitution from fluorine to chlorine to hydrogen and, in one case, to methyl, is to decrease the heat of chlorination (i to k), the heat of bromination (l to n), and the heat of hydrobromination (o to s) of the carbon–carbon double bond. Similarly, the substitution of hydrogen by methyl decreases the heat of hydrogenation of the carbon–oxygen double bond (g and h). It is interesting to note that the heat of hydrogenation of the carbon–oxygen double bond is significantly less than that of the carbon–carbon double bond. This is consistent with the presence on the former of two very electropositive groups, the lone pairs of oxygen, and leads to the conjecture that heats of hydrogenation (or chlorination, bromination, etc.) of double bonds may be found to decrease in the order C=C > C=N > C=O ≈ N=N > N=O (166).

TABLE 20

Some heats of addition to multiple bonds

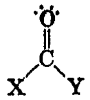
Compound	$-\Delta H$ (158, 159, 274)
Hydrogenation	
	kcal./mole
a. $ClCH=CH_2$	34.567
b. $CH_2=CH_2$	32.82
c. $CH_3CH=CH_2$	30.12
d. $CH_3CH=CHCH_3$ (trans)	27.6
e. $(CH_3)_2C=CCH_3$	26.92
f. $(CH_3)_2C=C(CH_3)_2$	26.63
g. $CH_3CH=O$	16.75
h. $(CH_3)_2C=O$	13.41
Chlorination	
i. $CF_2=CF_2$	57.3
j. $CF_2=CFCl$	48.8
k. $CH_2=CH_2$	43.7
Bromination	
l. $CF_2=CF_2$	38.4
m. $CF_2=CFCl$	32.1
n. $CH_2=CH_2$	29.2
Hydrobromination	
o. $CF_2=CF_2$	38.4
p. $CF_2=CFCl$	26.1
q. $CF_2=CCl_2$	23.0
r. $CH_3CH=CH_2$	20.4
s. $CH_3CH=CHCH_3$ (trans)	17.3

In general, *the more electronegative the substituents attached to a double bond, the greater the heat of addition.*

Triple bonds may be treated in an analogous manner. Two sets of data may be cited: the heats of hydrogenation of $HC\equiv CH$, $CH_3C\equiv CH$, and $CH_3C\equiv CCH_3$ are, respectively, 75.06, 69.70, and 65.58 kcal./mole (274); and the yield of amidine when ammonia is added to a nitrile ($R—C\equiv N$) is exceedingly small when R is CH_3, but is very large when R is CCl_3 or CF_3 (259).

5. *Interactions in the carbonyl group*

Carbonyl compounds provide many interesting illustrations of the inductive effect. Suppose, for example, that the electronegativities of X and Y in the compound XCOY were to increase.



This should cause the following to occur:

(*1*) closure of the X—C—Y angle, as carbon withdraws *s* character from the C—X and C—Y bonds;

(*2*) (*a*) diminution of the carbon–oxygen distance,
(*b*) diminution of the carbon–oxygen polarity, and
(*c*) enhancement of the carbon–oxygen bond strength, as measured by
    (*i*) the carbon–oxygen stretching force constant and
    (*ii*) the carbon–oxygen bond energy, as carbon feeds freed *s* character into the orbitals toward oxygen;

(*3*) rehybridization of oxygen, as this atom takes advantage of the enhanced electronegativity of carbon toward it and transfers some oxygen *s* character to the orbitals occupied by the unshared electrons, thus diminishing the electron-donor strength of the system and leading to
(*a*) a decrease in base strength and
(*b*) an increase in ionization potential.

These changes lead to numerous correlations. For example, the bond length of the carbonyl group should decrease as the ionization potential of the nonbonding oxygen electrons increases (301) (item 2,a with item 3,b); the polarity of the carbonyl group should decrease as the bond energy increases (304) (item 2,b with item 2,c,ii); the carbonyl stretching frequency, in the absence of conjugative effects, should increase as the electronegativities of the substituents on the carbonyl group increase (191) and the carbon–oxygen bond length decreases (156) (item 2,c,i, and item 2,c,i with item 2,a, respectively); and the basic properties of the carbonyl group should decrease, while the carbonyl stretching frequency should increase, as the ionization potential increases (53) (item 3,a with item 3,b, and item 2,c,i with item 3,b, respectively).

Steric effects may cause similar electronic adjustments in the carbonyl group. Suppose, for example, that the groups X and Y are brought closer together. For the bonding orbitals to follow this distortion of the X—C—Y valence angle, the carbon atom must withdraw some *s* character from the C—X and C—Y bonds. Conversely, were X and Y forced apart, orbital following on the part of carbon would require the introduction of additional *s* character into the C—X and C—Y bonds by the carbon atom (24). Either distortion should affect the *s* character in the carbon–oxygen bond, which one would expect to become shorter, less polar, and stronger as the X—C—Y angle becomes smaller. The data in table 21 illustrate the effect of angular distortions of the XCY group on the frequency of the carbonyl group (24). For X—C—Y angles smaller than normal (cases a and b), the C=O stretching frequency is larger than normal; for a larger than normal X—C—Y angle (case e), the C=O stretching frequency is smaller than normal. Other orbital-following effects are reviewed in this section in parts F, G, and H.

TABLE 21

Effect of valence-angle distortions on the C=O *stretching frequency*

Molecule	C=O Frequency (24)
	cm.$^{-1}$
a. Cyclobutanone	1780
b. Cyclopentanone	1740
c. "Normal acyclic ketones"	1700–1720
d. Cyclohexanone	1700
e. Hexamethylacetone	1690

Of the several aspects of the carbonyl group considered above, there is one, the C=O stretching frequency, that should depend, at least in part, on the stretching force constants of the C—X and C—Y bonds, the X—C—Y bending force constant, and the masses of X and Y. These factors have been considered by several authors (119, 229). The most recent analysis suggests that usually 85 to 90 per cent of the potential energy of the vibration of the carbonyl group resides in the carbon–oxygen bond (229); this result provides a measure of support for the suggestion that variations in the frequency of the carbonyl group are largely due to electronic effects (252).

C. ON THE NONADDITIVITY OF BOND LENGTHS

Bond lengths sometimes show marked deviations from simple additivity. For example, the carbon–fluorine distance in carbon tetrafluoride is 0.17 A. shorter than one-half the sum of the carbon–carbon and fluorine–fluorine distances in ethane and fluorine.

$$\begin{array}{llll}
\mathrm{CH_3{—}CH_3} & 1.54 \div 2 = & 0.77 & \\
:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}{—}\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: & 1.44 \div 2 = & \underline{0.72} & \\
 & & 1.49 & \text{(predicted)} \\
\mathrm{CF_3}{—}\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: & \multirow{2}{*}{C—F distances} \left\{ \right. & 1.32 & \text{(observed)} \\
\mathrm{CH_3}{—}\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: & & 1.39 & \text{(observed)}
\end{array}$$

Similar effects have been reported in other cases. Noting that the shortening frequently occurs for bonds joining atoms that differ in electronegativity, Schomaker and Stevenson (263) proposed the following empirical rule for predicting bond lengths:

$$r_{AB} = r_A + r_B - 0.09|x_A - x_B|$$

This rule has been criticized by Wells (309). The rule predicts no difference for the carbon–fluorine bond length in carbon tetrafluoride and methyl fluoride, for example, whereas the actual difference in bond length is 50 per cent of the electronegativity correction for the carbon–fluorine bond. Were repulsions between nonbonded atoms the important effect operating, the carbon–fluorine bond in carbon tetrafluoride would be longer than the carbon–fluorine bond in methyl fluoride. In fact, the carbon–fluorine bond in carbon tetrafluoride is the shorter of the two by 0.07 A. This may be explained in the following manner.

From symmetry, carbon must use four equivalent sp^3 orbitals in carbon tetrafluoride, while in methyl fluoride the large difference in electronegativity between hydrogen and fluorine causes the carbon atom to concentrate its *s* character preferentially in the carbon–hydrogen bonds, at the expense of the carbon–fluorine bond (Section VI), which is therefore richer in *p* character from the carbon side than the corresponding bond in carbon tetrafluoride, and longer (Section V). Admittedly, from the fluorine side, the H_3C—F bond is richer in *s* character than the F_3C—F bond, owing to the difference in electronegativity of carbon toward fluorine in these two compounds; however, unless the effective covalent radius of fluorine is by a significant amount more strongly dependent on hybridization than that of carbon, this effect will be of secondary importance so far as the carbon–fluorine bond length is concerned, since the initial perturbation (the change from CF_4 to CH_3F) is a perturbation on carbon.

A purely formal extension of the Schomaker–Stevenson rule leads to the wrong conclusion regarding the relative bond lengths in carbon tetrafluoride and methyl fluoride. Since hydrogen is less electronegative than fluorine, the effective electronegativity of the carbon atom toward fluorine in methyl fluoride is less than the effective electronegativity of the carbon atom toward fluorine in carbon tetrafluoride, i.e., the electronegativity difference between CH_3 and F is greater than that between CF_3 and F; hence the subtractive term in the Schomaker–Stevenson rule should be larger, and the carbon–fluorine distance shorter, in methyl fluoride than in carbon tetrafluoride, contrary to observation.

One may ask, Is the explanation offered above for the fact that the carbon–fluorine bond is shorter in carbon tetrafluoride than in methyl fluoride also applicable, perhaps in modified form, to the deviations from simple bond-length additivity considered by the Schomaker–Stevenson rule? Is it possible, for example, that the fluorine atom in going from F_2 to CF_4 rehybridizes in such a way as to shorten its effective covalent radius? In F_2 the fluorine atom is joined to an atom that is highly electronegative. Consequently, one may expect most of the *s* character of a fluorine atom in F_2 to be captured by the unshared electrons. In CF_4, however, the bonding orbital tilts down steeply toward fluorine. This increases the demand made by the bonding electrons for *s* character from the fluorine atom, and as the fluorine atom rehybridizes to meet this demand, the bond to carbon becomes richer in *s* character from the fluorine side, and shorter.

D. ELECTRONEGATIVITIES FROM BOND LENGTHS

1. Group electronegativities from the length of the carbon–fluorine bond

A change in hybridization ratio affects both the electronegativity of an atomic orbital (Section V,A) and its effective radius (Section V,C). It should be possible, therefore, to predict trends in bond lengths from inductive constants, or conversely, to infer from measured bond lengths trends in inductive constants.

Consider, again, the structure X—A—Y. As the electronegativity of X increases, or as A changes from sp^3- to sp^2- or sp-type hybridization, the *s* character in the A orbital toward Y (the A-to-Y orbital) increases. This tends to make the A—Y bond shorter. An inductively induced rehybridization of Y tends to counteract this, for as the *s* character in the A-to-Y orbital increases, A becomes effectively more electronegative with respect to Y, which causes Y to remove some *s* character from the Y-to-A orbital. This effect, of course, tends to increase the length of the A—Y bond. To preserve as much as possible the full effect of a change in hybridization of A on the length of the A—Y bond, Y should be an atom that uses little *s* character in its bond to A. Fluorine is such an atom.

Listed in table 22 are data that illustrate the composite effect of inductive influences and nominal changes in states of hybridization of carbon on the carbon–fluorine bond length. If a decrease in the carbon–fluorine bond length is taken to imply an increase in *s* content of the carbon-to-fluorine orbital, and if the latter implies an increase in electronegativity, the order from top to bottom in table 22 is the order of increasing group electronegativity. By and large, this order agrees well with chemical intuition and Taft's inductive constants (288, 289).

TABLE 22

Nine fluorine-containing compounds in order of decreasing carbon–fluorine bond length

Molecule	Carbon–Fluorine Distance	Reference
	A.	
a. $H_3C—F$	1.391	(38)
b. $CH_3\overset{\overset{O}{\|}}{C}—F$	1.3_7	(4)
c. $FH_2C—F$	1.358	(168)
d. $H\overset{\overset{O}{\|}}{C}—F$	1.351	(149)
e. $H\overset{\overset{CH_2}{\|}}{C}—F$	1.344	(208)
f. $F_2HC—F$	1.332	(115)
g. $F_3C—F$	1.323	(38)
h. $F\overset{\overset{CH_2}{\|}}{C}—F$	1.321	(151)
i. $F\overset{\overset{CF_2}{\|}}{C}—F$	1.313	(151)

In a quantitative sense, one may question whether it is reasonable, even as a first approximation, to attribute these changes in bond lengths entirely to changes in the hybridization ratio of the carbon orbital of the carbon–fluorine bond. Although the state of hybridization of carbon in these compounds is not known with great accuracy, it is known that the H—C—H angle in the methyl halides tends to be several degrees greater than the tetrahedral value (200). This leads to the estimate that the carbon orbital toward fluorine in $CH_3—F$ contains 15–20 per cent *s* character (60). The uncertainty in this figure arises from the uncertainty in the position of the hydrogen atoms, owing to their small mass or scattering power, and the sharp dependence of pyramidal hybridization ratios on the interbond angle between the equivalent hydrogen atoms. In $F_2C{=}CF_2$ the carbon orbital toward fluorine may be estimated to contain some 27–29 per cent *s* character. Thus, the change in *s* content from compound a to compound i is perhaps 7–14 per cent.

The corresponding change in bond length is 0.08 A. These figures may be compared with those cited earlier (Section V,C) for carbon–carbon bonds. The C(sp^3)—C(sp) bond is typically 0.08 A. or so shorter than the C(sp^3)—C(sp^3) bond. This corresponds to a nominal change in *s* content of 25 per cent. The actual change in *s* content is undoubtedly less than this figure, first, because the carbon orbitals of the carbon–carbon bond in ethane (though not in the diamond) are slightly richer in *s* character than the notation sp^3 indicates, and second and more importantly, because the lone σ orbital that projects from a triple bond is undoubtedly poorer in *s* character than the notation *sp* indicates (206). How much poorer is a moot question (220). If one adopts, as here, the σ–π description of multiple bonds and assumes that a triple bond preëmpts *s* character per π bond as effectively as does a double bond (part H), and while this is unlikely, it does afford some kind of first approximation, the lone "*sp*" orbital of carbon in, say, acetylene, might contain as little as 35–40 per cent *s* character. While exceedingly rough, these figures do yield for the carbon–carbon case a change in the covalent radius of carbon with hybridization ratio comparable to that estimated from the data on carbon–fluorine bonds.

2. Atom electronegativities from bond lengths in diatomic hydrides

There exists a correlation between the difference in bond length in a radical (or molecule) AH and the corresponding ion AH$^+$ and the electronegativity of A. It is found that in going from AH to AH$^+$ the bond length increases when A is electronegative and decreases when A is electropositive (table 23). It is possible, therefore, to estimate the electronegativity, x_A, of A from the interatomic distances in AH and AH$^+$; or, conversely, to estimate the interatomic distance R(AH$^+$) in AH$^+$ from R(AH) and x_A. The following explanation may be given for the correlation between x_A and the difference R(AH) $-$ R(AH$^+$).

TABLE 23

Bond lengths (284) in AH *and* AH$^+$, *their difference*, Δ, *and* x_A

Hydride, AH	R(AH)	R(AH$^+$)	$\Delta \equiv R$(AH) $-$ R(AH$^+$)	x_A (249)
	A.	*A.*	*A.*	
OH	0.9706	1.0289	−0.0583	3.5
NH	1.038	1.084	−0.046	3.0
HCl	1.27460	1.3153	−0.0407	3.0
HBr	1.414	(1.459)	$-(0.04_6)$	2.8
CH	1.1198	1.1308	−0.0110	2.5–2.6
BH	1.2325	(1.2146)	$+(0.01_8)$	1.8–2.0
BeH	1.3431	1.3121	+0.0310	1.4–1.5
AlH	1.64_7	1.601_6	$+0.04_6$	1.5
MgH	1.7306	1.649	+0.082	1.2–1.3

It is assumed that atom A has two or more valence electrons. This insures that the molecule or radical AH contains at least one unshared valence-shell electron. In abbreviated notation, the structure of AH may be indicated as $\cdot$A—H. Removal of an electron from this structure gives the ion AH$^+$. A convenient approximation to the structure of this ion is to regard the ion as a resonance hybrid of two extreme structures, which will be abbreviated as A—H$^+$ and $\cdot$A$\cdot$H$^+$. A—H$^+$ represents schematically the structure that would be obtained if the electron removed from $\cdot$A—H were to come from a predominantly nonbonding or antibonding orbital localized about A. $\cdot$A$\cdot$H$^+$ represents the hypothetical structure obtained when ionization occurs from a predominantly bonding orbital, one localized between A and H. An approximate wave function for the actual molecule AH$^+$ may be compounded from the wave functions for these two idealized structures.

$$\psi(\mathrm{AH}^+) = N[\psi(\mathrm{A—H}^+) + \lambda\psi(\cdot\mathrm{A}\cdot\mathrm{H}^+)]$$

where the proper value for λ is the value that minimizes the energy of AH$^+$. The dependence of this value of λ on the electronegativity of A may be established by the following argument.

The formal charge (166) on A in the structure A—H$^+$ is +1; in $\cdot$A$\cdot$H, $+^1/_2$. From this it is inferred (232, 233, 234) that the importance of the latter structure increases as the electronegativity of A increases; that is to say, it seems reasonable to suppose that

$$\partial\lambda/\partial x_A > 0$$

Also, it seems reasonable to suppose that $R(\cdot\mathrm{A}\cdot\mathrm{H}^+) > R(\cdot\mathrm{A—H})$ and that the difference $\Delta \equiv R(\mathrm{AH}) - R(\mathrm{AH}^+)$ becomes smaller (more negative) as λ increases; in short, that

$$\partial\Delta/\partial\lambda < 0$$

Hence, it follows that

$$\frac{\partial\Delta}{\partial x_A} = \frac{\partial\Delta}{\partial\lambda}\cdot\frac{\partial\lambda}{\partial x_A} < 0$$

The data in table 23 follow this pattern. With an increase in x_A, there follows a monotonic decrease in Δ.

The fact that Δ is actually positive for the more electropositive elements listed in table 23 implies that $R(\mathrm{A—H}^+) < \mathrm{R}(\cdot\mathrm{A—H})$. This is reasonable. In the parent hydride, $\cdot$A—H, most of the *s* character of A is captured by the unshared electrons about A; only part of its *s* character resides in the A—H bond (106, 144, 206, 207, 217, 218, 256). Removal of one of these unshared electrons decreases the number of unshared electrons that compete with the shared electrons for the *s* character of A. Therefore, the bonding orbital in A—H$^+$ should be richer in *s* character than the corresponding orbital in $\cdot$A—H, and shorter.

From the accepted value for the electronegativity of fluorine (3.9–4) (249) and the near linearity of Δ with

χ_A (table 23), it may be inferred that the interatomic distance in HF^+ is probably 0.98 ± 0.02 A.

3. Other scales of electronegativity

Electronegativity scales may be based on any molecular property that shows a systematic dependence on atom hybridization. This property might be a bond length (tables 16 and 22), a bond angle (table 15), a coupling constant (table 17), an inductive constant (table 18), an ionization potential (table 19; see, also, references 213 and 214); a heat of addition to a multiple bond (table 20), or a bond force constant—or its practical (though sometimes only approximate) equivalent: a characteristic group frequency. Group frequencies that have been treated in this manner include those for the cyanide group (90, 91, 155), the CH_2 group (315), the OH group (12), and the nitro group (94). The data in table 24 illustrate one such correlation: that between the electronegativity of R in R—NO_2 and the asymmetric stretching frequency of the nitro group. This frequency increases with remarkable regularity as the electronegativity of the attached group increases. Several explanations have been forwarded for this. One factor to consider is that an increase in the electronegativity of R in the compound R—NO_2 will cause the nitrogen atom to divert *s* character to the nitrogen–oxygen bonds (Section VI), thereby increasing the O—N—O angle (196) and the stretching force constant of the nitrogen–oxygen bonds (Section V,D). At the head of table 24 could be placed NO_2^+ (bond angle 180°, asymmetric stretching frequency 2375 cm.$^{-1}$); this represents one extreme (R *very* electronegative); at the other extreme stands NO_2^- (bond angle 115°).

TABLE 24

Effect of electronegative groups on the asymmetric valence vibration of the nitro group (94)

Molecule	Asymmetric Stretching Frequency	Molecule	Asymmetric Stretching Frequency
	cm.$^{-1}$		*cm.*$^{-1}$
F—NO_2	1793	RCl_2C—NO_2	1590
O_2N—NO_2	1735	$RH(O_2N)C$—NO_2	1580
O_2NO—NO_2	1715	RHClC—NO_2	1570
Cl—NO_2	1685	RH_2C—NO_2	1558
RO—NO_2	1640	R_2HC—NO_2	1553
F_3C—NO_2	1625	R_3C—NO_2	1540
$(O_2N)_3C$—NO_2	1618	^-O—NO_2	1375
Cl_3C—NO_2	1610	$:NO_2^-$	1270
Br_3C—NO_2	1592		

Walsh has suggested an electronegativity scale based on force constants of bonds to hydrogen (305). Such bonds are considered in part E of this section.

E. TRENDS IN HYDRIDE GEOMETRY

Removal of a hydrogen atom from a hydride like CH_4, NH_3, or H_2O increases by one the number of unshared electrons on the central atom. Were one unshared electron more demanding of *s* character than two shared electrons, removal of hydrogen atoms should cause the remaining bonds to become longer and remaining bond angles to become smaller. There seems to be little, if any, evidence contradictory to this view, and some in support of it. Bond lengths in the series NH_3, NH_2, NH do increase in the order 1.014 (284), 1.025 (251), 1.038 (284) A.; concomitantly, the bond angle decreases, from 106°46′ in NH_3 (284) to 103° in NH_2 (251). Similarly, the data in table 25 illustrate the fact that the bond length in a diatomic hydride is generally greater than the bond length in the corresponding stable polyatomic molecule. It is frequently said that the methyl radical is approximately planar (135); but so, too, is the methyl group. Thus, present data do not seem to rule out unequivocally the possibility that in the ground state bond lengths increase and bond angles decrease with increasing number of unshared electrons in the series CH_4, CH_3, CH_2, CH. (The ground states and chemistry of CH_2 and related carbenes have been discussed by several authors (76, 83, 92, 137–139, 281, 290).) Not considered in this discussion is the fact that there exists in the NH_2 radical, and still more so in the OH radical and the fluorine atom, a species of resonance not present in the CH_3 radical, which explains, perhaps, the monotonic decrease in bond dissociation energy along the isoelectronic series H_3C—CH_3, H_2N—NH_2, HO—OH, F—F (83, 60, 48, and 36 kcal./mole, respectively (58)).

TABLE 25

Corresponding bond lengths in diatomic and polyatomic hydrides (129, 284)

Bond	Bond Length	
	Polyatomic molecule	Diatomic molecule (ground state)
	A.	*A.*
CH	1.09_4	1.120
NH	1.014	1.038
OH	0.9584	0.971
SiH	1.480	1.521
PH	1.41	1.433
SH	1.334	1.35
GeH	1.527	1.591

Considering the effect that removal of a hydrogen atom has on atom hybridization, one would expect, *a fortiori*, that removal of a proton from, or the addition of an electron to, a neutral hydride would cause the *s* content of the remaining bonds to decrease, with its associated implications concerning bond lengths and bond angles, the former increasing, the latter decreasing, with decreasing *s* content. These considerations are applicable to the following molecule-ion pairs. In each case, one expects the ion to have less *s* character in its bond(s) than the parent molecule. Bond lengths and bond angles believed trustworthy are indicated in parentheses.

Removal of an extranuclear proton: CH_4 (1.094 A., 109°28′ (135)) and CH_3^-; NH_3 (1.038 A., 106°47′ (284)) and NH_2^-; H_2O (0.971 A., 104°27′ (134)) and OH^-.

Electron addition: CH_3 and CH_3^-; NH_2 (1.025 A., 103° (251)) and NH_2^-; OH (0.9584 A. (284)) and OH^-.

Addition of a hydride ion to a neutral, electron-deficient hydride should also decrease the *s* character in the original bonds. Thus, the bond in NH (1.014 A.) should be shorter than the bonds in NH_2^-; and the bonds in CH_2 (singlet state) should be shorter, and the bond angle greater, than those in CH_3^-.

Also, from the trends in table 15, it may be conjectured that removal of a proton from the nucleus of the central atom (this decreases its electronegativity) probably decreases the *s* character in the bonding orbitals. Thus, the bond angle in NH_2^- is expected to be smaller than the bond angle in H_2O (104°27′); similarly, the bond angle in CH_3^- is expected to be smaller than the bond angle in NH_3 (106°47′).

Finally, from the effect of the transfer of an extranuclear proton to the nucleus (a combination of ionization of an extranuclear proton, which decreases bond angles, and addition of a proton to the nucleus, which increases bond angles) on neutral molecules (NH_3 and H_2O, PH_3 and H_2S (table 15)), it is inferred that the bond angle in CH_3^- is probably several degrees greater than that in NH_2^-.

To summarize, six processes that may decrease *s* character in bonding orbitals have been considered: removal of a hydrogen atom, removal of an extranuclear proton, addition of an electron, addition of a hydride ion, removal of a nuclear proton, and transference of an extranuclear proton to the nucleus.

Linnett and coworkers have established a correlation between the difference in bond length in a radical AH and the corresponding hydride AH_n and the signs, and to a lesser extent the magnitudes, of the cross-terms in the potential-energy function of AH_n. This correlation is considered below in part F.

F. ORBITAL FOLLOWING

In methane, as one H—C—H angle opens, the one opposite to it tends to close (177, 181). This implies that the carbon orbitals follow to some extent the motion of the protons (64). An interesting application of this suggestion occurs in the methyl halides. Centrifugal stretching in the molecule CH_3—X as it rotates about the C—X axis forces open the H—C—H angles. To follow this change in geometry, the carbon atom must divert *s* character to the carbon–hydrogen bonds, at the expense of the C—X bond, which should (Section V,C), and does (293), become longer. Similar effects have been observed for planar, symmetrical molecules and ions of the type BX_3, BO_3^{3-}, CO_3^{2-}, and NO_3^-. In most cases, stretching one bond results in an increase in the angle opposite that bond (242).

Orbital following has been used by Linnett and Hoare to explain their observation that when the bond length in a symmetrical triatomic molecule ABA is less than that in the corresponding radical AB (*cf.* table 25), the bond–bond cross-term constant k_{12} in the potential-energy function for ABA is negative (179). This cross-term constant k_{12} measures the change in the strength of bond 1 as bond 2 changes length. A negative value means that bond 1 becomes weaker as bond 2 becomes longer. This implies that *s* character flows out of bond 1 and into bond 2 as bond 2 stretches.

Orbital following has also been applied to the difficult problem (142) of interpreting the intensities of infrared absorption bands in such molecules as water (48, 122), ammonia (48, 194), carbon dioxide (122), and ethylene (67, 114), and to the problem of interpreting and predicting the chemical and physical properties of small-ring compounds (this section, part G).

G. SMALL-RING COMPOUNDS

The fleeting distortions of bond angles and bond lengths that occur in vibrating molecules are caught greatly magnified in the geometries of three- and four-membered rings. If the ring atoms in such compounds attempt to adjust their orbitals to the local geometry, it would follow that orbitals participating in intraring bonds ought to be richer than usual in *p* character. This implies, in turn, that ring-atom orbitals not involved in intraring bonds ought to be richer than usual in *s* character. These statements carry certain definite implications. They suggest, for one thing, an explanation for the curious fact that the carbon–carbon interatomic distances in cyclopropane and cyclobutane alternate between being shorter and longer than normal (normal being the value for ethane, or diamond). In the paragraphs below, intraring bonds are considered first and then the external orbitals.

1. Interatomic distances in three- and four-membered rings

Interatomic distances in several small-ring compounds are given in figure 8. The statement that ring bonds are richer than usual in *p* character would seem to imply the existence of uncommonly large interatomic distances within small rings. Actually, the observed carbon–carbon distance in cyclopropane is 1.523 A., nearly 0.02 A. less than the carbon–carbon distance in ethane. For this reason, it is generally assumed that the ring bonds in cyclopropane and its analogs are

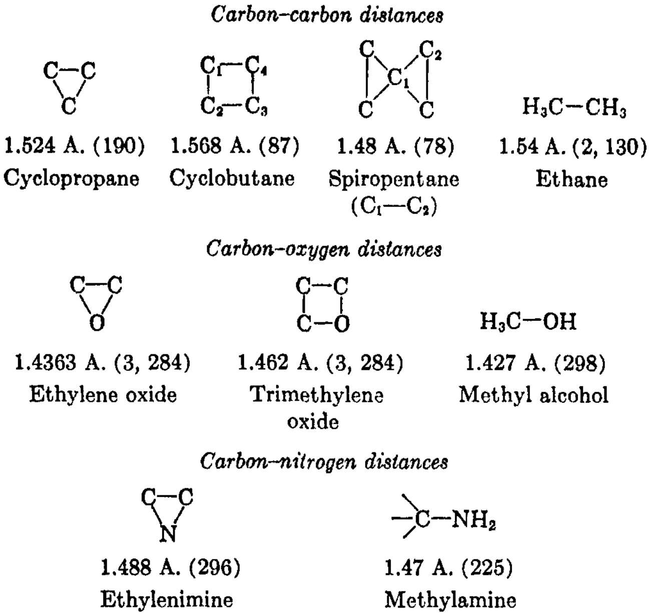


FIG. 8. Interatomic distances in several small-ring compounds (113).

bent bonds (66); although presumably the carbon–carbon bonds in cyclopropane actually do contain less *s* character than those in ethane. Indeed, in ethylenimine, the reported carbon–nitrogen distance of 1.488 A. is actually greater than the 1.47 A. reported for the carbon–nitrogen bonds in methylamine and dimethylamine. Similarly, in ethylene oxide the carbon–oxygen distance is reported to be 1.4363 A., compared to the smaller value of 1.427 A. for the carbon–oxygen distance in methyl alcohol. In both ethylenimine and ethylene oxide the bent-bond effect is apparently more than balanced by the effect anticipated for rehybridization induced by orbital following. Preponderance of the latter effect in these two compounds is perhaps attributable to the strong *s*-seeking character of unshared electrons.

Evidence that the same bond-lengthening effect is operative in hydrocarbons can be found in a comparison of the carbon–carbon distance, 1.524 A., in cyclopropane with the distance between the central carbon atom and the other ring atoms in spiropentane. This latter distance, which involves a carbon atom bound by symmetry to the use of sp^3 orbitals (78), is reported to be only 1.48 A.

In cyclobutane, where the bent-bond effect should be smaller than in cyclopropane, interatomic distances should reflect states of hybridization more faithfully. Indeed, the value reported for the carbon–carbon distance in cyclobutane is 1.56_8 A. (1.55–1.58 A. in 1,2,3,4-tetraphenylcyclobutane (85)), 0.02 A. greater than the corresponding distance in ethane. Similarly, in trimethylene oxide, the carbon–carbon distance is larger by 0.035 A. than the corresponding distance in methyl alcohol.

The abnormally long carbon–carbon distance in cyclobutane has also been attributed to repulsive forces between diagonally opposed (nonbonded) carbon atoms (figure 8: C_1 and C_3; C_2 and C_4) (87, 113); these atoms are closer to each other in cyclobutane than in *n*-butane. If repulsion between nonbonded atoms is the most important effect operating, it is not then immediately obvious, however, why the external H—C—H angle in cyclobutane is larger, rather than smaller, than normal.

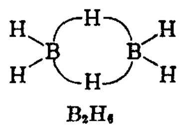
2. Hybridization of external orbitals

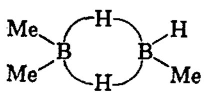
The H—C—H angle in cyclobutane, among other things, receives a ready explanation if it may be assumed that atomic orbitals that project from small rings are richer than usual in *s* character. Physical and chemical evidence in support of this assumption is summarized below (see, also, reference 253).

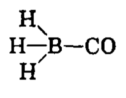
(*a*) *Evidence from bond angles:* The H—C—H angles in cyclopropane, ethylenimine, ethylene oxide, and cyclobutane have been reported as 118.2°, 116.7°, 116.7°, and 114 ± 8°, respectively. The Cl—C—Cl angle in 1,1-dichloropropane is given as 112° (227). In $Al_2(CH_3)_6$ the external C—Al—C angle, and in B_2H_6 the external H—B—H angle, are given as being 124° (167) and 121.5 ± 7.5° (130), respectively.

(*b*) *Evidence from bond lengths:* The carbon–chlorine distances reported for monochloropropane and dichloropropane are shorter by 0.02 A. than the usual $C(sp^3)$—Cl distance. In cyclopropane and cyclopropene the carbon–hydrogen distances seem to average about 0.01 A. less than the usual $C(sp^3)$—H distance (86, 152).

(*c*) *Evidence from stretching vibrations:* From their stretching force constants, Linnett has concluded that there is a large amount of *s* character in the carbon–hydrogen bonds of cyclopropane and ethylene oxide (175). The boron–hydrogen vibrations of the nonbridge hydrogen atoms in B_2H_6 (2522 and 2614 cm.$^{-1}$) and of the single nonbridge hydrogen atom in trimethylborane (2509 cm.$^{-1}$) are higher than the assigned boron–hydrogen vibrations in borine carbonyl (2164 and 2440 cm.$^{-1}$) (68). (See, also, table 21.)


B_2H_6


Trimethylborane


Borine carbonyl

(*d*) *Evidence from ionization potentials:* The first ionization potential of ethylene oxide is 10.565 e.v. The value for dimethyl ether is 10.00 e.v. (table 19). This indicates that the atomic orbitals occupied by the unshared electrons in ethylene oxide are richer in *s* character than the corresponding orbitals in dimethyl ether.

(*e*) *Evidence from dipole moments:* The dipole moments of monochlorocyclopropane and monochlorocyclopentane are, respectively, 1.76 and 2.04 debyes (66, 258). This indicates that the C(cyclopropane)—Cl bond contains more carbon *s* character than the C(cyclopentane)—Cl bond.

(*f*) *Evidence from proton–*C^{13} *coupling constants:* It is recalled that the value of J_{CH} increases as the *s* character in the carbon orbital of the carbon–hydrogen bond increases, the values for methane, benzene, and methylacetylene being, respectively, 125, 159, and 248 $sec.^{-1}$ The value reported for cyclopropane is 161 $sec.^{-1}$ (211), nearly the same as that of benzene.

(*g*) *Chemical evidence:* (*i*) Hydrolysis. It has been reported that the hydrolysis of chlorocyclopropane is relatively difficult (253). (*ii*) Basicity. Because ring opening is catalyzed by both acids and bases, it is difficult to determine experimentally whether, as would be expected, ethylene oxide and trimethylene oxide are weaker bases than ordinary ethers or not. However, it has been observed that hydrogen bonds to ethylene oxide, ethylenimine, and ethylene sulfide (264) and to cyclic ketones (319) are relatively weak. Also, it has been reported that the stability of the complex between trimethylene oxide and dinitrogen tetroxide is low, whereas the complexes with tetrahydrofuran and tetrahydropyran are moderately stable (272).

(*h*) *Additional evidence:* In the aluminum bromide dimer, the external aluminum–bromine bonds are shorter than the interatomic distances between the aluminum atoms and the bridge bromine atoms; also, the external Br—Al—Br angle is found to be 116° (52).

H. MULTIPLE BONDS

There exist today, side by side, two well-established, and equivalent (223, 236, 247), descriptions of the electron density in multiple bonds. One view, described in Section II, considers a multiple bond between two atoms to be formed by the overlap from one atom with similar orbitals from the other atom of one (σ) hybrid orbital (for carbon, either *tr-* or *di-*type hybrids) and one (for a double bond) or two (for a triple bond) pure $2p$ (π) orbitals. The other, more classical view considers a multiple bond between two atoms to be formed by the overlap from one atom with similar orbitals from the other atom of two (for a double bond, figure 9) or three (for a triple bond) equivalent hybrid orbitals (for carbon, *te*-type hybrids). These two descriptions will be referred to as the σ–π description and the bent-bond or banana-bond description, respectively.

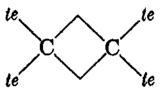


FIG. 9. Classical bent-bond description of a carbon–carbon double bond.

These two points of view are complementary. One point of view leads, for example, to the prediction that the interbond angle opposite a carbon–carbon double bond ought to be greater than 109°28′, while the other point of view leads to the prediction that this angle ought to be less than 120°. These predictions are described below in more detail.

1. Bent-bond description

From the bent-bond point of view (figure 9), a compound that contains a double bond may be viewed as a member of the class of small-ring compounds. Experimental evidence in support of this view has already been summarized (Section V). Bond angles, bond lengths, force constants, dipole moments, ionization potentials, inductive constants, coupling constants, bond dissociation energies, and acid–base strength testify to the fact that orbitals adjacent to a double bond are richer in *s* character than ordinary tetrahedral hybrids. It is well known, for example, that the normal interbond angle opposite a carbon–carbon double bond is greater than 109°28′. Figure 10 summarizes the information that the bent-bond description of multiple bonds provides concerning orbital hybridization ratios about a carbon atom involved in one double bond. The notation te^+ (te^-) indicates an orbital that contains more (less) than 25 per cent *s* character.

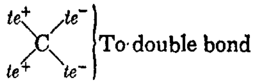


FIG. 10. Orbital hybridization ratios about a carbon atom involved in one double bond.

Orbital hybridization ratios about a carbon atom participating in a triple bond are summarized schematically in figure 11. This figure implies, and the implication is strongly supported by experiment, that the lone orbital projecting from a triple bond is richer in *s* character than either orbital of the pair that projects from a double bond.

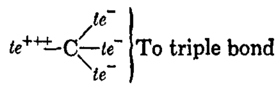


FIG 11. Orbital hybridization ratios about a carbon atom participating in a triple bond. Bent-bond approximation, with allowance for effect of orbital following.

Orbital hybridization ratios may, of course, be strongly influenced by the presence of lone-pair electrons or electronegative groups (Section VI). This point will be considered in part 3.

2. σ–π description

The overlap of the π component of a double bond would improve if the nuclei were brought closer together. The attractive force engendered by this effect must be balanced at equilibrium by an opposite force that may be identified with the σ component of the double bond. In this view, a double bond is envisaged as a two-component push-pull system, in which compression of one component is balanced at equilibrium by extension of the other. That the σ component of a normal double bond exists in a state of compression is shown by the fact, noted in Section V,C,2,(b), that superposition of a π bond on a σ bond leads to a marked decrease in interatomic distance, while the further decrease in interatomic distance that occurs when yet a second π bond is introduced shows that the π component of a double bond exists in a state of extension. Thus, the ionization potential of acetylene is greater than that of ethylene (11.42 e.v. compared to 10.50 e.v. (248)). Some relief of these stresses would occur if the natural length of the σ component were lessened by *increasing its s content.* Figure 12 illustrates this effect. In this figure tr^+ (tr^-) indicates an orbital that contains more (less) than 33 per cent s character.

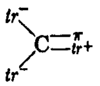


FIG. 12. Orbital hybridization ratios about a carbon atom participating in one double bond. σ–π approximation with allowance for π-bond compression of σ component of double bond.

Figure 12 implies that the normal interbond angle opposite a carbon–carbon double bond is less than 120°. This always seems to be the case.

A treatment for triple bonds similar to the one given above for double bonds has been mentioned in Section VII,D,1.

3. Comparison

Transformation to equivalent orbitals of the σ and π components of a multiple bond makes possible a direct comparison of the two prevailing views of multiple bonds. The sp^2 hybrid atomic orbital and pure $2p$ atomic orbital that a carbon atom uses in double-bond formation in the usual σ–π approximation to such a bond may be replaced by two equivalent orbitals, each one of which contains one-sixth s character and five-sixths p character, written $s^{1/6}p^{5/6}$ or sp^5 (223). Similarly, the sp hybrid and two pure $2p$ atomic orbitals used in the usual σ–π description of a triple bond may be replaced by three equivalent orbitals, each one of which is, again, an sp^5 hybrid orbital. These results are summarized in figure 13 (*cf.* figures 10 and 11).

Neither structure in figure 13 is a true representation of a multiple bond to carbon. Structure A may be described as the bent-bond representation of the conventional σ–π description of a carbon–carbon double bond. Real double bonds, by comparison, must be considered s-seeking centers; viewed against structure A, they appear to withdraw s character from adjacent single bonds. On the other hand, viewed against figure 9, carbon–carbon double bonds appear to release s character to adjacent single bonds. That these two statements are actually complementary may be seen by examining the effect of electronegative substituents on the hybridization of an ethylenic carbon atom.

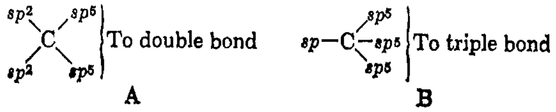


FIG. 13. Approximate equivalent orbitals for doubly and triply bonded carbon. Based on the σ–π convention of trigonal and digonal hydrids.

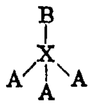
Take first the σ–π point of view and the double bond as an s-seeking center. The double bond preëmpts s character from adjacent single bonds more readily the more electronegative the attached substituents. Thus, the F—C—F angle in 1,2-difluoroethylene should depart from 120° downwards by a larger amount than the H—C—H angle in ethylene, and it does; the angles are 110° and 118°, respectively. Next, take the bent-bond point of view and the double bond as an s-releasing center. The double bond releases s character to adjacent single bonds more readily the more electropositive the attached substituents. Thus, the H—C—H angle in ethylene should depart from 109°28′ upwards by a larger amount than the F—C—F angle in 1,2-difluoroethylene. Both points of view lead to the same conclusion: namely, that the F—C—F angle in $F_2C{=}CH_2$ (or $F_2C{=}CF_2$) is less than the H—C—H angle in $H_2C{=}CH_2$.

I. APPLICATIONS TO COMPOUNDS CONTAINING SECOND-ROW ELEMENTS

1. Bond angles in compounds of Groups V and VI

The angle between two bonds that meet at an atom from Group V or VI generally decreases as the atomic number of the atom from Group V or Group VI increases. For example, the bond angle in H_2S is less than the bond angle in H_2O; and in Group V the bond angles decrease in the order $NX_3 > PX_3 > AsX_3$ for X = H or CH_3 (table 15). Explanation of these trends has been a troublesome problem in valence theory (202). While it is not within the province of the present review to consider in detail problems in which d orbitals possibly play an important part, it is perhaps admissible at this point to speculate briefly on the role that s and p electrons might be expected to play in these compounds.

Attention is directed to molecules of the type of BXA_3 (I) and B_2XA_2 (II), where A and B represent


I


II

substituents that may differ in electronegativity. Compounds of Group V are of type I, B representing a lone pair; compounds of Group VI are of type II. If, as before, unshared electrons are regarded as electrons in bonds to a substituent of zero electronegativity, the following account may be given of the effect on bond angles of the electronegativities of atoms A, B, and X.

(*1*) If A and B are identical (CH_4, NH_4^+, Ne, F^-), the four *s–p* hybrid orbitals of X are, of course, equivalent (Section III).

(*2*) If A is more electronegative than B, X should concentrate its *s* character in those orbitals that it directs toward B (Section VI), thus diminishing the A—X—A angle below and increasing the B—X—B angle above the tetrahedral value of 109°28′.

(*3*) If B represents an unshared pair, and the electronegativity of A remains fixed, a *decrease* in the electronegativity of X has the same effect on the A—X—A angle as an *increase* in the electronegativity of A (table 15). This seems reasonable. As the ability of X to contribute space of low potential energy to the electrons in the A—X bond diminishes, owing either to an increase in electronegativity of A or to a decrease in the electronegativity of X, X should concentrate more and more of its *s* character in the orbitals occupied by its unshared electrons; and, correspondingly, the A—X—A angle should become smaller, as observed.

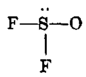
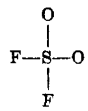
2. Bond angles and bond lengths in thionyl and sulfuryl fluorides

The shapes of several covalent molecules containing sulfur and phosphorus are examined below with a view to establishing in a qualitative manner the extent to which effects arising from hybridization ratios in σ bonds may be important in determining details of molecular geometry about atoms of the second row of the periodic table. Two sulfur compounds are considered first.

Accurate structural parameters are known for thionyl and sulfuryl fluorides. These are given in table 26 beneath the Lewis octet structures for these two molecules. Not shown in these valence-bond structures are d_π—p_π bonds between sulfur and the surrounding atoms. On formal charge grounds (232–234) it seems likely that such bonds are formed between sulfur and oxygen (204), but not between sulfur and fluorine. Accordingly, changes in the sulfur–fluorine bond in passing from one compound to the other may perhaps be viewed as arising at least in part from changes in hybridization of the σ orbitals of sulfur.

TABLE 26

Structures of thionyl and sulfuryl fluorides

	Thionyl Fluoride (95) 	Sulfuryl Fluoride (170) 
Sulfur–oxygen distance	1.412 A.	1.405 A.
Sulfur–fluorine distance	1.585 A.	1.503 A.
F—S—F angle	92°49′	96°7′

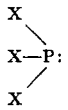
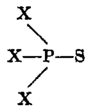
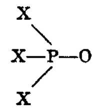
As shown in table 26, the two molecules SOF_2 and SO_2F_2 differ chiefly in the fact that the lone pair on sulfur in SOF_2 is shared with an oxygen atom in SO_2F_2. In view of the strong *s*-seeking character of unshared electrons (dimethyl sulfoxide is a nucleophilic reagent (278)), the sulfur–oxygen and sulfur–fluorine σ bonds in SOF_2 should receive less *s* character from sulfur than do the corresponding bonds in the more fully oxygenated compound. In fact, the sulfur–oxygen and sulfur–fluorine interatomic distances are greater, and the F—S—F angle is smaller, in SOF_2 than in SO_2F_2.

3. Structures of phosphorus, phosphoryl, and thiophosphoryl trihalides

Trends similar to those observed for thionyl and sulfuryl fluorides occur in the trihalides of phosphorus and their phosphoryl and thiophosphoryl derivatives. Structural parameters and Lewis structures for these molecules are given in table 27. One sees that as the substituent off the orbital on the right side of the phosphorus atom (table 27) changes from a lone pair to a sulfur atom, and then to the still more electronegative atom oxygen, *s* character appears to be diverted from this phosphorus orbital to the P—X bonds, causing these bonds to become shorter and the PX_3 group to become more open. Interestingly, the effects seem smallest in the fluorine derivatives and largest in the bromine derivatives, possibly because

TABLE 27

Structures of phosphorus, thiophosphoryl, and phosphoryl trihalides (284)

X =	Phosphorus Trihalide 		Thiophosphoryl Trihalide 		Phosphoryl Trihalide 	
	P—X	∠XPX	P—X	∠XPX	P—X	∠XPX
F	1.53_5	(100°)	1.53	100.3°	1.52	102.5°
Cl	2.04_4	99.9°	2.02	100.5°	1.99	103.6°
Br	2.23	100°	2.13	106°	2.06	108°

the phosphorus orbital plays a more important role in the slightly polar phosphorus–bromine bond than it does in the highly polar phosphorus–fluorine bond.

While most of the data in this review of the effects of orbital hybridization on molecular properties are for atoms from the first row of the periodic table free from complications of participating *d* orbitals, it seems likely from the examples just discussed that data of similar accuracy for heavier atoms would reveal trends similar to those observed for the lighter atoms. Provisional verification of this conjecture has been presented here for sulfur–fluorine, sulfur–oxygen, and phosphorus–halogen bonds. Sulfur–sulfur bonds in S_4N_4, $S_2O_4^{2-}$, $S_2O_6^{2-}$, and S_8 have been discussed recently from a similar point of view, the belief being expressed that bond lengths in these compounds are principally determined by the hybrid character of the orbitals that form the σ bonds (172, 173).

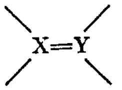
VIII. VALENCE-BOND SYSTEMATICS

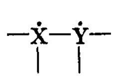
A. INTRODUCTION

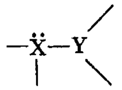
Longuet-Higgins (187) recently has proposed that the most restrictive and perhaps the most clear-cut definition of electron deficiency in covalently bonded molecules is "that the number of valency electrons is less than $2(n-1)$, where n is the number of atoms in the molecule." While, as noted, this definition does cover the boron hydrides, the volatile metallic borohydrides, the nonionic metal hydrides, the polymerized metal alkyls and certain unstable carbonium ions (187), it does not predict, for example, that $B_2H_6^-$, or $B_{10}H_{14}^{2-}$, or N_2^{2+} are electron-deficient, as, in fact, these species are. On the other hand, it does predict, for example, that the species CH_6 is electron-deficient, whereas such a species is, in fact, electron-rich. It is the purpose of this section to discuss another definition of electron deficiency.

B. THE OCTET RULE

Of the following three structures, most chemists would instinctively prefer the first structure over the


I


II


III

other two, on the grounds that it is the only structure of the three that satisfies the octet rule. One sees, also, that of the three structures, structure I is the structure with the least number of unshared electrons. This observation carries several interesting implications. To see this, it is convenient to introduce the following notation: U for orbitals occupied by unshared electrons and B for ordinary bonds. In practice, the following distinctions are important:

U_2 The number of orbitals in a valence-bond structure occupied by two unshared electrons (upper X orbital, structure III).

U_1 The number of orbitals occupied by one unshared electron (upper orbitals on X and Y, structure II).

U_0 The number of nonoverlapping atomic orbitals that are unoccupied (fourth Y orbital, not shown, structure III).

B_2 The number of ordinary two-centered bonds occupied by two electrons (valence-bond lines, structures I, II, and III).

B_1 The number of two-centered bonds occupied by one electron (none in structures I, II, and III).

For completeness, B_0 should be introduced for the number of empty two-centered bonds, although such a term is chemically absurd, and T_0, T_1, and T_2 for the number of three-centered bonds occupied by 0, 1, and 2 electrons, respectively. If, further, one symbolizes by

Σ the number of atomic orbitals involved in U_i, B_i, and T_i ($i = 0, 1, 2$), and by

V the number of valence electrons involved in U_i, B_i, and T_i ($i = 0, 1, 2$),

a direct accounting in any valence-bond structure of the number of valence orbitals and valence electrons yields these two basic relations:

Orbital count:

$$(U_0 + U_1 + U_2) + 2(B_0 + B_1 + B_2) + 3(T_0 + T_1 + T_2) = \Sigma \qquad (1)$$

Electron count:

$$U_1 + 2U_2 + B_1 + 2B_2 + T_1 + 2T_2 = V \qquad (2)$$

As it stands, this system of equations, two equations in eleven variables, has nine linearly independent solutions. For elements from the first row of the periodic table, the dimension of this subspace of solutions is immediately diminished by two by the following conditions on V and Σ:

$$V = \text{sum of the valence electrons} \qquad (3)$$

$$\Sigma = 4N + n \qquad (4)$$

where N is the number of heavy atoms and n is the number of hydrogen atoms in the molecule. The remaining conditions required to narrow down the possibilities to a unique solution are contained in the statement: *The total number of unshared electrons shall be as small as possible.* Let this number be called U_t.

$$U_t = U_1 + 2U_2 \qquad (5)$$

The problem is this: What numbers U_i, B_i, T_i consistent with equations 1 and 2 minimize U_t? It is instructive to seek an answer to this problem in a direct examination of equations 1 and 2. A moment's reflection shows it to be wasteful to constitute the remainder of the second sum (equation 2) from terms that occur with larger coefficients in the first sum (equation 1). Thus U_0, B_0, B_1, T_0, T_1, and T_2 should not be used. The opposite reasoning applies to U_1 and U_2. These conclusions may be confirmed algebraically. Equations 1 and 2 are solved for U_2 and B_2,

$$U_2 = (V - \Sigma) + (U_0 + 2B_0 + B_1 + 3T_0 + 2T_1 + T_2) \qquad (6)$$

$$B_2 = [\Sigma - (1/2)V] - [U_0 + (1/2)U_1 + 2B_0 + (3/2)B_1 + 3T_0 + (5/2)T_1 + 2T_2] \qquad (7)$$

and these values substituted into equation 5 to give

$$U_t = 2(V - \Sigma) + 2[U_0 + (1/2)U_1 + 2\mathrm{B}_0 + B_1 + 3T_0 + 2T_1 + T_2] \qquad (8)$$

Only by this procedure is the coefficient of each term within the brackets kept positive. Clearly the number of unshared electrons is a minimum when these terms vanish; i.e., when

$$U_0 = U_1 = B_0 = B_1 = T_0 = T_1 = T_2 = 0 \qquad (9)$$

A moment's reflection shows that this result is equivalent to the octet rule. The only nonvanishing terms are U_2 and B_2. Substituting from equations 9 and 4 into equations 6 and 7, one finds that

$$U_2 = V - (4N + n) \qquad (10)$$

$$B_2 = (4N + n) - (1/2)V \qquad (11)$$

C. CONNECTIVITY LIMITS

A valence-bond structure that purports to represent a stable molecule ought to appear at the very least as a singly connected whole, i.e., *the number of pairs of bonding electrons plus one must be equal to or greater than the number of atoms:*

$$B_2 + 1 \geq N + n \qquad (12)$$

On the other hand, owing to the orthogonality of atomic orbitals, *the number of unshared pairs plus the number of hydrogen atoms cannot total less than two if N is even* (acetylene, hydrogen cyanide, nitrogen, etc.) *or four if N is odd* (carbon dioxide, ketene, allene, etc.). That is,

$$U_2 + n \geq 2 \quad (N \text{ even}) \qquad (13)$$
$$\geq 4 \quad (N \text{ odd})$$

Substituting from equation 11 into 12 and from equation 10 into 13, one obtains the following conditions on V and N.

$$6N + 2 \geq V \geq 4N + 2 \quad (N \text{ even}) \qquad (14)$$
$$+ 4 \quad (N \text{ odd})$$

These limits on V are tabulated below for several values of N.

N	1	2	3	4	5	6	7	8
V_{max}	8	14	20	26	32	38	44	50
V_{min}	8	10	16	18	24	26	32	34
$\frac{1}{2}(V_{max.} - V_{min.}) + 1$	1	3	3	5	5	7	7	9

The last row of figures refers to the lengths of the horizontal periods in figure 14. In this figure, the vertical coördinate of each block is its heavy-atom number N, and the horizontal coördinate is its valence-electron number V. The two heavy steplike lines are plots of $V_{max.}$ and $V_{min.}$. Molecules of ordinary experience fall within these limits. Structures below the main sequence are electron-deficient, a condition defined by the failure of the right-hand inequality in equation 14, while structures above the main sequence are electron-rich, saturation being defined by the equality $V = 6N + 2$. Examination of the figure reveals that covalent molecules containing a *total* of twelve or twenty electrons cannot satisfy the octet rule. (The molecule C_3H_2, propargylene, has been reported; it is probably a diradical (273).) In general, structures containing four over a multiple of eight electrons are rare.

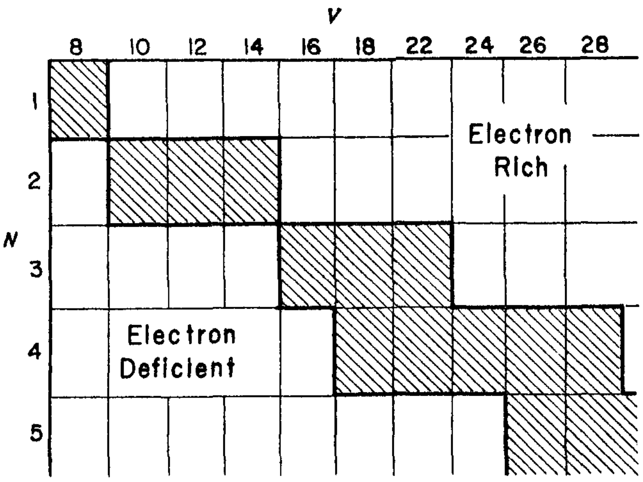


FIG. 14. Distribution of stable molecules on an N–V diagram. N = the number of heavy atoms; V = the number of valence electrons.

D. ELECTRON DEFICIENCY

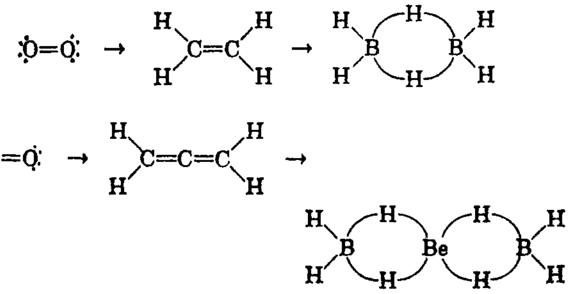
Implicit throughout the previous discussion is the assumption that the number of valence electrons, V, equals or exceeds the number of valence orbitals Σ:

$$V \geq \Sigma = 4N + n \qquad (15)$$

When this condition fails to hold, the combination of conditions 9 with equations 6 and 7 leads to anomalous results. $2B_2$, the number of electrons assigned to two-centered bonds, exceeds the number of valence electrons; correspondingly, U_2, the number of lone pairs, becomes a negative number. This may be avoided by relaxing the conditions that every term within the brackets in equation 8 must vanish. The question arises as to which term or terms it is best to retain.

E. THREE-CENTERED BONDS

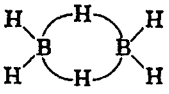
One is led to consider what happens when an isoelectronic sequence is developed one step past the hydrocarbon stage, where $U_2 = 0$ and condition 15 just prevails. Starting with oxygen and carbon dioxide, for example, and applying the principle that an extranuclear proton adds to the most basic site available, i.e., to unshared electrons, until such sites are exhausted, and then to double bonds (13, 14, 183, 198, 231, 250), one obtains the following structures.

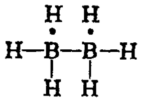


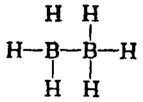
Secondly, one observes that equation 2 may be written in the form

$$U_t + B_t = V \tag{16}$$

where, as before, U_t represents the total number of unshared electrons and B_t represents the total number of electrons in bonds. Thus, the statement that U_t is to be minimized is equivalent to the statement that B_t is to be maximized, provided U_t does not vanish. When U_t vanishes, this statement must be amended, for at that point all structures have the same number of bonding electrons. This is illustrated by the following structures for B_2H_6.


I


II


III

The first structure is generally felt to be preferable to the other two on the grounds that it satisfies an extended form of the octet rule (88, 182). It is seen, also, that of the three structures, structure I is the structure with the most three-centered bonds. This leads to the not unreasonable conjecture that electrons in three-centered bonds are better off than electrons in two-centered bonds, much as electrons in two-centered bonds are better off than unshared electrons (187). For example, in the first reaction below, the number of electrons in two-centered bonds increases, while in the second reaction the number of electrons in three-centered bonds increases, and both reactions are exothermic (albeit the latter less so than the former).

$$2CH_3 = C_2H_6$$

$$2BH_3 = B_2H_6$$

An expression for the number of three-centered bonds in structures such as B_2H_6 and beryllium borohydride may be obtained from equation 8 by setting $U_t = 0$. To maximize the value of T_3, set $U_0 = U_1 = B_0 = B_1 = T_0 = T_1 = 0$. This gives

$$T_3 = \Sigma - V \tag{17}$$

Substitution in equation 7 then yields the following expression for the number of two-centered bonds.

$$B_2 = (3/2)V - \Sigma \tag{18}$$

Equation 17 shows that in the hydride of an element for which $U_t = 0$, the number of three-centered bonds per heavy atom is equal to 4 less the group number of the element. This number is 0 for carbon and 1 for boron. In the boron hydrides, the number of two-centered bonds is equal to one-half the total number of atoms.

F. SUMMARY

The following conclusions may be listed.

1. The octet rule is found to be equivalent to the condition that the number of unshared electrons in a valence-bond structure be as small as possible, or, when this number is zero, to the condition that the number of three-centered bonds be as large as possible.

2. For a molecule that is not electron-deficient, the number of pairs of electrons in two-centered bonds is $(4N + n) - (1/2)V$. This expression incorporates (*a*) the assumption of atomic orbitals and of their overlap to form two- and three-centered bonds (four- and other multicentered bonds are unlikely among s–p hybrid orbitals, on steric grounds), (*b*) the Pauli exclusion principle (subscripts ≤ 2), (*c*) the efficacy of the periodic classification of the elements (i.e., the neglect of all inner-shell electrons in the computation of V), (*d*) the neglect of all atomic orbitals with two or more nodes (i.e., the neglect of $3d$ orbitals in the computation of Σ for first-row elements), (*e*) the cardinal tenet of quantum mechanics that the energy be minimized, and (*f*) recognition of the fact that item (*e*) implies that the number of unshared electrons should be as small as possible. It may be added that expression 11 incorporates Zachariasen's rules (318).

3. A molecule is electron-deficient if the number of valence electrons V is less than $4N + 2$ if N is even or $4N + 4$ if N is odd, or if $V < \Sigma$.

4. The number of three-centered bonds per heavy atom in the hydride of an element for which $U_t = 0$ is equal to 4 less the group number of the element.

5. A covalent molecule that contains a total of twelve or twenty electrons cannot satisfy the octet rule.

IX. Summary and Conclusions

This review consists of two interwoven parts. One part, which may be considered independently of the other part, consists of a collection of selected experimental data on bond angles, bond lengths, inductive constants, dipole moments, force constants, ionization potentials, and heats of addition. The other part, which is more provisional, is an attempt to review in nonmathematical terms a self-consistent interpretation of these data. It is concluded that between the customary complexities of descriptive chemistry and the mathematical complexities of pure quantum chemistry there lies, rooted in the other two and complementary to them, a domain of pragmatic chemical theory that encompasses two familiar concepts, valence-bond structures and orbital hybridization, which separately from their inception and recently in union have proven useful in understanding and establishing correlations among molecular properties.

The author is indebted to his colleague Dr. Doyle Britton, who shared generously his knowledge of molecular structure and who acted as able advocate and friendly critic while this review was in preparation. The author is also indebted to the anonymous reviewers of the first draft of this review, which was written in the spring of 1959.

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