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ON INFERENCES OF BOND CHARACTER FROM BOND LENGTH; THE IMPORTANT ROLE OF NONBONDED INTERACTIONS[1]

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Abstract—Although experimental molecular structure is one of the oldest and most frequently applied diagnostic tools in studies of the nature of chemical bonds, it is concluded that its application to all but the grossest details of bonds such as carbon–carbon bonds remains entirely speculative. The concept of bond length is discussed to emphasize the need for careful consideration of ambiguities associated with the natural indeterminacy of atomic positions. A theoretical basis is given to the empirical Schomaker-Stevenson rule relating bond length to electronegativity. The divergent views of Pauling and Walsh on hybridization, ionic character, and bond strength are reconciled to some extent with the aid of a simple model. It is shown that structural effects commonly attributed to conjugation, hyperconjugation, hybridization, and partial ionic character can be rationalized to a remarkable extent in terms of nonbonded interactions. It is suggested that these factors are not fundamentally as distinct from each other as they are often assumed to be, and that much more serious attention should be given to the role of nonbonded interactions.

OF the numerous physical observables dependent in some way upon the nature of interatomic linkages, only a handful can be unambiguously ascribed to, and uniquely identified with, the various individual bonds. Such special observables have played important roles in our striving to understand chemical bonds. Of these the bond length, as measured by diffraction or spectroscopic methods, is one of the oldest and most popular, and the carbon–carbon bond has been one of the favorite subjects. That the detailed interpretation of results is still a matter of active controversy, even for such a simple linkage as the carbon–carbon bond, is a conclusive demonstration of the superficiality of our understanding of the chemical bond.

The pattern of response of C—C bond lengths to changes in environment is now reasonably well documented. In view of the firmness with which certain arbitrary interpretations of this response have become entrenched in much current writing, it seems worthwhile to consider alternative approaches to the problem.

The basis of interpretation of bond lengths is almost purely empirical. For covalent bonds, internuclear distances have been found to be reasonably well represented by sums of characteristic atomic radii.[2] Deviations from additivity are considered to reveal specific interactions which, in favorable cases, can be diagnosed. An unfortunate circumstance greatly impeding interpretations is that the data available for a given bond are far outweighed numerically by the large number of interactions of plausible physical significance that have been invented to account for the data. The factors most commonly acknowledged to influence bond lengths are:

(a) bond order, conjugation, hyperconjugation
(b) hybridization
(c) partial ionic character
(d) nonbonded interactions.

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[1] This research was supported by a grant from the National Science Foundation.

[2] L. Pauling, *The Nature of the Chemical Bond* (3rd Ed.) Chap. 7. Cornell University Press, New York (1960).

To this list should really be added another factor which, while so self-evident as to appear trivial, has, unhappily, played a significant role in the study of bonds:

(e) experimental errors and differences in operational definitions of bond length. Although the above terms [except for (e)] are considered to represent distinct bond characteristics, precisely definable in principle even if they have not yet been in practice, a little reflection shows that they are more subtly interwoven than commonly recognized. Perhaps the best established of them is (a) in aromatic hydrocarbons as predicted by Pauling and co-workers.[3] Structural effects of the others listed have been less conclusively demonstrated and even (a) is speculative in nonaromatic molecules, with which we shall be concerned in the remainder of the paper.

Curiously, at least for bonds to carbon atoms, the most neglected of the factors, (d), gives promise of becoming one of the most important. It was recently pointed out[4] that if a plausible set of potential functions describing interactions between nonbonded atoms were adopted, carbon carbon bond lengths in a variety of nonaromatic hydrocarbons could be closely computed without invoking hybridization, conjugation, or hyperconjugation. Since the arguments were also found to be applicable in large measure to bond energies and other thermochemical and kinetic effects[5] previously attributed to factors (a) and (b) above, it was suggested that nonbonded interactions might well be dominant factors in governing the changes in bonds accompanying changes in environment. The principal theme of this paper will be to point out some interrelationships between nonbonded interactions and the other factors listed which suggest that the concepts they represent are not as distinct as generally thought. In view of the preliminary nature of the new nonbonded model it seems best to present it in its most elementary form, keeping its oversimplifications obvious rather than masking them with physically reasonable corrections. Even in this form it leads to an unexpected range of correlation.

INTERPRETATIONAL UNCERTAINTIES IN BOND LENGTHS

Let us consider first factor (e) above, the problem of experimental errors and differences in definitions of bond length. The reason for concern is that the response of bond lengths to significant changes in environment is usually very small, and of a magnitude often not much greater than the above uncertainties. It has only been comparatively recently that experimental errors in the best diffraction studies have even approached a comfortable margin in this respect, say $\pm 0{\cdot}004$ Å or better, and that the full magnitude of interpretational uncertainties in spectroscopic studies has been recognized. In addition, virtually no effort has been made until recently to reduce bond lengths determined by different methods to comparable values.

When it is considered that the natural zero-point indeterminacy associated with atomic positions is of the order of 0·1 Å and that the probability distribution is asymmetric, it is readily apparent that the determination of interatomic distances will be sensitive to the method of averaging over bond vibrations. As simple schemes for treating the problem have not been fully worked out there are still interpretational uncertainties of the order of 10^{-2} Å in the case of C–C bonds. The C–H bond has

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[3] L. Pauling, L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.* 57, 2705 (1935); L. Pauling and L. O. Brockway, *Ibid.* 59, 1223 (1937). For a recent review see D. W. J. Cruickshank and R. A. Sparks, *Proc. Roy. Soc.* A **258**, 270 (1960).

[4] L. S. Bartell, *J. Chem. Phys.* 32, 827 (1960).

[5] L. S. Bartell, (to be published). A preliminary report is given in *Tetrahedron Letters* No. 6, 13 (1960).

received considerable attention, however, and it is instructive to study the results for the familiar series of hydrocarbons listed in Table 1. The parameters r_0, r_g, and r_e represent the spectroscopic average over the ground state,[6] the mean length, and the equilibrium length. The mean bond length, or center of gravity of the bond probability distribution, can be deduced from electron diffraction data for gas molecules.[7] X-ray crystal analyses, when corrected for thermal motions, give a parameter close to r_g.

TABLE 1 C–H BOND LENGTHS IN SEVERAL MOLECULES AS CHARACTERIZED BY VARIOUS DISTANCE PARAMETERS

Molecule	Hybridization[a]	Hybridization[b]	r_0[c]	r_g[d]	r_e[e]
HC≡CH	sp	sp^3	1·059[f]	(1·079)[g]	1·064[f]
H_2C=CH_2	sp^2	sp^3	1·086[h]	1·084[i]	(1·067)[j]
CH_4	sp^3	sp^3	1·094[k]	1·107[i]	(1·085)[j,l]
CH radical	p	sp^3 (?)	1·129	1·138	1·120[m]

[a] A. D. Walsh, reference 32; C. A. Coulson, reference 27.
[b] L. Pauling, reference 26 (CH radical not explicitly discussed).
[c] Spectroscopic average over ground state.
[d] Mean bond length, ground state.
[e] Equilibrium distance.
[f] B. D. Saksena, *J. Chem. Phys.* **20**, 95 (1952).
[g] Estimated from r_e.
[h] T. L. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958); Dowling and B. P. Stoicheff, *Canad. J. Phys.* **37**, 7034 (1959).
[i] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957); *Ibid.* **31**, 400 (1959).
[j] Estimated from r_g.
[k] T. L. Allen and E. K. Plyler, *J. Chem. Phys.* **26**, 972 (1957).
[l] L. S. Bartell, K. Kuchitsu, and R. J. deNeui, *J. Chem. Phys.* **33**, 1254 (1960).
[m] G. Herzberg, *Infrared Spectra of Diatomic Molecules*, Van Nostrand, New York (1950).

For most of the entries in Table 1 standard errors are reported to be ± 0·003 Å or less, but additional small uncertainties may arise. The important thing to observe is that the differences between r_0, r_g, and r_e, which are not always considered in comparing results for different molecules, are comparable to the differences from molecule to molecule. As a rule the C–C bond, with its smaller amplitude of vibration, will exhibit smaller differences between the various parameters than the C–H bond.

The value almost universally selected to represent the C–C single bond distance is the diamond X-ray value, 1·544 Å. Not only is this distance not an equilibrium distance as it is often taken to be (since zero-point motions undoubtedly expand the bond length in the lattice by the order of 0·01 Å), but it is appreciably higher than the C–C distances characteristic of paraffin hydrocarbons with r_g = 1·533 Å[9] and r_0 = 1·526 Å.[10] This is at least partly because of repulsions between nonbonded atoms.[11]

It is helpful to recognize that the decrease encountered in a given bond in going

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[6] Actually r_0 as customarily used does not signify a unique physical quantity. It may or may not, depending on the case, be subject to errors arising from assumptions of equivalence of positions of atoms of different isotopic mass. See C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).

[7] Unfortunately, the commonest parameter reported for electron diffraction determinations is an "effective length", generally intermediate between r_g and r_e and often slightly larger than r_0. See L. S. Bartell, *J. Chem. Phys.* **23**, 1219 (1955).

[8] K. L. Lonsdale, *Phil. Trans. Roy. Soc.* A **420**, 1219 (1947).

[9] For a summary of electron diffraction and X-ray data for n-hydrocarbons see R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.* **81**, 4765 (1959).

[10] For propane and isobutane D. R. Lide, *J. Chem. Phys.* **33**, 1514, 1519 (1960). Strictly, Lide's parameter is not r_0 but r_s, a related parameter presumed to lie somewhat closer to r_e.

[11] L. S. Bartell, *J. Amer. Chem. Soc.* **81**, 3497 (1959).

from r_g to r_e (i.e. from full to zero vibrational amplitudes) stems not only from the hypothetical settling of the bond to the bottom of its own anharmonic valence stretching potential well but also from the smaller nonbonded repulsions of neighboring atoms as they become quiescent. This latter factor leads us to predict that the mean C - C bond length in C_2H_6 should be a few thousandths of an angstrom longer than in C_2D_6 where the greater inertia of the D atoms restricts their vibrational amplitudes.

NONBONDED REPULSIONS

The underlying basis of the ideas in the remainder of the paper is that, contrary to prevalent opinion, the nonbonded repulsions between any two atoms bonded to a given carbon atom are enormous, and strongly influence structure and thermochemical properties. The factor that has obscured these repulsions is that they are balanced in tetrahedral compounds more closely than might have been expected. That is to say, interactions between the pairs H · · · H, C · · · C, Cl · · · Cl, H · · · C, and H · · · Cl, for example, are very similar in magnitude in substituted methanes. Notwithstanding, it has almost always been assumed that chlorine atoms are large and repel atoms strongly whereas hydrogens are small and quite negligible in comparison. Consequently it has been considered that bond angles, lengths, and energies in the series CH_nCl_{4-n} would show marked variations if nonbonded repulsions were large. The smallness of effects in this series was early interpreted[12] as indicating that atoms are greatly whittled down on the side of covalent bonds and hence exhibit small repulsions. Chemists have adhered to this belief.

The success of Pitzer and Catalano[13] in accounting for isomerization energies of paraffin hydrocarbons by a model invoking dispersion forces but altogether ignoring nonbonded repulsions (except for *gauche* configurations) is further evidence for the balance of the repulsions. The nonbonded interactions presently assumed, which have the dispersion forces of Pitzer and Catalano built into them, give a similar profile of interaction differences to account for isomerization energies.[14]

Confusing the picture have been the results of analyses of vibrational spectra. Urey Bradley analyses offer, in principle, perhaps the most direct experimental resolution of molecular force fields into valence and central force components that has yet been devised. The confusion arose because repulsions were found by analyses to be strong,[15–17] of the magnitude required for the present model and entirely comparable with repulsions computed for intermolecular van der Waals forces at the same distance, except in the case of hydrogen atoms. For methane, H · · · H interactions seemed to be negligible.[16] Inasmuch as structural and thermochemical evidence did not permit the large imbalance implied by the spectroscopic analyses, chemists tended to ignore all repulsions of atoms bonded to a given C atom. Nevertheless, the range of information simply accounted for by the assumption that interactions, including H · · · H interactions, are large, seemed too broad for the assumption to be

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[12] L. Pauling, *The Nature of the Chemical Bond* p. 193. Cornell University Press, Ithaca (1939).

[13] K. S. Pitzer and E. Catalano, *J. Amer. Chem. Soc.* **78**, 4844 (1956)

[14] The profile is not identical, however. It worked better for one reasonable model of molecular structure but not as well for the structural model of Pitzer and Catalano. Since our present emphasis is on the magnitude of, rather than the detailed differences between interactions, no parameter optimization has been attempted

[15] H. C. Urey and C. A. Bradley, *Phys. Rev.* **38**, 1969 (1931).

[16] T. Shimanouchi, *J. Chem. Phys.* **17**, 245, 734, 848 (1949).

[17] J. W. Linnett and D. F. Heath, *Trans. Faraday Soc.*, **44**, 873, 878, 884 (1948); **45**, 264 (1949). *J. Chem. Phys.* **19**, 801 (1951)

altogether spurious. Accordingly, the preliminary paper[4] in this series proposed a strong hydrogen interaction potential and presented many of the following arguments.*

Since publication of this paper[4] the vibrational spectra of several simple hydrides, including methane, have been re-examined using considerably more detailed and precise spectroscopic data. Strong H · · · H nonbonded interactions were found[18] which agreed closely with the predicted[19] values. The most important features obscuring the interpretation previously were (i) the effects of anharmonicity which are far greater for light hydrogen atoms than for other atoms, and (ii) the neglect of stretch-stretch interactions. Consideration of these factors in an approximate treatment of neopentane has also improved the agreement between spectroscopic C · · · C interactions and those suggested in reference 4.

What makes it possible for the small hydrogen atom to compete in repulsive force with the larger carbon and chlorine atoms is that the larger atoms are further from the central atom, and the resulting increase in nonbonded distances closely compensates for the larger size.

Whereas the balance of repulsions masks their effect in tetrahedral molecules, the change in *number* of the repulsions upon going to trigonal and digonal molecules, leads to marked effects, as discussed in the following. The balance is also destroyed in strained cyclic molecules as cyclobutane, where, according to the present model, the relief of C · · · H repulsions counteracts significantly the increase in C · · · C repulsions as the C—C—C angle decreases from 109·5° to 90°. The magnitudes of the terms, which have been generally neglected in previous calculations of strain energies, are analysed in ref. 4. It is expected that similar considerations will prove to be important in conformational analysis. It is to be stressed, however, that the present interactions are entirely insufficient to explain the barriers to rotation around the C—C bond in ethane. They do yield, nevertheless, quite accurate values for the difference in energy between *trans* and *gauche* configurations of normal hydrocarbons.

Finally, it is fitting to mention that several theoretical papers[20,21] have appeared recently which seem to justify, at least partly, the present assumption that intramolecular interactions can be treated in much the same way as intermolecular van der Waals forces.

BOND ORDER

The principal environmental variation of bonds to be discussed in this paper is the variation in the number of adjacent bonded atoms.[22] A concise summary of behavior of carbon bond lengths is shown in Fig. 1. While the figure is schematic it quite

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* After the present manuscript was completed, Professor E. B. Wilson, Jr., kindly brought to my attention a paper presenting similar ideas by J. B. Conn, G. B. Kistiakowsky, and F. A. Smith, *J. Amer. Chem. Soc.* **61**, 1868 (1939).

[18] L. S. Bartell and K. Kuchitsu (to be published). See also K. Kuchitsu and L. S. Bartell (submitted to *J. Chem. Phys.*). It is the second derivative of the nonbonded potential that is most accurately given by the data. Forces are less well established by direct analysis but can be estimated from $V''(r)$ with the aid of mild assumptions about $V(r)$.

[19] Reference 4. A recent estimate of interatomic H · · · H interaction energies very similar in magnitude at small r to the energies of reference 4 was published by J. T. Vanderslice and E. A. Mason, *J. Chem. Phys.* 33, 492 (1960).

[20] R. McWeeny, *Proc. Roy. Soc.* A **253**, 242 (1959).

[21] O. Sinanoglu, *J. Chem. Phys.* 33, 1212 (1960).

[22] The structural consequences of few other types of environmental changes have been followed sufficiently reliably for C—C bonds to warrant discussion here. But see J. D. Dunitz and V. Schomaker, *J. Chem. Phys.* **20**, 1703 (1952).

accurately characterizes a large body of data, as stressed by Bernstein, Costain, and Stoicheff.[23]

It has been customary to attribute a substantial part of the downward slope of the line representing single bonds to conjugative or hyperconjugative interactions. The point of view has been that delocalization of electrons from adjacent bonds into the bonding region of the single bond increases the effective bond order and shortens the C—C distance. Originally hyperconjugation was thought to be strongly effective only when the adjacent single bonds were to hydrogen atoms, but substitution of the hydrogens by other atoms has been found to have surprisingly little effect on the C—C bond length.

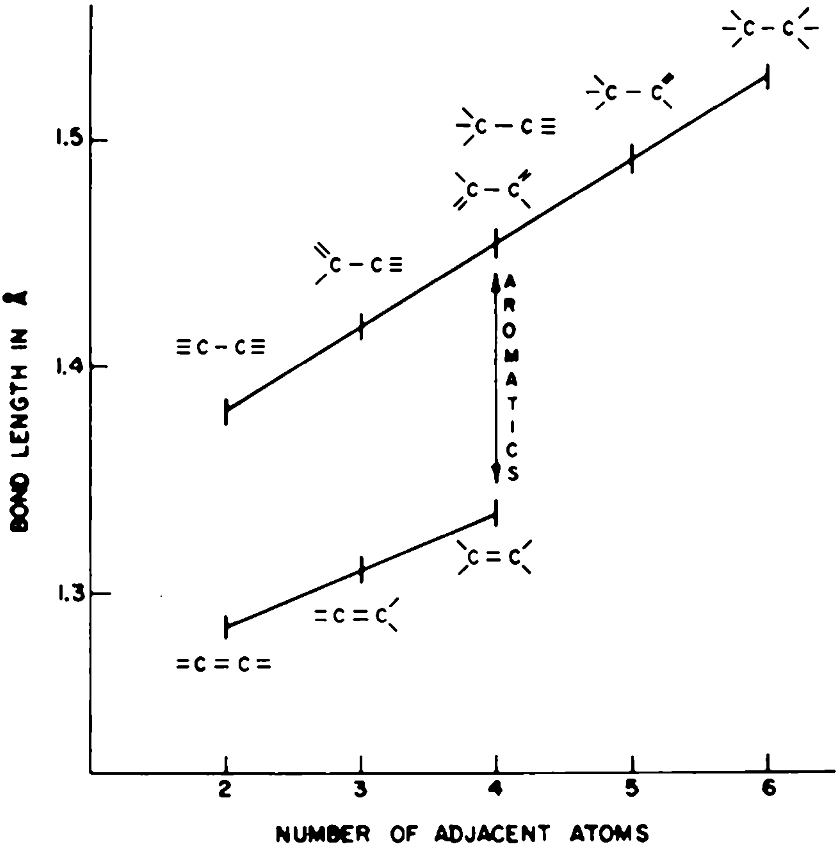

FIG. 1. Variation of bond length with environment.

Recently considerable doubt has been cast on the role of conjugation and hyperconjugation in the ground state of nonaromatic molecules on the basis of empirical evidence summarized by Dewar and Schmeising.[24] The character of the argument is not so much that conjugation and hyperconjugation are unreasonable as that, if proper account is taken of other factors, there remains little evidence for conjugative interactions in the molecules considered. It is interesting that the representation of

[23] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959); C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

[24] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

Bernstein[23] suggests a similar conclusion. Aromatic molecules, for which there is strong evidence[3] relating bond lengths to π bond orders, fall on a line terminated at Bernstein's pure single bond limit by the ---C C - and · C C · bond lengths. Even before the idea of conjugation was seriously challenged it had often been observed that extrapolation of aromatic bond lengths to zero π bond order led to a value appreciably below that of the "normal" single bond.

A theoretical investigation of butadiene by Berry[25] has also lent weight to the idea that conjugation is of only minor importance in bond lengths. Moreover, Berry showed that there is no meaningful way, even granting that an adequate electronic wave function be known for a molecule, of exactly separating the contributions to bond stability of the electronic factors he examined. The reason for this is that components of the wave functions associated with the factors were not mutually orthogonal. It is perhaps along the lines of this argument that a theoretical test can be made of the present empirically justified suggestion that conjugation, hybridization, electronegativity and nonbonded interactions do not represent entirely distinct quantities. For the present, since pure theory as yet offers scant help, there is utility in continuing our empirical search for the simplest and most fruitful description of molecules.

To return to the theme of nonbonded interactions, it is to be noted that atomic repulsions across bonds increase in number as we proceed from left to right across Fig. 1. This is true both for single bonds and double bonds. Furthermore, if the nonbonded potential functions are known as a function of distance, repulsive forces can be evaluated and resolved along bond directions, and the influence on bond distance can be calculated from known force constants. It is interesting that the potential functions of ref. 4, constructed from considerations of intermolecular van der Waals forces, reproduce not only the directions but also the magnitudes of the slopes of the lines in Fig. 1. Since adjacent multiple bonds would be expected to introduce no appreciable π bond character into C H bonds, it might be argued that a comparison of C C and C· H bond shortenings would reveal the π character of C C bonds. Pauling,[26] Coulson,[27] and others have indeed attributed the difference between C C and the analogous but smaller C H bond shortenings illustrated in Table 1 to π electron conjugation. It is found, however, that the nonbonded model also accounts for the smaller shift of the C H bonds,[28] partly because of the larger force constants, and partly because of the geometry and magnitudes of repulsions. Similarly, the difference between C—Cl bonds in methyl and vinyl chlorides, which is larger than the analogous difference between C—C bonds, can be accounted for by the nonbonded model as well as by the conjugation model.[29] The present model would also predict

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[25] R. S. Berry *J. Chem. Phys.* **30**, 936 (1959).

[26] L. Pauling, *loc. cit.* (2), Sec. 5.

[27] C. A. Coulson, *Valence* Chap. VIII. Clarendon Press, Oxford (1952).

[28] Note, however, that the present nonbonded model, as applied using the potential functions of ref. 4, is not intended to treat bonds which are adjacent to unshared electrons, as the bond in the C—H radical. It has often been remarked that unshared electrons behave as bulkier groups than attached atoms, as suggested, for example, by bond angles and distances in NH_3 and the NH_2 radical (and the long bond in the C H radical).

[29] The field gradient perpendicular to the bond observed at the chlorine nucleus in vinyl chloride has been interpreted in terms of a finite but small C—Cl double bond character. See J. H. Goldstein, *J. Chem. Phys.* **24**, 106 (1956). It seems possible that the different field asymmetries in vinyl chloride and methyl chloride may arise from polarization differences induced in the chlorine atoms by the different nonbonded environments.

shortenings in single bonds adjacent to three and four membered rings where increased nonbonded distances presumably relieve repulsions.

Another effect which has been regarded as strong evidence for hyperconjugation is a kinetic beta deuterium isotope effect discovered by Lewis[30] and Shiner[31] in solvolysis reactions. Here again nonbonded repulsions can be shown to provide an alternative explanation.[6] Hydrogen atoms, with characteristically larger amplitudes of vibration than deuteriums, behave as if they were bulkier and, accordingly, strive more vigorously to force off the leaving group and to make the carbon skeleton assume the trigonal configuration associated with the carbonium ion transition state. Numerical computations show the effect is entirely reasonable in magnitude, but the numerical values depend so strongly upon assumed bond angles and lengths (which at present are largely conjectural) that a definite conclusion cannot yet be made. The best estimate suggests that some hyperconjugative delocalization occurs but that this has the effect, in turn, of enhancing the nonbonded effect.[6] In any event, physical arguments for hyperconjugation in carbonium ion transition states seem much more convincing than for ground states of olefins.

As suggested above, even if conjugation were inescapable, considerations of nonbonded repulsions would inevitably arise. Valence bond structures written with π bonds across (nominally) single bonds imply, by the altered pairing scheme and charge distribution, a substantial reduction of certain nonbonded repulsions in the vicinity of the bond.

HYBRIDIZATION

By hybridization we shall mean to imply not only the geometry (tetrahedral, trigonal, digonal) but also s, p, etc. character of the sigma bonds. Walsh[32], especially, has stressed the number of properties that can be correlated in terms of hybridization and his ideas have gained widespread support. The original unavoidable over-simplifications have become deeply rooted with repeated usage and hybridization is now commonly regarded as a true physical property. In reality, of course, s character has always been used only as a parameter of correlation and never as an observable. There is no difficulty, given a simple valence bond or localized molecular orbital wave function, in assessing the hybridization. The difficulty is that there is as yet no unique way of defining hybridization in a many electron polyatomic wave function of sufficient complexity to treat rigorously such delicate things as bond angles. Granting this, no combination of experimental observables can be expected to establish hybridization. Nevertheless, the concept of hybridization is so attractive that we may confidently look forward to its ultimate clarification.

Two well-known alternative representations of hybridization of carbon orbitals in unsaturated molecules, the conventional σ-π description used for example by Walsh[32] and Coulson,[27] and Pauling's bent bond scheme[33] are listed for C—H bonds in Table 1. Neither scheme can yet be said to have been demonstrated clearly superior, and both are, at best, rough approximations.

The commonest diagnostic criterion used to infer hybridization in molecules is the angle between bonds. If a simple valence bond wave function is adopted, if it is

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[30] E. S. Lewis and C. F. Boozer, *J. Amer. Chem. Soc.* 74, 6306 (1952). *Ibid* 76, 791, 795, (1954).

[31] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* 75, 2925 (1953). *Ibid* 76, 1603 (1954).

[32] A. D. Walsh, *Trans. Faraday Soc.* 43, 60 (1947).

[33] L. Pauling, *loc. cit.* (2), p. 137

assumed that only *s* and *p* orbitals are involved, and if it is assumed that bonds are not bent, then it is an easy problem to compute bond angles as a function of hybridization.[34] None of the assumptions are clearly justified and much evidence has recently been cited regarding the failure of the last assumption.[4,35] Since the reasoning behind the assumption about unbent bonds is based on the principle of maximum orbital overlap, it is appropriate to point out an inconsistency. If Slater orbitals as tabulated by Mulliken *et al.* are used for ethylene,[36] and the H—C—H bond angle is increased or decreased symmetrically from the equilibrium angle, the sum of the overlaps of the bonding orbitals can be readily calculated. It is found to be about fivefold less costly in loss in overlap to *fix* the hybridization of the carbon orbitals at an optimum value and "bend" the C—H bonds than it is to *vary* the carbon hybridization to follow the angular displacements. Moreover, the known weakness of the bond bending restoring forces allows even modest nonbonded repulsions to alter bond angles by many degrees. These arguments reinforce the empirical observation of ref. 4 that bond angles seem closely correlated with "intramolecular van der Waals radii". They also strongly indicate that equilibrium bond angles are poor gauges of hybridization.

Dewar and Schmeising,[24] having presented impressive evidence against the importance of conjugation and hyperconjugation in nonaromatic molecules, chose to attribute the effects under discussion to hybridization changes,[37] following Walsh[32]. The authors pointed out that if the differences between tetrahedral and trigonal sigma bonds were taken explicitly into account, little thermochemical evidence for conjugation remained. The necessary differences in bond energy, $(E'_{CC} - E_{CC})$ and $(E'_{CH} - E_{CH})$ were determined empirically from experimental curves of bond energy versus bond length in conjunction with measured differences between trigonal and tetrahedral bond lengths. Again it may be remarked that direct use was not made of hybridization, but only of the geometry customarily associated with hybridization.

It is extremely interesting and probably significant that the nonbonded model leads only not to the same qualitative results as the model of Dewar and Schmeising, but in addition, permits a rough theoretical calculation of the slope, dE/dr, of the curve of bond energy versus bond length evaluated empirically by Dewar and Schmeising. Let us, naively, assume that bond energy is of the form

$$E = E_0 + \tfrac{1}{2}k(r - r_m)^2 - V_{nb} \tag{1}$$

where k is the force constant, r the bond distance, r_m a constant, and V_{nb} represents a variable environment of nonbonded repulsions across the bond between the atoms in the bond and atoms adjacent to the bond (of variable number). If we give V_{nb} the Lennard-Jones repulsive form, λr_{ij}^{-12}, it follows that

$$dE/dr \sim -kr_{ij}/12(\partial r_{ij}/\partial r), \tag{2}$$

independently of assumptions about the magnitude of λ. If the representative values $k \sim 4\cdot5 \times 10^5$ dynes/cm, $r_{ij} \sim 2\cdot5 \times 10^{-8}$ cm, and $(\partial r_{ij}/\partial r) \sim \sin(109\cdot5/2) \sim 0\cdot8$

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[34] The converse problem of computing hybridization from an arbitrary set of bond angles may not always have a solution.

[35] D. F. Heath, J. W. Linnett, and P. J. Wheatley, *Trans. Faraday Soc.* 46, 137 (1950). N. V. Cohan and C. A. Coulson, *Ibid.* 52, 1163 (1956). I. Burnelle and C. A. Coulson, *Ibid.* 53, 403 (1957). N. Muller and D. E. Pritchard, *J. Chem. Phys.* 31, 1471 (1959). Casabella, Bray, and Barnes, *Ibid.* 30, 1393 (1959).

[36] R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.* 17, 1248 (1949). The conventional σ-π double bond representation was assumed in the present computation and all bond lengths were fixed.

[37] Paper II by M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* 11, 96 (1960), introduces, however, the qualification that nonbonded interactions are to be considered absorbed into hybridization.

are substituted into equation (2), it is found that the magnitude of dE/dr is 170 kcal/mole per angstrom. Dewar and Schmeising, by solving simultaneous equations involving energies of formation of various hydrocarbons of known structure, found slopes at normal single bond distances of about 250[24] or 190[37] for C–C and 150[24] or 250[37] for C–H bonds, in the same units. Glockler[38] has reported analogous values of 140–190 and 140, respectively. The fact that the nonbonded model gives slopes agreeing with slopes determined with the use of C–C bonds of obviously variable bond order is of obscure significance.[39] The fact that it provides correct magnitudes for Dewar and Schmeising's model to work is provocative evidence that the nonbonded model may be substituted in part, or in total, for the "hybridization" model with little change in effective result.

IONIC CHARACTER AND ELECTRONEGATIVITY

Although there is general agreement that the strength and length of bonds is markedly influenced by ionic character, the direction of the effect is still a matter of dispute. Pauling[40] has advanced a scheme, rationalized on the basis of ionic-covalent resonance, in which ionic character enhances bond energies and decreases lengths. The scheme, in which the concept of electronegativity plays a central role, is so successful in a wide variety of correlations that it is unthinkable to disregard it. This, of course, does not mean that the physical basis of its rationalization is necessarily correct. On the other hand Walsh[32] has given quite reasonable arguments that increasing ionic character weakens and lengthens bonds, and has concluded that ionic-covalent resonance is not a significant factor. Several illuminating discussions of of the two points of view have appeared.[41] It seems worthwhile to present a few additional ideas which, in a simple way, cast a little more light on interrelations between the two points of view. They will also give some insight into the nature of carbon carbon bonds despite the fact that such bonds are not usually discussed in terms of ionic character.

In the case of the C–H bonds listed in Table 1, the hydrogens become more acidic as the bond configurations progress from tetrahedral to digonal. Presumably a similar shift of charge occurs in the analogous series of C–C bonds when H is replaced by CH_3. According to Walsh[32] and Coulson[27], among others, a dominant factor in the above series of bonds is that the electronegativity operative in the direction of a bond varies as the hybridization varies, and increasing the *s* character of a carbon orbital decreases the orbital radius, increases the electronegativity, and shortens the bond. Alternatively, Pauling[28] suggests a fixed hybridization where, as the bonds adjacent to a given single bond are bent to form double bonds or triple bonds, the nonbonding charge is bent away from the given bond direction. This would be expected to decrease nuclear screening, increase electronegativity and shorten the single bond. The essential similarity between the concept of bond–bond repulsions and interactions between pairs of nonbonded atoms,[42] implies a close similarity between Pauling's model and the nonbonded model of this paper.

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[38] G. Glockler, *J. Chem. Phys.* 21, 1291 (1953). *J. Phys. Chem.* 61, 31 (1957).

[39] A partial explanation is given in the next section.

[40] L. Pauling, *loc. cit.* (2), Chapter 3.

[41] See, for example, A. D. Walsh, *Ann. Rev. Phys. Chem.* Vol. 5, p. 163, (1954) and "A discussion of bond energies and bond lengths," *Proc. Roy. Soc.* A 207, 1–133 (1951).

[42] See T. L. Allen, *J. Chem. Phys.* 31, 1039 (1959). H. J. Bernstein, *J. Chem. Phys.* 19, 140 (1951). *Ibid.* 20, 263, 524, 1328 (1952).

The relationship between bond lengths and electronegativity was first critically examined by Schomaker and Stevenson[43] who formulated the empirical rule for pure single bonds

$$r_{AB} = r_A + r_B - \beta\,|x_A - x_B|, \tag{3}$$

where r_A and r_B are "covalent radii", β is a constant equalling 0·09 Å and x_A and x_B are electronegativities. Pauling[40] has recently revised the rule by varying β in order to diminish discrepancies discussed by Wells,[44] and has adjusted the value to 0·08 Å for bonds to carbon atoms. No theoretical justification of equation (3) seems to have been given, though frequent criticism has been expressed that it holds only roughly and fails appreciably in many individual cases. Its failures can hardly be surprising in view of the abundance of effects thought to influence bonds, and in view of the fact that a satisfactory explanation of why bond lengths should be additive in the first place, has never been found. Nevertheless the trend successfully reproduced by the rule warrants further attention.

A clue to the possible significance of the Schomaker Stevenson rule is provided by the ideas which led to Pauling's original definition of electronegativity. It is to be emphasized that the empirical definition in terms of deviations, Δ, from additivities of bond energies (or deviations, Δ', from the geometric mean of bond energies) seems almost accidentally to have captured considerable truth in terms of what we normally understand by electronegativity. Let us proceed with Pauling's original argument that a bond A-B, formed in the absence of an electronegativity difference has a bond energy, D_{AB}, given by the mean of D_{AA} and D_{BB}. Similarly, we assume r_{AB} is the mean of r_{AA} and r_{BB}, or sum of r_A and r_B. We then imagine that an "electronegativity difference" be turned on which results in an additional potential, $\lambda V'(r)$. For sake of argument we shall represent the bond potential energy by the sum of a Morse curve and $\lambda V'(r)$ as follows,

$$V(r) = D_0\{e^{-2a\Delta r} - 2e^{-a\Delta r}\} + \lambda V'(r) \tag{4}$$

where $\Delta r = r - (r_A + r_B)$ and D_0 is the mean of D_{AA} and D_{BB}. For any assumed form of $V'(r)$ it is possible to eliminate λ and establish a functional relationship between total depth, $D_{AB} = D_0 + \Delta$, of $V(r)$ and the position, $r_{AB} = r_A + r_B - \Delta r_{AB}$, of its minimum. Finally, the shift in bond length, Δr_{AB}, is related to electronegativity by Pauling's definitions

$$|x_A - x_B| = (\Delta/23)^{\frac{1}{2}} \tag{5}$$

or

$$|x_A - x_B| = (\Delta'/30)^{\frac{1}{2}}, \tag{6}$$

where energy is expressed in kcal/mole. The result of this elementary approach is shown in Fig. 2 for several simple forms of V', and compared with the Schomaker-Stevenson curve.

Fluorine, as it is the most electronegative element by far, is the element for which the need for corrections is most conspicuous. Since the unusually low bond energy and associated long bond length of elemental fluorine have been explained in terms of exceptionally large nonbonded repulsions on the one hand,[45] or low dispersion forces

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[43] V. Schomaker and D. P. Stevenson, *J. Amer. Chem. Soc.* **63**, 37 (1941).

[44] A. F. Wells, *J. Chem. Soc.* 55 (1949).

[45] See, for example, J. K. Wilmshurst, *J. Chem. Phys.* **33**, 813 (1960). K. S. Pitzer, *Quantum Chemistry* p. 166, Prentice-Hall, New York (1953), discusses the analogous weakness of the O—O single bond on much the same basis.

on the other,[46] and since these interactions might be disproportionately relieved or augmented on bonding with other atoms, it seemed not unreasonable to try forms $e^{-r/\rho}$ and r^{-6} for V'. An alternative explanation of the electronegativity effect on the basis of nuclear repulsions[41] suggested as a lower limit of rate of variation the form r^{-1}. The effect of enhanced covalent binding was examined by using as V' the attractive part, of form $-e^{-ar}$, of the Morse curve. The effect of nonbonded neighbors as given in equation (1) was also calculated. For the purpose of application to bonds similar to C—C bonds, the values chosen for D_0, a, and ρ were 81 kcal/mole, 2 Å^{-1}, and 0·32Å, respectively. The general magnitude of the results was not sensitive to these parameters.

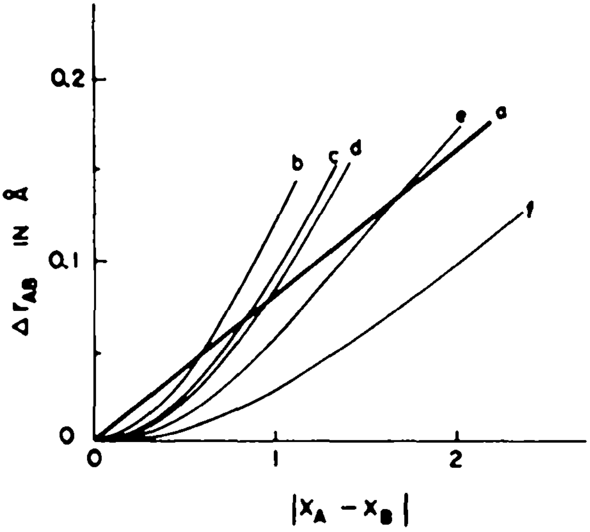

FIG. 2. Bond shortening as a function of electronegativity difference according to the Schomaker-Stevenson rule (a), and models where V' represents (b) nonbonded atoms (equation 1), (c) $\exp(-r/\rho)$, (d) r^{-6}, (e) Morse bonding, (f) r^{-1}.

The most remarkable result is that the various forms assumed for V', *with no freely adjustable parameters*, lead to rather similar curves, and show a striking area of agreement with the empirical Schomaker-Stevenson rule[47]. For electronegativity differences that are not too large, except for $V' = r^{-1}$, the disagreement is of a magnitude comparable with experimental errors characteristic of the time of formulation of the rule. It seems reasonable to conclude, then, that the present arguments constitute a rough justification of the Schomaker-Stevenson rule[48]. Further, they remind us of how much more complex a property electronegativity is than a simple gauge of polarity.

We have now arrived at an approximate relation between bond length and electronegativity, and between bond length and shift from tetrahedral to trigonal bonds. This permits us to assess, or at least to speculate upon, the shift in electronegativity

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[46] K. S. Pitzer, *J. Chem. Phys.* **23**, 1735 (1955).

[47] Schomaker and Stevenson always had reservations about the analytic form of their rule at zero electronegativity difference (c.f. their footnote 5). The present curves give a more appropriate slope in this region.

[48] Wilmshurst, ref. 45, also proposes an equation of the form of the Schomaker–Stevenson rule but concludes that increases in electronegativity difference tend to *increase* bond lengths. Allowances are made in the same equation for amount of *s* character, however, and the rather numerous assumptions introduced to establish *s* character markedly influence the apportionment between hybridization and electronegativity effects.

with the nonbonded relief or altered nuclear screening attending the shift from tetrahedral to trigonal bonds. For C—C bonds such a shift (in conventional but possibly misleading language, from "sp^3-sp^3 bonds" to "sp^2-sp^3 bonds") results in a decrease in bond length of 0·03 Å.[4] According to the various curves of Fig. 2, this is associated with an electronegativity shift of 0·4 to 0·6. From Pauling's relationship between ionic character and electronegativity[40] we deduce an "ionic character" of about 0·06 which, for a bond 1·5 Å long implies a dipole moment of 0·4 D.[49] This may be compared with the experimental dipole moments of 0·35 D when CH_3 is attached to a vinyl group, and 0·37 D when it is attached to a phenyl group.[50] It is quite common to attribute these moments to hybridization or hyperconjugation. Other hydrocarbon moments in nonaromatic networks as, say, methyl acetylene, methylcyclopropane, and methylcyclobutane can be accounted for similarly.

The fact that the moment in chlorobenzene is smaller than that in methyl chloride is likewise understandable in terms of the greater "electronegativity" of the carbon in the unsaturated compound. This leads us, however, directly to the apparent inconsistency which was alluded to at the beginning of this section, and indicates that *group* electronegativities, as portrayed by our scheme, do not share the same range of simple correlations as atomic electronegativities. The C—Cl bond length is shorter and bond energy is greater in chlorobenzene or vinyl chloride than in methyl chloride, and by the amount required by our parametric relation involving electronegativity. Accordingly it is natural to consider the electronegativity difference between $H_2C{=}CH$— and Cl as being *greater* than between H_3C and Cl on the basis of the relation between electronegativity and energy. But, as we also showed from the model, the "hybridization" of carbon is such as to *reduce* the electronegativity and polarity differences in the unsaturated halides. A similar inconsistency is encountered in comparing the fluroides of CF_3 and CH_3 or halides of $C(CH_3)_3$ and CH_3. Whether this is at all related, by analogy to the present model, to the notably small size of fluorine atoms or large size of carbons in comparison with their covalent radii is not certain. Presumably, completely analogous arguments are also applicable to the C=O bond as it exists in, say, acetone and ketene. It was carbon-oxygen bonds, especially, that led Walsh to his conclusions about ionic character weaking bonds.[51] In any event, the ambivalent

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[49] The above argument is oversimplified to draw quick attention to the principal point. Obviously in toluene, for example, the para hydrogen has a demand made upon it that is similar to that made upon the methyl group, and if its response were the same, the model would give zero dipole moment. But the present model implies a smaller $\Delta\nu_{CH}$ than $\Delta\nu_{CC}$, and accordingly a smaller energy, electronegativity, and polarity shift for the hydrogen. It is striking that the discrimination needed between $(E'_{CC} - E_{CC})$ and $(E'_{CH} - E_{CH})$ for the model of Dewar and Schmeising to work is also needed to yield the correct dipole moments. So again we see a familiar correlation of the hyperconjugation theory, involving the donor capacity of H and CH_3, arising naturally from the present model.

[50] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 108. Cornell University Press, New York (1953).

[51] In applying our nonbonded model the important effects of substituting atoms of different intrinsic electronegativity must, unfortunately, be neglected. That is because such cases would involve differential steric effects and we claim at present to know at most the magnitudes of the interactions, not the detailed differences between them. In the limited scope of environmental variations left for us to explore we should choose to express Walsh's connection differently, stating that the environmental factors leading to bond strengthening also lead, in Walsh's bonds, to smaller polarity differences. If the bond from carbon were to an atom, Y, of *lower* intrinsic electronegativity than carbon, bond strengthening in our model would be associated with *increased* bond polarity. The hybridization model of Walsh would seem to imply the same thing. As discussed in footnote 49, increasing bond polarity would not necessarily increase the net molecular dipole moment, for Y would be competing with H. There is some experimental evidence that the tetrahedral-to-trigonal $\Delta\nu_{CY}$ decreases as the electronegativity of Y decreases. Thus C—Y bond strengthening and polarity increasing might still result in a lower net molecular dipole moment.

role of "electronegativity" with respect to intrinsic atomic polarity differences and environmental group polarity differences, and the connection with bond energies, is brought somewhat more into the open by the present simple model.

CONCLUSION

Effects customarily attributed to conjugation, hybridization, and group electronegativity can be rationalized to a remarkable extent in terms of nonbonded interactions. This suggests the foregoing factors are by no means as distinct from each other as they are often assumed to be. As a consequence it is improbable that unambiguous inferences of the nature of bonds in terms of these factors can be drawn from any set of experimental data, let along simple bond distances, until much more fundamental meanings are worked out. This conclusion is not really as pessimistic as it seems, for the model of nonbonded interactions that led to its formulation correlates a very extensive body of data in an extremely elementary way. Even in its present rudimentary form it is readily susceptible to the computation of numerical values of observables. If experience confirms the present proposal that intramolecular interactions between nonbonded atoms are comparable with intermolecular interactions at a given internuclear distance, such interactions *must* play a dominant role in the foregoing effects. If atoms are "whittled down" on the side of covalent bonds, nonbonded interactions may still often be of the same magnitude as the other interactions discussed.