THE INTERPRETATION OF BOND PROPERTIES

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It is our aim in this Review to discuss some recent attempts to interpret variations in length and strength of bonds. The extent of the subject—which includes in principle the whole of structural chemistry—makes it impossible for us to do more than consider a few of what appear to be the most interesting suggestions which have been advanced. In particular, we shall not discuss recent treatments of the structure of metals and intermetallic compounds by valence-bond methods.[1]

Before discussing the interpretation of these quantities, it is desirable to examine what they are and how they are obtained. There is no ambiguity, other than that involved in the method of observation, in the determination of bond length. The same is not true of bond strength.

Bond energies are quantities which may be assigned so that their sum in a molecule gives its heat of formation from separated atoms.[2-4] E. T. Butler and M. Polanyi [5] prefer to call them " bond energy terms " and reserve bond energy for the dissociation energy of a bond. For molecules for which an unambiguous valence bond structure may be written, the energy is regarded as an additive bond property, and the component terms as constants. It has been noted [5] that additivity is not evidence for a constant heat of formation of the bonds concerned. Consider two kinds of bonds formed, for example, by carbon with two different atoms X and Y. Whatever the variation in the energies of the C–X and C–Y bonds with the position of the C atom, no deviation from the additivity rule would result, so long as the variations are equal for both kinds of bond.

It has been pointed out by various authors [6-9] that heats of formation at ordinary temperatures include vibrational, rotational, and translational energy as well as chemical binding energy, and that although there is some theoretical justification for considering that the last of these is an additive bond property, the others are unlikely to be. The question has been quantitatively discussed for hydrocarbons by T. L. Cottrell,[10] who concludes

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[1] L. Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.
[2] K. Fajans, *Ber.*, 1920, **53**, 643; 1922, **55**, 2826.
[3] L. Pauling, " The Nature of the Chemical Bond ", Cornell, 1940.
[4] N. V. Sidgwick, " The Covalent Link in Chemistry ", Cornell, 1933.
[5] *Trans. Faraday Soc.*, 1943, **39**, 19.
[6] V. Dietz, *J. Chem. Physics*, 1935, **3**, 58.
[7] R. Serber, *ibid.*, p. 81.
[8] M. J. S. Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767.
[9] M. V. Wolkenstein, *Compt. rend.* (*Doklady*), *Acad. Sci. U.R.S.S.*, 1946, **51**, 213.
[10] *J.*, in the press.

that bond energies obtained conventionally may be used instead of " binding energy terms ", without introducing serious error. Tables of bond energies have been given by Sidgwick,[4] Pauling,[3] and, more recently, by G. E. Coates and L. E. Sutton,[11] and by Y. K. Syrkin.[12]

The bond energy of a diatomic molecule is the same as its dissociation energy if the atoms are produced in their ground states ; or may readily be derived from it if the state of excitation of the atoms produced is known. In molecules such as H_2O, NH_3, CH_4, where there is only one type of bond, the bond energy is obtained by dividing the heat of formation from atoms by the number of bonds. The bond energy need not be the same as, and in general differs slightly from, the dissociation energy of a bond in the molecule. This is because the energy of dissociation of a bond in a polyatomic molecule includes the energy of reorganisation of the radicals formed. There is the further difficulty in carbon compounds that the latent heat of sublimation of carbon to the valence state is not accurately known. This comes into the bond energy obtained from the heat of formation of the compound, but not into the dissociation energy.[13] The same is true of nitrogen compounds.

For a molecule in which there is more than one type of bond, it is necessary to know the energies of all types but one from other data, and to obtain the remaining bond energy as the residuum. This leads to rather large differences in the energy of the " same " bond in different molecules because the total environmental effects causing deviations from additivity in the bond energies as a whole are lumped into an effect on the one bond considered last. If allowance is to be made for the effects of differences in environment on the individual bonds in a molecule, it is necessary to make an assumption of the type which we wish to test about the effect of distortion, on at least one sort of bond, and then to see if this leads to self-consistent conclusions. For example, for organic compounds, it is necessary to assume a relationship between the energy and length of the CH bond, since all CH bonds are not the same and the CH bond in methane is the only bond in any organic compound whose energy may be determined unambiguously.

The observed variation of length of the CH bond is from $1{\cdot}059_7$ A. in acetylene to $1{\cdot}093_6$ A. in methane.[14] At first sight the question to be answered appears to be : " How much does the CH bond energy change from acetylene to methane ? " This question is not only unanswerable but meaningless. We have defined bond energy as the quantity of energy which must be assigned to each bond so that the sum gives the heat of formation of the molecule. It is not an observable property of a bond but a conveniently chosen part of the energy of a molecule. The question is more properly put : " How much of the difference between the energies of formation of methane and acetylene should be attributed to the fact that the CH bond is shorter in acetylene than in methane, in order to

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[11] *J.*, in the press.

[12] *J. Phys. Chem. Russia*, 1943, **17**, 347.

[13] L. H. Long and R. G. W. Norrish, *Proc. Roy. Soc.*, 1946, *A*, **187**, 337.

[14] G. Herzberg, " Infra Red and Raman Spectra ", New York, 1945, Chap. IV.

arrive at a scheme of bond energies which fits in as well as possible witl other bond properties ? "

The simplest answer is to regard the CH bond energy as constant because the change in length is small compared with changes in lengtl of other bonds. J. J. Fox and A. E. Martin [15] have assumed that th energy difference between two CH bonds of differing length is given b $\Delta E = \frac{1}{2}k(\Delta r)^2$, where k is the mean of the CH force constant in methan and acetylene, and Δr is the difference in length. This is only abou 0·5 kcal./mole, so they consider it negligible. Their procedure is unsound because the difference of the equilibrium bond lengths in the two compounds indicates that there is some difference in bond character and also that we are dealing with separate potential energy minima between which there need not be any simple relation. Nevertheless W. Gordy,[16] assuming the constancy of the CH bond energy, has shown that CO, CC, and CN links obey a simple relationship of the form $E = lr^{-2} + m$, where l and m are constants.

H. A. Skinner,[17] on the other hand, starts with the general assumption that short bonds are stronger than long bonds, and therefore that the variation in length of CH is important. To allow for this, he took the point corresponding to CH in methane and that to " ideal covalent " CH, of length equal to the sum of the covalent radii of C and H (the latter from H_2), and of energy the arithmetic mean of the latent heat of sublimation of carbon and the H–H bond energy, drew a straight line between the two, and extrapolated linearly to shorter bond lengths. This arbitrary procedure gives reasonably smooth energy–length curves for derived bond energies for CC, CO, CN, CCl, and CS bonds, of the form $Er^n =$ constant, with $n = 3$—4. The numerical results are quite sensitive to the energy–length relationship assumed for the CH bond, but they all show energy varying with length more rapidly than was supposed for CH.

We may compare the OH bond. The OH distance in the OH radical is 0·971 A.,[18] in water 0·958 A.[14] (these are r_e values). The OH bond energy in the radical is $\sim$ 100 kcals.,[19] in water 110·4 kcals.[17] The straight line joining these points on an energy–length graph has a much steeper slope than that joining either to " ideal covalent " OH, which also suggests that for the CH bond Skinner has underestimated the variation of energy with length.

We have stated that our aim in arriving at corrected bond energies should be to produce a scheme which fits in as well as possible with other bond properties. If the latter can be satisfactorily inter-related, then the bond energies should be chosen to fit in with such a scheme ; *e.g.*, if both force constant and dissociation energy of a bond increase, then we should consider that the bond energy increases too. We may now consider the

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[15] *J.*, 1938, 2106.

[16] *J. Chem. Physics*, 1947, **15**, 305.

[17] *Trans. Faraday Soc.*, 1945, **41**, 645.

[18] G. Herzberg, " Molecular Spectra and Molecular Structure ", New York, 1939, Chap. VIII.

[19] R. J. Dwyer and O. Oldenburg, *J. Chem. Physics*, 1944, **12**, 351.

CH bond in that light. In the compounds CH, CH_4, C_2H_4, C_2H_2 we know the CH distances, the force constants, and the dissociation energies; and the type of orbital hybridisation has been considered theoretically.[20] The properties of CH in these molecules are set out in Table I.[21]

TABLE I

Properties of CH *bonds*

Molecule.	Hybridisation.	r_0(CH), A.	k(CH), dynes/cm. × 10^5.	D(CH), kcals.
CH	p	$1{\cdot}131^{14}$	$4{\cdot}3^{*}$	80^{18}
CH_4	sp^3	$1{\cdot}094^{14}$	$5{\cdot}0^{22}$	102^{23}
C_2H_4	sp^2	$1{\cdot}071^{14}\dagger$	$5{\cdot}1^{22}$	100^{24}
C_2H_2	sp	$1{\cdot}059^{14}$	$5{\cdot}9^{22}$	$104,^{23}$ 121^{25}

* From the value for the vibration frequency given by Herzberg [18] (cf. J. W. Linnett [26]).

† This value, quoted by Herzberg,[14] is due to W. S. Gallaway and E. F. Barker,[27] and presumably must be regarded as superseding earlier values still frequently quoted. An uncertainty of ± 0·01 has been assigned to the length by F. Halverson.[28] Linnett [26] has estimated the length as 1·088 from the force constant.

These variations do not appear to have any simple inter-relation. As mentioned in the footnote to the table, the estimate of the CH length in ethylene from the force constant is in disagreement with the experimental value, although apart from this the length changes smoothly with force constant; and the dissociation energies do not show a regular trend. Thus it is not certain whether one should make the bond energy change or not.

Discussion of bond strength may be concerned with bond energies, force constants, or dissociation energies. Because of the difficulties mentioned above, the bond energy is not a wholly satisfactory measure of it. The force constant is often used for bonds in simple molecules, such as the CH bonds mentioned above, where an unambiguous assessment of bond energy is not possible. On the other hand, there are many more molecules for which we have thermochemical data than for which it is possible to make the assignment of the fundamental vibration frequencies necessary for the derivation of force constants. Moreover, many force constants depend markedly on the type of force field assumed.[29] There is no entirely satisfactory relationship between force constant and energy, although some

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[20] Cf. C. A. Coulson, *Quart. Reviews*, 1947, **1**, 144.

[21] Cf. A. D. Walsh, Faraday Society Discussion, 1947, " The Labile Molecule ".

[22] G. Herzberg, " Infra Red and Raman Spectra ", New York, 1945, Chap. II.

[23] E. W. Steacie, " Atomic and Free Radical Reactions ", New York, 1946, Chap. III.

[24] K. J. Laidler, *J. Chem. Physics*, 1947, **15**, 712.

[25] R. Cherton, *Bull. Soc. roy. Sci. Liége*, 1942, **11**, 203

[26] *Trans. Faraday Soc.*, 1945, **41**, 223.

[27] *J. Chem. Physics*, 1942, **10**, 88.

[28] *Rev. Mod. Physics*, 1947, **19**, 87.

[29] J. W. Linnett, *Quart. Reviews*, 1947, **1**, 73.

regularities have been found.[30] The use of dissociation energies is limited because of the possible effect of radical reorganisation energy.

We have now discussed the property of the bond which we hope to correlate with its length, and incidentally we have given the form of the correlation, *viz.*, the longer the bond the weaker. Instead of directly correlating length with strength, it is more illuminating to consider the interpretation of changes in each from a more theoretical standpoint. There are three obvious factors which have to be taken into account: the multiplicity, *i.e.*, whether the bond is single, double, or triple, the polarity, and the type of orbital hybridisation involved. We shall consider these separately.

(1) *Bond Multiplicity and Bond Order.*—The realisation, brought about by the application of quantum mechanics to problems of molecular structure, that bonds are not necessarily pure single, double, or triple, but might have intermediate characteristics, made it necessary to devise some more elastic type of description for a bond than that permitted by the simple valency picture, and the term bond order thus came into use.

For bonds which might be between single and double, an early approach was to relate empirically " double-bond character " to bond length, using a knowledge of the lengths of " pure " bonds and of those bonds where an easy assessment of " double-bond character " seemed possible, and thence to estimate the latter in other cases. If only the Kekulé forms of benzene are considered, each bond has 50% " double bond character ", and in graphite the bonds have 33% " double bond character ".[3] Thus, with the values for ethane and ethylene, there are four points through which a smooth curve may be drawn. More recently, Pauling [1] has extended the idea by defining " bond number " as the number of shared electron pairs involved in the bond, and has drawn a smooth curve of bond number against length through the points for ethane, ethylene,* and acetylene. This is fitted by a logarithmic relation involving only one constant. However, the point for a bond of order 1·5 does not give the bond distance in benzene. Pauling therefore makes the assumption that resonance shortens the bond, and gives a correction factor for use with resonating structures. In connection with later discussion it is of interest to note that, without this resonance correction, the bond number in benzene is required to be 1·64 to make the relation hold. Pauling has applied it in a discussion of internuclear distances and bond numbers in metals which, however, we shall not consider further. " Indices de liaison ", corresponding to Pauling's bond numbers, have been calculated for many molecules by Daudel *et al.*[31-33]

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[30] Cf. J. W. Linnett, *Trans. Faraday Soc.*, 1940, **36**, 1123; 1942, **38**, 1.

[31] P. Daudel, R. Daudel, R. Jaques, and M. Jean, *Rev. sci.*, 1946, **84**, 489.

[32] C. A. Coulson, P. Daudel, and R. Daudel, *ibid.*, 1947, **85**, 29.

[33] C. A. Coulson and W. E. Moffitt, in course of publication.

* Pauling takes 1·330 A. as the C–C length in ethylene. The more recent value of 1·353 A. given by Gallaway and Barker [27] does not fit the form of the curve so well.

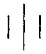
Pauling's definition of bond order has been criticised by W. G. Penney.[34] If the bond in benzene has 50% double-bond character, and if we seek, as we reasonably might, to make " character " indicate all the properties of a bond, including its energy, then we would expect the heat of formation of benzene to be given by the sum of the bond energies of six C–H bonds, three C–C bonds, and three C=C bonds. In fact, of course, the heat of formation of benzene is greater because of resonance energy. Thus the bond order in benzene would be better expressed by a number somewhere between 1·5 and 2·0.

Penney's other criticism is based on the effect of including the three Dewar structures on the resonance energy of benzene. We consider that, after the formation of a ring of single C–C bonds and the C–H bonds, benzene may be regarded as a hexagonal structure of univalent atoms. L. Pauling and G. W. Wheland [35] have shown that, if only the two Kekulé structures (I) and (II) are taken into account, the wave function and exchange energy are given by


(I.)


(II.)


(III.)


(IV.)


(V.)

$$\Psi = 0{\cdot}632(\psi_{\mathrm{I}} + \psi_{\mathrm{II}})\,;\quad W = 2{\cdot}40J$$

where J is the exchange integral. If the full canonical set (I)—(V) is taken into account, the wave function and energy become

$$\Psi = 0{\cdot}410(\psi_{\mathrm{I}} + \psi_{\mathrm{II}}) + 0{\cdot}178(\psi_{\mathrm{III}} + \psi_{\mathrm{IV}} + \psi_{\mathrm{V}})\,;\quad W = 2{\cdot}61J$$

This inclusion improves the energy by about 9%. But if the excited structures (III)—(V) are taken into account in obtaining the bond order as defined by Pauling, it is found that the order drops from 1·5 to 1·46.

Penney therefore proposed another definition. It is assumed that all electron orbits are equivalent and that the energy of the most stable state of the system can be calculated as a function of J, the appropriate exchange integral. There are assumed to be k equivalent pairs of neighbouring orbits, so the average energy per pair is W/k. According to the electron-pairing approximation, within a pair the coefficient of the exchange integral is $+1$, while it is $-\frac{1}{2}$ between two electrons not belonging to the same pair.[36, 37] The actual linkage of the system can be expressed as p (the bond order) times a single bond plus $(1 - p)$ times " no bond ", and this is equated to the calculated energy thus :

$$W/k = p(J) + (1 - p)(-\tfrac{1}{2}J)$$

whence

$$p = \tfrac{1}{3}(1 + 2W/kJ)$$

Penney's definition of bond order is based on spin theory : we quote the above equivalent, but less fundamental derivation, for simplicity.

For benzene, structures (I)—(V) being taken into account, p is 0·623.

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[34] *Proc. Roy. Soc.*, 1937, *A*, **158**, 306.

[35] *J. Chem. Physics*, 1933, **1**, 362.

[36] Cf. J. H. Van Vleck and A. Sherman, *Rev. Mod. Physics*, 1935, **7**, 167.

[37] Cf. L. Pauling and E. B. Wilson, " Introduction to Quantum Mechanics ", New York, 1935, Chap. XIII.

The total bond order is therefore 1·623. Penney has shown that his bond orders give a reasonably good value for the energy of other aromatic compounds, and Fox and Martin[15] have pointed out that Penney's order for benzene fits fairly well on an energy–order curve drawn through points for bonds of order 0, 1, 2, 3. It also gives a smooth order–length curve, including the point for a bond of order 3, the CC distance in ethylene being taken to be 1·33 A.

Coulson has treated bonds of fractional order by the method of molecular orbitals, and has given a definition of bond order in terms of the coefficients used in building up molecular orbitals by the linear combination of atomic orbitals (L.C.A.O.).[38, 39, 20] The order of a bond is, as before, considered to be the sum of two parts, one of magnitude unity, corresponding to the single localised σ bond between two atoms, and the other part, p, contributed by the mobile electrons. For ethylene, p is 1, and the total bond order is 2; for acetylene, the total bond order is 3. p in a conjugated system is evaluated as follows. If a given electron occupies a molecular orbital represented by

$$\Upsilon = a_1\psi_1 + a_2\psi_2 + \dots + a_n\psi_n$$

where

$$a_1^2 + a_2^2 + \dots + a_n^2 = 1$$

and where the ψ's are atomic orbitals, its contribution to the mobile order of a bond between atoms R and S is $a_{\mathrm{R}}a_{\mathrm{S}}$. More generally, if the a's are complex, p_{RS}, the contribution of one mobile electron to the order of the bond R–S, is given by $p_{\mathrm{RS}} = \frac{1}{2}(a_{\mathrm{R}}a_{\mathrm{S}}^* + a_{\mathrm{R}}^*a_{\mathrm{S}})$. The total mobile bond order is the sum of contributions p_{RS} from each mobile electron present. On this basis, the total bond order in benzene is 1·667.

Coulson derives the relation between p_{RS} and β_{RS}, the resonance integral, and the total resonance energy of the system. Using J. E. Lennard-Jones's[40] identification of 2β with the difference in energy between a pure double bond and a pure single bond, $E_d - E_s$, each corrected for compression or extension to the length of the actual bond (usually by Hooke's law), the energy of a bond of mobile order p is shown to be $pE_d + (1-p)E_s$. There appears to be some confusion in the literature about this. Gordy[16] uses the above relation without correction for compression and extension, and even Coulson seems to have done so at times.[32] For benzene, the bond energies considered appropriate by T. L. Cottrell and L. E. Sutton[41] being used, the C–C energy is 85·3 kcals. if compression and extension are taken into account, and 88·6 kcals. otherwise. The actual value is 87·6 kcals., but the significance of this test is doubtful, because, as Penney[34] has pointed out, the value of the latent heat of sublimation affects the relative as well as the absolute values in this case. Further, since the interpretation of the resonance integral is not certain, it would in any case be unwise to attach too much importance to small differences.

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[38] C. A. Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413.

[39] J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811.

[40] *Proc. Roy. Soc.*, 1937, *A*, **158**, 280.

[41] *J. Chem. Physics*, 1947, **15**, 685.

Another difficulty is that if, for C–C bonds, the energy is plotted against the order for the points 0, 1, 2, 3, the curve is concave towards the order axis.[11, 15] If the compressional and stretching effects are neglected, Coulson's relation (see above) gives a straight-line plot between total order 1 and 2, while if these effects are taken into account, the curve is convex to the order axis. There are two possible reasons for this discrepancy. First, as we have already pointed out, the uncertainty in the interpretation of β means that the relationship between order and energy on the M.O. approximation is not rigorous. Secondly, it is not obvious that the curve representing bonds which are intermediate between single and triple should pass through the point corresponding to a double bond.

For NN bonds, the empirical energy–order curve is convex to the order axis, while for CN bonds the plot is nearly linear.

Using the above interpretation of p, and a Hooke's law allowance for compressional and extensional effects, Coulson [38] obtains for the length, R of a bond

$$R = R_s - (R_s - R_d)\left[1 + \frac{k_s}{k_d}\left(\frac{1 - p}{p}\right)\right]^{-1}$$

where k_s/k_d is the ratio of the force constants of a single and a double bond. Pauling [3] has given the same relation, putting $k_s/k_d = 1/3$, and with x, the " double-bond character ", in place of p. In fact, the ratio of k(CC) in ethane to that in ethylene is more nearly 1/2 than 1/3 [29], and Coulson has given reasons for believing that the fraction here applicable is even greater. Thus Pauling's value of the term $k_s(1 - p)/k_dp$ is about correct, although his value of 0·5 for x in benzene is low compared with the bond order. From an empirical curve of length against order, using as fixed points ethane, graphite, benzene, ethylene, and acetylene, the value 0·765 for k_s/k_d is obtained. Coulson [38] has calculated the order of the links in several conjugated hydrocarbons, and has determined the lengths from the curve, good agreement with the observed results being obtained.

C. A. Coulson [42] has calculated mobile bond orders in systems containing the carbonyl group, and H. C. Longuet-Higgins and Coulson [43] have done the same for some heterocyclic molecules containing nitrogen. These authors [44] have also given a formal discussion of the application of the molecular orbital method to conjugated systems and the calculation of bond orders and related properties. In connection with the calculations on the carbonyl group, it is worth emphasising that the mobile bond order as defined by Coulson is the *covalent* bond order, and, because of the partial ionic character of the bond, $p < 1$ for pure C=O. Coulson gives for C=O, $p = 0{\cdot}895$. A more exact treatment of the CO link in carboxyl and amide groups has been given by K. Wirtz,[45] who finds that taking into account compressional and stretching energy makes some difference to the bond order and a considerable difference to the estimated value of the resonance integral. Calculations involving heteronuclear systems are less reliable than those for homonuclear systems, because the resonance integrals are

[42] *Trans. Faraday Soc.*, 1946, **42,** 106.

[43] *Ibid.*, 1947, **43,** 87.

[44] *Proc. Roy. Soc.*, 1947, *A*, **191,** 39.

[45] *Z. Naturforsch.*, 1947, **2,** *a*, 264.

no longer equivalent for all the links, and no satisfactory interpretation of the Coulomb integrals has been given.

The assumption that the bonds in ethane, ethylene, and acetylene are pure single, double, and triple bonds depends upon the view that the CH bonds are completely localised. R. S. Mulliken, C. A. Rieke, and W. G. Brown [46] (hereafter denoted by M.R.B.) have concluded that this is not quite true and have considered the extent to which "hyperconjugation" takes place.[20, 47] Briefly, in ethane, for example, the CH_3 group is considered to act as an electron donor to the C–C link, since it is possible to construct molecular orbitals for CH_3 of the required symmetry. This means that the C–C link in ethane has a contribution from mobile electrons, making its bond order greater than unity. M.R.B. have calculated bond orders in a number of compounds which give a smooth curve when plotted against length, except that the formal single bond of systems C—C≡C is shorter than indicated by the curve. This agrees with a suggestion of L. Pauling, H. D. Springall, and K. J. Palmer [48] that bonds with much *s* character in the σ bond are shorter than usual. Bond orders given by this method have been found by Gordy [16] to fit a relationship of the form $N = aR^{-2} + b$, where N is the order and R the length of the bond. A plot of N against R^{-2} gives a good straight line for CC, NN, and OO bonds.

Many other empirical relationships connecting order—or multiplicity—with length and energy have been suggested.[49–52] In view of the relatively small alterations in length for large alterations in order, it is hardly surprising that it is possible to get agreement between the observed and the calculated lengths with a variety of functional forms of the relationship. The accuracy of some of the predictions is not as good as might be desired. For example, Lagemann [50] obtains an equation and constants which predicts lengths of 1·50, 1·36, and 1·31 A. for the CC links in ethane, benzene, and ethylene, respectively, compared with the experimental values of 1·55,[53] 1·40,[54] and 1·353 A.[27] There is no general agreement on what is to be regarded as the order of a bond. Lagemann and Gordy use M.R.B. bond orders; Kavanau considers that his equation fits the Coulson bond order best. Better results are always obtained for the prediction of lengths than of energies.

A. D. Walsh [55] has criticised previous definitions of bond order as being oversimplified, and has suggested that it should be possible to obtain an experimental measure of a suitably defined bond order. The bond order

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[46] *J. Amer. Chem. Soc.*, 1941, **63**, 41.

[47] C. L. Deasy, *Chem. Reviews*, 1945, **36**, 145.

[48] *J. Amer. Chem. Soc.*, 1939, **61**, 927.

[49] J. L. Kavanau, *J. Chem. Physics*, 1944, **12**, 467; 1947, **15**, 77; *J. Amer. Chem. Soc.*, 1947, **69**, 1827.

[50] R. T. Lagemann, *J. Chem. Physics*, 1946, **14**, 743

[51] H. J. Bernstein, *ibid.*, 1947, **15**, 284, 339, 688.

[52] R. Cherton, *Bull. Soc. chim. Belg.*, 1943, **52**, 26.

[53] L. Pauling and L. O. Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223.

[54] J. H. Archer, C. Finbak, and O. Hassel, *Tids. Kjemi Berg.*, 1942, **2**, 33.

[55] *Trans. Faraday Soc.*, 1946, **42**, 779.

is defined as the "summed total electronic energy per bond". The ionisation potential of the electrons concerned in the bond is considered to be a measure of this, in a manner which will be clarified by an example : ethylene has two π electrons, the ionisation potential for one π electron in ethylene is 10·45 v.,* so the mobile bond order is proportional to 20·90 v. Acetylene has four π electrons, each of ionisation potential 11·35 v., giving a mobile order of 45·40 v. Ionisation, in fact, is used as a perturbation to discover how tightly an electron is bound. Benzene has four π electrons with an ionisation potential 9·19 v. and two at 11·7 v. ; the mobile order therefore corresponds to $\frac{1}{6}(4 \times 9{\cdot}19 + 2 \times 11{\cdot}7) = 10{\cdot}03$ v. σ electrons have an ionisation potential of 12·0 v. The total bond order is obtained by adding this to the mobile bond order. The results are scaled to ethylene having a mobile bond order of 1, or total bond order 2. This scheme shows that the π bond in ethylene is only 0·87 as strong as the σ bond, and that the mobile bond order in acetylene is more than twice that in ethylene. This is surprising, since bond energies show that the second π bond in acetylene is not so strong as the first. Environmental factors are automatically taken into account ; for example, the bond order in tetramethylethylene is different from that in ethylene. There is a smooth relation between length and order, and a straight line is obtained by plotting a selected set of values for CC force constants against order. A fairly smooth curve is obtained from a plot of bond order against bond energy, although here some of the energies are obtained from an empirical energy–length curve. One interesting result of this approach is that the bond order of *cyclo*hexane is rather less than the bond order in ethane, a conclusion which is indicated by other evidence.[10]

We conclude this section with Table II, comparing the various bond orders given for some C–C bonds.

TABLE II

C–C Bond orders

Bond in :	Pauling.	Penney.	Coulson.	M.R.B.	Walsh.
Ethane	1	1	1	1·12	1·07
Ethylene	2	2	2	2·12	2·00
Acetylene	3	3	3	3	3·10
Benzene	1·5	1·623	1·667	1·667	1·51
Graphite	1·33	1·45	1·53	1·53	1·3
Formal C=C in butadiene .	1·81	1·911	1·894	1·945	1·91
Formal C–C in butadiene .	1·18	1·333	1·447	1·325	1·175

It is worth pointing out that all these definitions of order are concerned with *covalent* bonds only, as is to be expected since the idea grew from multiplicity of carbon–carbon bonds. An extension of the idea to include ionic bonds by W. Gordy [56] will be discussed in the section on polarity.

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[56] *Physical Rev.,* 1946, **69,** 130 ; *J. Chem. Physics,* 1946, **14,** 305.

* The ionisation potentials quoted in this review are all taken from Walsh's papers.

(2) *Polarity.*—Pauling [3] has suggested that bonds are stabilised by covalent–ionic resonance, and that therefore the energy of a bond A–B is greater than the arithmetical, or more properly the geometrical, mean of the A–A and B–B energies. That this is not the whole story is shown by the following results for the calculated energy of the hydrogen molecule: pure covalent, 3·76 e.v.; covalent–ionic hybrid, 4·00 e.v.; variation treatment with no reference to covalent or ionic structures, 4·70 e.v.; observed, 4·72 e.v.[57, 58, 59] Furthermore, as A. Burawoy [60] has remarked, there are bonds where a large contribution from the ionic form might be expected, but where stabilisation is not found. Nevertheless, Pauling's generalisation seems to apply in many cases.

E. Warhurst [61] has considered the effect of covalent–ionic resonance on lengths and force constants. His calculations are not rigorous—they involve neglect of the non-orthogonality integral—and are inconclusive so far as they bear on bond lengths. He has, however, given a successful treatment of the decrease of vibration frequency, which occurs when certain gases are liquefied or dissolved in non-ionising solvents, by considering the effect of alteration of the dielectric constant of the medium on the energy of the ionic form. Ionic character in diatomic molecules has also been treated by F. T. Wall,[62] who shows that if the wave function is written $\Psi = \psi_c + a\psi_i$, a^2 is given by the relation

$$a^2 = (H_{cc} - W)/(H_{ii} - W)$$

where the subscripts c and i refer to covalent and ionic forms, and H_{cc} and H_{ii} are integrals of the type $\int \psi_c H \psi_c d\tau$ and therefore represent the energies of the covalent and ionic forms respectively. E. C. Baughan, M. G. Evans, and M. Polanyi [63] derived a for a series of CH_3–X compounds from the dipole moment, and thence calculated the resonance energy, obtaining values agreeing very roughly with those derived from Pauling's geometric mean rule.

On the basis that stabilisation in bonds between unlike atoms is due to ionic contributions, Pauling [3] derived a scale of "electronegativity" values for the elements from thermochemical data. R. S. Mulliken [64, 65] showed that "electronegativities" are related to the average of the ionisation potential and electron affinity of the atom, and W. Gordy [66] has related them to the effective nuclear charge of the atom and its covalent radius. Bond dipole moments are roughly proportional to the electronegativity difference between the linked atoms.[67] C. P. Smyth [68] observed that some moments, notably those for carbon attached to large atoms such as sulphur

[57] C. A. Coulson, *Trans. Faraday Soc.*, 1937, **33,** 1479.

[58] S. Weinbaum, *J. Chem. Physics*, 1933, **1,** 593.

[59] H. M. James and A. S. Coolidge, *ibid.*, p. 825

[60] *Trans. Faraday Soc.*, 1943, **39,** 79.

[61] *Ibid.*, 1944, **40,** 26.

[62] *J. Amer. Chem. Soc.*, 1939, **61,** 1051.

[63] *Trans. Faraday Soc.*, 1941, **37,** 377.

[64] *J. Chem. Physics*, 1934, **2,** 782.

[65] *Ibid.*, 1935, **3,** 573.

[66] *Physical Rev.*, 1946, **69,** 604.

[67] J. G. Malone, *J. Chem. Physics*, 1933, **1,** 197.

[68] *J. Physical Chem.*, 1937, **41,** 209; *J. Amer. Chem. Soc.*, 1938, **60,** 183; 1941, **63,** 57.

or iodine, are larger than expected ; he remarked that the reason why better results are given for small atoms may be their smaller polarisability.

In the discussions mentioned, with the exception of Mulliken's,[65] it has been assumed that the dipole moment is due solely to contributions from ionic forms. This assumption is unjustified, as has been shown by Mulliken, and in more detail by C. A. Coulson.[69] Analysis using the L.C.A.O. molecular orbital approximation shows that there are four terms in the expression for the dipole moment of a bond.* The first is that arising from the formal charge effect. The second is the " homopolar dipole ", *i.e.*, that due to the asymmetry of the electron distribution relative to the bond given by Heitler–London type of terms even when the component atomic functions are symmetric about their nuclei : this may be quite large if the atoms differ much in size. The third term is the " atomic dipole ", *i.e.*, that due to the asymmetry of the atomic orbitals about their nuclei, which is large if we are dealing with a hybridised orbital.

The fourth term represents the secondary dipole moment which may be induced in any non-bonding electrons. This is unlikely to be important unless a " lone pair " is present ; when also it may be that orbital hybridisation will cause these to have a moment of the " atomic dipole " type. The moment of the covalent form may be large : Coulson [69] has calculated that for the CH bond the " pure covalent " structure has a moment 1·97 D. (C^+H^-), whereas the ionic form has a moment 1·53 D. (C^-H^+). The overall moment is calculated to be 0·40 D. (C^+H^-). To assume that moments are due only to ionic forms may therefore introduce serious error.

It is, however, worth considering the relation of electronegativity to other bond properties. V. Schomaker and D. P. Stevenson [70] have suggested the relation

$$r_{AB} = r_A + r_B + \beta(x_A - x_B)$$

for the length r_{AB} of a bond between atoms A and B, where r_A and r_B are the covalent radii in A., x_A and x_B are the electronegativities, and $\beta = 0{\cdot}09$ for single bonds. The rule has also been used for double bonds.[71, 72] It is not altogether satisfactory. For example, the Sn–Cl distances in $SnMe_3Cl$, $SnMe_2Cl_2$, $SnMeCl_3$, and $SnCl_4$ are 2·37, 2·34, 2·32, and 2·30 A., respectively.[73] The sum of the covalent radii of Sn and Cl is 2·39 A. ; the Schomaker–Stevenson rule gives 2·28 A. For $AsCl_3$ and $AsMe_2Cl$ the As–Cl distances are 2·16 and 2·18 A.,[73] the sum of the covalent radii is 2·20 A., and the Schomaker–Stevenson rule gives 2·11 A.

Gordy [56] has suggested that the force constant of a bond depends on

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[69] *Trans. Faraday Soc.*, 1942, **38**, 433.

[70] *J. Amer. Chem. Soc.*, 1941, **63**, 37.

[71] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J.*, 1945, 146.

[72] W. Gordy, *J. Chem. Physics*, 1947, **15**, 81.

[73] H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, 1944, **40**, 164.

* $\mu = Q_bR - 4eabS(R/2 - x_{ab}/S) + 2e(a^2x_{aa} - b^2x_{bb}) + \mu_s$ where Q_b is the formal electronic charge on nucleus B, R is the internuclear distance, a and b are the coefficients of ϕ_a and ϕ_b (the atomic orbitals combined to give the molecular orbital), S is the overlap integral $\int\phi_a\phi_b d\tau$, and x_{ab}, x_{aa}, and x_{bb} are given by $\int x\phi_a\phi_b d\tau$, $\int x\phi_a{}^2 d\tau$, and $\int(R - x)\phi_b{}^2 d\tau$; x is the distance measured from A.

the *product* of the electronegativities of the atoms, and is given fairly accurately by

$$k = aN(x_A x_B / r^2_{AB})^{3/4} + b$$

a and b are constants (equal to 1·67 and 0·30 respectively if lengths are in A. and the force constants in dynes/cm. $\times$ 10^{-5}) which are the same for all bonds ; N is the bond order, defined as the effective number of covalent *or ionic* linkages involved. For covalent linkages the bond order used is that defined by M.R.B.,[46] which may be non-integral ; but bonds with partial ionic character are considered integral, *e.g.*, HCl as single, C=O as double. It does not always work, however ; one reason for this may be that there is no method of including changes of electronegativity due to environmental effects. The CH bond in aldehydes, for example, has a very low force constant,[26] which is not predicted. A. D. Walsh [74] discusses other exceptions to Gordy's rule in a forthcoming paper.

Walsh [75] has suggested that in a given bond, *ceteris paribus*, the force constant and bond energy decrease and the length increases with increasing polarity. The statement seems in contradiction to Pauling's rule for bond energies and to the Schomaker–Stevenson rule for bond lengths. This is not necessarily so. The last two rules compare a bond between atoms A and B with one between atoms C and D. The second of them states that if the electronegativity difference between A and B is greater than that between C and D the AB bond will be shorter than $r_A + r_B$ (the sum of the covalent radii) by an amount greater than that by which the CD bond is shorter than $r_C + r_D$; the first applies *mutatis mutandis* to strengths. On the other hand, Walsh's rule is that, if environmental factors in polyatomic molecules X and Y both containing a bond AB cause the polarity of the bond to be greater in X than in Y, then its length will be greater, and its strength less, in X than in Y. It is conceivable that decrease in electronegativity of atom A, if initially $x_B > x_A$, may reduce the *covalent* strength of AB, so that although the ionic–covalent resonance may be increased, the total bond energy may nevertheless decrease. Similar considerations apply to the length. Walsh's rule would then be compatible with the idea of covalent–ionic resonance. Walsh, on the other hand, has suggested that the internuclear distances of the covalent and ionic forms are too different to allow resonance.

We now consider some of the evidence bearing on this rule. Skinner and Sutton [73] have shown that substitution of Cl for methyl in the methyltin chlorides reduces the Sn–Cl distance. A similar shortening of the M–Hal link on further halogen substitution is shown by fluorinated methanes, chlorinated silanes, brominated silanes, methyltin bromides, methyltin iodides, methylarsenic chlorides, and methylchloroamines.[73] Such substitution might be expected to reduce the polarity of the M–Hal link. Dipole-moment data [76] show that this drop in polarity does occur in the chlorosilanes and chloromethanes. This seems to be evidence for Walsh's

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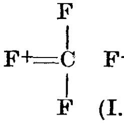
[74] *J.*, in the press.

[75] *Trans. Faraday Soc.*, 1947, **43**, 60.

[76] Cf. L. O. Brockway and I E. Coop, *ibid.*, 1938, **34**, 1429.

rule, though there is no evidence in most instances to show whether the energies increase as the bonds shorten ; furthermore, there are other possible descriptions of the effect. L. O. Brockway and H. O. Jenkins [77] ascribe the shortening in tetrafluoromethane to structures such as (I), so that the decrease in polarity is incidental to the strengthening due to increased multiplicity. Skinner and Sutton [73] suggest that substitution of a less by a more electronegative outer grouping increases the electronegativity of the central atom and hence decreases its effective radius—a suggestion which is in agreement with Gordy's [66] expression for electronegativity—and that successive substitutions of halogen decrease the radius of the central atom. The halogen atoms will be enlarged by their negative charges ; but it is likely that the charge on each atom will be less the more such atoms there are, and thus this enlargement will decrease progressively.


$$\mathrm{F^{+}{=}\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}\quad F^{-}}$$
(I.)

The evidence for the effect of polarity on the strengths of less ambiguously single bonds is suggestive rather than rigorous. For example, the experimental data allow us to be fairly arbitrary in our choice of CH bond energies ; and little is known with certainty about its polarity. According to Coulson,[69] the polarity is about the same in almost all CH bonds, but his calculations are more reliable for CH in methane than in other compounds. Thus any discussion of the effect of polarity on the CH link must be very tentative.

The application of the polarity rule to multiple bonds is obscured by the possibility of change of multiplicity. The —C≡N and C=O links are both polar, with the negative end of the dipole at the nitrogen and the oxygen atom. We would expect therefore, that substitution of Cl for H in these compounds, if it did not alter multiplicity, would reduce the polarity and increase the strength of the bonds. Some experimental data are given in Table III.

TABLE III

Molecule.	CN length.	CN force constant.	Molecule.	CO length.	CO force constant.
HCN	1·157[14]	17·9[22]	H_2CO	1·21[79]	12·0[81]
ClCN	1·15[78]	16·7[22]	Cl_2CO	1·18[80]	12·14[81]

The CN force constant in ClCN is less than in HCN. This is not in accordance with the rule. Instead, it indicates that $Cl^{+}{=}C{=}N^{-}$ is an important structure, a view supported by the shortening of the C–Cl bond to 1·64 A. On the other hand, carbonyl chloride shows the expected polarity

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[77] *J. Amer. Chem. Soc.*, 1936, **58**, 2036.

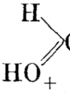
[78] C. H. Townes, A. N. Holden, and F. R. Merritt, *Physical Rev.*, 1947, **71**, 64.

[79] D. P. Stevenson, J. E. LuValle, and V. Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 2508.

[80] V. Schomaker, private communication.

[81] C. R. Bailey and J. B. Hale, *Phil. Mag.*, 1938, **25**, 98.

effect: there is no important contribution from $Cl^{+}{=}CCl{-}O^{-}$,* the C–Cl length being 1·74 A.[80] Walsh's explanation is that the importance of $Cl_2C{-}O^-$ is reduced compared with $Cl_2C{=}O$; Schomaker's is that $Cl^{-}CCl{\equiv}O^{+}$ is important.

The carbonyl link is of particular interest, because Walsh [83] has, in a series of compounds, attributed thereto polarities obtained from the ionisation potential of the non-bonding $p\pi$ electrons on the oxygen atom. This is the energy difference between the ground state and the ion: to regard it as exclusively concerned with the ground state of the molecule is therefore somewhat arbitrary. Furthermore, a theoretical discussion by W. E. Moffitt [84] of the electronic configuration of simple compounds containing CO shows that it is not strictly correct to attribute variations in the ionisation potential to change in the carbonyl group alone. A possible example of this difficulty is that the ionisation potentials of carbon dioxide and carbon oxysulphide are 13·73 and $\sim$ 12 v., the difference being almost 40% of the total variation for all compounds considered. This indicates, according to Walsh, a considerable difference in polarity in the carbonyl links, whereas the CO lengths are almost the same in each compound—1·163 [14] and 1·161 A.,[85] respectively. Again, the ionisation potential of formic acid is 11·3 and that of formaldehyde is 10·8 v., which should mean that the bond in formic acid is shorter and stronger than that in formaldehyde, whereas in fact the lengths are 1·24 [86] and 1·21 A.,[79] respectively, and the vibration frequencies are 1740 cm.$^{-1}$ and 1750 cm.$^{-1}$.[87] These facts agree with the view that  $\overset{H}{\underset{HO^{+}}{\gg}}C{-}O^{-}$ is an important structure.

It appears that it is more difficult than was expected to disentangle polarity effects.

(3) *Orbital Hybridisation.*—Hybridisation is important in the discussion of bond properties apart from its contribution to stereochemistry, because it affects the overlap of the bonding orbitals, and thus the extent and density of the electron cloud between the nuclei, which is responsible for the bond being formed. Energy is required to form hybridised orbitals from atomic orbitals, because to do so involves moving electrons further from the nucleus; but this can be more than offset by the energy of forming the bond.

We intend to discuss here only hybridisation of *s* and *p* orbitals. CH bonds are particularly suitable in this connection, because changes in the property of the bond are likely to be due mainly to changes in the carbon atom. We have shown (Table I) that as we pass from methane to acetylene

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[82] L. O. Brockway, L. Pauling, and J. Y. Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2693.

[83] *Trans. Faraday Soc.*, 1946, **42**, 56; 1947, **43**, 158.

[84] To be published.

[85] T. W. Dakin, W. E. Good, and D. K. Coles, *Physical Rev.*, 1947, **71**, 640.

[86] J. Karle and L. O. Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 574.

[87] G. Herzberg, "Infra Red and Raman Spectra", New York, 1945, Chap. III.

* An earlier electron-diffraction study [82] gave CO in carbonyl chloride as 1·28 A., and a large contribution from this structure was assumed to explain the result.

the CH length decreases and the force constant increases. Most authors consider that at the same time the *s* character increases.[20] Approximate calculations by L. Pauling and J. Sherman [88] showed that tetrahedral * or sp^3 orbitals give the maximum projection along the bond axis and therefore presumably the maximum strength of bond. The facts therefore seem in disagreement with the theory.

Walsh [21] has enunciated the principle : " the more *s* character in a carbon valency, the more electronegative is the carbon atom in that valency ". He has combined this with the two rules that the strength of a bond increases with the product of the electronegativities of the bound atoms, and that increase in polarity causes a decrease in the strength of a bond to explain the order of strengths in CH bonds.

The question may be looked at as follows : *s* character brings the overlap zone nearer the carbon atom—thus incidentally altering the homopolar moment—and, because an *s* orbital has no directional properties, the charge cloud becomes more diffuse. Thus in a volume element on or near the line joining the nuclei, the electron density is reduced, and the screening of the nucleus thereby becomes less, with the result that the carbon atom behaves as if it were more positive. To take account of this in the description of the bond, we should have to adjust the ionic terms in the electron-pair approximation, or alter the relative magnitudes of the coefficients of the atomic orbitals in the L.C.A.O. molecular orbital approximation, in such a way as to increase the proportion of electron round the carbon. In the particular case of the CH link, it may be that, although increase of *s* character decreases the overlap, the loss in strength may be outweighed by additional stabilisation due to resonance with ionic structures.[91]

J. Duchesne [92] has suggested that substitution of a more for a less electronegative group on carbon increases the electronegativity of the carbon with respect to other groupings attached to it, causing these bonds to have more *s* character and therefore the bond to the electronegative group more *p* character. His evidence is from the CH force constants of certain methyl compounds, derived from their Raman spectra in the liquid state. Considering the changes in vibration frequency which often occur in passing from the liquid to the vapour, this evidence is not completely satisfactory. Walsh [21] has extended the application of the idea. It provides an explanation of the weakness of secondary CH bonds, but as T. L. Cottrell and R. E. Richards [93] have pointed out, there seem to be cases where it does not apply. For example, since carbon is more electronegative than hydrogen, we would expect that the CH links in ethylene

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[88] *J. Amer. Chem. Soc.*, 1937, **59**, 1450.

[89] *Ibid.*, 1931, **53**, 1367.

[90] *Ann. Reports*, 1940, **37**, 67.

[91] Cf. E. Warhurst, Faraday Society Discussion, 1947, " The Labile Molecule ".

[92] *Nature*, 1947, **159**, 62.

[93] Faraday Society Discussion, 1947, " The Labile Molecule ".

* Pauling [89] pointed out in 1931 that it is also possible to form tetrahedral orbitals which give strong bonds from *s*, *p*, and *d* orbitals. Sutton [90] has suggested that these might occur in tetrahedral silicon compounds, such as SiF_4, possibly accounting for the shortness of the link.

would have more *s* character than sp^2, and that the HCH angle would be greater than 120°. In fact it is 119° 55′.[27]

It is, however, not clear why an electronegative group should desire to have more *p* character in its bond with carbon beyond sp^3, because sp^3 orbitals have the greatest projection along the bond axis. On the other hand, if sp^3 hybridisation had not occurred completely, it is easy to see that such effects might be appreciable.

Conclusions.—In planning this Review we intended to consider how far there has been given a consistent interpretation of variations in bond lengths and strengths. Such an interpretation would appear to require simultaneous consideration of the effects of multiplicity, polarity, and orbital hybridisation. This, in fact, has hardly been attempted in the literature, probably because it is extremely difficult either to apply the necessary theoretical treatment or to analyse the data in such a way as to distinguish with certainty the effects of these factors. A rigorous treatment would doubtless short-circuit these terms, but they are the concepts with which it has been found useful to work. All we have been able to do within the limits available has been to follow a sectional treatment, though we have tried to indicate the inter-relations between the concepts. Our opinion is that this inter-relation needs to be carried a good deal further.

At present the subject abounds in hypotheses which have a limited success but which are *ad hoc* and probably not unique. To say this is no disparagement of the advances which have been made, nor to deny the importance of the striking changes which have taken place in structural chemistry in the past twenty years.

In addition to the general unification of the whole subject indicated above, further work on the effect of orbital hybridisation and of polarity seems to be particularly desirable.

In conclusion, we wish to express our thanks to Mr. W. E. Moffitt for many valuable discussions.