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RESONANCE AND CONJUGATION—II[1]

FACTORS DETERMINING BOND LENGTHS AND HEATS OF FORMATION

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Abstract—Two previous papers[1,3] presented interim reports of an investigation into the importance of resonance in conjugated systems. Further work has confirmed our earlier conclusions that resonance effects are unimportant in classical molecules, the bond lengths in them being determined by the state of hybridization of carbon; that the observed stabilization of such molecules is due to changes in bond energy with hybridization rather than to resonance; and that resonance stabilization plays a surprisingly small role even in benzene. A calculation is described which, starting from very limited experimental data, provides values for several CC bond lengths (ethylene, benzene, graphite) which agree excellently with experiment, a value for the sp^2-sp^2 C—C bond length which agrees well with the value found in butadiene, diphenyl, etc., and a set of bond energies for CC and CH bonds of various types. Heats of formation for a number of hydrocarbons are calculated from these bond energies and compared with experiment. Agreement is excellent for paraffins, olefines, and acetylenes, confirming the lack of hyperconjugative stabilization in the latter. Deviations in cycloparaffins are ascribed to conformational effects (CH—CH dipole repulsions). Butadiene shows an apparent resonance energy of 2 kcal/mole, less than a quarter of the stabilization energy; reasons are given for believing even this value to be much too large. The lack of resonance in butadiene is confirmed by a MO calculation of its effect on the bond lengths. When allowance is made for the effect of σ-bond compression, the resonance energy of benzene is found to be only about 10 kcal/mole, less than a quarter of the stabilization energy. Previous ideas [1,3] concerning the importance of electron correlation in conjugated systems are clarified: it is shown that the neglect of such correlation invalidates existing methods of calculation, particularly in the case of classical molecules, and a method is suggested whereby such correlation effects might be taken into account. The significance of resonance theory is discussed. Various criticisms made by Mulliken in a recent paper[4] are shown to be unjustified.

THIS paper describes a general investigation into the factors determining bond lengths and heats of formation in conjugated systems. Preliminary accounts[1,3] were given in Paris in September, 1957, at the C.N.R.S. Colloquium on the calculation of molecular wave functions, and at Bloomington in June, 1958, at the Conference on Hyperconjugation. These earlier studies led to the conclusion that, in contrast to most current opinion, resonance effects are relatively unimportant in classical* molecules and that the arguments commonly cited as evidence for resonance in such molecules are vitiated by their neglect of changes in the properties of carbon bonds with hybridization. Here we present the results of our completed investigation. This has not only confirmed our earlier conclusions but it has also provided further cogent

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* A classical molecule is defined as one for which only a single classical (unexcited) resonance structure can be written; e.g. $CH_2{=}CH{-}CH{=}CH_2$, $CH_3{-}C{\equiv}CH$.

[1] Part I: M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

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[3] M. J. S. Dewar and H. N. Schmeising, *Collogues Internationaux du Centre National de la Recherche Scientifique* **82**, 51 (1958).

evidence that resonance effects are very generally of less importance than has commonly been supposed.

1. *Lengths of carbon bonds*

We argued in Part I[1] that the available data on carbon bond lengths could be explained in terms of changes in effective covalent radius of carbon with its state of hybridization. The idea that bond lengths should vary with hybridization was put forward some years ago by Walsh[4] and by Coulson[5]; but subsequent authors have agreed with Coulson's[5] conclusion that the changes in covalent radius are not sufficient to account for the observed changes in bond length, and that resonance effects must also be important.

If the lengths of single bonds C—X between carbon and some other atom X are determined only by the state of hybridization of carbon, one might expect the length to vary more or less linearly with the percentage *s*-character of carbon,[*] the length of a given type of bond being always the same. By an obvious extension, one would expect the lengths of carbon–carbon bonds to be a linear function of the mean percentage *s*-character of the two carbon atoms, the length of a given type of bond always being the same. These relations would not be expected to hold if resonance effects were important; for the resonance interactions would involve bonds adjacent to the bond in question. One would not expect the resonance interaction between the CH and CC bonds in $\mathrm{C}\vdots\mathrm{H}_3-\mathrm{C}\vdots\mathrm{CH}$ to be the same as that between CCl and $\mathrm{C}{:}\mathrm{N}$ bonds in $\mathrm{CCl}_3-\mathrm{C}{:}\mathrm{N}$, and so one would not expect the C—C single bonds to have the same length if resonance were important.

Herzberg and Stoicheff[7] pointed out some years ago that the data then available suggested that the lengths of C—C single bonds in acetylenes depend only on the state (saturated or acetylenic) of the terminal carbon atoms. Table 1 lists all the accurate data now available for C—C single bonds of various types. All the values were derived from spectroscopic measurements except those for the sp^2–sp^2 bonds; these were measured by Bastiansen *et al.* using refined electron diffraction techniques. Note that the lengths of the sp^3–sp and sp–sp bonds are remarkably constant, confirming the earlier work.[7] These values should be accurate to a few thousandths of an angstrom. The rather scanty data for sp–sp^2 and sp^2–sp^2 bonds are subject to larger errors.

The mean lengths for the bonds of various types (last column of Table 1) are plotted against percentage *s*-character of carbon in Fig. 1. The value assumed for the sp^3–sp^3 bond (1·544 Å) is that observed in diamond; that for the sp^2–sp^3 bond (1·515 Å) is the mean of fourteen recent[8] X-ray determinations. All six points are seen to lie close to a straight line.

The data listed in Table 1 and Fig. 1 strongly suggest that the lengths of C—C single bonds in classical molecules, even in conjugated molecules such as diacetylene

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[*] This argument has been misquoted by Professor R. S. Mulliken in a recent criticism[6] of our work. The shortening in passing from sp^3 carbon (25% *s*) to sp^2 carbon (33-1/3% *s*) should not be the same as that in passing from sp^2 to sp carbon (50% *s*); the second contraction should be—and is—about double the first.

[4] A. D. Walsh, *Trans. Faraday Soc.* **43**, 60 (1957).

[5] C. A. Coulson, *Victor Henri Memorial Volume* p. 15. Desoer, Liège (1948); cf. *J. Phys. Chem.* **56**, 311 (1952).

[6] R. S. Mulliken, *Tetrahedron* **6**, 68 (1959).

[7] L. F. Herzberg and B. P. Stoicheff, *Nature, Lond.* **175**, 79 (1955).

[8] L. E. Sutton, *Tables of Interatomic Distances*. Special Publication No. 11 of The Chemical Society. London (1958).

TABLE 1. LENGTHS OF C—C SINGLE BONDS IN CLASSICAL MOLECULES

Compound	Type of bond	Length (Å)	Mean length (Å) of bonds of given type
$CH_3{-}C{\equiv}CH$	sp–sp^3	1·459[a]	
$CH_3{-}C{\equiv}CCl$	sp–sp^3	1·458[b]	
$CF_3{-}C{\equiv}CH$	sp–sp^3	1·464[b]	
$ClCH_2{-}C{\equiv}CH$	sp–sp^3	1·458[c]	
$CF_3{-}C{\equiv}C{-}CH_3$	sp–sp_3	1·455[d]	
$CH_3{-}C{\equiv}N$	sp–sp^3	1·458[a]	
$CF_3{-}C{\equiv}N$	sp–sp^3	1·464[b]	
$CCl_3{-}C{\equiv}N$	sp–sp^3	1·460[e]	
$CH_3{-}C{\equiv}C{-}C{\equiv}N$	sp–sp^3	1·458	1·459
	sp–sp	1·379[b]	
$HC{\equiv}C{-}C{\equiv}CH$	sp–sp	1·379[b]	
$HC{\equiv}C{-}C{\equiv}N$	sp–sp	1·378[a]	
$N{\equiv}C{-}C{\equiv}N$	sp–sp	1·380[b]	1·379
$CH_2{=}CH{-}C{\equiv}CH$	sp–sp^2	1·446[f]	
$CH_2{=}CH{-}C{\equiv}N$	sp–sp^2	1·426[f]	
$O{=}CH{-}C{\equiv}CH$	sp–sp^2	1·445[g]	1·439
$CH_2{=}CH{-}CH{=}CH_2$	sp^2–sp^2	1·483[h]	
diphenyl	sp^2–sp^2	1·492[i]	
4:4′-dipyridyl	sp^2–sp^2	1·470[i]	1·482

[a] C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).

[b] L. E. Sutton, *Tables of Interatomic Distances*. Special Publication No. 11 of The Chemical Society, London (1958).

[c] E. Hirota, T. Oka and Y. Morino, *J. Chem. Phys.* **29**, 444 (1958).

[d] B. Bak, D. Christiansen, L. Hansen-Nygaard and E. Tannenbaum, *J. Chem. Phys.* **26**, 134 (1957).

[e] J. B. Baker, D. R. Jenkins, C. W. Kenney and T. M. Sugden, *Trans. Faraday Soc.* **53**, 1397 (1957).

[f] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

[g] C. C. Costain and J. R. Morton, *J. Chem. Phys.* **31**, 389 (1959).

[h] A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).

[i] (values for the central bond) A. Almenningen and O. Bastiansen, *Kgl. Norske Videnskab. Selskabs. Skrifter* No. 4, 1 (1958).

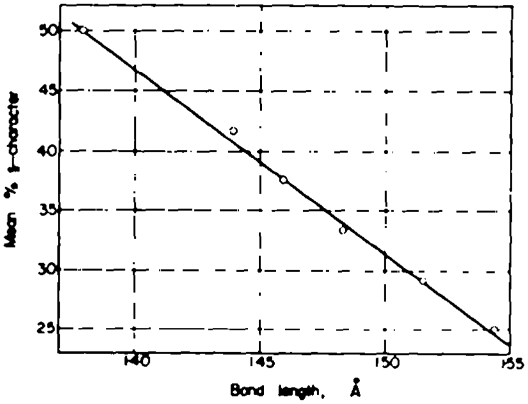

FIG. 1. Plot of bond lengths vs. mean percentage *s*-character of carbon for C—C single bonds.

or butadiene, depend only on the state of hybridization of carbon and are little affected by resonance.*

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* The multiple bonds also show no variation in length greater than the limits of experimental error; this, however, is less significant since it is well known that current theory predicts much smaller increases in length of multiple bonds in resonating systems than decreases in the lengths of single bonds; cf. H. C. Longuet-Higgins and F. H. Burkitt, *Trans. Faraday Soc.* **48**, 1077 (1952).

It is a pity that so few accurate determinations are available for the lengths of other bonds. Some recent values for CH, CCl, CBr, and CI bonds are listed in Table 2 and plotted against percentage *s*-character of carbon in Fig. 2. In each case the points for sp^3, sp^2, and sp carbon lie accurately on a straight line.

TABLE 2. LENGTHS OF CH, CCl, CBr, AND CI BONDS OF VARIOUS TYPES

Hybridization of carbon	H	Length of C—X bond (Å): X = Cl	Br	I
sp^3	1·102[a]	1·781[d]	1·939[d]	2·139[d]
sp^2	1·086[b]	1·736[a]	1·891[a]	2·092[a]
sp	1·057[c]	1·637[c]	1·739[a]	1·991[e]

[a] bond lengths in C_2H_6, CH_2:CHCl, CH_2:CHBr, CH_2:CHI, MeC ⋮ CBr, MeC ⋮ CI; L. E. Sutton, *Tables of Interatomic Distances*. Special Publication No. 11 of The Chemical Society, London (1958).

[b] bond length in C_2H_4; see ref.[15–17]

[c] bond length in C_2H_2; J. H. Callomon and B. P. Stoicheff, *Canad. J. Phys.* **35**, 373 (1957).

[d] bond lengths in CH_3Cl, CH_3Br, CH_3I; C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).

[e] bond length in MeCC ⋮ CI; C. C. Costain, *J. Chem. Phys.* **23**, 2037 (1955).

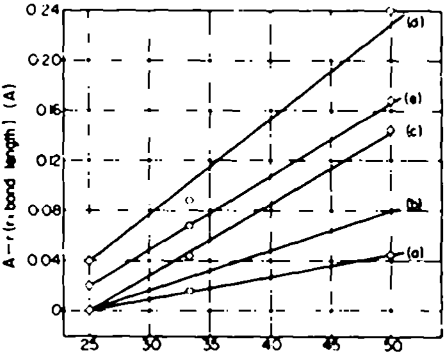

FIG. 2. Plot of bond length vs. percentage *s*-character of carbon for C—X bonds: (a) X = H, A = 1·102; (b) X = C, A = 1·540; (c) X = Cl, A = 1·781; (d) X = Br, A = 1·979; (e) X = I, A = 2·159.

These results suggest that the lengths of CH, CCl, CBr, and CI bonds are also determined by the state of hybridization of carbon rather than by resonance; this agrees with the conclusion reached from measurements of nuclear quadrupole coupling constants[9] that the C—Cl bond in vinyl chloride has little double bond character (ca. 5%).

As we pointed out in Part I,[1] this argument seems open to criticism in that one would expect the lines in Fig. 2 to be parallel if the rule of additivity of covalent radii held. Mulliken has stressed this point in his criticism[6] of our work. However the rule of additivity of covalent radii has no good theoretical basis and numerous experimental exceptions to it are known—as we pointed out in Part I.[1] The following argument shows that one would not expect it to hold except as a rough first approximation, and that the results indicated in Fig. 2 are consistent with the idea that the

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[9] J. H. Goldstein, *J. Chem. Phys.* **24**, 106 (1956).

bond lengths plotted there are determined almost entirely by changes in hybridization of carbon.

Accepting the criterion of maximum overlap,[10] we would expect the variation in length of carbon bonds with hybridization to reflect changes in size and shape of the carbon hybrid AO. If the atom X forming a bond C—X is much smaller than carbon, overlap will be best if the AO of X is centred at the point of maximum density of the carbon AO. If on the other hand X is much larger than carbon, overlap will be best when the centre of gravity of the carbon AO is centred at the point of maximum density of the AO of X. Therefore in the first case the change in bond length with hybridization of carbon should parallel changes in the distance from the carbon nucleus to the *point of maximum orbital density* in its AO, in the second case it should parallel changes in the distance from the carbon nucleus to the *centre of gravity* of its AO. There is no reason why these two distances should change in the same way with hybridization.

Note that the plots in Fig. 2 for bonds to Cl, Br, and I all atoms which are much larger than carbon, are approximately parallel; this would be expected from the argument given above. It is not surprising to find a different result for CH bonds, H being much smaller than carbon; and it is satisfactory to find that the slope for the intermediate case of carbon carbon bonds (X—C) is intermediate between the extremes when X is much smaller, or much larger, than carbon.

This argument shows that the rule of additivity of covalent radii should not be expected to hold accurately and that attempts to explain away small deviations from it are misguided. It is perhaps unfortunate that so much confidence has been placed on a rule based on inaccurate data and lacking any valid theoretical justification.

It should be added that since publication of our previous papers[1,3] several other authors have come out in support of the idea that resonance effects are unimportant in classical molecules. Costain and Stoicheff[11] pointed out that the lengths of a C—C bond depends only on the number of atoms or groups attached to the carbon atoms forming the bond; this number is determined by the state of hybridization of the two carbon atoms. Brown[12] and Somayajulu[13] have concluded that the lengths of such bonds are determined by the hybridization of the carbon atoms and not by resonance. Bartell[14] suggests that the bond lengths are determined by Van der Waal's interactions between the adjacent groups; although this interesting idea seems to differ from that proposed here, Professor Bartell at any rate agrees with us in ascribing little importance to resonance. A detailed analysis of the relation between non-bonded interactions and hybridization would be of interest.

II. *The bond order–bond length relation*

We pointed out in our previous papers[1,3] that if the CC bond lengths in ethylene, benzene, and graphite are plotted against their π-bond orders (found using LCAO MO coefficients calculated with inclusion of overlap; cf. Appendix 3. Thus the π-bond order for ethylene is $(1 + S)^{-1}$), the three points lie approximately on a straight line which extrapolates to a value ca. 1·47 Å for zero π-bond order. Since that time the

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[10] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 4493 (1950).

[11] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.* **30**, 777 (1959).

[12] M. G. Brown, *Trans. Faraday Soc.* **55**, 694 (1959).

[13] G. R. Somayajulu, *J. Chem. Phys.* **31**, 919 (1959).

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

length of the CC bond in ethylene has been redetermined and found to be nearly 0·02 Å less than the "old" value. With the new values 1·333,[15] 1·337,[16] or 1·339,[17] Å, the points for ethylene, benzene, and graphite become accurately collinear, extrapolating to a value (1·488 Å) which is within experimental error of the observed length (1·483 Å) of the central bond in butadiene (Fig. 3). This suggests that the length of a single bond between sp^2 carbon atoms is about 1·485 Å, and that the bond order-bond length plot is linear, the curvature in published plots being due to the neglect of changes in bond length with hybridization and the consequent assumption that the bond length for zero bond order is 1·54 Å. Brown[12] has independently reached the same conclusion.

III. *Heats of formation and bond energies*

(a) *General considerations and terminology.* In Part I[1] we pointed out that if the lengths of carbon bonds vary with hybridization, so also must their bond energies; and that in this case current calculations of "resonance energies" would have no significance, since they neglect such changes in bond energy with hybridization. We also criticized the calculation of resonance energies by comparison of the heats of hydrogenation of conjugated compounds with those of partial reduction products (e.g. butadiene with 1-butene, benzene with cyclohexene). These "reference compounds" are themselves stabilized by a structural feature (presence of a saturated carbon next to a multiple bond) which is not present in the conjugated original. Whether or not this stabilization is a resonance effect ("hyperconjugation") is entirely irrelevant; the "resonance energies" calculated in this way are a meaningless conglomeration of two different effects, one of which does not appear in the parent conjugated system.

We suggested as a measure of the stabilization of an unsaturated molecule a comparison of its heat of formation with that of an equivalent number of simple molecules (e.g. ethylene, acetylene) where no resonance can occur. Following Mulliken we termed this purely empirical quantity the *stabilization energy* (*SE*). The chemical behaviour will be determined by the stabilization energy, rather than by the fictitious resonance energies estimated by current methods.

We showed that the stabilization energy of butadiene must contain a component δH due to changes in bond energy with hybridization, and given by

$$\delta H = (E' - E) - 2(\epsilon' - \epsilon) \qquad (1)$$

where E', E are respectively the bond energies of C–C bonds between sp^2 and sp^3 carbon atoms, and ϵ', ϵ are the corresponding CH bond energies. We showed that the whole of the observed stabilization energy of butadiene might be explained in this way,* resonance stabilization being negligible. The same is true for "hyperconjugated" molecules such as propene.

This implies that the chemically very significant stabilization in such molecules may not be due to resonance; in this case there is a real need for terms to describe

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* We must draw attention to a further misquotation in Professor Mulliken's paper.[6] We did not postulate[1] that $\epsilon' = \epsilon$; we postulated only that $(E' - E) \gg 2(\epsilon' - \epsilon)$, on the grounds that if CC bonds vary in length more with hybridization than do CH bonds (cf. Fig. 2 in this paper) they should show correspondingly greater changes in bond energy with hybridization.

[15] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **31**, 400 (1959).

[16] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.* **80**, 2673 (1958).

[17] J. M. Dowling and B. P. Stoicheff, quoted by Costain and Stoicheff[13].

the structural features leading to such stabilization without any reference to their cause. The term "conjugation" has always had a structural connotation in organic chemistry; here one need only abandon its improper identification with resonance. The term "hyperconjugation" has, however, always been used in the literature in its original sense, implying[18] a special type of resonance interaction. We wish to suggest the term *semiconjugation* to describe the corresponding structural feature. Thus conjugation implies the presence of a single C—C bond between unsaturated carbon atoms, semiconjugation the presence of a bond between a saturated and an unsaturated carbon atom.

The next problem is to determine how much, if any, of the stabilization energies of conjugated and semiconjugated molecules are to be ascribed to resonance. To do this one needs to know the various bond energies involved [cf. equation (1)].

We first tried to estimate bond energies directly, by equating the calculated and observed heats of formation of a number of hydrocarbons and solving the resulting set of equations for the bond energies. This attempt failed for technical reasons (see Appendix 1), an unfortunate circumstance, since if successful it would have provided directly an unambiguous set of bond energies.

We therefore adopted the expedient of assuming relations between bond energy and bond length for CC and CH bonds. Glockler[19] and Feilchenfeld[20] have proposed relations of this kind in which bond energy (E) is expressed as a power of, or power series in, r^{-1}, r being the bond length. Their work was, however, based on the "old" value (1·353 Å) for the length of the C:C bond in ethylene. When we tried to repeat their calculations using the newer values[15] [17] of 1·333–1·339 Å we could not obtain satisfactory results.

If there is a relation between bond energy and bond length, it must be such that E is finite at $r = 0$ and vanishes as $r \to \infty$, and it must satisfy everywhere the conditions.

$$\frac{\partial E}{\partial r} < 0; \quad \frac{\partial^2 E}{\partial r^2} > 0; \quad E > 0 \quad (r > 0) \tag{2}$$

Glockler's function does not fulfil these conditions when the new value for the ethylene bond length is used; while Feilchenfeld's relation cannot be made to fit the data. Even a five-term polynomial in r^{-1} proved unsatisfactory.

The obvious solution was to find some function other than a power series in which to express the relation between E and r. The tractrix [equation (3)] seemed a good choice since it automatically fulfils the necessary conditions and has only two disposable parameters, a, b.

$$r = \frac{1}{b}\left[\mathrm{a} \log\left(a + (a^2 - E^2)^{1/2}\right) - a \log E - (a^2 - E^2)^{1/2}\right] \tag{3}$$

Attempts to fit a pair of tractrices to the data on bond lengths and heats of formation proved awkward, however, owing to the cumbersome nature of the tractrix function. We therefore decided to combine the determination of the disposable parameters (a_C, b_C, a_H, b_H) in the tractrix equations for CC and CH bonds with the calculation of the sp^2–sp^2 C—C bond length outlined in Part I.[1] This procedure enabled us to

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[18] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 40 (1941).

[19] G. Glockler, *J. Chem. Phys.* **21**, 1242, 1249 (1953); *Ibid.* **61**, 31 (1957).

[20] H. Feilchenfeld, *J. Chem. Phys.* **61**, 1133 (1957).

calculate a number of bond lengths which could be compared with experiment, and so provided a useful check on the general validity of our assumptions.

IV. *Calculation of the* C—C *bond energy-bond length relation*

In Part I[1] we outlined a technique for calculating the equilibrium bond lengths in benzene (r_b) and graphite (r_g) in terms of the following parameters:

r_e' E_e' (equilibrium bond length and equilibrium bond energy for the sp^2-sp^2 C—C single bond)

r_e'' E_e'' (corresponding values for C:C double bond)

k_e' k_e'' (force constants for single and double bonds between sp^2 carbon atoms at equilibrium bond length)

The force constants are either known (k_e'') or can be found by interpolation. The tractrix equations (3) provide relations between bond length and bond energy. One

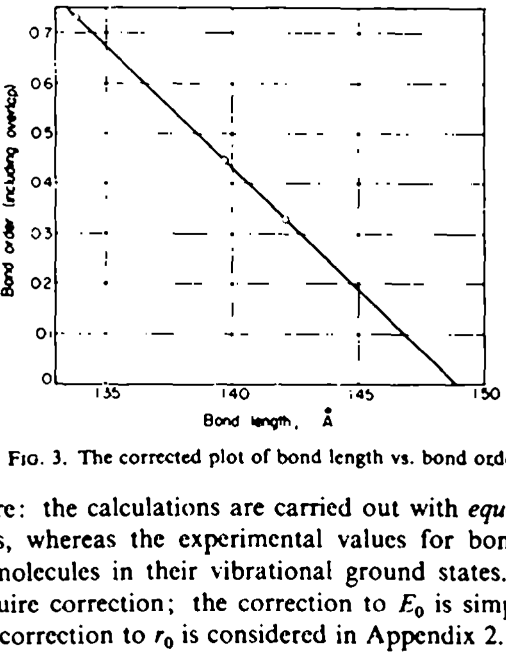

Fig. 3. The corrected plot of bond length vs. bond order.

difficulty arises here: the calculations are carried out with *equilibrium* bond lengths and bond energies, whereas the experimental values for bond lengths and bond energies refer to molecules in their vibrational ground states. These ground-state values (r_0, E_0) require correction; the correction to E_0 is simply equal to the zero point energy; the correction to r_0 is considered in Appendix 2.

In order to minimize the amount of experimental data used, and to check the validity of our conclusion (cf. Fig. 3) that the bond order-bond length plot is linear, we assumed in our calculation that this was the case. The only experimental data* we used were the following:

heat of formation and CC bond length in diamond.
heat of formation and CH bond lengths in methane and ethylene.
heat of formation of acetylene.
the CC force constants in ethane, ethylene and acetylene.

We were then able to calculate without any further assumptions the following sixteen quantities:

r_0', E_0' (the mean bond length and bond energy of the sp^2-sp^2 C—C bond in its vibrational ground state)

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* The thermochemical data are referred to 0°K; see section V, p. 104.

r_e', E_e' (the corresponding equilibrium values)
r_0, E_0, r_e, E_e (corresponding values for the sp^3–sp^3 CC bond)
r_b, r_g (equilibrium bond lengths in benzene and graphite respectively)
r_0'' (mean C:C bond length in ethylene in its vibrational ground state)
r_e'' (corresponding equilibrium value)
a_C, b_C, a_H, b_H (constants in the tractrix equations)
Details of the calculation are given in Appendix 3.

Table 3 shows a comparison of the observed and calculated values for r_g, r_b and r_0''. The remarkable agreement strengthened our confidence in the conclusions we had reached and assumptions we had made in reaching them.

TABLE 3. COMPARISON OF CALCULATED AND OBSERVED BOND LENGTHS

CC bond in	Symbol	Bond length in Å	
		Calculated	Observed
benzene	r_b	1·397	1·397 ± 0·001
graphite	r_g	1·421	1·4211
ethylene	r''	1·338	1·333[15] 1·337[16] 1·339[17]

Table 4 compares three different theoretical estimates for r_0' with experimental values for the lengths of sp^2–sp^2 single bonds (Table 1). The agreement between these four values provides further evidence that no significant resonance shortening of the central bond occurs in molecules such as diphenyl or butadiene.

TABLE 4. ESTIMATES OF THE LENGTH (r_0') OF THE sp^2–sp^2 C—C BOND

Method	Length (Å)
r/s-character plot	1·486
r/bond order plot	1·489
benzene–graphite calculation	1·489
experiment	1·483, 1·492, 1·470[a]

[a] See Table 1.

Table 5 lists the values of the parameters a_C, b_C, a_H, b_H in the tractrix equations.

TABLE 5. PARAMETERS IN THE TRACTRIX EQUATIONS

Type of bond	a (kcal/mole)	b (kcal/mole Å)
CC	2919·8828	6116·1936
CH	4144·6424	13022·007

V. *Derivation of bond energies*

The values found in this way for the various C—C and CH bond energies were (in kcal/mole):

$$E_0 = 84{\cdot}56;\quad E_0' = 94{\cdot}99;\quad \epsilon_0 = 98{\cdot}19;\quad \epsilon_0' = 100{\cdot}52 \tag{4}$$

These values when substituted into equation (1) give an estimated value for the stabilization energy of butadiene at 0°K of 5·8 kcal/mole, compared with the experimental value (see Table 10, p. 109) of 8·6 kcal/mole. This suggests that at least the major part of the stabilization of butadiene can be ascribed to changes in bond energy with hybridization rather then to resonance.

A similar calculation can be carried out for semiconjugated hydrocarbons. The bond energy of the sp^3-sp^2 C—C bond can be estimated from its length (1·515 Å) using the tractrix equation; this (89·59 kcal/mole) leads in turn to an estimated value of 2·7 kcal/mole for the stabilization energy per sp^3-sp^2 C—C bond in semiconjugated systems, in good agreement with experiment (Table 10).

These results are gratifying in view of the extremely scanty thermochemical data used in calculating the bond energies; they suggest that our estimates of the variation in bond energy with hybridization for CC and CH bonds are not far from the truth. This in turn supports our suggestion that the theoretical interpretation of the thermochemistry of carbon compounds needs complete revision; the assumption that bond energies do not vary with hybridization is not even a passable first approximation.

One further difficulty remained, however, in our interpretation. It is known that the heats of formation of paraffins cannot be expressed accurately as sums of bond energies, and it is generally agreed[21] that the discrepancies are due to non-bonded interactions of some kind. Not wishing to commit ourselves to any specific interpretation of these interactions, we decided to allow for them empirically by absorbing them into the sp^3 CH bond energies. The value given in Table 4 refers to methane where there are no non-adjacent bonds; we found that the available data could be well interpreted by introducing just two empirical parameters, the CH bond energies in methyl, and in methylene or methine groups. No correction was needed for any of the other CC or CH bond energies; their values were estimated from the experimentally determined bond lengths by using the appropriate tractrix equations.

Table 6 lists the bond energies found in this way, together with the assumed bond lengths. Note that all our thermochemical calculations are for compounds in the gas phase at the absolute zero. The use of data corrected to 0°K avoids complications from specific heat differences and from conformational isomerism (cf. Section VI, p. 106); at 0°K each hydrocarbon will be in its most stable conformation.

Table 7 compares the observed heats of formation from atoms in the gas phase at 0°K of a number of hydrocarbons with those calculated from the bond energies in Table 6. The agreement is excellent for the paraffins and satisfactory for the semiconjugated olefines and acetylenes, especially in view of the fact that all but two of the bond energies were calculated from limited experimental data by a clear-cut theoretical method, rather than fitted to the available values for heats of formation; and in view of the fact that the experimental values are liable to errors of a few tenths of a kcal/mole. Table 7 suggests that one or two of the bond energies may be in error by small amounts; these will be discussed below. There seem to be marked deviations (~2 kcal/mole) for cycloparaffins and conjugated dienes and large deviations for the benzene derivatives.

[21] cf. J. R. Platt, *J. Chem. Phys.* **15**, 519 (1947); M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 1625 (1954); K. S. Pitzer, *J. Chem. Phys.* **23**, 1735 (1955); K. S. Pitzer and E. Catalano, *J. Amer. Chem. Soc.* **78**, 4844 (1956); L. S. Bartell, *J. Chem. Phys.* **32**, 827 (1960).

TABLE 6. BOND ENERGIES AND BOND LENGTHS[a]

Type of bond		Symbols used in text for length and bond energy	Bond length (Å)	Bond energy (kcal/mole) at 0°K.
C–C	sp^3–sp^3	r_0, E_0	1·544	84·56
	sp^3–sp^2	r_0^*, E_0^*	1·517[b]	89·59[b]
	sp^3–sp		1·459	100·74
	sp^2–sp^2	r_0', E_0'	1·479[c]	94·99[c]
	sp^2–sp		1·432	105·82
	sp–sp		1·379	119·75
C=C	sp^2–sp^2	r_0'', E_0''	1·338	130·44
	sp^2–sp		1·310[d]	138·25
	sp–sp		1·282[d]	146·71
C≡C	sp–sp		1·205	170·55
C—H	sp^3 (methane)		1·094	98·19
	sp^3 (primary)	ε_p	1·102	97·01
	sp^3 (sec, tert)	ε_s	?	96·30
	sp^2	ε'	1·086	100·52
	sp	ε''	1·059	109·46

[a] Values for bonds in their vibrational ground states (i.e. r_0, E_0).
[b] These values for r_0^*, E_0^* may need revision ; see Section VII.
[c] The values for r_0' may be too large and for E_0' too small; see Table 9.
[d] Bond lengths in ketene, allene, butatriene; see Costain and Stoicheff[7].

VI. *Conformational effects in cyclohexane*

The deviations in cyclohexane derivatives are probably a conformational effect, due to dipole–dipole repulsions between adjacent CH bonds. Repulsions of this kind should make the all-*trans* conformation (Fig. 4a) of a polymethylene chain the most stable, there being just two pairs of adjacent CH bonds. Cyclohexane, in its stable chain form, has an all-*gauche* conformation (Fig. 4b) in which there are three pairs of adjacent CH bonds on neighbouring carbon atoms; the heat of formation per methylene group in cyclohexane should therefore be less than that for methylene in an open chain by the repulsion energy per pair of adjacent CH bonds.

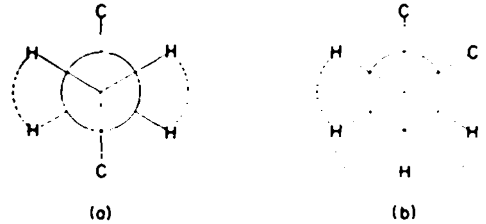

FIG. 4. Conformations of CH_2 groups (a) in centre of polymethylene chain at 0°K; (b) in cyclohexane (chain form). Broken lines indicate interactions between adjacent CH dipoles.

Taking the value 0·4 *D* for the CH bond moment and assuming the dipoles localized at the midpoints of bonds, we find for the CH repulsion energy 0·3 kcal/mole. The heat of formation of cyclohexane should be less than that calculated from the bond energies in Table 6 by six times this amount, i.e. 1·8 kcal/mole; this is just the observed discrepancy (Table 7). An extension of this argument shows that the discrepancy should be the same for alkylcyclohexanes, as also seems to be the case.

TABLE 7. COMPARISON OF CALCULATED AND OBSERVED[22] HEATS OF FORMATION OF HYDROCARBONS IN THE GAS PHASE AT 0°K

Hydrocarbon	Heat of formation (kcal/mole)		
	Calculated	Observed	Difference
methane	392·7	392·7	(0)
ethane	666·6	666·8	−0·2
propane	943·8	943·3	0·5
n-butane	1220·9	1221·0	−0·1
n-pentane	1498·1	1498·1	(0)
n-hexane	1775·3	1775·3	(0)
i-butane	1223·1	1222·6	0·5
i-pentane	1500·2	1499·6	0·6
neopentane	1502·4	1502·1	0·3
cyclohexane	1663·0	1661·1	1·9
methylcyclohexane	1942·3	1940·9	1·4
1 : 4-dimethylcyclohexane	2221·6	2220·1	1·5
propene	812·6	812·1	0·5
1-butene	1089·8	1089·1	0·7
l-pentene	1366·9	1366·5	0·4
1 : 4-pentadiene	1235·8	1234·7	1·1
trans-2-butene	1092·7	1091·8	0·9
1 : 3-butadiene	959·0	961·1	−2·1
1 : 3-pentadiene	1239·1	1241·0	−1·9
propyne	671·8	671·3	0·5
1-butyne	948·9	948·1	0·8
2-butyne	954·1	952·7	1·4
benzene	1279·4	1307·4	28·0
toluene	1559·5	1587·4	27·9
p-xylene	1839·6	1867·4	27·8

VII. *Heats of formation of semiconjugated hydrocarbons*

Not only do the calculated and observed heats of formation of semiconjugated olefines and acetylenes agree quite well (Table 7) but also the calculated values are consistently the higher. Therefore insofar as our calculations have any validity they imply that resonance stabilization (hyperconjugation) in such molecules is negligible.

The small deviations in the case of the olefines seems to be proportional to the number of sp^2–sp^3 bonds, and those in the acetylenes proportional to the number of of sp–sp^3 bonds. This suggests that the corresponding bond energies in Table 6 are too high, by about 0·5 and 0·7 kcal/mole respectively, corresponding to increases of 0·003 Å in each bond length. This is surprising; for several recent determinations (Table 8) of the sp^2–sp^3 C–C bond length suggest that the value listed in Table 6 is already too great.

The matter needs further investigation. The values in Table 8 seem to be consistently less than those reported from X-ray diffraction. Although X-ray methods are less precise than those based on spectroscopy of electron diffraction, they are also less subject to systematic errors. Spectroscopic methods are particularly difficult to apply to asymmetric molecules owing to the complications caused by centrifugal distortion

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[22] Calculated from Rossini *et al.*, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* Carnegie Press, 1953.

and anharmonicity of vibrations. It is perhaps significant that the bond length data for sp^2–sp^3 and sp–sp^2 bonds show far more scatter than those for sp–sp^3 or sp-sp bonds; bonds of the latter type appear in linear or symmetrical top molecules whose rotational spectra are much easier to interpret, whereas bonds of the former type have been studied only in unsymmetrical molecules. However it does seem likely on balance that the bond length listed in Table 6 for the sp^2–sp^3 bond is too great.

TABLE 8. RECENT DETERMINATIONS OF THE LENGTH OF THE sp^3–sp^2 C—C BOND

Compound	Length (Å)
CH_3COF	1·503 ± 0·003[a]
CH_3COCN	1·490 ± 0·01[b]
CH_3COOH	1·497 ± 0·01[c]
$(CH_3)_2C{:}CH_2$	1·506[14]

[a] L. Pierce and L. C. Krisher, *J. Chem. Phys.* **31**, 875 (1959).

[b] L. C. Krisher and E. D. Wilson, *J. Chem. Phys.* **31**, 882 (1959).

[c] W. J. Tabor, *J. Chem. Phys.* **27**, 974 (1959).

TABLE 9. VALUES OF E' AND CORRESPONDING RESONANCE ENERGY OF BUTADIENE FOR VARIOUS VALUES OF r'

r' (Å)	E' (kcal/mole)	Resonance energy (kcal/mole)
1·489	94·99	2·07
1·486	95·41	1·65
1·484	95·99	1·07
1·481	96·58	0·48
1·479	97·00	0·06

It is also possible that the value for the C—C bond length in hydrocarbons may be less than that in diamond; a recent spectroscopic study of ethane has given[23] a value 1·534 Å for the CC bond length.

VIII. *Conjugated dienes*

In the case of butadiene and 1:3-pentadiene the calculated heats of formation (Table 7) are less than those observed by about 2 kcal/mole; this difference could be ascribed to resonance stabilization. Note that the value for pentadiene is *less* than that for butadiene; here again there is no evidence for resonance stabilization due to hyperconjugation.

The value of 2 kcal/mole for the resonance energy may not be genuine. It depends on the bond energy (E') ascribed to the sp^2–sp^2 C—C bond, and this in turn depends on its length (r'). The values listed in Table 4 suggest that r' could have a value anywhere in the range 1·479–1·489 Å; Table 9 lists corresponding values of E' and of the derived resonance energy of butadiene, which can have any value between zero and 2 kcal/mole.

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[23] H. C. Allen and E. K. Plyler, *J. Chem. Phys.* **31**, 1062 (1959).

It is evident that the resonance shortening of the sp^2–sp^2 bond in butadiene must be small; taking the maximum value for r' (1·489 Å), the shortening would be less than 0·01 Å—and this would have to correspond to a resonance stabilization of 2 kcal/mole. This seems rather unlikely. The data certainly suggest that r' does not appreciably exceed the measured length (1·483 Å) of the central bond in butadiene and that the resonance energy is less than 1 kcal/mole.

TABLE 10. HEATS OF HYDROGENATION OF HYDROCARBONS IN THE GAS PHASE AT 0°K, AND VARIOUS DERIVED QUANTITIES

Compound	Heat of hydrogenation[a]	*SE*[a]	*HE*[a]	*CE*[a]
ethylene	31·04	-	—	—
propene	27·95	3·09	2·93	0·15
1-butene	28·63	2·41	2·93	−0·52
1-pentene	28·36	2·68	2·93	−0·25
1:4-pentadiene	56·86	5·22	5·86	−0·64
trans-2-butene	25·91	5·13	5·86	−0·73
1:3-butadiene	53·45	8·63	6·24	2·39
1:3-pentadiene	50·62	11·46	9·17	2·29
benzene	44·01	49·11	18·72	30·39
toluene	43·80	49·32	19·52	29·80
p-xylene	43·06	50·06	20·32	29·74

[a] in kcal/mole for reaction in the gas phase at 0°K.

IX. *Heats of hydrogenation; stabilization energies*

Table 10 lists heats of hydrogenation in the gas phase at 0°K for several hydrocarbons, calculated from published data.[23] The third column gives corresponding stabilization energies. Note that the values for classical molecules correspond to a stabilization of about 2·7 kcal/mole per sp^2–sp^3 bond, and 8·6 kcal/mole per sp^2–sp^2 bond.

The equations given in Part I[1] for the contribution to *SE* due to such hybridization effects (a quantity we may term *hybridization energy*, *HE*) need modification for the effects of non-bonded interactions in the paraffinic reduction products (Section V). When these are taken into account as here by ascribing different bond energies ϵ_p, ϵ_s to primary, and to secondary or tertiary, CH bonds, the equation for *HE* in olefines becomes:

$$HE = m\{(E_0^* - E_0) - (\epsilon' - \epsilon_p)\} + n\{(E_0' - E_0) - 2(\epsilon' - \epsilon_p)\} + (2m + 4n - 3b)(\epsilon_p - \epsilon_s) \quad (7)$$

where m, n are respectively the numbers of sp^3-sp^2, and sp^2-sp^2 C—C bonds, and b is the number of unsaturated branches in the olefine (i.e. the number of groupings $R_1R_2C = C<$); for the other symbols see Table 6. The first two terms in equation (7) are those previously derived,[1] the last term is the correction for the difference between primary and secondary CH.

The fourth column of Table 10 lists *HE* values calculated in this way. The values for simple olefines are essentially identical with the *SE*'s, confirming that the thermochemical data provides no evidence for resonance; in the case of butadiene and 1:3-pentadiene, the difference between *SE* and *HE*—which could be ascribed to resonance stabilization—is again about 2 kcal/mole, in agreement with the estimate from heats of formation (Table 7). This calculation of course also depends on the values ascribed to E', and hence to r'; if $r' < 1{\cdot}489$ Å, the difference between SE and HE would be less, vanishing if $r' = 1{\cdot}479$ Å [cf. Table 9 with equation (7)].

Even with the highest reasonable value (1·489 Å) for r', the resonance energy of butadiene is less than a quarter of the observed stabilization energy; and, as was pointed out in the previous section, the true value is probably less. This confirms our earlier[1] conclusion that resonance plays a minor role in the stabilization of classical conjugated hydrocarbons.

TABLE 11. CALCULATION OF THE RESONANCE ENERGY OF BENZENE FOR EXTREME VALUES OF r'

	CE[*]	SRE[*]	RE[*]
from heat of formation:			
$r' = 1{\cdot}479$ Å	21·94	15·27	6·7
$r' = 1{\cdot}489$ Å	27·94	14·84	13·1
from heat of hydrogenation:			
$r' = 1{\cdot}479$ Å	23·98	15·27	8·7
$r' = 1{\cdot}489$ Å	29·98	14·84	15·1

[*] in kcal/mole.

X. *Benzene*

Benzene and its derivatives appear to have large resonance energies, whether these are estimated from heats of formation (Table 7) or from heats of hydrogenation (Table 8). The values in all cases are about 30 kcal/mole. The fact that the values for benzene, toluene, and *p*-xylene are the same indicates that hyperconjugation between the methyl groups and the ring leads to no significant additional stabilization.

These values are subject to correction for changes in the sp^2–sp^2 C—C bond energy (E'); if $r' = 1{\cdot}479$ Å, the apparent resonance energy of benzene would fall to 22 kcal/mole. Table 11 gives mean values for benzene, toluene, and *p*-xylene derived from heats of formation, and from heats of hydrogenation, for the highest and lowest values of E' listed in Table 9.

As was pointed out in Part I,[1] there is a further factor to be considered. The "resonance energies" listed in the first column of Table 11 represent the calculated differences in total energy between benzene and a classical cyclohexatriene with double bonds of length 1·338 Å, and single bonds of length 1·479 or 1·489 Å. But these differences in energy cannot be equated to the difference in π-electron energy between benzene and classical cyclohexatriene—which alone can properly be termed resonance energy (RE); the values in Table 11 also contain[1] a contribution due to the difference in σ-bond length, and consequently in σ-bond compression, between the two structures. The energy required to compress *three* single bonds to the lengths (1·338 Å) of the double bonds in cyclohexatriene is greater than that required to compress *six* such single bonds to the lengths (1·397 Å) of the bonds in benzene. This effect stabilizes benzene by a quantity which may be termed *σ-strain relief energy* (SRE), the values of which are listed in the second column of Table 11. The last column gives the true resonance energies, found by difference. The quantity in the first column (i.e. SRE +

RE) may be termed *conjugation energy* (*CE*); it is equal to the difference between the stabilization energy and hybridization energy.

Inspection of Table 11 shows that the true resonance energy of benzene probably lies in the range 5–15 kcal/mole. These values are much less than those commonly quoted and support our contention[1] that only about a quarter of the stabilization of benzene is due to resonance.

Current estimates of the resonance energy of benzene have neglected the effect of hybridization, and most of them have also neglected σ-bond compression.

TABLE 12. CALCULATION OF BOND LENGTHS AND ENERGY FOR BUTADIENE

Structure	Equilibrium bond lengths (Å)		Total CC bond energy at equilibrium (kcal/mole)
	1:2 Bond	2:3 Bond	
classical	1·334	1·485	362·49
actual	1·336	1·479	361·80
(difference)	0·002	−0·006	−0·69

XI. *Calculation of bond lengths in butadiene*

When we began this investigation our object was to calculate bond lengths in conjugated systems allowing for the effect of σ-bond compression. Further investigation has shown that the method we at first proposed[1,3] for doing this suffers from a curious defect (Appendix 4). We have, however, been able to develop a technique for calculating bond lengths by directly minimizing the total energy of the molecule with respect to variations in the lengths of the individual bonds (Appendix 4) and we have applied this technique to butadiene. The results of this calculation are given in Table 12. The first row gives equilibrium bond lengths and total energy for a classical structure with localized single and double bonds. The second row gives corresponding values for the actual molecule. The third row shows the differences in bond lengths and energy due to resonance interactions.

Note that the changes in bond length are very small and the calculated resonance energy *negative*. This certainly supports our conclusion that resonance effects in butadiene are insignificant, particularly since we used a simple MO method which is known to overestimate resonance in butadiene.

It should be pointed out that the resonance effects found by us are much less than those given by apparently more precise methods. We think that our calculation is in fact the more reliable in spite of its simplicity since, unlike other investigators, we proceeded by minimizing the total energy of the molecule rather than relying on relations between bond order and bond length. Moreover the bond order–bond length relation used by other workers is probably incorrect. A further difficulty arises in the case of one-electron resonance integrals. These cannot be evaluated theoretically, and we feel that our empirical method for estimating them is better than the methods used by other authors (e.g. the assumption that resonance integrals are proportional to overlap). As will be seen presently, current methods must in any case overestimate resonance effects in butadiene, due to their neglect of electron correlation; we may have made some tacit allowance for this through our empirically determined resonance integrals.

XII. *Electron correlation;* the importance of vertical correlation*

In Part I[1] we drew attention to the effects of electron correlation in conjugated molecules and we concluded that the relatively high bond order ascribed by current treatments[6] to the central bond in butadiene is an artefact of an illegitimate assumption inherent in all of them. Since the argument has been misunderstood, we repeat it here in a clearer and more definite form.

The coulomb repulsion energy between two electrons occupying orbitals in a given atom or molecule can be calculated by standard methods. If we calculate in this way the repulsion energy for a pair of electrons occupying the same $2p$-AO of a carbon atom we obtain a value which is much too large. The reason for this discrepancy is well known; it is due to the neglect of electron correlation in simple orbital calculations.

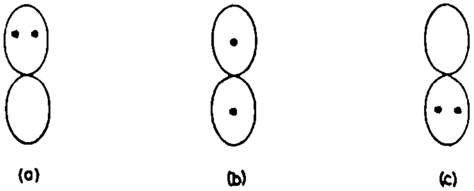

FIG. 5. Configurations of two electrons occupying a p-AO.

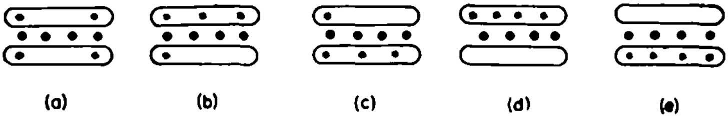

FIG. 6. Configurations of the π-electrons in butadiene; the dots denote the carbon nuclei.

We can distinguish three configurations for the pair of electrons (Fig. 5).† In (a), (c) the electrons occupy the same lobe of the p-AO, in (b) different lobes.

In a simple orbital treatment each electron is supposed to move independently of the other, so that the chance of finding it in a given lobe is always 1/2. The weights of the three configurations would then be in the statistical ratio, (a):(b):(c) = 1:2:1. Configuration (b) is, however, favoured by the fact that in it the mean distance between the electrons is greater and the repulsion between them correspondingly less; the mean coulomb repulsion is therefore less than that calculated on the basis of simple orbital theory. In other words the electrons reduce their mutual repulsion by correlating their motions, so that most of the time they occupy different lobes of the p-AO.

A similar situation arises in the case of butadiene, when four electrons occupy in pairs two four-centre π-MO's. Here the electrons can keep apart in two ways; either by occupying different lobes of the π-MO, or by spreading themselves out along a given lobe. We shall refer to correlation of the first kind as *vertical correlation*, that of the second kind as *horizontal correlation*.

Fig. 6 indicates the main types of configuration: in (a), two electrons occupy each

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* In this paper we again use[1] the term "electron correlation" in its naive sense, to imply the tendency of electrons in a molecule to correlate their motions, throughout the effects both of the Pauli principle and of coulomb repulsion.

† In order to make the argument clearer, the p-AO has been represented in the form corresponding to a real wave function.

π-lobe, in (b), (c) three electrons occupy one π-lobe, and in (d), (e) all four electrons are in the same π-lobe.

Simple orbital theory assumes that the probability of finding a given electron in a given π-lobe is always 1/2, independent of the positions of the other electrons; in this case the weights of the configurations would be in the ratio (a):(b):(c):(d):(e) 6:4:4:1:1. However the mutual repulsion of the electrons will favour configuration (a) since in it the electrons are less bunched together; the weight of configuration (a) will therefore be greater than that implied by simple orbital theory.

This favouring of configuration (a), vertical correlation has the effect of reducing the overall coulombic repulsion between the π-electrons, and so reducing the total energy of the molecule. This is exactly analogous to the effect of correlation in atoms (cf. Fig. 5) and it can be taken into account to some extent by empirical adjustment of interelectronic repulsion integrals.[23,24] There is, however, a second much more serious consequence of electron correlation which cannot be approximated in this way.

In an atom the mean electron distribution is determined by symmetry; correlation cannot alter this mean electron distribution– it affects the instantaneous motions of electrons, not their mean positions averaged over a long period. This is not true for molecules. Consider the case of butadiene. The electrons in a given π-lobe will tend to spread out along it in response to their mutual repulsion (horizontal correlation). In the configuration of Fig. 6(a), each pair of electrons will tend to occupy the terminal bonds, due to their mutual repulsion. Configuration 6(a) therefore corresponds to high π-electron density in the terminal bonds, and low π-electron density in the central bond. When on the other hand three or four electrons occupy the same π-lobe [Fig. 6 (b) (e)], the extra electron or electrons will tend to be forced into the central bond. Neglect of vertical correlation leads one to overestimate the importance of these latter configurations and so to overestimate the average electron density in the central bond.

Now *not one* of the existing treatments of π-electron systems takes this effect of vertical correlation into account. Adjustment of integrals[24] compensates to some extent for the effect of vertical correlation on the energy, but not for its effect on the wave function—and consequently on the electron distribution. Inclusion of configuration interaction in its conventional form[25] allows only for the effect of horizontal correlation. There can therefore be no doubt that all current treatments of butadiene *must* overestimate the electron density in the central bond of butadiene and the consequent resonance shortening; and there is at present no way of estimating the magnitude of this error.

Mulliken[6] based much of his criticism of our work on the results of such calculations; the argument given above shows that no valid conclusions can be drawn from such calculations and so refutes his criticisms.

An extension[1] of this argument suggests that current methods should always overestimate the effect of resonance in classical unsaturated molecules, and that these may well conform closely both in structure and in energy to the pattern predicted for a configuration with essentially localized single and double bonds. In such

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[24] W. E. Moffitt, *Proc. Roy. Soc.* A **210**, 224, 245 (1951); R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 (1953).

[25] D. P. Craig, *Proc. Roy. Soc.* A **200**, 474 (1950).

molecules vertical correlation tends to share them equally between the two π-lobes, and horizontal correlation then spreads out the electrons in each π-lobe so that they tend to be concentrated in alternate bonds. But such a set of alternate bonds in a conjugated system must be the set written as double in one classical structure; electron correlation therefore tends to concentrate the electrons in each π-lobe into the bonds written as double in a classical structure for the molecule. If there is only one such structure, the π-electrons tend to be concentrated in pairs in the double bonds; the electron distribution will then conform more closely to that of a single classical structure than one would expect from current theoretical treatments in which electron correlation is neglected.

The situation is entirely different in non-classical molecules for which two or more classical structures can be written, i.e. aromatic molecules and mesomeric ions and radicals such as allyl. Here the two sets of π-electrons have a choice of classical structures and there is no question of their being localized in definite bonds. Consequently vertical correlation will not affect the smearing of electrons over the whole conjugated system; vertical correlation should affect the energy of a non-classical molecule but should not much affect the electron distribution in it. In this case conventional treatments have much more chance of success, particularly if allowance is made for the effect of vertical correlation on the energy.[24]

XIII. *The significance of classical structures*

Our argument implies that vertical correlation of the π-electrons in a conjugated system favours configurations in which the electrons are evenly distributed between the two π-lobes, and that horizontal correlation then tends to concentrate each such set of electrons into the bonds written as double in a classical structure for the conjugated system. According to this view classical structures take on a new significance; they represent instantaneous electron distributions favoured by electron correlation. This suggests that a special weight should be given to such structures in a resonance interpretation of conjugated systems; and that in such an interpretation the individual structures have a much more profound significance than is ascribed to the canonical structures of the VB theory.

This is interesting; for it is well known that simple resonance theory, in which excited structures are neglected, gives a very good account of chemical behaviour, although detailed calculation[26] has shown that excited canonical forms can be of dominant importance in the VB wave functions of aromatic molecules. We ascribe this apparent anomaly to the neglect of vertical correlation in VB theory.

The same conclusion, that the inclusion of excited structures in resonance theory is wrong in principle has also been reached by a different line of reasoning,[27] not incompatible with that given here.

Our argument does, however, suggest that resonance structures other than classical ones should be important. Each classical structure represents a preferred correlation pattern for the set of electrons occupying a given π-lobe. If both sets of π-electrons conform to the same classical structure, the resulting configuration as a whole will conform to the classical formulation in which each line represents a pair of electrons concentrated in the region between two nuclei. If, however, there are two or more

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[26] A. Pullman and B. Pullman, *Experientia* 2A, 364 (1946).

[27] M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc.* A 214, 482 (1952).

possible classical structures, the two sets of π-electrons may adapt different distribution patterns, giving rise to a quasi-classical configuration in which certain "π-bonds" contain single electrons. Thus in the case of benzene, if both sets of electrons match up, we have the two Kekulé structures, Fig. 7 (a), (b); but if the two sets of electrons conform to different classical structures, we have the quasi-classical structures (c), (d) with one π-electron per CC bond.

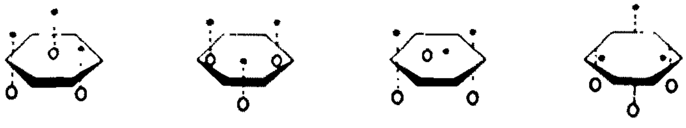
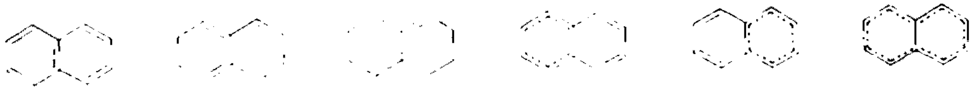

(a) (b) (c) (d)

Fig. 7. Favoured configurations for π-electrons in benzene.

The structures (c), (d) correspond to the structure for benzene proposed by Thomson[28] with three electron bonds; they may be described as *Thomson structures.* Our argument implies that benzene can be represented as a hybrid of two Kekulé structures and to Thomson structures; the Thomson structures can be represented conventionally by writing broken lines for one electron π-bonds; Naphthalene pro-


Kekulé structures Thomson structure

vides a further illustration; here there are three classical structures; combination of these in pairs (corresponding to the two sets of π-electrons exhibiting different correlation patterns) gives three classical (Kekulé) and three semi-classical (Thomson) configurations; i.e.


(a) (b) (c) (a) + (b) (a) + (c) (b) + (c)

In the simple MO treatment, effects of electron repulsion are included in the empirical resonance integrals. If these are evaluated, as in our treatment, from ethylene, they will correspond to the electron repulsion between pairs of electrons occupying the same C:C bond (i.e. a classical or Kekulé configuration). The electron repulsion in the staggered semi-classical Thomson configuration should be less than this; our treatment of benzene should therefore give too high a value for the energy, the difference being due to the contributions of the two lower-energy Thomson structures to the ground state. This certainly seems to be the case. The conjugation energy calculated for benzene (Section V) was only 1·9 kcal/mole compared with the experimental value (Table 11) of 20–30 kcal/mole. A rough calculation shows that this difference is of the same order of magnitude as the difference on electron repulsion energy between Kekulé and Thomson structures.

It is noteworthy that our method gave such a good value for the bond length in benzene (Table 3) although the value for the energy was much too high. This would

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[28] J. J. Thomson, *Phil. Mag.* 27, 784 (1914).

not be surprising if our explanation for the discrepancy is correct since the difference in electron repulsion between the Kekulé and Thomson structures is insensitive to bond length. Only the derivative of this difference with respect to bond length would enter our calculation, and this should be small.

XIV. *Possible methods for including vertical correlation*

Vertical correlation can be included in calculations of conventional type in one of two ways. Either one can use weighting factors involving the interelectronic distances directly (cf. the Hylleraas treatment of helium) or one can use a configuration interaction treatment in which vertical correlation is taken into account in the individual configurations, using configurations with varying numbers of electrons in the two π-lobes.

A treatment of the first kind had been described by Kolos[29] but so far he has applied it only to molecules such as ethylene or benzene where the π-MO's are determined by symmetry; any extension to more complex molecules would be very difficult. The second type of treatment has not yet been carried out.

There is, however, a third approach, suggested recently by Dr. C. E. Wulfman and one of us[30] and based on the relation between the MO and VB approximations.

The simple MO method is known to overestimate the importance of ionic structures, due to its neglect of electron correlation. An alternative approach is to make the opposite assumption, that electron correlation is so extreme that the chance of finding both electrons in a bond simultaneously on the same terminal atom is zero --in other words that ionic structures can be neglected. This leads to the VB approximation.

We can make the same simplifying assumption in the case of conjugated systems. We can assume that vertical correlation is so extreme that only configurations with equal numbers of electrons on either side of the nodal plane are important. A treatment of this kind was applied[30] to simple polyenes, the FEMO approximation being used for the electrons in each π-lobe; extension of this work seems most desirable since a comparison with the results of conventional treatments (in which vertical correlation is ignored) would indicate the maximum effect that vertical correlation can have.

It should be added that the experimental value for the mutual repulsion between two electrons occupying a $2p$-AO of carbon corresponds[30] to complete correlation implying that the chance of finding both electrons in the same lobe of the AO is small. This calculation suggests that the completely correlated model for π-electron systems may correspond closely to reality.

XV. *Significance of hybridization*

A number of authors have considered the possibility of a continuous transition between pure p and pure s bonds, the division of carbon bonds into sp^3, sp^2 and sp types being arbitrary. This view has been recently stressed by Mulliken[6]; if it were correct, our distinction of bonds into distinct hybridization types would lose much of its significance.

This argument is tacitly based on the assumption that σ-bond orbitals are linear, so that the valence orbital of carbon must point along the bond axis. It ignores the

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[29] W. Kolos, *Acta Phys. Polonica* **16**, 257, 267, 299 (1957).

[30] M. J. S. Dewar and C. E. Wulfman, *J. Chem. Phys.* **29**, 158 (1958).

possibility of non-collinear overlap giving rise to bent bonds ("banana bonds"). Coulson and Moffitt[31] have shown that the structure of cyclopropane can be very well interpreted in terms of such bent bonds; and the experimental evidence concerning bond lengths, etc., provides no support for the continuous transition of bond properties with bond angles that would be expected if hybridization changed in conformity with bond angles.

Electron correlation should favour symmetrical distributions of the valence electrons of carbon, particularly near the nuclei; this in turn will favour bent bonds in cases where mutual repulsion or geometrical constraint forms the adjacent atoms out of the most symmetrical arrangement. Thus in the case of quadricovalent carbon, the four bond orbitals should set out symmetrically from the nucleus; this corresponds to (possibly non-collinear) overlap of four ligand orbitals with sp^3 hybrid orbitals of carbon. The idea of continuous variation of hybridization parameters probably implies an underestimate of the effects of electron correlation.

The significance of hybridization is in any case uncertain. The properties of a molecule depend only on the overall electron distribution, as expressed in the density matrix. Orbitals, hybridization, etc. are purely artificial concepts made necessary by our inability to calculate the electron distribution accurately or more directly. In this sense the correlations we have established between bond properties and co-ordination number may have a deeper significance than our interpretation would suggest; we have, however, preferred to formulate it in terms of hybridization for lack of a better theoretical model.

Appendix 1

Attempted calculation of bond energies. If the heats of formation of hydrocarbons can be expressed in terms of bond energies, then for a given hydrocarbon;

$$\sum_i n_i E_i + \sum_j n_j \epsilon_j = \mathrm{H} \tag{8}$$

where E_i is the bond energy of a given type of CC bond and n_i the number of such bonds, ϵ_j and n_j the corresponding quantities for CH bonds, and H the heat of formation.

If a number of hydrocarbons are considered, the set of equations (8) form a set of simultaneous equations for the bond energies. These can be written in the form

$$\mathbf{A} \,.\, \mathbf{E} = \mathbf{H} \tag{9}$$

where **E** is the vector of bond energies, **H** the vector of heats of formation, and **A** the matrix of bonds of various types.

If we take a set of compounds whose heats of formation are known, **A** and **H** are known; equation (9) should then give the bond energies for bonds of various types. Unfortunately **A** proves to be a degenerate matrix; attempts to reduce the degeneracy of **A** sufficiently to solve equation (9) proved fruitless. Moreover random errors in the experimental values for heats of formation introduced enough "noise" to make the set of equations self-inconsistent.

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[31] C. A. Coulson and W. E. Moffitt, *Phil. Mag.* **40**, 1 (1949).

Appendix 2

Correction of bond lengths for vibrational anharmonicity. If the vibration of a bond is anharmonic, the mean length (r_0) will differ from the equilibrium length (r_e). The relation between r_0 and r_e can be derived[32] but it is very cumbersome. Since the corrections in our case are small, we made the simplifying assumption that r_0 can be equated to the mean of the extreme bond lengths for a classical oscillator. Using the Morse potential, this leads to the expression

$$r_0 - r_e = -\left(\frac{2D_0 + hV_0}{k}\right)^{1/2} ln\left[1 - hV_0(2D_0 + hV_0)^{-1}\right] \tag{10}$$

where D_0 is the ground state bond energy, V_0 the ground state vibration frequency, and k the force constant.

TABLE 13. THE FORCE CONSTANT–BOND LENGTH RELATION

Compound	Equilibrium bond length	Force constant
ethane	1·540	4·57
ethylene	1·334	10·90
acetylene	1·205	15·48

$k = -46{\cdot}978r_e^{-2} - 194{\cdot}813r_e^{-4} - 136{\cdot}486r_e^{-6}$
bond lengths in Å, force constants in millidyne/Å

The corrections calculated from equation (10) for CC bonds are small (ethane, 0·0044 Å; ethylene, 0·0036 Å. acetylene, 0·0032 Å); the corrections for CH bonds are somewhat larger. Our crude method must overestimate the corrections, but the errors certainly cannot be important for the present purpose.

Appendix 3

The benzene–graphite calculation. The condition for equilibrium in benzene can be written

$$\frac{\partial E}{\partial r} = \frac{\partial E\sigma}{\partial r} + \frac{\partial E\pi}{\partial r} = 0 \tag{11}$$

where E is the total energy, E_σ, E_π the energies of the σ- and π-electrons, and r the bond length. The first term can be expressed in terms of the equilibrium force constant (k_e') for the sp^2–sp^2 C—C bond, from which together with its equilibrium length (r_e') one can calculate the Morse function parameters. The second term can be calculated by the method indicated in Part I,[1] using the simple LCAO method with inclusion of overlap; the values taken for the overlap integrals were those calculated from Hartree–Fock AO's. A similar equation can be written for the condition for equilibrium in graphite.

In order to estimate k_e', we assumed a relation between force constant and bond length of the form

$$k = ar^{-2} + br^{-4} + cr^{-6} \tag{12}$$

The constants a, b, c were found by fitting the force constants for ethane, ethylene, and acetylene; the data used and values found are listed in Table 13.

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[32] cf. G. Herzberg, *Spectra of Diatomic Molecules*. Van Nostrand, New York (1950).

Sixteen quantities have to be determined (Section VI); viz. r_0', E_0', r_e', E_e', r_0 E_0, r_e, E_e, r_b, r_g, r_0'', r_e'', a_C, b_C, a_H, b_H. The equations available are:

equation (8) applied to r, r', r'' (three relations)
equation (4) applied to (r, E), (r', E'), (r'', E'') (three relations)
equation (9) applied to benzene and graphite (two relations)
equation (4) applied to diamond and methane (two relations)
equation for zero point energy, applied to find $(E_0 - E_e)$ and $(E_0 - E'_e)$ (two relations) heats of formation of ethylene and acetylene, expressed as sums of bond energies (two relations)
condition that the plot of bond order vs. r should be linear for four cases (ethylene, benzene, graphite, and pure sp^2-sp^2 single bond) (two relations).

There are therefore sixteen relations available, sufficient to determine the sixteen unknowns in terms of the experimental quantities listed in Section VI. The calculation was complicated by the fact that the computer available to us (a HEC 2M) had a limited store (1024 words); this made it impossible to put the whole problem on the machine. A solution was reached by varying E' until the equations became self-consistent. Full details of the calculation, which took 200 hours of machine time, are given in a thesis by one of us.[33]

Appendix 4

Calculation of bond lengths. In our previous papers[1,3] we proposed the following method for calculating bond lengths in conjugated systems.

The total energy (E) of the CC bonds in a conjugated system may be written

$$E = nE_0' + \sum C_{rs} + E_\pi \tag{13}$$

where n is the number of CC bonds and E_0' the corresponding σ-bond energy, C_{rs} is the energy required to compress the σ-bond between atoms r, s to the length it has in the conjugated system, and E_π is the total π-bond energy. In simple MO theory,

$$E_\pi = \sum_r q_r \alpha_r + 2 \sum_{r<s} \sum p_{rs} \beta_{rs} \tag{14}$$

where q_r, α_r are the change density at, and coulomb integral of, atom r, and p_{rs}, β_{rs} are the bond order and resonance integral of the bond between atoms r, s. In the MO treatment E_π is found by minimizing it with respect to the AO coefficients.

Combining equations (13) and (14),

$$E = nE_0' + \sum_r q_r \alpha_r + 2 \sum_r \sum_s p_{rs} \beta'_{rs} \tag{15}$$

where

$$\beta'_{rs} = \beta_{rs} + \frac{C_{rs}}{2p_{rs}} \tag{16}$$

Since equations (14) and (15) are similar in form, it would appear that a standard MO calculation, with β replaced by β', should give the total energy (including σ-bond compression) rather than π-energy. The replacement seems valid, since β, c, and p are all one-valued functions of bond length in molecules in equilibrium; β' should also be a one valued function of bond length.

[33] H. N. Schmeising, Ph.D. Thesis, London (1959).

In order to calculate E, an iterative procedure must be used. Values for the bond lengths are assumed; β_{rs}, c_{rs}, p_{rs}, and hence β'_{rs} are calculated for each bond; solution of the appropriate secular equations gives the orbital coefficients from which bond orders are calculated; and from these together with the p/r relation a new set of bond lengths are calculated. The cycle is repeated until the bond lengths become self-consistent.

The trouble with this idea is that p_{rs} does not have the same meaning in equations (15) and (16). In equation (15), p_{rs} is a bond order found from orbital coefficients; in equation (16) p_{rs} is found from the assumed bond lengths using the p/r relation. If the molecule were in its equilibrium state, the p's would be identical; but in the minimization procedure there is the danger of arriving at a false solution. This happened when we tried to apply the method to butadiene.

The difficulty might have been overcome, had not the following alternative and better based procedure made it superfluous. The problem is to minimize the total energy of butadiene with respect to simultaneous variation in two parameters (lengths of the 1:2 and 2:3 bonds). As Mr. F. Beck* pointed out to one of us, the problem can be solved by fitting parabolas to the energy surface and finding the total minimum of these. It can be shown that if x_0 is an approximation to the minimum of a two-dimensional curve $f(x)$, then a second approximation x'_0 is given by

$$x'_0 = x_0 - d(f_+ - f_-)/2(f_+ + f_- - 2f) \tag{17}$$

where d is a suitable increment, and f_+, f_- the values of $f(x)$ for $x = x_0 \pm d$.

If d is kept constant, then successive applications of equation (17) may not lead to a solution, since it may be that at some stage f_+, f_- become equal. This difficulty cannot occur if d is halved after each iteration.

Equation (17) can be applied for any number of variables provided the initial approximations are sufficiently good. A proof of the relation, and further discussion, will be found in a thesis[33] by one of us.

In applying the method to butadiene one needs to know β, s, and c as functions of bond length. The values of s, the overlap integral, were taken from tables,[34] calculated for Hartree-Fock orbitals. The values of β were found by the modified Lennard-Jones method described previously.[1] The compression energy was found from a Morse function.

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* Research Laboratories, General Electric, England.

[34] R. S. Mulliken, *J. Chem. Phys.* 19, 900 (1951).