Tetrahedron, 1959, Vol. 5, pp. 166–178 Pergamon Press Ltd. Printed in Great Britain.

A RE-EVALUATION OF CONJUGATION AND HYPER-CONJUGATION: THE EFFECTS OF CHANGES IN HYBRIDISATION ON CARBON BONDS

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THIS paper falls into three sections.

In the first, we examine the currently accepted evidence for the delocalisation of bonds in polyenes, olefines, etc., and show it to be inconclusive.

In the second, we give three independent estimates of the length of a pure single σ bond between sp^2 carbon atoms which indicate that it is close to the value for the central bond in butadiene. We also estimate the bond energies of bonds formed by sp^2 carbon atoms, and find that the apparent "resonance energy" of butadiene can be ascribed quantitatively to the variation in bond energy with hybridisation.

In the third section we consider the status of conjugation in general terms; we shall conclude that the naive resonance picture is correct, in that resonance is important only in molecules for which more than one classical (unexcited) structure can be written.

The evidence for bond delocalisation

Five lines of evidence are commonly quoted as evidence for the delocalisation of bonds in conjugated and hyperconjugated systems*:

(*a*) The shortening of σ bonds in such systems; for example, the single C–C bonds in butadiene and methylacetylene are approximately 1·46 Å in length, much less than the value (1·54 Å) found in saturated hydrocarbons or diamond.

(*b*) The fact that the heats of formation of such molecules are greater than the sum of their bond energies; and the heats of hydrogenation per double bond are less than the heat of hydrogenation of ethylene.

(*c*) The fact that hyperconjugated hydrocarbons such as toluene are polar.

(*d*) The fact that conjugated and hyperconjugated molecules show a light absorption very different from that of unconjugated analogues.

(*e*) The fact that conjugated and hyperconjugated molecules differ in chemical reactivity from unconjugated analogues.

Criticism of the evidence for delocalisation

(*a*) It has long been recognised[1, 2] that bonds formed by sp^2 carbon atoms must

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* The terms conjugation and hyperconjugation are used here as designations of structural features, with no reference to their theoretical interpretation.

[1] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).

[2] C. A. Coulson, *Victor Henri Memorial Volume*; *Contribution à l'Étude de la Structure Moléculaire* p. 15. Desoer, Liège (1948); *Proc. Roy. Soc.* A **207**, 91 (1951).

be shorter than analogous bonds formed by sp^3 carbon. Unless the degree of shortening can be estimated, no conclusions can be drawn from the lengths of single bonds in molecules such as butadiene or methylacetylene. Mulliken *et al.*[1] and Coulson[2] estimated the length (r_1) of the pure sp^2–sp^2 C–C bond by assuming additivity of covalent radii, and estimating the covalent radius of sp^2 carbon by comparison of the CH bond lengths in methane or ethane (1·095 Å) with that in ethylene (1·07 Å). This leads* to a predicted value of about 1·50 Å for r_1. This argument is certainly not conclusive; for there is no theoretical justification for the rule of additivity of covalent radii, and it tends in any case to fail for hydrides.

(*b*) Likewise the bond energies of bonds formed by sp^2 carbon must be greater than those of analogous bonds formed by sp^3 carbon. This obviously invalidates any calculations of "resonance energies" by comparison of observed heats of formation with those calculated from current tables of bond energies; for the latter are based on the assumption that bond energies are unaffected by changes in hybridisation. Thus the C=C bond energy is deduced from the heat of formation of ethylene by assuming that the bond energies of the CH bonds are the same as in a paraffin; this cannot be the case.

The same applies to the calculation of resonance energies from heats of hydrogenation. Consider the following thermochemical argument, x being the heat of hydrogenation of ethylene, E_{RS} the bond energy of a single bond between atoms R, S involving sp^3 carbon atoms and E'_{RS} the corresponding value for sp^2 carbon atoms:

$$\begin{aligned}
&2\,CH_2{=}CH_2 + 2H_2 \rightarrow 2\,C_2H_6 + 2\,x\\
&2\,CH_2{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2 + E'_{CC} + E_{HH} - 2E'_{CH}\\
&2\,CH_3{-}CH_3 \rightarrow C_4H_{10} + H_2 + E_{CC} + E_{HH} - 2E_{CH}
\end{aligned}$$

hence

$$\begin{aligned}
CH_2{=}CH{-}CH{=}CH_2 + 2\,H_2 \rightarrow C_4H_{10} + 2\,x - [(E'_{CC} - E_{CC})\\
- 2(E'_{CH} - E_{CH})] \qquad (1)
\end{aligned}$$

The "resonance energy" of butadiene is defined† as the difference between the heat of hydrogenation of butadiene and that of two molecules of ethylene. Clearly this will include a term E_h, given by:

$$E_h = (E'_{CC} - E_{CC}) - 2(E'_{CH} - E_{CH}) \qquad (2)$$

which represents the effect of the different hybridisation of the carbon atoms in the unsaturated and saturated hydrocarbons. Obviously E_h has nothing to do with delocalisation of electrons or resonance; and unless we can estimate E_h and show it to be less than the observed "resonance energy", we cannot tell from heats of hydrogenation whether resonance is, or is not, important in butadiene.

Exactly the same situation arises in the case of hyperconjugation, as is shown by the following argument for propene:

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* Recent estimates[3, 4] of the CH bond length in ethylene (1·085 Å) lead to a value of 1·52 Å for r_1.

† The use of this naive definition, in the place of comparisons with "reference compounds" (here butene-1), will be justified later.

[3] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.* **27**, 1414 (1957).

[4] O. Bastiansen, Lisa Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).

$$\begin{aligned} &CH_2{=}CH_2 + H_2 \rightarrow C_2H_6 + x \\ &CH_2{=}CH_2 + CH_4 \rightarrow CH_2{=}CH\cdot CH_3 + H_2 + E''_{CC} + E_{HH} - E_{CH} - E'_{CH} \\ &C_2H_6 + CH_4 \rightarrow C_3H_8 + H_2 + E_{CC} + E_{HH} - 2\,E_{CH} \end{aligned} \qquad (3)$$

where E''_{CC} is the bond energy for a σ bond between an sp^2 carbon and an sp^3 carbon.

Hence:

$$CH_2{=}CH\text{–}CH_3 + H_2 \rightarrow C_3H_8 + x - [(E''_{CC} - E_{CC}) - (E'_{CH} - E_{CH})] \qquad (4)$$

Therefore the apparent "resonance energy" of propene will contain a term E'_h, given by

$$E'_h = (E''_{CC} - E_{CC}) - (E'_{CH} - E_{CH}) \qquad (5)$$

The same situation will arise quite generally. The experimental resonance energy will contain a contribution due to changes in hybridisation given by:

$$(E_h)_{\text{total}} = mE_h + nE'_h \qquad (6)$$

where m is the number of single bonds between pairs of sp^2 carbon atoms, and n that of bonds between sp^2 and sp^3 carbon atoms in a classical structure for the hydrocarbon.

Obviously, similar arguments will apply to compounds containing heteroatoms; for example to $\alpha\beta$-unsaturated ketones.

(c) As Walsh[5] has emphasised, sp^2 carbon must be more electronegative than sp^3 carbon. Therefore bonds between sp^2 and sp^3 carbon atoms must be polar, for example:

$$\underset{sp^3}{CH_3} \rightarrow \underset{sp^2}{CH{=}CH_2} \qquad \underset{sp^3}{CH_3} \rightarrow \underset{sp^2}{C_6H_5}$$

Unless the magnitude of this dipole can be estimated and shown to be less than the observed moment of propene or toluene, one cannot conclude from the polarity of those hydrocarbons that the bonds to methyl are not single.

(d) The light absorption of a compound is determined by the *difference* in energy between two different states, the ground state and an excited state. One cannot therefore conclude from the light absorption of a conjugated molecule that the ground state is non-classical; the differences from analogous unconjugated molecules may lie entirely in the excited states. One would certainly expect a much greater degree of electron delocalisation in the excited state than in the ground state, where all the electrons are paired; so this argument is by no means merely a piece of provocative sophistry.

(e) Exactly the same argument applies to chemical reactivity, which again is determined by the difference in energy (strictly free energy) between *two* different states, the initial state and the transition state. Here again one would expect the transition state for the reaction of a molecule such as butadiene to be more delocalised than the parent hydrocarbon; for the products of such reactions (e.g., addition of ions or radicals) are either allyl derivatives of π-complexes, in which the electrons must be more highly delocalised than they are in butadiene.

The arguments for delocalisation or resonance in simple conjugated systems, or in hyperconjugated systems, are therefore inconclusive. Obviously there *are* systems in

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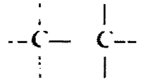
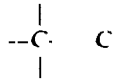
[5] A. D. Walsh, *Trans. Faraday Soc.* 43, 60 (1947).

which delocalisation must be important; for example, benzene or graphite, where all the bonds have the same length. But the extrapolation to systems such as butadiene or propylene has no justification. We have also seen that most of the current interpretation of the thermochemistry of carbon compounds needs complete revision.

Preliminary estimate of the length of the $C(sp^2)$–$C(sp^2)$ *bond*

Accurate measurements of bond lengths in a variety of compounds containing triply bound carbon have shown[6] that the lengths of adjacent C–C single bonds are constant to within two or three thousandths of an angström, having the values shown in Table 1.

TABLE 1. EQUILIBRIUM LENGTHS OF VARIOUS CC BONDS

Bond	Equilibrium length (Å)
 $-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	1·542 ± 0·001
 $-\overset{|}{\underset{|}{C}}-C$	1·460 ± 0·003
C— C	1·380 ± 0·002
$H_2C \cdot CH_2$	1·353
$H_2C=C\ CH_2$	1·309

The same value for the "hyperconjugated" C–C single bond is observed not only in a range of methylacetylenes, but also in acetonitrile and trifluoroacetonitrile; and the value for the "conjugated" single bond is likewise the same in cyanoacetylene or cyanogen as in polyacetylenes. The constancy of these bond lengths in compounds of very different types, and the fact that the contraction (0·082 Å) in passing from an sp^3–sp^3 bond to an sp^3–sp one is, within the limits of experimental error, the same as that (0·080 Å) in passing from an sp^3–sp bond to an sp–sp one, suggest very strongly indeed that the contractions are due to a change in covalent radius of carbon with hybridisation and not to any resonance or delocalisation effect.

If one assumes that the covalent radius of carbon is a linear function of its s-character, one finds for the covalent radius of sp^2 carbon (33 per cent s) the value 0·745 Å, corresponding to a value of r_1, the $C(sp^2)$–$C(sp^2)$ bond length, of 1·49 Å. This argument suggests that the values assumed for r by previous workers are too great.

Table 1 also gives values[6] for the bond lengths in ethylene and allene. Here no resonance effects are possible and the contraction in allene must be due to the different hybridisation (sp) of the central carbon atom. If we assume that the change in hybridisation affects the lengths of single and double bonds equally, we then find for the various covalent radii of carbon:

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

E

$$(sp^3)\text{-}(sp) = 0{\cdot}08\ \text{Å} : (sp^2)\text{-}(sp) = 0{\cdot}044\ \text{Å} \tag{7}$$

whence:

$$(sp^3)\text{-}(sp^2) = 0{\cdot}036\ \text{Å} \tag{8}$$

and so:

$$r_1 = 1{\cdot}543 - 2(0{\cdot}036) = 1{\cdot}471\ \text{Å} \tag{9}$$

This argument is uncertain at two points. First, the length of the C=C bond in ethylene is uncertain, a recent study[3] by electron diffraction having given the value 1·334 Å. This value implies $r_1 = 1{\cdot}43$ Å, which seems too small. Secondly, the assumption that changes in covalent radius affects both C–C and C=C bond length equally is suspect, though one can show that the differences should not be large.

Inclusion of σ bond compression energy in MO *calculations*

A second estimate of r_1 was obtained in the course of a different investigation, one which led us to consider in detail the properties of bonds involving sp^2 carbon atoms.

Various attempts[7] have been made to include σ-bond compression in MO calculations; most of these have either used unrealistic (parabolic) potential functions, or have depended on symmetry properties of special molecules (e.g., benzene). No general method has been published for including in MO calculations the effects of σ-bond compression, using an arbitrary potential function. The following considerations provide such a method.

Making the usual assumption that σ and π electrons can be treated independently, we can write the total energy (E) of a conjugated molecule in the form:

$$E = E_\pi + E_c \tag{10}$$

where E_π is the total energy of the π electrons and E_c is the energy required to compress the σ bonds to the lengths they have in the actual molecule. We may write:

$$E_c = \sum_{r<s}\sum C_{rs} \tag{11}$$

where C_{rs} is the compression energy of the σ bond between the (adjacent) atoms r, s. Now in the simple Hückel treatment, with or without inclusion of overlap,

$$E_\pi = \sum_r q_r \alpha_r + 2 \sum_{r<s}\sum p_{rs}\beta_{rs} \tag{12}$$

where q_i, p_i are the π-electron charge density at, and Coulomb integral of, atom i; and p_{ij}, β_{ij} are the bond order and resonance integral of the bond between atoms i and j. Combining equations (10) and (12):

$$\begin{aligned} E &= \sum_r q_r \alpha_r + 2 \sum_{r<s}\sum p_{rs}\beta_{rs} + \sum_{r<s}\sum c'_{rs} \\ &= \sum_r q_r \alpha_r + 2 \sum_{r<s}\sum p_{rs}\beta'_{rs} \end{aligned}$$

where:

$$\beta'_{rs} = \beta_{rs} + \frac{C_{rs}}{2p_{rs}} \tag{14}$$

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[7] E. S. Lennard-Jones, *Proc. Roy. Soc.* A **158**, 280 (1937); H. C. Longuet-Higgins and F. H. Burkitt, *Trans. Faraday Soc.* **48**, 1077 (1952).

Since β, c and p are all one-valued functions of bond length, so also is β'. Moreover equations (12) and (13) are identical in form. It follows that if we carry out a Hückel treatment, replacing β by β', and making the treatment self-consistent for the variation in β' with bond length, we obtain a value for E instead of E_π; and the corresponding values of the bond lengths are those which minimise E, the *total* energy of the molecule. This treatment therefore allows explicitly for the effect of σ-bond compression. To complete the calculation, we need to know β as a function of bond length. This can be done as follows. Consider the conversion of a pure C–C single bond of length r_1 to a double bond of length r. This can be done in stages (Fig. 1). The bond is first compressed to length r, with an increase in energy C', equal to the compression energy of the single bond; and then the π-component is introduced, with a change in energy calculated by MO theory as some function $f(\beta)$ of β.

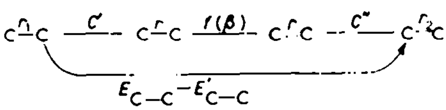

Fig. 1. Estimation of β as a function of bond length.

Now the energy change can also be estimated in another way. First we convert the C–C single bond of length r_1 to a C=C double bond of equilibrium length r_2, the energy difference being equal to the difference between the C=C bond energy (E_{C-C}) and that (E'_{CC}) for a single bond between sp^2 carbon atoms. Next we stretch the double bond to length r, with a change in energy C''. Equating these two estimates:

$$C' + f(\beta) = E_{C-C} - E'_{CC} + C'' \tag{15}$$

whence

$$f(\beta) = E_{C-C} - E'_{CC} + C'' - C' \tag{16}$$

In this equation E_{C-C} is known, and C'' can be found from any suitable potential function. In order to estimate β, we also need to know E'_{CC} and C'. It is natural to assume Morse functions for calculating compression energies; if so, the function for C' will involve r_1 and E'_{CC}, and that for C'', r_2 and E_{C-C}. This shows why we became interested in estimating r_1 and E'_{CC}.

Note that, although the above argument has been based on the simple Hückel form of the MO method, exactly the same treatment can be used in the SCF approach; for the one-electron terms in the Roothaan equations are identical in form with the Hückel expressions, and so if the one-electron resonance integrals β are replaced by the modified quantities β' [equation (14)] the SCF treatment will automatically lead to results corrected for σ-bond compression. Since solution of the Roothaan equations involves in any case an iterative procedure, no extra labour would be involved in this refinement.

In our preliminary work on bond lengths we have used the Hückel treatment, but we plan to carry out similar calculations by the SCF method.

A second estimate of r_1, and estimates of E'_{CC}

The treatment outlined in the previous section can be used to estimate bond lengths in conjugated systems in terms of the quantities r_1 and E'_{CC}. We were thus able to calculate* the bond lengths in benzene and graphite in terms of these quantities; the resulting expressions could be treated as a pair of simultaneous equations for r_1 and E'_{CC}, and we were able to solve these with the aid of a digital computer. The results were:

$$r_1 = 1{\cdot}479\ \text{Å}; \quad E'_{CC} = 100\ \text{kcal/mole} \tag{17}$$

The agreement of r_1 with previous estimates, and with the experimental value for the length of the central bond in butadiene, is remarkable, and certainly supports the idea that the length of that bond is not due to any significant resonance effects in butadiene; for the calculation treated r_1 and E'_{CC} as a pair of parameters whose values were in no way prejudged.

The values given in equation (13) were checked in three independent ways. First, the calculations also led to values for the total heats of formation of benzene and graphite, and these agreed well with experiment. Secondly, the values for r_1 and E'_{CC} fitted well an empirical relation between bond energy and bond length, the derivation of which is described below. Thirdly, the resulting bond energies led [cf. equation (1)] to a predicted heat of hydrogenation of butadiene in good agreement with experiment; this point, which is discussed in detail later in this paper, shows that both the central bond length and the heat of hydrogenation of butadiene can be consistently interpreted with a non-resonating model.

Empirical relations between bond energy and bond length

Glockler[8] and others have shown that the heats of formation of carbon compounds can be consistently interpreted on the assumption that bond energy is a one-valued function of bond length. We preferred, however, to derive new relations of this kind for CC and CH bonds, since we felt that the published ones were open to criticism.

We adopted three-parameter relations of the form:

$$E = a_1 r_1^{-1} + a_2 r_2^{-2} + a_3 r_3^{-3} \tag{18}$$

for both carbon–carbon and carbon–hydrogen bonds. The six parameters were evaluated by assuming the heats of formation (with L_c = 170 kcal/mole) and bond lengths for diamond, methane, ethane, ethylene, benzene and acetylene, the spectroscopic bond lengths being corrected for residual energy to make them compatible with thermochemical data. The relations so obtained for the bond energies (in kcal/mole) at 25° were:

$$(E_{CC})_r = -\frac{1140{\cdot}593}{r} + \frac{3252{\cdot}755}{r^2} - \frac{1991{\cdot}129}{r^3} \tag{19}$$

$$(E_{CH})_r = \frac{1125{\cdot}03}{r} - \frac{2477{\cdot}006}{r^2} + \frac{1376{\cdot}444}{r^3} \tag{20}$$

As a check, the heat of atomisation of graphite was calculated, the value (171 kcal/mole) being in satisfactory agreement with experiment. The values for r_1 and E'_{CC} in equation (17) fit equation (19).

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* These calculations were carried out by the simple MO treatment, with inclusion of overlap: the overlap integrals were those calculated for SCF AO's.

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

The corresponding values of bond lengths and bond energies for the various CC and CH bonds are listed in Table 2; here E_e and r_e are the equilibrium values for the bond energy and bond length, and E_0 and r_0 are the values appropriate to thermochemical calculations at 25°C.

TABLE 2. BOND ENERGIES AND BOND LENGTHS FOR CARBON BONDS

Bond	Bond lengths (Å)		Bond energies (kcal/mole)	
	r_e	r_0	E_e	E_0
C=C	1·350	1·353	131·6	129·1
C–C sp^2 sp^2	1·476	1·479	102·2	100·4
C–C sp^3 sp^3	1·540	1·543	82·5	83·9
C–H sp^2	1·071	—	—	100·9
C–H sp^3	1·095	—	—	97·2

Conjugation energies and resonance energies

With the values in Table 2, we can estimate the spurious "resonance energy" E_R of butadiene from equation (2):

$$E_R = (100{\cdot}4 - 83{\cdot}9) - 2(100{\cdot}9 - 97{\cdot}2) = 9{\cdot}1 \text{ kcal/mole} \tag{21}$$

This value is actually *greater* than the experimental "resonance energy" of butadiene relative to two molecules of ethylene, which from heats of hydrogenation is found to be 8·1 kcal/mole. This implies that conjugation effects in butadiene are unimportant—in which case the central bond must be essentially a single bond, and its length (~1·46 Å) a measurement of r_1. The agreement with r_1 is within the limits of error claimed for the electron-diffraction measurements.

A further check was provided by a self-consistent treatment of butadiene by the method indicated above (equations (10) to (16)). The results were as follows:

Assumed initial values for bond lengths	1:2, 1·36 Å	2:3, 1·46 Å
Final self-consistent values	1:2, 1·359 Å	2:3, 1·445 Å

Calculated resonance energy, −0·5 kcal/mole.

These results provide useful confirmation of the argument in the previous paragraph; evidently conjugation alters the bond lengths and total energy very little—so that the length of pure single and double CC bonds must be close to those observed in butadiene. The discrepancy between theory and experiment is, however, serious; reasons will be given later for believing that the simple MO treatment, though excellent for aromatic molecules such as benzene or graphite, should be less successful for butadiene. Note that the resonance energy is *negative*. This negative "resonance energy" is compensated by a greater decrease in σ-bond compression energy. Delocalisation occurs at all only in order to reduce the σ-bond compression energy, not because it is favourable in itself. The overall stabilisation is very small.

This argument is illustrated still more strikingly by benzene. The empirical "resonance energy" R is given by the difference in heat of hydrogenation between benzene and three molecules of ethylene:

$$R = 47{\cdot}9 \text{ kcal/mole} \tag{22}$$

Now a Kekulé structure for benzene contains three single bonds between sp^2 carbon atoms; the total spurious "resonance energy", R_h, due to hybridisation effects is given by:

$$R_h = 3 \times 8{\cdot}1 = 24{\cdot}3 \text{ kcal/mole} \tag{23}$$

The "true" resonance energy R_0 of benzene is then given by

$$R_0 = R - R_h = 23{\cdot}6 \text{ kcal/mole} \tag{24}$$

But this still includes differential effects of σ-bond compression. The total compression energy of the σ bonds in three molecules of ethylene is 30·5 kcal/mole, that of the six σ bonds in benzene 19·7 kcal/mole. Therefore benzene is stabilised to the extent of 10·8 kcal/mole by the relief of σ-bond strain. Consequently the real resonance energy, R_π, of benzene, due to decrease in total π energy, is given by:

$$R_\pi = R_0 - 10{\cdot}8 = 12{\cdot}8 \text{ kcal/mole} \tag{25}$$

In other words only about *a quarter* of the "observed resonance energy" of benzene is due to resonance; half is due to changes in bond energy of carbon bonds with hybridisation, and a quarter to the relief of σ-bond strain. The relief of strain is much greater than in the case of butadiene simply because the symmetrical structure of benzene allows a uniform sharing of π electrons—and so a uniformity of bond lengths—without *loss* of π energy.

"*Hyperconjugation*"

If resonance is unimportant in the ground state of butadiene, it must be completely unimportant in hyperconjugated structures such as propene. The "resonance energies" of such molecules must arise entirely from changes in bond energy with hybridisation [equations (3) to (5)]. This idea is supported very strongly by the data[9] in Table 3; the hyperconjugation energies of monoalkylethylenes are remarkably constant, and the mean hyperconjugation energies of both *sym*- and *as*-dialkylethylenes are in each case almost exactly double the value for monoalkylethylenes. It certainly seems very reasonable to ascribe the hyperconjugation energy (HCE) to a hybridisation effect [equation (5)].

We may take the mean hyperconjugation energy per alkyl group to be 2·3 kcal/mole. Hence from equation (5):

$$E''_{CC} = E_{CC} + (E'_{CH} - E_{CH}) + E'_h = 89{\cdot}9 \text{ kcal/mole} \tag{25}$$

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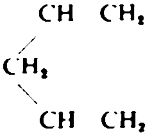
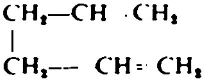
[9] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Amer. Chem. Soc.* **58**, 137, 146 (1936); M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *Ibid.* **59**, 831 (1937); M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, H. A. Smith and W. E. Vaughan, *Ibid.* **60**, 440 (1938).

TABLE 3. HEATS OF HYDROGENATION[*] AND DERIVED HYPERCONJUGATION ENERGIES (HCE) OF OLEFINES (kcal/mole)

C_2H_7	32·58
MeCH$=$CH$_2$	30·12
EtCH$-$CH$_2$	30·34
AmCH$=$CH$_2$	30·14
Pr^{i}CH CH$_2$	30·33
Bu^{t}CH CH$_2$	30·34
 $CH_2(CH{=}CH_2)_2$	2 × 30·40
 CH_2—CH=CH$_2$ CH_2—CH=CH$_2$	2 × 30·26
Mean	30·29
Mean HCE	2·29

Me$_2$C CH$_2$	28·34
MeHC$=$CH$_2$	28·49
MePr^{i}C$=$CH$_2$	28·00
MePe^{neo}C$-$CH$_2$	27·24
Mean	28·02
Mean HCE	4·56 = 2 × 2·28

trans-Butene-2	27·62
cis-Butene-2	28·57
Pentene-2	27·94
*cyclo*Hexene	28·59
*cyclo*Pentene	27·93
Mean	27·93
Mean HCE	4·65 = 2 × 2·32

The corresponding value for the bond length (equation (19)) is found to be:

$$(sp^2) - (sp^3) : 1{\cdot}523 \text{ Å} \tag{27}$$

The value reported for the exocyclic C–C bond in toluene (1·51 Å) agrees with this within the limits of experimental error.

Conjugation and resonance

The arguments given above suggest that resonance is unimportant in a molecule such as a polyene or olefine for which only one classical (unexcited) structure can be written. The "evidence" commonly quoted for resonance in such systems can be better interpreted in terms of changes in bond properties with hybridisation.

A different situation arises in aromatic compounds, and in odd conjugated systems (ions, radicals, and compounds such as cyanin dyes, which are iso-conjugate with carbanions). Here the bonds have intermediate lengths and the molecules possess stabilities greater than one would expect on the basis of hybridisation changes alone.

It would appear, therefore, that a naive form of the resonance theory, in which excited structures are neglected, gives a good qualitative account of conjugated systems.

This conclusion conflicts with the results of direct calculations by the MO method, which require considerable delocalisation of the π electrons in polyenes and corresponding changes in the lengths of bonds. This discrepancy can be ascribed to a neglect of electron correlation.

Two types of correlation can be recognised in π-electron systems: correlation effects tending to keep electrons in different AO's, and correlation effects tending to keep electrons on opposite sides of the nodal plane. Only effects of the first kind are taken into account in normal SCF MO calculations, even if configuration interaction is included. Now the second type of correlation enables electrons more easily to occupy similar positions along the carbon chain; it is due to neglect of this effect that the integrals representing mutual repulsion of pairs of electrons occupying the same AO's are overestimated in the usual treatment. As a result the SCF MO method must overestimate the delocalisation of electrons along the chain, even if configuration interaction is included. The success of the Pariser–Parr treatment, and Moffitt's "atoms-in-molecules" treatment, are undoubtedly due to their correction of these integrals; in this way they allow implicitly for the second type of electron correlation. These treatments should lead to pictures of molecules in which electron delocalisation is greatly reduced: Berry[10] has indeed found that an atoms-in-molecules treatment of butadiene leads to a picture of the ground state which corresponds closely to complete fixation of the 1 : 2 and 3 : 4 double bonds.

This question could be resolved only by direct calculation of π-electron distributions and energies by treatments in which electron correlation is explicitly taken into account. The following intuitive argument does, however, suggest that an exact treatment will lead to a picture close to that given by simple resonance theory, i.e., one in which resonance effects are significant only in molecules for which more than one classical structure can be written; and it also explains the success of current MO theory in dealing with aromatics and odd conjugative systems as well as its failure in the "classical" conjugated systems for which only one resonance structure can be written.

Consider the four π electrons in butadiene, occupying the two lobes of the π orbital. Mutual repulsion will tend to keep them apart; we may therefore expect at any instant to find two in each lobe. The two electrons in a given lobe will repel each other; they will also tend to linger in the regions between nuclei where the nuclear field is strongest. Hence the most probable distribution of the electrons should be that indicated in Fig. 2(a); these correlation effects will therefore tend to make the π electrons congregate

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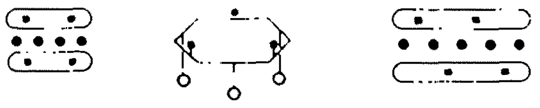
[10] J. S. Berry, *J. Chem. Phys.* **26**, 1660 (1957).

in pairs in the terminal bonds—thus accentuating the difference between "single" and "double" bonds and making the molecule approach more closely its single classical structure.



(a) (b) (c)

Fig. 2. Correlation diagrams for: (a) butadiene; (b) benzene; (c) the ion $C_5H_7^+$.

Now consider benzene. Here again the π electrons are most likely to be evenly distributed between the two π lobes, and to occupy alternate bonds; but here the two sets can be staggered (Fig. 2b) so that there is an average one π electron per bond. Here correlation effects do not hinder delocalisation of the π electrons over all the bonds in the conjugated system. The same thing can happen in "odd" systems such as the pentadienate cation (Fig. 2c).

A little consideration will show that if the electrons in a given π lobe occupy alternate bonds, they must distribute themselves in accordance with a classical structure for the molecule. Therefore, if only one classical structure is possible, both sets of π electrons distribute themselves likewise, and this correlation effect makes the molecule approach the classical structure more closely than one would otherwise expect. If more than one classical structure can be written, the two sets of π electrons can conform to different structures, giving the effect of electron delocalisation. This provides an elegant explanation for the success of simple resonance theory.

Although these arguments have been applied to conjugated systems, they must also apply to systems which are hyperconjugated. One may therefore expect significant resonance effects due to hyperconjugation only in ions or radicals, when more than one unexcited (classical) structure can be written. The fact that some of these are "no-bond" structures does not matter; the total number of real bonds is the same in all. This is illustrated in Fig. 3 for the ethyl cation.

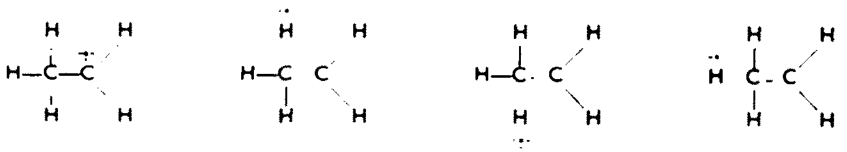


Fig. 3. Classical structures for the ion $C_2H_5^+$; note that in each case there are six real covalent bonds.

Conjugative stabilisation

The special chemical properties of benzene arise from its abnormally large heat of formation; this extra stability, compared with unconjugated analogues, is an experimental fact, and its efficacy is independent of its theoretical interpretation. The use of the term "resonance energy" for these experimentally measured quantities is therefore unsatisfactory, particularly since the argument given above suggest that only a small part of the extra heat of formation is due to resonance. It would be much better if the experimentally measured stabilisations were described as *stabilisation energies*, the term resonance energy being reserved for that part of the overall stabilisation that is due to delocalisation of electrons.

In most published work, "resonance energies" have been estimated by comparison with "reference compounds"; for example, the "resonance energy" of benzene is commonly given as the difference in heat of hydrogenation between three molecules of *cyclo*hexene and one of benzene. Our arguments indicate that this procedure is wrong in principle. A molecule such as *cyclo*hexene is conjugatively stabilised by the presence of bonds of a type (sp^2–sp^3) that are absent in benzene; the resonance energy found in this way is not only ambiguous (since it depends on the arbitrary choice of a reference compound) but it also contains irrelevant contributions from hyperconjugation in the reference compound. There will also be irrelevant steric effects, owing to conformational differences (e.g., between *cyclo*hexane and *cyclo*hexene).

Conjugation energy should be defined as the difference in heat of hydrogenation between the compound in question, and an appropriate number of molecules of simple compounds such as ethylene in which neither conjugation nor hyperconjugation is important. The same quantity can be calculated without difficulty from heats of combustion. Conjugation energies so defined are unambiguous and have an obvious chemical significance.

Further evidence for the effects of hybridisation

After the calculation described above had been completed, Bastiansen *et al.*[4] described a precision study of *cyclo*octatetraene by electron diffraction, leading to the bond lengths listed in Table 4.

TABLE 4. BOND LENGTHS (Å) IN ETHYLENE[3] AND *cyclo*OCTATETRAENE[4]

	C–C	C=C	C–H
Ethylene	-	1·334 ± 0·005	1·085 ± 0·005
*cyclo*octatetraene	1·462 ± 0·001	1·334 ± 0·001	1·090 ± 0·005

Now the bond angles in *cyclo*octatetraene preclude any significant resonance interaction between adjacent double bonds; the lengths of the CC bonds should therefore approximate closely to those of pure double and single bonds between sp^2 carbon atoms. The C=C bond length in fact agrees exactly with that found for ethylene by Bartell and Bonham[3]; but the value (1·462 Å) for the C–C bond is, if anything, *less* than that for the central bond in butadiene.

These results seem to provide unequivocal support for the argument developed in this paper. Moreover, the heat of hydrogenation of *cyclo*octatetraene agrees very closely with the value calculated from equation (1), using the bond energies listed in Table 2. It seems difficult to escape the conclusion that resonance effects are indeed unimportant in the ground state of butadiene.

The bond lengths for sp^2 carbon listed in Table 2 are, however, probably a little too large, owing to our assumption of the old value (1·353 Å) for the C=C bond. We are investigating this matter in detail; it seems unlikely that our general conclusions will be affected.

Acknowledgements—We are greatly indebted to the General Electric Company Ltd., for computational facilities, including the use of a HEC 2M computer.