418. *Hyperconjugation. Part I. Conjugation and Hyperconjugation Energies.*

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By improved calculations for a series of methyl-benzenes and -ethylenes the hyperconjugation energy per methyl group has been found to be constant.

A detailed comparison of the empirical and theoretically computed delocalisation energies of benzene and butadiene yields a value of approximately -74 kcal. for β_0, the resonance integral (including overlap) for the C═C bond distance of 1·39 Å.

The strengthening of single and double bonds by hyperconjugation is found to be less than previous estimates, the total contribution of third-order conjugation to the bond energies of both single and double bonds being only about 1·6 kcal.

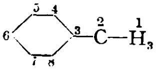
The conjugation of alkyl groups with multiple bonds is known as hyperconjugation. Methyl groups, because of their symmetry, are more effective for this purpose than higher alkyl groups. However, since alkyl groups are saturated, the degree of delocalisation is much smaller than that which occurs in ordinary conjugated systems. Nevertheless, the occurrence of hyperconjugation in certain molecules is revealed by small but definite changes in the static and dynamic characteristics of such molecules. Thus progressive alkylation of a double bond in an unsaturated molecule results not only in displacement of its ultra-violet absorption spectrum towards longer wave-lengths but also in progressive stability of the molecule, as shown by diminution of its heat of hydrogenation. In reaction kinetics the usual inductive-effect order of alkyl groups is inverted in strongly electron-demanding reactions. (For a comprehensive review see Crawford, *Quart. Reviews*, 1949, **3**, 226.)

In a study of the phenomenon, Mulliken, Rieke, and Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 41) computed the hyperconjugation energies and bond orders for a number of methylated compounds. Their work took cognisance of the fact that the resonance integral β varies with bond length and they determined its mode of variation from empirical evidence. In like manner they deduced an empirical resonance integral for hyperconjugated C–H bonds but assumed the Coulomb integral for H_3 in CH_3 to be the same as for C in C═C. On this basis they derived a value for β of about 45 kcal. per mole for a C═C bond-length of 1·33 Å and showed that hyperconjugation strengthens ordinary single and double bonds by about 2·5 and 5·5 kcal. per mole, respectively.

In a similar way Roberts and Skinner (*Trans. Faraday Soc.*, 1949, **45**, 339) calculated the hyperconjugation energies in certain hydrocarbon molecules and radicals. They determined the dependence of the resonance integral on C–C distance but neglected the non-zero values of the orthogonality integrals.

It is the purpose of the present work to improve and to extend the calculations referred to above. This we do by accepting the main feature of Mulliken's model in which the three hydrogen atoms function as a single pseudo-atom with one π-electron. The improvements consist (i) in regarding the pseudo-atom H_3 as a hetero-atom with an electronegativity different from that of carbon and (ii) in allowing for the variation of the resonance integral with distance by assuming it to be proportional to the overlap integral. In this way it will be shown that a value for β can be deduced which is close to the spectroscopic value. The delocalisation energies for a series of methyl-benzenes and -ethylenes are reported here.

Method of Calculation.—The method of calculation is that of molecular orbitals with inclusion of the overlap integral S between adjacent atomic orbitals. It will be illustrated for the case of toluene, the numbering shown in the annexed figure being used for convenience. Associated with the pseudo-atom H_3 is a π orbital formed by grouping of the three hydrogen atom $1s$ atomic orbitals. Consequently the molecule has eight π electrons, each of which is supposed to move in a molecular orbital ψ embracing all the nuclei and represented by a linear combination of the π orbitals ϕ_i so that



$$\psi = \sum_{i=1}^{8} c_i \phi_i$$

The energies of the electron levels are given by the roots of the secular equation $|H_{ij} - ES_{ij}| = 0$ in which

$$E = \int \psi^* H \psi \mathrm{d}\tau ; \; H_{ii} = \int \phi_i^* H \phi_i \mathrm{d}\tau = \alpha_i ; \; H_{ij} = \int \phi_i H \phi_j \mathrm{d}\tau = \gamma = H_{ji} ;$$

$$S_{ij} = \int \phi_i \phi_j \mathrm{d}\tau ; \; S_{ii} = \int \phi_i \phi_i \mathrm{d}\tau = 1 ; \text{ and } \beta = \gamma - S\alpha$$

In these definitions we have preserved the original significance of β and γ to facilitate comparison with Mulliken's work. Care is needed since it frequently happens now that β and γ are interchanged. All the ϕ_i are purely real functions.

In order to solve the secular equations for E and the coefficients c_i, values must be assumed for S and γ (and hence for β). These latter quantities are functions of the lengths of the individual bonds and are therefore different from S_0 and γ_0 (and β_0), the corresponding values for unsubstituted benzene. The assumption (Wheland, *J. Amer. Chem. Soc.*, 1941, **63**, 2025) that γ is proportional to S permits parameters to be defined such that

$$\rho_{12} = \gamma_{12}/\gamma_0 = S_{12}/S_0 ; \; \rho_{23} = \gamma_{23}/\gamma_0 = S_{23}/S_0 .$$

The $2p\pi$ overlap integrals which are required are easily evaluated for various lengths of bond, Slater wave functions being used and a value of 3·25 for Z, the effective nuclear charge of carbon. The results, which show a surprisingly large variation between single and triple bonds, are recorded in Table 1. They agree excellently with values interpolated from the comprehensive collection of integrals recently published by Mulliken, Rieke, Orloff, and Orloff (*J. Chem. Phys.*, 1949, **17**, 1248).

A value must also be assumed for the Coulomb term of the pseudo-atom H_3. In order to ensure π-electron migration from the methyl group into the ring, as required by the *op* directing property of the substituent in electrophilic reactions, this was taken to be a more electropositive atom than carbon, and the corresponding diagonal element H_{11} in the secular equation set equal to $\alpha + \delta_1\beta_0$ with $\delta_1 = -0{\cdot}5$. This electropositivity of H_3 was shared somewhat with the adjacent carbon atom whose Coulomb term was taken as $\alpha + \delta_2\beta_0$, with $\delta_2 = -0{\cdot}1$. There is some arbitrariness in this choice of parameters. Since, however, they are chosen to reproduce the dipole moment of toluene, assuming it to be a resonance moment, they are unlikely to be very seriously wrong. If it is agreed that δ_2 must be considerably smaller than δ_1, then values similar to those which we have selected would be almost inevitable.

TABLE 1. *Variation of* S *with bond length.*

r(C–C), Å	1·20	1·33	1·35	1·39	1·46	1·54	C–H_3
S	0·336	0·273	0·264	0·247	0·219	0·191	0·64

Now the presence of a substituent in an aromatic molecule induces a change in the electronic structure of the molecule. This effect is usually regarded as manifesting itself in two ways (Coulson, *Proc. Phys. Soc.*, 1952, **65**, *A*, 933; Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341; Longuet-Higgins and Sowden, *J.*, 1952, 1404): (i) If the substituent X possesses π electrons these will interact with or perturb the π electrons of the aromatic molecule. As a result the effective length of the conjugation path is increased. This is the conjugative effect and it results in charge shifts, and changes in π electron energies, etc.

It is taken into account by considering the appropriate number of π electrons in molecular orbitals extending over the whole nuclear framework. (ii) Since in general the electronegativity of the substituent X will be different from that of the carbon centre to which it is attached, a polarised C–X σ bond results. This in turn polarises adjacent bonds in the aromatic molecule and so the effect is transmitted. This is the inductive effect. It diminishes in magnitude with distance from the C–X bond and can be taken into account by assigning a value to H_{ii} for the carbon centre to which the substituent is attached different from α_c. As a first approximation, this latter effect is ignored in the present study except insofar as it is partly included in the parameter δ_2, the hyperconjugative effect chiefly being dealt with.

Rounded values for ρ, *viz.* $\rho_{12} = 2{\cdot}5$ and $\rho_{23} = 0{\cdot}7$, were chosen and the determinantal equation was solved to yield all eight energy values; the most negative of these corresponds to the lowest, *i.e.*, the most stable, molecular orbital. These energies are all of the form $E_j = \alpha + k_j\beta_0$, where the various k_j are found from the secular determinant. The energies are therefore computed in terms of β_0 which is here taken as a standard. Its value will subsequently be determined by comparing computed and empirical conjugation energies in benzene and butadiene which are taken as reference molecules. This procedure is superior to the previous rather troublesome trial-and-error method of determining the variation of β with distance. The four lowest energy values which result being assumed to be each doubly-filled, the total π-electron energy E^{mobile} is found to be

$$E^{\text{mobile}} = 8\alpha + 8{\cdot}6102\beta_0.$$

To obtain the delocalisation energy the total energy E^{loc} of the π-electrons in a localised bond structure must be computed. This is simply

$$\begin{aligned} 2E_{\mathrm{C\equiv H_3}} + 6E_{\mathrm{C=C(benzene)}} &= 2(\alpha + 1{\cdot}3613\beta_9) + 6(\alpha + 0{\cdot}8000\beta_0) \\ &= 8\alpha + 7{\cdot}5226\beta_0 \end{aligned}$$

The total delocalisation energy is therefore $1{\cdot}0877\beta_0$. Deducting from this the conjugation energy of benzene, *viz.*, $1{\cdot}0666\beta_0$, we obtain $0{\cdot}0211\beta_0$ as the extra stability of the molecule due to conjugation between the methyl group and the benzene ring. Hyperconjugation energies obtained in this way for several methyl-benzenes and -ethylenes are recorded in Table 2 in units of β_0.

Empirical Conjugation Energies.—For the empirical determination of conjugation energies two methods are available. They are based on the heats of hydrogenation and combustion. Although heats of hydrogenation normally provide the most accurate data for the determination of conjugation energies, these are not as extensive as might be desired. Consequently, heats of combustion (National Bureau of Standards, Project **44**) which have been determined with greater accuracy have been used for this purpose. It has been shown (Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41) that the following expression fits with great fidelity the data for non-conjugated hydrocarbons:

TABLE 2. *Hyperconjugation Energies (H.E.) of Methyl-benzenes and -ethylenes.*

	Computed (in units of β_0)			Empirical (in kcals.)	
Molecule	H.E.	No. of Me groups	H.E. per Me group	H.E. (Δ)	H.E. per Me group
Toluene	0·0211	1	0·0211	1·5	1·5
o-Xylene	0·0423	2	0·0211	2·54	1·27
m-Xylene	0·0422	2	0·0211	2·96	1·48
p-Xylene	0·0422	2	0·0211	2·79	1·39
Mesitylene	0·0632	3	0·0211	4·54	1·51
Durene	0·0845	4	0·0211	5·66	1·41
Propylene	0·0242	1	0·0242	1·20	1·20
cis-Butene	0·0485	2	0·0242	1·06	0·53
*iso*Butene	0·0477	2	0·0239	2·11	1·55
Tetramethyl ethylene	0·0961	4	0·0240	3·05	0·76

$$-\Delta H_{298} = 54{\cdot}625N_{\mathrm{CH}} + 48{\cdot}25N_{\mathrm{CC}} - 1{\cdot}5N_{\mathrm{Me}} + 22{\cdot}18N_{\mathrm{C=C}} + 56{\cdot}6N_{\mathrm{C\equiv C}} \quad . \quad (1)$$

Here, N_{CH}, N_{CC}, $N_{\mathrm{C=C}}$, $N_{\mathrm{C\equiv C}}$ are the numbers of C–H bonds, C–C bonds, C=C double bonds, C≡C triple bonds, respectively, and N_{Me} is the number of methyl groups. Negative departures Δ from heats of combustion predicted by this equation yielded the figures recorded in column 5 of Table 2. (The figures for the methylbenzenes were obtained after subtraction from the total conjugation energy of that due to benzene.)

Corrections for Extension and Compression of Bonds and Third-order Conjugation.—The direct comparison of theoretically computed and empirically determined conjugation energies is not a completely fair one for two reasons:

(i) The total energy of a conjugated molecule involves not only the energy of the π electrons, but also the energy of compression and extension of the C–C σ bonds. In the calculation of empirical conjugation energies, therefore, account must be taken of the changes in the lengths of the bonds. The importance of doing this has recently been stressed by several workers (*e.g.*, Lennard-Jones, *Proc. Roy. Soc., A*, 1937, **138**, 280; Mulliken, Rieke, and Brown, *loc. cit.*; Hornig, *J. Amer. Chem. Soc.*, 1950, **72**, 5772; Coulson and Altmann, *Trans. Faraday Soc.*, 1952, **48**, 293). Here the compression and extension energies $C_s(r)$ and $C_d(r)$ were calculated from Morse functions

$$C(r) = D\{\exp[-a(r - r_e)] - 1\}^2$$

in which the exponent a was obtained from the expression

$$a = (k_e/2D)^{\frac{1}{2}}$$

where k_e is the bond force constant and D the bond dissociation energy. The following reasonable values of these parameters were used:

Bond type	D (kcal.)	$10^8 r_e$	$10^5 k_e$, dyne cm.$^{-1}$
C—C	83	1·54	4·5
C=C	141·5	1·33	8·2

and the results obtained set out in Table 3. Small variations from these values of the parameters would not sensibly affect our results.

TABLE 3. *Compression energies (kcal./mole).*

r(C–C), Å ...	1·54	1·52	1·49	1·46	1·43	1·39	1·36	1·33	1·30	1·27	1·24	1·22	1·20
$C_s(r)$	0·00	0·13	0·90	2·43	4·98	9·98	15·27	23·09	30·78	41·61	54·72	65·15	83·17
$C_d(r)$	17·42	14·81	11·11	7·78	4·88	1·90	0·50	0·00	0·56	2·41	5·80	9·01	13·10

(ii) Since the single bond in ethane is strengthened by third-order conjugation, the ideal single bond is one which is slightly longer (Mulliken, Rieke, and Brown, *loc. cit.*) than that found in ethane. Similarly the ideal double bond is one which is weaker and slightly longer than that of ethylene. In computing the total conjugation energy therefore in a system containing single and double bonds, allowance must be made for the strengthening of these bonds compared with the ideal standards. For example, in benzene where all the bonds are of equal length, this additional strengthening (R_y) is simply six times that per single bond calculated for the length obtaining in benzene. The total conjugation energy computed theoretically is therefore given by

$$R = R_x + R_y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where R_x is the ordinary or first-order conjugation.

Here the third-order conjugation energies for both ethane and ethylene were obtained on the basis of the same secular equations, it being assumed that $\rho_{C\equiv H_3}$ is the same as $\rho_{C=H_2}$. When overlap is included, the calculation of third-order conjugation energy is straightforward. It may readily be shown to be

$$2\beta_0 \left\{ \frac{2S_0\rho_{12}{}^2 + (\rho_{23}{}^2 + 4\rho_{12}{}^2)^{\frac{1}{2}}}{1 + S_0{}^2\rho_{12}{}^2 + S_0(\rho_{23}{}^2 + 4\rho_{12}{}^2)^{\frac{1}{2}}} - \frac{2\rho_{12}}{1 + S_0\rho_{12}} \right\}$$

per dimension where ρ_{12} and ρ_{23} refer to the $C\equiv H_3$ and C=C bonds, respectively. This expression being used, values of R_y per bond were computed for various bond lengths. The results obtained are set out in Table 4.

Now it has been shown (Mulliken, Rieke, and Brown, *loc. cit.*) that

$$R = \Delta + C + 2\delta_{1\cdot 54}N_{C-C} + \delta_{1\cdot 33}N_{C=C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where C is the energy correction for changes in bond length due to conjugation, and δ is the hyperconjugation energy per bond per dimension for bond lengths of 1·54 and 1·33 Å, respectively.

Comparison of expressions (2) and (3) shows that

$$\Delta + C = R_x + R_y - 2\delta_{1\cdot54}N_{C-C} - \delta_{1\cdot33}N_{C=C} \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

Table 5 (drawn up in a similar manner to Table 6 of the paper by Mulliken, Rieke, and Brown) contains the theoretically computed quantities occurring on the right side of equation (4). In addition, for the reference molecules benzene and butadiene, the theoretically computed $\Delta + C$ (in column 7) is compared with the empirical value (column 10).

Discussion.—Table 2 shows clearly that the hyperconjugation energy per methyl group is constant in both series of compounds. However, the computed magnitude of this quantity is slightly greater in the ethylene than in the benzene series. This is accounted for by the fact that the magnitude of the delocalisation energy is sensitive to the value of ρ which will be different for the two series of compounds because of the slightly different bond lengths.

TABLE 4. *Third-order conjugation energies*: $\delta(r)$ *values.*

r(C–C), Å	1·54	1·46	1·39	1·35	1·33
$\delta(r)$, in units of β_0	0·0092	0·0122	0·0154	0·0176	0·0187

The almost exact constancy of the hyperconjugation energy per methyl group is parallel to a similar additivity relation for charge migrations caused by hyperconjugation, reported in the following paper. This provides a partial justification for treating the whole effect as a perturbation one and considering only first-order perturbation theory. Such an approach to the problem has sometimes been made in the past, though without the detailed support provided by our present calculations.

There are two values of the delocalisation energy of *cis*- and *trans*-butene because in expression (1) no distinction is made between isomeric compounds. Since, however, the thermal data for these compounds do differ, this is reflected in differences in the delocalisation energies.

TABLE 5. *Conjugation energies.*

		Theoretical, in units of $\lvert\beta_0\rvert$					Empirical, in kcals.			
Molecule	r(C–C), Å	R_x	R_y	R	Deduction *	$\Delta + C$	Δ	C	$\Delta + C$	β_0
Benzene	1·39	1·0666	0·0924	1·1590	0·1113	1·0477	39·46	35·49	74·95	−71·6
Toluene	1·39 1·54	1·0877	0·1016	1·1893	0·1297	1·0596	—	—	—	—
o-Xylene	1·39 1·54	1·1089	0·1108	1·2197	0·1481	1·0716	—	—	—	—
m-Xylene	1·39 1·54	1·1088	0·1108	1·2196	0·1481	1·0715	—	—	—	—
p-Xylene	1·39 1·54	1·1088	0·1108	1·2196	0·1481	1·0715	—	—	—	—
Mesitylene	1·39 1·54	1·1298	0·1200	1·2498	0·1665	1·0833	—	—	—	—
Durene	1·39 1·54	1·1511	0·1292	1·2803	0·1849	1·0954	—	—	—	—
Propylene	1·33 1·54	0·0242	0·0279	0·0521	0·0371	0·0150	—	—	—	—
cis-Butene	1·33 1·54	0·0485	0·0371	0·0856	0·0555	0·0301	—	—	—	—
Tetramethyl-ethylene	1·33 1·54	0·0961	0·0555	0·1516	0·0923	0·0593	—	—	—	—
Butadiene	1·35 1·46	0·1253	0·0474	0·1727	0·0558	0·1169	5·45	3·43	8·88	−75·9

* $2\delta_{1\cdot54}N_{C-C} + \delta_{1\cdot33}N_{C=C}$.

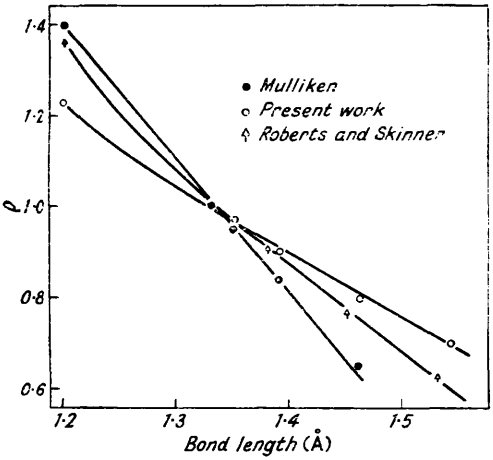
The values obtained for $|\beta_0|$ by comparison of the theoretical and empirical conjugation energies (see Table 5, columns 7, 10, and 11) of benzene and butadiene are 71·6 and 75·9 kcal., respectively. An average value for $|\beta_0|$ of 73·8 kcal. being used, the third-order conjugation energies computed here are set out in Table 6 together with those of Mulliken, Rieke, and Brown (M.R.B.), and Roberts and Skinner (R.S.).

The magnitudes of the third-order conjugation energies presented here are appreciably less than the M.R.B. and R.S. values. The large difference between the results contained in the third and the fourth rows of the Table is no doubt due to the fact that, although Roberts and Skinner determined the variation of β with distance, the overlap integral was neglected. Although Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025) concluded that for unsubstituted hydrocarbons its neglect is not a source of error, Skinner himself points out that Wheland's calculations were not made from the starting point of a dependence of β on distance.

A further reason for the discrepancy between the figures in rows two and three and those in the fourth row is ascribed to the different rates of variation of β with distance in the three sets of calculations. This is shown clearly in the Figure in which the variation of ρ with bond length is plotted. It is at once evident that the variation of β with distance in the present work is much less rapid than that previously obtained.

Although there is no means of directly determining third-order conjugation energies, the values obtained in the present study would seem to be more reasonable than the results of the two previous computations. Even allowing for the fact of a more intense conjugation across a shorter bond, a third-order conjugation energy of 5—7 kcal. in ethylene seems rather large. If it were indeed so, this would mean that the third-order conjugation in ethylene is comparable with ordinary conjugation between the two double bonds, as in butadiene. This is hardly likely.

Variation of C–C *resonance integral* $\beta(\rho = \beta/\beta_0)$ *as a function of bond length.*



The value of β_0 (= —73·8 kcal./mole) which we have obtained is larger than the value to be expected without the inclusion of overlap integrals, and a little larger than that recently obtained by Mulliken (*J. Chem. Phys.*, 1949, **46**, 497), but it lies in the region which is now considered plausible. In particular it corresponds closely with the " spectroscopic " value, chosen to fit the ultra-violet absorption of ethylene or benzene. It must be considered reasonably satisfactory that although our value of β_0 is greater than that of Mulliken, Rieke, and Brown, our third-order conjugation energies are smaller.

TABLE 6. *Third-order conjugation energies in kcal./mole (per dimension of pseudo π-electrons).*

r(C–C), Å	1·55	1·53	1·45	1·39	1·34
M.R.B.	—	1·35	2·37	3·93	5·54
R.S.	2·50	2·76	4·20	5·6	7·08
Present work	0·78	—	0·90	1·14	1·58

In conclusion it is important that the uncertain nature of some of our assumptions should be stressed. Three of these appear to us to be of greater significance than the rest. The first—and most important—is the chief point of the model, whereby an H_3 group is represented by a single pseudo-atom with one π-electron. This carries with it the assumption that the carbon atom also has π-electron orbitals (to permit the extended conjugation). This suggests strongly that this carbon atom should be regarded as digonally hybridised—a conclusion which is at variance with more conventional and simple descriptions of normal saturated carbon compounds. The second assumption is that when the system is treated as a π-electron system, there is no π–σ resonance. Recent work (Altmann, *Proc. Roy. Soc.*, *A*, 1952, **210**, 327, 343) suggests that even in ethylene there may be some resonance interaction between π and σ bonds. It might be expected that this would be more important still in the conjugation of methyl groups with unsaturated and aromatic systems. Finally—though this is partly included in our second assumption—the hypothesis that one single configurational wave-function is adequate to describe the molecule would appear unjustified in view of the work of Coulson, Craig, and Jacobs (*Proc. Roy. Soc.*, *A*, 1950, **202**, 498; 1951, **206**, 287, 297), on configurational interaction.

These three difficulties are in addition to those associated with the method of molecular orbitals itself, and which are well known. Notwithstanding the semi-empirical character which these difficulties force upon our calculations, we believe that they do provide further support for the general picture of the phenomenon of hyperconjugation as put forward by Mulliken.

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