methane does not give rise to rotational motion around all axes.

The curve for trichlorofluoromethane in Fig. 2 shows no transition in the solid, although the slightly higher than usual dielectric constant of the solid, together with its appreciable decrease with decreasing temperature, suggests some dipole orientational freedom, possibly, arising from loosening caused by rotation around the C–F axis.

When these results are regarded as a whole, it is evident that the rounded-off tetrahedra formed by the molecules of the tetrahalogenated methanes, CX_xY_y, can rotate over hindering potential energy barriers in the crystal lattice in a temperature region extending not far below the melting point, when the ratio of the van der Waals C–X radius to the C–Y radius lies between 1.00 and 1.09. When the ratio is 1.31 or larger, the hindering potential barrier is too high to permit passage by rotational motion. This might be expressed in a different and obvious way by saying that, when one halogen on the central carbon atom exceeds another in "crystal" radius by as much as 33%, and, possibly, by more than 9%, they cannot exchange lattice positions by rotation of the molecule. Of the last six substances in Table II, which have a single threefold axis of symmetry in the molecule, rotation is apparently permitted about this axis in trifluorochloromethane, bromotrichloromethane and tribromofluoromethane above a transition point. For tribromochloromethane, where the ratio is only 1.09, it appears that rotation like that in the CX_4 class is permitted. For trichlorofluoromethane and bromotrifluoromethane, the decrease of dielectric constant with decreasing temperature for some distance below the freezing point suggests the possibility of a gradually decreasing amount of rotation about the axis of symmetry in contrast to a discontinuous transition. The extreme sharpness of the drop in the dielectric constant on freezing of dichlorodifluoromethane (Fig. 2), dibromodifluoromethane (Fig. 2), bromochlorodifluoromethane (Fig. 3) and bromotrifluoromethane (Fig. 3) testifies to the high purity of the materials. It appears, therefore, that some molecular mobility exists for several degrees below the freezing point, as evidenced by the rounding off of the vertical drop of the curves. Since this effect is most pronounced in the symmetrical trichlorofluoromethane, decreases in the less symmetrical dichlorodifluoromethane and dibromodifluoromethane, and is least in unsymmetrical bromochlorodifluoromethane, it seems probable that this is a true lattice property and not the effect of traces of liquid due to impurities. The large effect of specific volume changes upon the shape of the dielectric constant–temperature curve for substances of small molecular dipole moment is shown in the curves for dibromodichloromethane and bromotrichloromethane, which have moments, 0.25×10^{-18} and 0.21×10^{-18}, respectively,[6] and, consequently, small dielectric constants. For substances of large moment and dielectric constant, neglect of volume changes normally does not affect the conclusions to be drawn from the curves.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Hyperconjugation

BY ALF LOFTHUS[1]

RECEIVED JULY 16, 1956

The original work on hyperconjugation of Mulliken, Rieke and Brown has been repeated, including overlap between adjacent atoms, and using some improved assumptions regarding parameters to be used in the semi-empirical LCAO-MO method, and improved empirical data. With the chosen parameters the calculations lead to fairly consistent results for the different examples of conjugated molecules under investigation. The second-order hyperconjugation was found to be small; the contribution is only about 1.4 kcal./mole and 1.1 kcal./mole for a single and double bond, respectively.

Introduction

It has since long been known that groups such as CH_3 and CH_2 should be able to conjugate with multiple bonds. This effect has been called hyperconjugation.[2]

A theoretical approach to the problem of hyperconjugation, based on semi-empirical molecular orbital calculations, was first made by Mulliken, Rieke and Brown.[3] Their basic principle was that two or three ordinary single bonds from a carbon atom to any two or three other atoms may be regarded as constituting a quasi-double or quasi-triple bond whenever there is opportunity for conjugation with a second (quasi or ordinary) multiple linkage. Thus the difference in the conjugation power of $—C{\equiv}H_3$, $—C{\equiv}N$, $—C{\equiv}C—$, etc., are quantitative rather than qualitative in character.

Further, Mulliken, Rieke and Brown classified conjugation in general in the following way

$HC{\equiv}C—C{\equiv}CH$ $N{\equiv}C—C{\equiv}N$	ordinary (first-order) conjugation
$H_3{\equiv}C—C{\equiv}CH$ $H_3{\equiv}C—C{\equiv}N$	second-order conjugation (first-order hyperconjugation)
$H_3{\equiv}C—C{\equiv}H_3$	third-order conjugation (second-order hyperconjugation)

---

[1] Royal Norwegian Council for Scientific and Industrial Research Fellow. Permanent address: Department of Physics, The University of Blindern, Oslo, Norway.

[2] For a general review, see V. A. Crawford, *Quart. Rev.*, **3**, 226 (1949), and J. W. Baker: "Hyperconjugation," the Clarendon Press, Oxford, 1952. See also the papers by Mulliken, Rieke and Brown,[3] Coulson and Crawford[5] and I'Haya[6,7] and references cited there.

[3] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

According to this viewpoint, nearly all saturated organic molecules are stabilized by second-order hyperconjugation, usually of a rather complicated character.

The ordinary conjugation energy for conjugated molecules has been computed by several writers, with the result that it is very nearly proportional to the number of C–C single bonds. Mulliken, Rieke and Brown therefore found it reasonable to postulate that the hyperconjugation energy of saturated hydrocarbons is to a good approximation proportional to the number of C–C bonds. The hyperconjugation energy per C–C bond should then be constant, which is in harmony with the constancy of the C–C bond length (1.54 Å.) in saturated molecules. They pointed out that it is not feasible to make computations of the second-order hyperconjugation energy except for relatively simple or symmetrical molecules. For saturated molecules one has to rely largely on computations for ethane in order to establish the normal contributions of second-order hyperconjugation to the total binding energy.

It has been found that second-order hyperconjugation is of minor importance in ordinary organic reactions. On the contrary, however, the first-order hyperconjugation between CH_2, CH_3, CH_3R and similar groups and multiple bonds is of major importance in the interpretation of the abnormal reaction rates and increase in dipole moments of alkyl-substituted molecules, displacements of the ultraviolet absorption spectrum toward longer wave lengths, increase in stability with progressive alkylation of a double bond in unsaturated molecule, and similar phenomena. The general term "Hyperconjugation" is usually used for this type of conjugation.

In their work, Mulliken, Rieke and Brown[3] calculated the hyperconjugation energies and both orders for some methylated hydrocarbon molecules, and found that about 2.5 kcal./mole of the normal bond energy of the 1.54 Å. C–C bond, and about 5.5 kcal./mole of the 1.33 Å. C=C bond is due to second-order hyperconjugation. They made allowance for variation of the resonance integral with bond length, but assumed the Coulomb integral for H_3 to be the same as for the carbon atom in the system. The overlap integrals were neglected.

Roberts and Skinner[4] calculated the hyperconjugation energies in some hydrocarbon molecules and radicals, assuming a certain dependence of the resonance integral on the C–C distance. Overlap integrals were neglected. Their results gave somewhat higher second-order hyperconjugation energies than those by Mulliken, Rieke and Brown, but of the same order of magnitude.

Coulson and Crawford[5] improved and extended the calculations referred to above. The improvements consisted in (1) regarding the atom group H_3 as a heteroatom with an electronegativity different from that of carbon, (2) including of overlap integrals between adjacent atoms, and (3) allowing for the variation of the resonance integral with bond distance by assuming it to be proportional to the overlap integral. The conjugation energies for a series of methylbenzenes and -ethylenes were reported. The second-order hyperconjugation energies were much less than those found by Mulliken, Rieke and Brown and by Roberts and Skinner.

Recently, I'Haya[6,7] in two papers discussed the extension and application of the hyperconjugation theory to computations of (1) the electronic structure of methyl- and ethyl-substituted acetylenes and benzenes, not including overlap integrals and (2) conjugation and first- and second-order hyperconjugation energies for a series of alkylbenzenes, including overlap integrals for adjacent atoms. The second-order hyperconjugation energies were found to be considerably less than any previous evaluations.

In a subsequent paper I'Haya[8] repeated the computations of the second-order hyperconjugation energies under some new assumptions, the most important of which were (1) the resonance integral β to be proportional to the overlap integral S, while in the previous work $\gamma = \beta + S\alpha$ was assumed to be proportional to S and (2) a value -0.3 for the electronegativity parameter δ as determined semi-theoretically, while a δ value -0.5 was used previously. The results gave considerably larger values for the second-order hyperconjugation energies, and were now more in accordance with those given by Coulson and Crawford.

In the present work the calculations made by Mulliken, Rieke and Brown[3] were repeated under extended and improved assumptions: (1) overlap integrals for adjacent atoms were included; (2) both Slater and SCF AOs were used, and the results compared; (3) allowance was made for an electronegativity of the H_3 and H_2 groups different from that of the adjacent C-atom; (4) the resonance integral β was assumed to be proportional to the overlap integral S[9]; (5) correction for an error in a previous formula for the total conjugation energy was made; (6) more accurate bond distance measurements were used, probably leading to better values for the compression and extension energies; (7) an improved formula for the observed conjugation energies was used.

The purpose of these calculations was twofold—first either to show that the whole mass of data on "observed" conjugation and hyperconjugation energies is consistent as between the different examples of conjugation and first-order hyperconjugation, or else to find out under what conditions or what assumptions as to parameter values this would be true. The second purpose of the calculations, then, was to calculate second-order hyperconjugation energies as functions of bond distance by using the chosen parameters.

Method of Calculation

In these calculations the simple method of molecular LCAO orbitals with inclusion of overlap integrals S between adjacent atoms was used. Each of the π-electrons of a conjugated molecule is sup-

---

[4] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

[5] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

[6] Y. I'Haya, *Bull. Chem. Soc.* (*Japan*), **28**, 369 (1955).

[7] Y. I'Haya, *ibid.*, **28**, 376 (1955).

[8] Y. I'Haya, *J. Chem. Phys.*, **23**, 1171, 1165 (1955).

[9] R. S. Mulliken, *J. chim. phys.*, **46**, 675 (1949), sec. 28.

posed to move in a molecular orbital ψ of the type $\psi = \sum_i c_i\phi_i$, where the ϕ_i's are the atomic π orbitals. The energies of the electron levels are then given by the roots of the secular equation $|H_{ij} - S_{ij}E| = 0$, where

$$E = \int\psi H\psi d\tau,\ H_{ii} = \int\phi_i^*H\phi_i d\tau = \alpha_{ii}$$

$$H_{ij} = H_{ji} = \int\phi_i^*H\phi_j d\tau = \gamma_{ij}$$

$$S_{ij} = S_{ji} = \int\phi_i^*\phi_j d\tau,\ S_{ii} = 1$$

We now introduce the quantities

$$\beta_{ij} = \gamma_{ij} - {}^1/_2 S_{ij}\,(\alpha_{ii} + \alpha_{jj}),\ x_{ij} = {}^1/_2(\alpha_{ii} + \alpha_{jj}) - E$$

such that

$$\gamma_{ij} - S_{ij}E = \beta_{ij} + S_{ij}x_{ij}$$

and the secular equation takes the form

$$|\beta_{ij} + S_{ij}\,x_{ij}| = 0$$

In order to take into account the variance of β_{ij} with bond lengths, we assume $\beta_{ij} = \rho_{ij}\beta_0$, where the parameter $\rho_{ij}(r)$ is supposed to be of the form[9]

$$\rho_{ij}(r) = S_{ij}(r)/S_0(1.353)$$

where $S_{ij}(r)$ is the overlap integral between two atoms of arbitrary distance, $S_0(1.353)$ the overlap integral for a pure C=C bond, and β_0 the resonance integral for the same bond.

The different electronegativities for various atoms are accounted for by introducing a parameter δ defined by the expression

$$\alpha_{kk} = \alpha_0 + \delta_{kk}\beta_0$$

such that

$$\begin{aligned} x_{ij} &= {}^1/_2(\alpha_{ii} + \alpha_{jj}) - E \\ &= {}^1/_2(\alpha_0 + \delta_{ii}\beta_0 + \alpha_0 + \delta_{jj}\beta_0) - E \\ &= x_0 + ({}^1/_2\delta_{ii}\beta_0 + {}^1/_2\delta_{jj}\beta_0) \end{aligned}$$

where

$$x_0 = \alpha_0 - E$$

In these calculations we assume that α has the same value for all carbon atoms in the system, *i.e.*, $\delta_{CC} = 0$, but that α for the H_2 or H_3 group may be equal to or different from that of carbon, *i.e.*, δ_{H_3} or $\delta_{H_2} \leqq 0$. Three different values for δ were used, namely, 0, −0.25 and −0.50.[10]

The values of the overlap integrals required were taken from tables by Mulliken, Rieke, Orloff and Orloff[12] for Slater AO, and from tables by Mulliken[13] for SCF-AO.

The overlap integrals for the $C\equiv H_3$ and $C=H_2$ groups were calculated in a different way. Following Mulliken, Rieke and Brown,[3] the three hydrogen atom ls AO's of an H_3 group, called a, b and c, are arranged in an equilateral triangle, with atom c in the *yz*-plane. Then the following linear combinations of these resemble AO's of the kind mentioned at the right

$$\begin{aligned} [\sigma] &= (a + b + c)/(3 + 6S)^{1/2} \text{ like } 2pz \\ [x] &= (a - b)/(2 - 2S)^{1/2} \text{ like } 2px \\ [y] &= (a + b - 2c)/(6 - 6S)^{1/2} \text{ like } 2py \end{aligned}$$

Similarly, for the $C=H_2$ group we have

$$\begin{aligned} [\sigma] &= (a + b)/(2 + 2S)^{1/2} \text{ like } 2pz \\ [x] &= (a - b)/(2 - 2S)^{1/2} \text{ like } 2px \end{aligned}$$

It can be shown by simple trigonometry that the overlap integral between the H_3 group and the C atom is independent of a rotation of the triangle relative to the C atom 2p orbitals, and is given by

$$S(C\equiv H_3) = 2^{1/2}S(\text{ls, } 2p\sigma)\ \sin{}^1/_2\chi/(1 - S_{HH})^{1/2}$$

where χ is the HCH angle. Exactly the same formula applies to the $C=H_2$ group.

The S and ρ values used in these calculations are listed in Table I.[14]

The solutions of the secular equations are all of the form $x_0 = \alpha_0 - E_j = k_j(-\beta_0)$, and give the energy per electron per orbital. β_0, which is taken as energy standard, will be determined by comparison between computed and empirical energies.

The total non-localized energy is found as the sum of the energies of the lowest filled orbitals. The energy of a localized orbital i-j is found by forming secular equations of the type

$$\begin{vmatrix} d_{ii} & d_{ij} \\ d_{ij} & d_{jj} \end{vmatrix} = 0$$

where the *d*'s are the same elements as in the secular equations for the non-localized orbitals.

Finally, the total conjugation energy is found as the difference between the total localized and the total non-localized energy of the lowest filled orbitals

$$\text{C.E.} = E_{loc} - E_{non-loc}$$

The conjugation energies thus found are recorded in Table III as $(\Delta + C)_{calcd}$ in units of $-\beta_0$.

TABLE I

VARIATION OF S AND ρ WITH BOND LENGTH

R(CC), Å.	Slater AO S_{CC}	Slater AO ρ_{CC}	SCF AO S_{CC}	SCF AO ρ_{CC}
1.207	0.334	1.265	0.426	1.191
1.22	.327	1.237	.419	1.174
1.35	.268	1.005	.360	1.004
1.353	.264	1.000	.358	1.000
1.356	.262	0.994	.355	0.996
1.37	.256	.970	.350	.977
1.397	.246	.930	.340	.950
1.460	.220	.833	.315	.870
1.47	.218	.820	.312	.862
1.53	.195	.740	.292	.816
1.543	.191	.723	.288	.808
	$S_{CH_3(2)}$	$\rho_{CH_3(2)}$	$S_{CH_3(2)}$	$\rho_{CH_3(2)}$
Ethane	0.629	2.382	0.692	1.933
Ethylene	.665	2.519	.731	2.042
Propylene	.626	2.371	.691	1.930
Methylacetylene	.626	2.371	.691	1.930
Dimethylacetylene	.626	2.371	.691	1.930

---

(10) Coulson and Crawford[5] chose $\delta_1 = -0.5$ and $\delta_2 = -0.1$, so as to reproduce the dipole moment of toluene. Muller, Pickett and Mulliken[11] gave theoretical evidence in favor of a δ_1 in neighborhood of −0.5. Recently, Y. I'Haya[8] from theoretical calculations found δ_1 to be approximately −0.3.

(11) N. Muller, L. W. Pickett and R. S. Mulliken, THIS JOURNAL, **76**, 4770 (1954).

(12) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(13) R. S. Mulliken, *ibid.*, **19**, 900 (1951).

(14) The bond distances listed in column 1 of Table I and III are from the most recent measurements. Note that the C=C distance in ethylene now is supposed to be 1.353 Å.,[15] while 1.33 Å. has been used in previous calculations.

(15) G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 215 (1952).

TABLE II

HEATS OF FORMATION AND "OBSERVED" CONJUGATION ENERGIES

Mole	ΔH_f^0(0°K.), kcal./mole Calcd.	Obsd.	Δ, kcal./mole
Ethane	−16.30	−16.517	0.22
Ethylene	14.52	14.522	0
Benzene	65.82	24.000	41.82
1,3-Butadiene	36.46	29.78	6.68
Diacetylene	114.52	?	?
Propylene	10.08	8.468	1.61
Methylacetylene	49.11	46.017	3.09
Dimethylacetylene	45.45	38.09	7.36

TABLE III

CONJUGATION ENERGIES

				Computed, in terms of $-\beta_0$				Obsd., in kcal./mole				
	r(CC), A.	R_x		$N_s\delta_s$		$(\Delta + C)_{\text{calcd}}$		$\Delta_{\text{obsd.}}$	C	$(\Delta + C)_{\text{obsd}}$	$-\beta_0$kcal.	
		Slater	SCF	Slater	SCF	Slater	SCF				Slater	SCF
Benzene	1.397	1.0004	0.8440	0.0453	0.0426	0.9551	0.8014	41.82	32.5	74.3	77.8	92.7
		1.0004	.8440	.0444	.0393	.9560	.8047				77.7	92.3
		1.0004	.8440	.0384	.0282	.9620	.8158				77.2	91.1
1,3-Butadiene	1.470	0.1152	.0864	.0118	.0120	.1034	.0744	6.68	2.1	8.8	85.1	118.3
	1.356	.1152	.0864	.0115	.0111	.1037	.0753				84.9	116.9
		.1152	.0864	.0100	.0080	.1052	.0784				83.7	112.2
Diacetylene	1.37	.1032	.0760	.0164	.0153	.1736	.1214	?	6.0			
	1.22	.1032	.0760	.0160	.0142	.1744	.1236					
		.1032	.0760	.0139	.0103	.1796	.1314					
Propylene	1.53	.0314	.0314	.0096	.0107	.0218	.0207	1.61	0	1.6	73.4	77.3
	1.35	.0324	.0322	.0094	.0099	.0230	.0223				69.6	71.7
		.0340	.0362	.0081	.0072	.0259	.0290				61.8	55.2
Methylacetylene	1.460	.0312	.0270	.0122	.0122	.0380	.0296	3.09	1.1[a]	4.2	110.5	141.9
	1.207	.0318	.0276	.0119	.0113	.0398	.0326				105.5	128.8
		.0334	.0306	.0103	.0082	.0462	.0448				90.9	93.8
Dimethylacetylene	1.460	.0642	.0566	.0244	.0244	.0796	.0644	7.36	2.2[a]	9.6	120.6	149.1
	1.207	.0650	.0576	.0238	.0226	.0824	.0700				116.5	137.1
		.0678	.0616	.0206	.0164	.0944	.0904				101.7	106.2

[a] Allowance is also made for a certain shortening of the single bond distance as due to decreased single bond radius of acetylenic carbon (see ref. 3, Table VI, footnote *g*).

Comparison of Computed and Observed Conjugation Energies

Observed Conjugation Energies.—The "observed" conjugation energies are found as differences between calculated and observed heats of formation, ΔH_f^0(0°K.), where ΔH is in kcal./mole.

The following formula[16] was used for the calculated ΔH

$$\Delta H_f^0(0°\text{K.}) = -3.55N_{\text{C-H}} + 5.00N_{\text{C-C}} + 28.72N_{\text{C=C}} + 61.43N_{\text{C}\equiv\text{C}} - 0.78n$$

where

$$n = n_{\text{C-C}} + n_{\text{C=C}} + n_{\text{C}\equiv\text{C}}$$

$n_{\text{C-C}}$ is the sum, taken over all C–C single bonds, of the number of bonds going out from the two carbon atoms of the given bond to other carbon atoms; $n_{\text{C=C}}$ and $n_{\text{C}\equiv\text{C}}$ are similar sums for C=C and C≡C bonds.

The observed heats of formation were taken from the API tables.[17] $\Delta H_f^0(0°\text{K.})_{\text{calcd}}$, $\Delta H_f^0(0°\text{K.})_{\text{obsd}}$, and the "observed" conjugation energies Δ_{obsd} are recorded in Table II. Δ_{obsd} is also recorded in Table III.

Corrections for Extension and Compression of Bonds.—In addition to the π-electron energy, the total conjugation energy of a molecule also involves the energy of compression and extension of the C–C bonds. Account must therefore be taken of changes in bond lengths due to conjugation.

The compression and extension energies were calculated from Morse functions

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

where $a = (K/2D)^{1/2}$, K the bond force constant, D the bond dissociation energy, r the actual bond length, and r_e the "ideal" single or double bond distance.

The following values of these constants were used

Bond type	D(kcal.)	$10^8 r_e$(cm.)	$10^6 K$(dyne cm.$^{-1}$)
C—C	83	1.543	4.5
C=C	141.5	1.353	8.2

The $C(r)$ values thus found, and $(\Delta + C)_{\text{obsd}}$, are recorded to the right in Table III.

Correction for Second-order Hyperconjugation.—Before we can compare the observed energies with the calculated ones, it is necessary to deduct from the calculated ones the amount of second-order hyperconjugation which must, according to the assumptions, be present in normal molecules. This is because a single bond in ethane and a double bond in ethylene are strengthened by second-order hyperconjugation, such that an ideal single and an ideal double bond are slightly weaker and longer than found in ethane and ethylene, respectively.

In the following we use the same procedure as given by Mulliken, Rieke and Brown.[3]

---

(16) R. S. Mulliken and R. G. Parr, *J. Chem. Phys.*, **19**, 1271 (1951), eq. 23a. A misprint in this equation ($-5.00\ N_{\text{C-C}}$) is corrected for and a term for triple bonds to fit acetylene is added.

(17) "Selected Values of Chemical Thermodynamics Properties," National Bureau of Standards, Washington, D. C.

The total conjugation energy R, of all orders, can be written as[18]

$$R = \Delta + C + 2\delta_s N_s + \delta_d N_d$$

where

Δ is "obsd." conjugation energy
C is the energy correction for changes in bond lengths by conjugation
δ_s and δ_d are the hyperconjugation energy per bond dimension for actual bond lengths of a single bond and a double bond, respectively

N_s and N_d are the the no. of single and double bonds, respectively

Further, the total conjugation energy is given by

$$R = R_x + R_y$$

For the molecules dimethylacetylene, methylacetylene, diacetylene and ethane, R_x and R_y are equal and of the same conjugation order, and consequently

$$\Delta + C = 2R_x - 2\delta_s N_{\text{C-C}}$$

since $N_{\text{C=C}}$ is equal to zero for these molecules.

For benzene, butadiene and propylene R_x is the ordinary conjugation energy and R_y the second-order hyperconjugation energy

$$R_y = \delta_s N_{\text{C-C}} + \delta_d N_{\text{C-C}}$$

and consequently

$$\Delta + C = R_x - N_s\delta_s$$

Per dimension, the formula

$$\Delta + C = R_x - N_s\delta_s$$

applies in both cases.

Using the secular equation for ethane, $N_s\delta_s$ was calculated for the bond distances corresponding to the molecules under investigation. The results are given in Table III.

Summary and Discussion

Table III contains the computed quantities expressed in units of $-\beta_0$ at the left, and the experimental quantities expressed in kcal./mole at the right. A comparison should now be possible, thus yielding values of the resonance integral β_0, the results of which are given in the last column of the table.

Due to the approximate character of these calculations and the possible inaccuracy of the observed data, a complete consistency of the obtained β_0 values for the different examples of conjugated systems can of course not be expected. However, the consistency seems acceptable if we choose a high numerical value of the electronegativity parameter δ. It can also be seen that the consistency is somewhat better for SCF-AO than for Slater AO.

In order to see if $(\Delta + C)_{\text{calcd}}$ could be increased, *i.e.*, $|\beta_0|$ decreased, by another choice of $\rho(\text{C}{\equiv}\text{H}_3)$ than $\rho = S(\text{C}{\equiv}\text{H}_3)/S(r_0)$ in cases of small numerical values of the electronegativity parameter δ, the variation of $(\Delta + C)_{\text{calcd}}$ with ρ was calculated for methylacetylene. The result indicated that $(\Delta + C)_{\text{calcd}}$ is very insensitive to even a large variation in ρ. Only by varying δ can $(\Delta + C)_{\text{calcd}}$ (or β_0) be affected substantially.

According to these conclusions, we shall in the following discussions choose $\delta = -0.5$, and $-\beta_0 =$ 81 and 102 kcal./mole as an appropriate average for Slater AO and SCF-AO, respectively. The value 81 kcal./mole is in good accordance with 78 kcal. obtained by Coulson and Crawford, and 74 kcal. obtained by I'Haya.[19]

Using these values of the parameters, the second-order hyperconjugation energies in kcal./mole were calculated for the actual bond lengths. The results are recorded in Table IV, together with the results obtained by other authors previously cited, for comparison.

The present calculations confirm Coulson and Crawford's conclusion that the second-order hyperconjugation is quite small. Actually, the values obtained here are smaller than those obtained by any other authors. Only about 1.4 kcal./mole of the normal bond energy of the ordinary 1.543 Å. C–C bond comes from second-order hyperconjugation, and about 1.1 kcal/mole for the ordinary 1.353 Å. C=C bond.

TABLE IV

SECOND-ORDER HYPERCONJUGATION ENERGIES IN KCAL./MOLE (PER DIMENSION OF PSEUDO-ELECTRONS)

r(CC), Å.	M.R.B.[3]	R.S.[4]	C.C.[5]	I'H[6-8]	Present work Slater AO	Present work SCF-AO
1.33	5.54			2.33		
1.34		7.08	1.58			
1.35	5.00			2.19		
1.353					1.20	1.10
1.37					1.13	1.05
1.38		5.90				
1.39	3.93	5.60	1.14	1.92		
1.397					1.04	0.96
1.41		5.10				
1.45	2.37	4.20	0.90			
1.46				1.55	0.83	.84
1.47					.81	.82
1.49		3.40				
1.53	1.35	2.76		1.22	.65	.73
1.54	1.25					
1.543					.63	.72
1.55		2.50	0.78	1.13	.63	.72

Acknowledgment.—The author is much indebted to Professor R. S. Mulliken for suggesting the work, and for his much valuable advice.

CHICAGO, ILL.

---

[18] Mulliken, Rieke and Brown[3] originally used the formula $R = \Delta + C + 2\delta_{1.54}N_{\text{C-C}} + \delta_{1.33}N_{\text{C=C}}$, where $\delta_{1.54}$ and $\delta_{1.33}$ always were to be taken for the bond lengths 1.54 and 1.33 Å., respectively, but R referred to the total conjugation energy at bond lengths equal to the actual ones in the molecules. However, Mulliken in a later paper (ref. 16, footnote 30) pointed out that in the formula just cited δ_s and δ_d should be substituted for $\delta_{1.54}$ and $\delta_{1.33}$ (also that footnote 35, ref. 3, is incorrect). Coulson and Crawford,[5] and I'Haya[7] also used the incorrect formula, but the error introduced in this way is of minor importance.

[19] These authors used β_0 (1.39 Å.) as energy standard. In order to compare them with the present values, their original values were multiplied by $S(1.353)/S(1.39) = 1.05$.