Hyperconjugation. I. General Theory and Its Applications to Simple LCAO MO Calculations

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I. Introduction[#]

It has been noticed by several writers that the alkyl group may have the power to conjugate with other resonating systems. In 1935, Baker and Nathan[1] introduced the concept later called hyperconjugation in order to explain the abnormal reaction rates of alkyl-substituted compounds. After that, the large increases in dipole moments of alkyl-substituted compounds were attributed by several authors[2-6] to a charge migration from the alkyl radical to the attached resonating systems. On the other hand, it has been found[7-9] that the length of the C-Me bond in such systems is less than the normal C-C bond length of 1.54Å. In 1939, Mulliken[10] has given a theoretical explanation on the basis of hyperconjugation to the red shifts of spectra and increases in the exaltation of molecular refractivity in alkylsubstituted resonating systems. Concerning the heats of hydrogenation of hyperconjugated systems, several investigations[11,13] have been published; for instance, Cullis, Hinshelwood and Mulcahy[12] state that the phenomenon of hyperconjugation seems to be significant in the oxidation of hydrocarbons.

[#] For reviews on experimental aspects, see C.L. Deasy, *Chem. Revs.*, **36**, 145 (1945), and more recently, V.A. Crawford, *Quart. Revs.*, **3**, 226 (1949).

[1] J.W. Baker and W.S. Nathan, *J. Chem. Soc.*, 1840, 1844 (1935).

[2] J.W. Baker and L.G. Groves, *J. Chem. Soc.*, 1144 (1939).

[3] J.W. Baker, *J. Chem. Soc.*, 1150 (1939).

[4] Mariott, Hobbs and Gross, *J. Am. Chem. Soc.*, **63**, 659 (1941).

[5] H.C. Hurdis and C.P. Smyth, *J. Am. Chem. Soc.*, **64**, 2829 (1942).

[6] H.C. Hurdis and C.P. Smyth, *J. Am. Chem. Soc.*, **65**, 89 (1943).

[7] G. Herzberg, F. Patat and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937).

[8] L. Pauling, H.D. Springall and K.J. Palmer, *J. Am. Chem. Soc.*, **61**, 927 (1939).

[9] D.P. Stevenson, H.D. Burham and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2922 (1939).

[10] R.S. Mulliken, *J. Chem. Phys.*, **7**, 121, 339, 356 (1939).

[11] J.B. Conant and G.B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937).

[12] C. F. Cullis, C. N. Hinshelwood and M. F. R. Mulcahy, *Proc. Roy. Soc.* (London), **A196**, 160 (1949).

Mulliken, Rieke and Brown[13] give a description of an application of the molecular orbital method to the computation of hyperconjugation energies and bond orders in methylated hydrocarbon molecules. Explanations were given for the observed shortening of C-Me bonds and decrease in heats of hydrogenation in hyperconjugated molecules. They estimated an empirical exchange integral for C-H_3 bond, but assumed a coulomb integral for H_3 to be the same as for carbon atoms in a conjugated hydrocarbon. Thus, their new interpretations involve some bold assumptions, nevertheless their work seems to be very successful. Sklar[14] has computed the extent of migration of an electron from the methyl radical into the benzene ring by the method of antisymmetrized molecular orbitals, and obtained results which were in agreement with the experimental data. Roberts and Skinner[15] discussed the dissociation energies of carbon bonds in hydrocarbon radicals in terms of hyperconjugation

Herzfeld[16] and Matsen[17] independently discussed the effect of the migration of an electron from the substituent in the ring on the red shift and intensity of spectra; however they treat the methyl radical not as $-C\equiv H_3$ but as one group. More recently, Coulson and Crawford[18,19] have computed the hyperconjugation energies, charge distributions and red shifts in the spectra in methyl-substituted ethylenes and benzenes using the MO method.

Thus, although considerable work has been done in recent years in discussing hyperconjugation[20], no attempt has been made to compute the electronic structures of either methyl- or ethyl-substituted molecules with the common parameters. In this series, the effect of hyperconjugation is discussed in ethyl-substituted π-electron systems as well as in methyl-substituted ones using the LCAO MO method with common numerical parameters determined from the experimental aspects.

II. General Theory of Hyperconjugation*

From the MO view point, the methyl group should have orbitals of π-character in order to conjugate with the π-orbitals of the resonating systems; namely it should have a structure of $-C\equiv H_3$. Now if the hydrogen atoms with 1s AO's ψ_a, ψ_b, ψ_c, (ψ_a in yz plane) are called H_a, H_b, H_c, respectively, then we may form the following group orbitals with approximate contours (z-axis perpendicular to the paper) shown in Fig. 1#.

$$\begin{aligned} \phi_\sigma &= (\psi_a+\psi_b+\psi_c)/(3+6S)^{1/2} && \sigma\text{-type} \\ \phi_y &= (2\psi_a-\psi_b-\psi_c)/(6-6S)^{1/2} && \pi_y\text{-type} \qquad (1) \\ \phi_x &= (\psi_b-\psi_c)/(2-2S)^{1/2} && \pi_x\text{-type} \end{aligned}$$

where S is the overlap integral between hydrogen atoms. The MO's such as ϕ_x and ϕ_y of Eq. (1), which may be called quasi-x and quasi-y MO's following Mulliken, are strictly equal in energy. Thus, in general, hyperconjugation is a two dimensional affair, namely in methylacetylene we have both x- and y- hyperconjugations, but in toluene we may have only one species of hyperconjugation for the reason that the other type of hyperconjugation perpendicular to the above one may be assumed to make no more contribution to the resonance energy for double bond than is present for simple unsaturated molecules like methylacetylene itself.

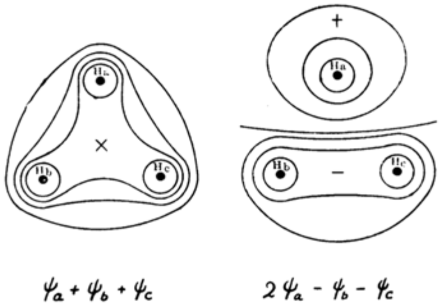

Fig. 1. σ and π_y group orbitals in methyl group.

Besides the π-character of the $-C\equiv H_3$ group, in ethylacetylene and ethylbenzene the quasi double bond between C and H_2 involves one σ-bond and one π-bond with the following quasi MO's:

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

[14] A.L. Sklar, *J. Chem. Phys.*, **7**, 184 (1939).

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

[16] K.F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).

[17] F.A. Matsen, *J. Am. Chem. Soc.*, 72, 5243 (1950).

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

[19] V.A. Crawford, *J. Chem. Soc.*, 2058, 2061 (1953).

[20] More interesting calculations concerning aromatic carbonium ions have recently been made; (a) E. Heilbronner and M. Simonetta, *Helv. Chim. Acta*, **35**, 1049 (1952), (b) N. Muller, L.W. Pickett and R.S. Mulliken, *J. Am. Chem. Soc.*, **76**, 4770 (1954).

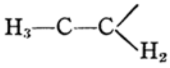
* The interpretation of hyperconjugation is a little different according to molecular orbital or valence bond descriptions. See, C. A. Coulson, "Valence", Oxford Univ. Press (1951), p. 310.

\# This figure is reproduced from Professor Coulson's "Valence" with his kind permission.

[21] The hyperconjugative effect may be accompanied with the inductive effect, as the former always causes polarities in various bonds to some extent. In this paper, however, the inductive effect except for next neighboring carbon atom is ignored because the hyperconjugative effect is to be chiefly dealt with.

$$\begin{aligned}\phi_\sigma&=(\psi_a+\psi_b)/(2+2S)^{1/2}\\ \phi_\pi&=(\psi_a-\psi_b)/(2-2S)^{1/2}\end{aligned}\qquad(2)$$

Here ψ_a and ψ_b refer to the two hydrogen atoms on opposite sides of the yz plane. If the orientation of the ethyl radical is assumed to be,



we have another type of hyperconjugation perpendicular to the above one. The proper quasi y-orbital would be

$$\phi_y=N\{2\times 2te\sigma-(\psi_a+\psi_b)/(2+2S)^{1/2}\}\qquad(3)$$

where $2te\sigma$ is the tetrahedral orbital of the carbon atom of the methyl group which extends toward the other carbon atom of the ethyl group to make the C-C single bond within the ethyl group, and N is the normalization factor. This quasi y-orbital is to be hyperconjugated with the y-orbital of the carbon atoms of the attached conjugated systems, namely of the triple bond of acetylene. Thus in ethylacetylene we have two-dimensional hyperconjugation, but in ethylbenzene the treatment of x-hyperconjugation only is probably satisfactory just as it is in toluene.

After all, in the present study, it is assumed that the hyperconjugation of the substituted ethyl group is essentially the same as of the methyl group itself.

III. Outline of Method and Empirical Parameters

It is convenient to express the molecular orbitals of the electrons as linear combinations of atomic orbitals (LCAO). If each MO is constructed out of n definite AO's $\phi_r(r=1,2,\ldots\ldots,n)$, we may write it down in the form,

$$\chi_j=\sum_{r=1}^{n}C_{jr}\phi_r\qquad(4)$$

We have then following equations:

$$(\alpha_r-\mathcal{E})C_r+\sum_{s\neq r}(\gamma_{rs}-S_{rs}\mathcal{E})C_s=0\qquad(r=1,2,\ldots\ldots,n)\qquad(5)$$

where

$$a_r=\int\phi_r\mathrm{H}\phi_r d\tau,\qquad \gamma_{rs}=\int\phi_r\mathrm{H}\phi_s d\tau,\qquad \mathrm{S}_{rs}=\int\phi_r\phi_s d\tau\qquad(6)$$

and $\mathcal{E}$'s are the energies of LCAO MO's. We write $\gamma_{rs}=\beta_{rs}+\frac{1}{2}\mathrm{S}_{rs}(\alpha_r+\alpha_s)$ and assume that the Coulomb integral α_r has the same value α for all the carbon atoms in the system, and is $\alpha+\lambda_1\beta$ and $\alpha+\lambda_2\beta$ for pseudo atom H_3 or H_2 and next neighboring carbon atom respectively. Here β corresponds to the benzene C-C, and λ_1 and λ_2 are empirical parameters to be determined from experimental aspects; particularly λ_2 is a measure of the inductive effect[21]. We also assume that β_{rs} is proportional to the overlap integral between atoms r and s if r and s are bonded, otherwise zero[22,23]. That is

$$\beta_{rs}=(S_{rs}/S)\beta\equiv\rho_{rs}\cdot\beta\qquad(7)$$

where S is the overlap integral between adjacent carbon atoms in benzene (C-C distance is 1.39Å).

With these assumptions and neglecting the overlap integrals, the equations (5) take the following forms,

$$(\alpha_r-\mathcal{E})C_r+\sum_{s\neq r}\rho_{rs}\beta C_s=0\qquad(r=1,2,\ldots\ldots,n)\qquad(8)$$

where the summation is carried out over all s bonded to r. Then we get the sets of coefficients C_{jr} corresponding to each eigenvalue $\mathcal{E}_j$. According to the definitions[24,25], the total π-electron density of atom r is given by

$$q_r=2\sum_j C_{jr}^2\qquad(9)$$

and the bond order of a bond r-s by

$$p_{rs}=2\sum_j C_{jr}C_{js}\qquad(10)$$

where q_r and p_{rs} are given as a sum over all occupied MO's.

The overlap integrals needed to evaluate the ρ values are computable from the table given by Mulliken et al[26]. using the experimental data for internuclear distances, and are shown in Table I. Although the overlap integral of the group orbitals such as C-H_3 and C-H_2 is also computable by the method of Mulliken et al. ($S=0.541$)[27], the parameter ρ which was derived from the above overlap integral value was found to be not suitable for the present calculations probably because of neglecting all overlap integrals. If the

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22) G.W. Wheland, *J. Am. Chem. Soc.*, 64, 900 (1942).

23) R.S. Mulliken and C.A. Rieke, *J. Am. Chem. Soc.*, 63, 1770 (1941).

24) G.W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, 57, 2086 (1935).

25) C.A. Coulson, *Proc. Roy. Soc.* (London), A169, 413 (1939).

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

27) The overlap integral of the group orbital C-H_3 is computed as follows:

$$S(\mathrm{C},\mathrm{H_3})=\sqrt{\frac{2}{3}}\sin\alpha\,[1-S\,(1s,\,1s;\,\mathrm{H-H})]^{-\frac{1}{2}}\times S(1s,\,2te\sigma;\mathrm{C-H})$$

where 2α is the tetrahedral valence angle 109.5°. See ref. 26), Section Vd.

28) See references 7) and 8).

overlap integral between C and H_3 or H_2 is estimated as the one between carbon sp_3 tetrahedral hybrid-AO and hydrogen 1s AO using the C-H internuclear distance 1.09Å[28], then we get $S(1s,\ 2te\sigma)=0.685$ and ρ_{CH_3} or $\rho_{CH_2}=2.77$. The more suitable value was found to be chosen as 2.92[29] through calculations.

TABLE I

C(π)-C(π) OVERLAP INTEGRALS AND ρ VALUES

r(C-C), Å	S(2pπ,2pπ)	ρ_r*
1.53	0.196	0.794
1.51	0.203	0.822
1.50	0.206	0.834
1.47	0.217	0.879
1.42	0.236	0.955
1.39	0.247	1.000
1.205	0.335	1.356

* $\rho_r=S(r)/S(1.39)$.

The overlap integral between the quasi π_y-orbital (3) and the tetrahedral orbitals of the attached carbon atom of the ethyl group is computed as 0.435[30] by the method of Mulliken et al., but the ρ value derived from this was not adequate as mentioned above, ρ_{CH_2-C} value is therefore taken as 2.35 in proportion to ρ_{CH_3} or ρ_{CH_2} (2.92).

As for another parameter λ_1, it seems certainly to be negative according to a theoretical explanation which was recently given by Muller, Pickett and Mulliken[20b], and probably in the neighborhood of -0.5. In this paper -0.5[31] was most suitable for reproducing experimental data, particularly dipole moments of hyperconjugated systems. Since the trigonal and digonal carbon atoms of the double and triple bonds are more electronegative than the tetrahedral carbon of the methyl group, parameter λ_2 will be also negative and is chosen as -0.1 taking account of the inductive effect from the adjacent H_3 group.

Since no precise method gives the numerical values of these quantities, the above assumed values involve considerable uncertainties. Therefore, as far as the reliability of these parameters is concerned, we should be contented with the agreement between predicted and observed values when these parameters are used in computations.

IV. Application to Methyl and Ethylacetylenes

Following the ideas of Sec. II, methylacetylene has eight delocalized π-electrons and ethylacetylene ten delocalized ones. Therefore, the secular determinants are

$$\begin{vmatrix} z+\lambda_1 & \rho_{12} & 0 & 0 \\ \rho_{12} & z+\lambda_2 & \rho_{23} & 0 \\ 0 & \rho_{23} & z & \rho_{34} \\ 0 & 0 & \rho_{34} & z \end{vmatrix}=0 \quad \text{twice} \qquad (11)$$

for methylacetylene, and

$$\begin{vmatrix} z+\lambda_1 & \rho_{12} & 0 & 0 & 0 & 0 \\ \rho_{12} & z+\lambda_2 & 0 & \rho_{24} & 0 & 0 \\ 0 & 0 & z+\lambda_1 & \rho_{34} & 0 & 0 \\ 0 & \rho_{24} & \rho_{34} & z+\lambda_2 & \rho_{45} & 0 \\ 0 & 0 & 0 & \rho_{45} & z & \rho_{56} \\ 0 & 0 & 0 & 0 & \rho_{56} & z \end{vmatrix}=0,$$

$$\begin{vmatrix} z+\lambda_1 & \rho^* & 0 & 0 \\ \rho^* & z+\lambda_2 & \rho_{45} & 0 \\ 0 & \rho_{45} & z & \rho_{56} \\ 0 & 0 & \rho_{56} & z \end{vmatrix}=0 \qquad (12)$$

for ethylacetylene. In Eqs. (11) and (12), $z=(\alpha-\varepsilon)/\beta$ and the numberings of atoms are shown in Fig. 2.

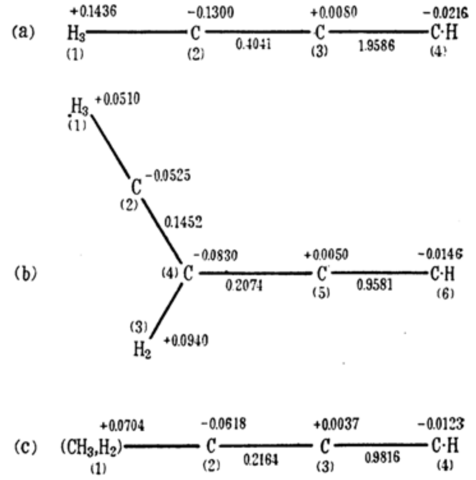

Fig. 2. The numberings of the atoms and the π-electron charge distribution and mobile bond order diagrams in methylacetylene (a) with both x and y-hyperconjugations and ethylacetylene (b) with x-hyperconjugation only and (c) with y-hyperconjugation only (taking the x-axis to be perpendicular to the plane of the paper and omitting bond orders between C and quasi-π group orbitals).

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[29] In ref. 13), the ρ_{CH_3} value was taken as 4; Pullman and Metzger took it as 2.5; *Bull. Soc. Chim.*, **57**, 1021 (1948). The same value 2.5 was chosen by Coulson and Crawford in ref. 18) in calculations including overlap. Mulliken and Rieke found that if the overlap integral is included in the computations, the magnitude of the parameter ρ_{CH_3} is reduced from 4 to about 2; see ref. 23) or R.S. Mulliken, *Rev. Modern Phys.*, **14**, 265 (1942). The author has checked this evaluation, and obtained the value 2.19. The self-consistent computation including overlap integrals using such a parameter is in course of computation.

[30] This value is obtained as follows:

$$S(CH_2,C)=N_1[\sin\alpha\times S(2te\sigma,2te\sigma;\ C-C) \\ +2N_2\cos^2\alpha\times S(1s,2te\sigma;C-H)],$$

where N_1 and N_2 are the normalization factors.

[31] In ref. 18), Coulson and Crawford also took as $\lambda_1=-0.5$ and $\lambda_2=-0.1$ from the dipole moment evidence.

Using the following values of empirical parameters: for methylacetylene,
$\lambda_1=-0.5$, $\lambda_2=-0.1$, $\rho_{12}=2.92$, $\rho_{23}=0.879$ (as 1.469 Å)³²⁾, $\rho_{34}=1.356$ (as 1.205 Å)³²⁾,
and for ethylacetylene,
$\lambda_1=-0.5$, $\lambda_2=-0.1$, $\rho_{12}=2.92$, $\rho_{24}=0.834$ (as 1.50 Å)³³⁾, $\rho_{45}=0.879$ (as 1.47 Å)³³⁾, $\rho_{56}=1.356$, $\rho^*=2.35$,
computational results are given in Table II, and final charge distribution diagrams in Fig. 2.

TABLE II

THE OCCUPIED ENERGY LEVELS AND DIPOLE MOMENTS OF METHYL AND ETHYLACETYLENES

	Occupied energy levels	μ (D)	
	z^a	calcd.	obsd.
Methyl-acetylene	$+1.260226_b$	0.727	0.72^d
	$+2.915310^{b,c}$		0.77^e
Ethyl-acetylene	$+1.195202$	0.783	0.80^e
	$+1.243628$		
	$+2.280381^c$		
	$+2.391106^c$		
	$+3.251446^c$		

a. Note $z=(\varepsilon-\alpha)/\beta$, where ε's are the energies of MO's.

b. In methylacetylene, the occupied energy levels are doubly degenerate.

c. These are attributable to the hyperconjugated quasi-π orbitals.

d. H. E. Watson and K. L. Ramaswamy, Proc. Roy. Soc. (London), **A156**, 130 (1936).

e. F. J. Krieger and H. H. Wenzke, J. Am. Chem. Soc., **60**, 2115 (1938).

Bond Order and Bond Length.—Using the bond order and bond length curve³⁴⁾, we can estimate the approximate bond lengths from the calculated bond orders shown in Fig. 2. Thus we obtained C_2-C_3(1.47 Å), C_3-C_4(1.20 Å) in methylacetylene and C_2-C_4(1.52 Å), C_4-C_5 (1.47 Å), C_5-C_6(1.20 Å) in ethylacetylene. The experimental values of internuclear distance are given only for methylacetylene, and the agreements between the calculated and observed values are complete. Consequently, we may consider that the values of parameters assumed before are certainly adequate. In ethylacetylene, no appropriate experimental data for C-C length have been given, but the calculated values shown above might be very suggestive if experimental data could be available on the bond length of the carbon-carbon bond adjacent to the triple bond in ethylacetylene.

Resonance Moment.—The dipole moment due to the migration of electrons from alkyl group to carbon atoms of acetylene, assuming it to be a resonance moment only, may be calculated from the charge distribution diagrams. In Table II, the calculated values are compared with the observed ones and agreements are very satisfactory in both cases. Attention should be called to the neglect of dipole moment which may arise from the σ-electrons (mainly C-H moment).

The comparison of the computed and the empirical conjugation energies will be investigated in the subsequent paper including overlap integrals³⁵⁾.

V. Application to Methyl and Ethylbenzenes

When making computations by the MO method, the total effective number of π-electrons is taken to be eight and ten respectively for toluene and ethylbenzene each numbered as in Fig. 3. In these cases, the treatment of x-hyperconjugation only is probably satisfactory as mentioned in Sec. II.

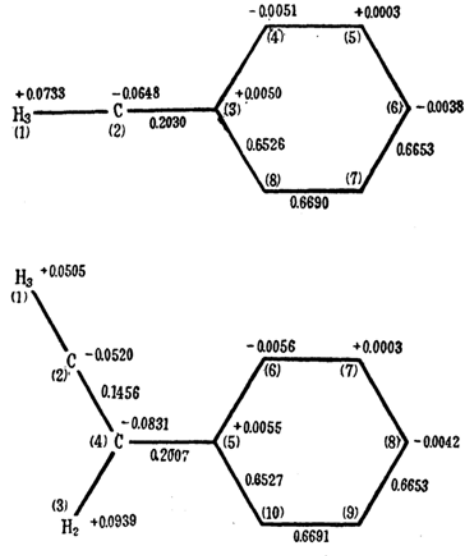

Fig. 3. The numberings of the atoms and the π-electron charge distribution and mobile bond order diagrams in toluene and ethylbenzene (omitting bond orders between C and quasi-π group orbitals).

Using the same empirical parameters in secular equations as those for substituted acetylenes (cf. Sec. IV.), the energy levels of molecular orbitals (in Table III), charge distributions (in Fig. 3) and resonance moments (in Table IV) are obtained.

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32) Spectroscopic data; G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules" (D. Van Nostrand, New York, 1945).

33) These are estimated values.

34) C. A. Coulson, *Proc. Roy. Soc.*, A169, 413 (1939), A207, 91 (1951).

35) In ref. 13) and 18), Mulliken et al. and Coulson and Crawford computed the empirical conjugation energies from heats of combustion and compared with the theoretical values corrected for extension and compression of the σ-bonds. See Series II of this article.

TABLE III

THE CALCULATED ENERGY LEVELS OF TOLUENE AND ETHYLBENZENE

Toluene z^{a}	Ethylbenzene z^{a}
-1.000000	-1.000000
-0.986142^{b}	-0.994367^{b}
$+0.952463$	$+0.950784$
$+1.000000$	$+1.000000$
$+1.936516$	$+1.914324$
$+2.823428^{c}$	$+2.324890^{c}$
	$+3.156861^{c}$

a. See foot-note (a) of Table II.

b. These correspond to the lowest unoccupied levels.

c. These are attributable to the hyperconjugated quasi—orbitals.

The Red Shifts of the Near Ultraviolet Absorption Spectra.—The above computed migration of electrons from alkyl group to the ring causes wave-length shift and the variation of intensity of 0–0 band in the absorption spectra of alkylsubstituted benzene. In order to compute the extent of these shifts, we must estimate the nature of the transition in alkylbenzene. In benzene, the excitation of the electron from the highest occupied orbitals in the ground state to the lowest unoccupied orbitals produced singlet and triplet states. Excitation energies computed without electron repulsion may be thought to give the average values of the actual levels[36]. In alkyl-substituted benzenes, the original orbital degeneracy is removed by the perturbation of the attached alkyl group. Therefore, in this case, we may assume that the average values of the theoretical excitation energies will give the approximate transition energy of alkylbenzene.

Thus for toluene, we assume a set of hypothetical states with the electron configurations as follows[37]:

$$\begin{array}{rl} Y: & (\chi_0)^2\ (\chi_1)^2\ (\chi_2)\ \ (\chi_3)^2\ (\chi_5) \\ Y': & (\chi_0)^2\ (\chi_1)^2\ (\chi_2)^2\ (\chi_3)\ \ (\chi_4) \\ Z: & (\chi_0)^2\ (\chi_1)^2\ (\chi_2)\ \ (\chi_3)^2\ (\chi_4) \\ Z': & (\chi_0)^2\ (\chi_1)^2\ (\chi_2)^2\ (\chi_3)\ \ (\chi_5) \end{array} \qquad (13)$$

For instance, a transition from the ground state N to the upper hypothetical state Y would involve transition of an electron from χ_2 to χ_5, leaving a second electron in χ_2 and all other electrons in closed shells. Therefore,

$$\Delta\varepsilon_{\text{av.}} = (1/2)(\varepsilon_5+\varepsilon_4-\varepsilon_3-\varepsilon_2) = h\nu \qquad (14)$$

where ε_j is the j'th MO energy, and ν is the frequency of a transition from the ground state to an averaged hypothetical state which corresponds to the average height of the actual state.

Now we show that the relative shift in frequency between the ν of Eq. (14) and the corresponding mean frequency of benzene, $\nu' = -2\beta/h$, is given by

$$(\nu'-\nu)/\nu' = 1+(\varepsilon_5+\varepsilon_4-\varepsilon_3-\varepsilon_2)/4\beta \qquad (15)$$

These quantities are computed for toluene and ethylbenzene from the energy levels in Table III, and are shown in Table IV with the ones calculated from our observed 0–0 bands of the near ultraviolet absorption spectra (see Sec. VI). We find that they are in complete agreement with each other. A prediction for the 0–0 band frequencies in alkylbenzenes is also possible if the corresponding position in benzene is estimated. The calculated frequencies both in vapor and in solution are shown in Table IV, taking the values for benzene as 2625 Å[38] and 2640 Å[39] corresponding to vapor and solution states respectively.

TABLE IV

DIPOLE MOMENTS, ABSORPTION FREQUENCIES AND OSCILLATOR STRENGTHS OF TOLUENE AND ETHYLBENZENE

		Toluene	Ethylbenzene
μ (D)	calcd.	0.362	0.549
	obsd.	0.37^{a}	0.58_{a}
$\frac{\nu'-\nu}{\nu'}$	calcd.	0.016	0.014
	obsd.	0.019^{b}, 0.016^{c}	0.015^{b}
Vapor λ, (Å)	calcd.	2666	2661
	obsd.	2668^{d}	2664^{d}
Solution λ, (Å)	calcd.	2681	2678
	obsd.	2692^{b}	2680^{b}
$f \times 10^4$	calcd.	20.5	14.2
	obsd.	15^{b}, 10^{e}, 30^{f}	9^{b}

a. J. W. Baker and L. G. Groves, J. Chem. Soc., 1144 (1939).

b. Our experimental data. See Sec. VI and Fig. 4.

c. H. Sponer and E. Teller, Rev. Modern Phys., **13**, 75 (1941).

d. F. A. Matsen, W. W. Robertson and R. L. Chuoke, Chem. Revs., **41**, 273 (1947).

e. R. S. Mulliken and C. A. Rieke, "Reports on Progress in Physics", vol. 8, p. 331 (1941).

f. Sponer and Löwe, J. Opt. Soc. Am., **39**. 840 (1949).

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[36] C.C.J. Roothaan and R.S. Mulliken, *J. Chem. Phys.*, **16**, 118 (1948).

[37] R.S. Mulliken, *J. Chem. Phys.*, **7**, 353 (1939).

[38] H. Sponer, G. Nordheim, A.L. Sklar and E. Teller, *J. Chem. Phys.*, **7**, 207 (1939).

[39] F.A. Matsen, W.W. Robertson and R.L. Chuoke, *Chem. Revs.*, **41**, 273 (1947).

Oscillator Strength.—Before calculation of the oscillator strength[40],

$$f=1.085\times10^{11}\nu Q^2 \tag{16}$$

where ν is the frequency of the transition in cm^{-1}, we need to calculate the dipole strength Q for the transition. In alkylbenzenes, the wave function of the lowest-lying singlet state is approximately given as follows by analogy with the corresponding one ($^1B_{2u}$) of benzene[41].

$$\psi(\mathrm{V})=[\psi(\mathrm{Z})-\psi(\mathrm{Z}')]/2^{1/2} \tag{17}$$

where $\psi(\mathrm{Z})$ and $\psi(\mathrm{Z}')$ correspond to the electron configurations of third and forth lines shown in (13) respectively. The Q-values of the $N\rightarrow Z$ and $N\rightarrow Z'$ transitions in alkylbenzenes are z-polarized (figure axis is taken to be z), and

$$\begin{aligned}Q(N\rightarrow V)=[&\textstyle\int\psi_N(z_1+z_2)\psi_Z d\tau\\&-\textstyle\int\psi_N(z_1+z_2)\psi_{Z'}d\tau]/2^{1/2}\end{aligned} \tag{18}$$

where z_1 and z_2 refer to the two electrons occupied initially in the χ_2 or χ_3 orbitals (cf. (13)). The transition moments for the other axis which is perpendicular to z-axis in the benzene plane are zero. In the case of toluene, for example, this reduces to

$$Q(N\rightarrow V)=2^{1/2}[\textstyle\int\chi_2 z\chi_4 d\tau-\int\chi_3 z\chi_5 d\tau] \tag{19}$$

Using Eq. (4) and calculated coefficients C_{jr}, we get

$$\begin{aligned}Q(N\rightarrow V)=[&1-2(C_{23}C_{43}+C_{24}C_{44}\\&-C_{25}C_{45}-C_{23}C_{46})]r/2^{1/2}\end{aligned} \tag{20}$$

where r is the carbon-carbon distance in benzene. Then we can calculate f by Eq. (16). The f-value thus obtained theoretically is shown in Table IV with the one for ethylbenzene, in which the procedure of computation is the same as above.

The discussions for the conjugation energy are delayed in the subsequent paper.

VI. The Near Ultraviolet Absorption Spectra of Alkylbenzenes

On account of the lack in the data of the near ultraviolet absorption spectra of alkylbenzenes, the solution spectra were obtained in normal hexane on a Beckman quartz spectrophotometer DU (see Fig. 4). The 0–0 band of benzene in solution was estimated to be 2640 Å (note the 0–0 band in benzene is forbidden). The oscillator strengths for the transitions were computed from the integrated areas under the extinction curves, by the following equation[42],

$$f=4.32\times10^{-9}\textstyle\int\varepsilon_\nu d\nu \tag{21}$$

where ν is the frequency in cm^{-1}. No correction was made for the effect of solution on the f-value.

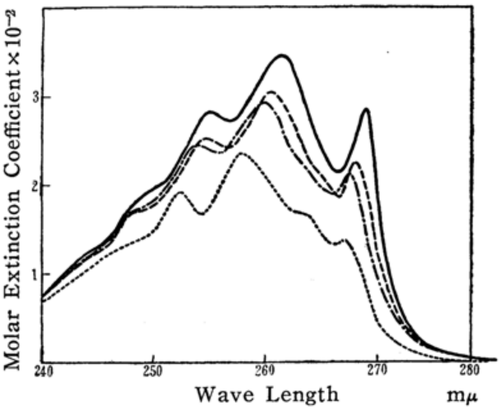

Fig. 4. The near ultraviolet absorption spectra in normal hexane of toluene (——), ethylbenzene (– – – –), iso-propylbenzene (–·–·–·–) and tert-butylbenzene (······).

VII. Critical Discussion

From the outset, it was our intention to calculate the electronic states of alkylbenzenes with a view to extending the theory of hyperconjugation. However, the precise computations of the electronic states in such complicated molecules are impossible for the present, so we cannot help making use of the empirical LCAO MO method with empirical parameters. Since no precise computations can be made for the Coulomb integrals of H_3 or H_2 groups or for the exchange integrals between C and H_3 or H_2, we meet first of all with a difficulty when we attempt to give reasonable values to these quantities. Consequently, values of these parameters which were chosen from several assumptions, so as to reproduce the observed dipole moments as well as possible were applied not only to alkylbenzenes but to alkyl-substituted acetylenes, and fairly satisfactory results were obtained. Therefore, these empirical parameters seem to be considerably reliable when the overlap integrals are ignored.

The calculations show that the theory of

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[40] R. S. Mulliken and C. A. Rieke, "Reports on Progress in Physics", Vol. 8, p. 231 (1941).

[41] For benzene $\psi(Z)$ and $\psi(Z')$ are degenerated so that the coefficients of $\psi(Z)$ and $\psi(Z')$ should be equal in magnitude, for the alkylbenzenes, however, $\psi(Z)$, $\psi(Z')$ are no longer degenerate and the coefficients should be slightly unequal. This inequality will not affect the center of gravity of the excited states, but it must not give sufficiently correct Q-values for the transitions since equal mixing should not be expected. Matsen discussed the resulting errors in an appendix of ref. 17). See also reft. 37) and A.L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937), M. Goeppert-Mayer and A.L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

[42] J.R. Platt and H.B. Klevens, *Rev. Modern Phys.*, **16**, 182 (1944).

hyperconjugation introduced by Mulliken, Rieke and Brown has a real importance for the study of the electronic structure not only of methylated organic molecules but of other alkyl-substituted ones; namely even when the methyl group is substituted for a hydrogen atom of the methyl group, the hyperconjugation is recognized as being the same as in the case of methyl group only. For such a complicated organic molecule, the usual method consists of computing its electronic structure taking only π-electrons of carbon atoms involved; however the phenomenon of hyperconjugation suggests that to a large extent the 1s electrons of the hydrogen atoms and even the tetrahedral hybridized orbital of the carbon atoms in the alkyl group take part in π-conjugation. More accurate calculations are made in the subsequent papers using the LCAO MO and LCAO SCF MO methods including the overlap integrals.

Summary

The theory of hyperconjugation has been extended and applied to computations of the electronic structures of methyl and ethyl-substituted acetylenes and benzenes using the empirical LCAO MO method not including the overlap integrals. The common empirical parameters introduced from experimental aspects were used consistently through the calculations. Charge distributions of the π-electrons, bond orders, resonance moments, relative shifts of near ultraviolet absorption spectra and oscillator strengths were calculated, and fairly satisfactory results, compared with the observed values, were obtained. Because of the lack of appropriate absorption data, the near ultraviolet absorption spectra of alkylbenzenes in normal hexane were obtained. The calculations show that when the methyl group is substituted for a hydrogen atom of the methyl group, the hyperconjugative effect is recognized as same as before.

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