Hyperconjugation. II. The Electronic Structures and Conjugation Energies of Alkylbenzenes

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I. Introduction

It was shown in Part I⁽¹⁾ that even in ethyl-substituted acetylene and benzene the ideas of extended hyperconjugation could be also applied. In this paper, the author gives more detailed calculations of the electronic structures and conjugation energies not only in toluene and ethylbenzene but in *tert*-butylbenzene by the empirical LCAO MO method including overlap integrals for neighboring atoms. Since such a computation including overlap has been made only by Coulson and Crawford⁽²⁾ for a series of methyl-substituted benzenes and ethylenes, it is desirable to investigate the electronic structures of the other alkyl-substituted resonating systems, particulary of alkylbenzenes which have long been a question, using the same method as in the case of toluene.

The models for the methyl and ethyl groups were already established in Sec. II of Part I, but a model for the *tert*-butyl group remains unsettled. In this case, it seems fairly reasonable to consider the three CH_3 as one group such as H_3 in toluene; that is

$$—C—(CH_3)_3.$$

Therefore, we have two dimensional hyperconjugation to be conjugated with an attached resonating system, but in *tert*-butylbenzene only one type of hyperconjugation is probably effective for just the same reason as in toluene.⁽³⁾

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* A part of this work was presented at the 7th Annual Meeting of the Chemical Society of Japan, Tokyo University, April 3, 1954.

1) The preceding paper.

2) (a) C.A. Coulson and V.A. Crawford, *J. Chem. Soc.*, 2052 (1953); (b) V. A. Crawford, ibid., 2058, 2061 (1953).

3) See Sec. II of Part I.

II. Method of Computations

The method of LCAO MO (Linear Combination of Atomic Orbitals Molecular Orbital) with inclusion of the overlap integrals between adjacent atomic orbitals requires certain changes in the forms of the equations and the definitions mentioned in Sec. III of Part I. If we denote different atoms by a Greek suffix μ, ν,…… and molecular orbitals (MO) by a Latin suffix i, j,……, each MO ψ_j is represented by n AO's ϕ_μ in the form

$$\psi_j=\sum_{\mu=1}^{n} x_{j\mu}\phi_\mu \tag{1}$$

where tne coefficients $x_{j\mu}$ are determined by minimizing the total energy. The energy levels of MO's ψ_j are given by the roots of the secular determinant

$$\det|H_{\mu\nu}-\varepsilon S_{\mu\nu}|=0 \tag{2}$$

where

$$\begin{aligned} H_{\mu\mu}&=\int\phi_\mu H\phi_\mu d\tau=\alpha_\mu, \\ H_{\mu\nu}&=\int\phi_\mu H\phi_\nu\, d\tau=\gamma_{\mu\nu}, \\ S_{\mu\nu}&=\int\phi_\mu\phi_\nu\, d\tau. \end{aligned}$$

Neglecting interactions of non-neighbor atoms, making replacements $\beta=\gamma-\alpha S$, $\xi_\mu=1-\lambda_\mu S$, and $z=(\alpha-\varepsilon)/(\gamma-S\varepsilon)$, and assuming $\gamma_{\mu\nu}$ is proportional to $S_{\mu\nu}$ ⁴⁾, the above secular determinant is simplified as a polynomial of z. (note α, β, γ and S correspond to benzene).

Illustration for the case of toluene, the numbering of atoms shown in the diagram, is as follows; this molecule has eight π-electrons in orbitals made by combining the six 2pπ carbon AO's and the two quasi-π orbitals of the methyl group. Because of the C_{2v} symmetry of the molecule⁵⁾, the MO's are divided into two groups, one is a_2 and the other is b_1 symmetries.

$$\Delta(a_2)=\begin{vmatrix} z & 1 \\ 1 & z \end{vmatrix}=0 \tag{3}$$

$$\Delta(b_1)=\begin{vmatrix} \xi_1 z+\lambda_1 & \rho_{12} & 0 & 0 & 0 & 0 \\ \rho_{12} & \xi_2 z+\lambda_2 & \rho_{23} & 0 & 0 & 0 \\ 0 & \rho_{23} & z & 1 & 0 & 0 \\ 0 & 0 & 2 & z & 1 & 0 \\ 0 & 0 & 0 & 1 & z & 2 \\ 0 & 0 & 0 & 0 & 1 & z \end{vmatrix}=0 \tag{4}$$

In these determinants, ρ's are the proportional constants of the exchange integrals to overlap ($\rho_{\mu\nu}=S_{\mu\nu}/S$) and λ's are the correction terms for the Coulomb integrals in units of β. Solution of above determinantal equations (3) and (4) provides us with the orbital energies ε_j (shown in Table II) using the relation

$$\varepsilon_j=\alpha-\frac{z}{1-Sz}\beta \tag{5}$$

and the corresponding coefficients $x_{j\mu}$'s.

TABLE I

EMPIRICAL PARAMETERS

	λ_1	λ_2	ρ_{12}	ρ_{23}
Toluene	−0.5	−0.1	2.92	0.834
tert-Butylbenzene	−1.0	−0.1	3.0	0.777
	λ_1,λ_3	λ_2,λ_4	ρ_{12},ρ_{34}	ρ_{24},ρ_{45}
Ethylbenzene	−0.5	−0.1	2.92	0.822

TABLE II

ORBITAL ENERGIES w_i OF ALKYLBENZENES*

	Toluene	Fthylbenzene	*tert*-Butylbenzene
$2a_2$	−1.328021	−1.328021	−1.328021
$4b_1$	−1.297212	−1.297330	−1.320806
$3b_1$	+0.767269	+0.768415	+0.770480
$1a_2$	+0.801925	+0.801925	+0.801925
$2b_1$	+1.305127	+1.290928	+1.298214
$1b_1$	+1.623852	+1.439167	+1.515066
$0b_1$		+1.745722	

* $w_i=(\varepsilon_i-\alpha)/\beta$, and orbital energies higher than $2a_2$ are not recorded.

The empirical parameters used are the same as that of Part I excepting *tert*-butylbenzene and some refinements made in ρ_{23} both in toluene and ethylbenzene, and are recorded in Table I. Since the choice of parameters for *tert*-butylbenzene are quite arbitrary, considerable uncertainties remain. Judging from a result of calculations, however, they seem not to be very seriously wrong. The author of course wishes that further support will be provided for these numerical values of the empirical parameters.

The influences of the inductive effect to the Coulomb integrals of the ring carbon atoms are ignored.⁶⁾

III. Conjugation Energies and Hyperconjugation Energies

In order to obtain conjugation and hyperconjugation energies, the total energies E(L) and E(S) of the π-electrons in localized and semi-localized bond structures must be calculated, in addition to the total energy of the delocalized model E(D). Here what is called the total energy of the semi-localized bond structure E(S) is the total sum of each π-electron energies in $C-H_3$ group and the delocalized benzene. Now we get the vertical conjugation (or vertical π-resonance) energy

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4) G.W. Wheland, *J. Am. Chem. Soc.*, 63, 2025 (1941); ibid., 64, 900 (1942).

5) In this paper, the benzene ring in ethylbenzene is approximately treated to be also C_{2v} symmetry.

6) See foot-note 21) of Part I.

E(CJ)7) and the vertical hyperconjugation energy E(HCJ) as follows:

$$E(\mathrm{CJ})=E(\mathrm{L})-E(\mathrm{D})$$
$$E(\mathrm{HCJ})=E(\mathrm{S})-E(\mathrm{D}). \qquad (6)$$

These energies computed theoretically for a series of alkylbenzenes are listed in column 3 of Table IV (E(HCJ) is given in bracket).

On the other hand, it has been shown by Mulliken, Rieke and Brown8) (hereafter called M. R. B.) that the following empirical formula for the heats of combustion fits the available data for saturated hydrocarbons with considerable accuracy:

$$-\Delta H_{298^\circ}=54.625N_{\mathrm{CH}}+48.25N_{\mathrm{CC}}-1.5N_{\mathrm{Me}}+22.18N_{\mathrm{C=C}}+56.6N_{\mathrm{C\equiv C}} \qquad (7)$$

where N_{CH}, N_{CC}, N_{Me}, $N_{\mathrm{C=C}}$ and $N_{\mathrm{C\equiv C}}$ are the numbers of C–H bonds, C–C bonds (counting each bond in a multiple bond; e.g., nine in benzene), methyl groups, C=C double bonds, and C≡C triple bonds, respectively. Then the difference Δ between the value empirically predicted by Eq. (7) and observed heat of combustion9) is 39.46, 40.96 and 40.91 kcals. for benzene, toluene and ethylbenzene respectively. Therefore, the value Δ(HCJ), which is obtained after subtraction from the Δ of benzene, is 1.5 kcal. for toluene and 1.45 kcal. for ethylbenzene.

IV. Third-Order Conjugation

It has been noticed that when comparing empirical and theoretically computed (vertical) conjugation energies, we should make two corrections; the one to the energy of compression and extension of the C–C bond length, the other to the energy of the third-order conjugation. The importance of doing the former correction for the empirically determined conjugation or resonance energies from the formula (7), has been demonstrated by several writers10,11,12) and more recently Coulson and Crawford2a) have recalculated the compression and extension energies using Morse functions. In this paper, the value C=35.49 kcal. for benzene which was given by above authors is used without revision.

The latter correction for the theoretically computed conjugation energies which was first stressed by M. R. B., is based upon the fact that ideal single (or double) bond is one which is slightly weaker and longer than that found in ethane (or ethylene), because the single (or double) bond in ethane (or ethylene) is strengthened by third-order conjugation. The corrected total conjugation energy is therefore given by the sum of the ordinary of first-order (E(CJ) in Eq. (6)) and third-order conjugation energies; that is

$$E(\mathrm{CJ})=E_1(\mathrm{CJ})+E_3(\mathrm{CJ})$$

The third-order conjugation energies per bond are readily computed for various bond lengths on the basis of the variation method including overlap integrals between adjacent atomic orbitals:

$$\varepsilon(r)=2\left\{\frac{z_1(\mathrm{D})}{1-Sz_1(\mathrm{D})}+\frac{z_2(\mathrm{D})}{1-Sz_2(\mathrm{D})}-\frac{2z(\mathrm{L})}{1-Sz(\mathrm{L})}\right\} \qquad (8)$$

per dimension where $-z_1(\mathrm{D})$ and $-z_2(\mathrm{D})$ are the lower two roots of the secular equation for both delocalized ethane and ethylene and take the following forms;

$$\left.\begin{matrix}z_1(\mathrm{D})\\ z_2(\mathrm{D})\end{matrix}\right\}=\frac{1}{2\xi_1\xi_2}\Big[\xi_1\lambda_2+\xi_2\lambda_1\pm\xi_1\rho_{23}+\Big\{(\xi_1\lambda_2+\xi_2\lambda_1\pm\xi_1\rho_{23})^2-4\xi_1\xi_2(\lambda_1\lambda_2-\rho_{12}^2\pm\lambda_1\rho_{23})\Big\}^{1/2}\Big] \qquad (9)$$

and $-z(\mathrm{L})$ is a doubly degenerated root of the quadric secular equation for localized two $\mathrm{CH_3}$ groups.

$$z(\mathrm{L})=\frac{1}{2\xi_1\xi_2}\left[\xi_1\lambda_2+\xi_2\lambda_1+\{(\xi_1\lambda_2+\xi_2\lambda_1)^2-4\xi_1\xi_2(\lambda_1\lambda_2-\rho_{12}^2)\}^{1/2}\right] \qquad (10)$$

In Eqs. (9) and (10), ρ_{12} and ρ_{23} refer to the $\mathrm{C\equiv H_3}$ or $\mathrm{C=H_2}$ and C–C bonds respectively, and λ's and ξ's have the same meaning mentioned in Sec. II.

Taking the C–C overlap integral S in benzene as 0.247, values of $\varepsilon(r)$ are evaluated for various bond lengths and are listed in Table III.

TABLE III

THIRD-ORDER CONJUGATION ENERGIES

r(C–C), in Å	ε(r), in units of β
1.54	0.001267
1.53	0.001308
1.52	0.001350
1.51	0.001396
1.50	0.001445
1.46	0.001659
1.39	0.002115
1.33	0.002595

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7) This vertical conjugation energy corresponds to a quantum-mechanical resonance energy named by Coulson and Altmann in ref. 12).

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

9) Heat of combustion for benzene, toluene and ethylbenzene is 789.08, 943.58 and 1101.13 kcals., respectively; W.C. Price, *Chem. Revs.*, **41**, 257 (1947). No appropriate data is given for *tert*-butylbenzene.

10) J.E. Lennard-Jones, *Proc. Roy. Soc.* (London), **A138**, 280 (1937).

11) D.F. Hornig, *J. Am. Chem. Soc.*, 72, 5772 (1950).

12) C.A. Coulson and S.L. Altmann, *Trans, Faraday, Soc.*, 48, 293 (1952).

Now it has been shown (M. R. B.)

$$\varDelta+C=E_1(\mathrm{CJ})+E_3(\mathrm{CJ})-2\varepsilon(1.54)N_{\mathrm{C-C}} \\ -\varepsilon(1.33)N_{\mathrm{C=C}} \qquad (11)$$

where C is the conjugation energy correction due to compression and extension of the bonds, and ε is the hyperconjugation energy per bond per dimension for bond distance 1.54 and 1.33 Å respectively. The right hand sides of Eq. (11) computed theoretically for three alkylbenzenes are given in Table IV together with the value for benzene, for the purpose of comparison between the theoretical and empirical conjugation energies $\varDelta+C$ for benzene and of computing the hyperconjugation energies in three alkylbenzenes.

The value β obtained by comparison of both $\varDelta+C$ for benzen is -70.0 kcal.[13], and is somewhat larger than that of the spectroscopic value -60 kcal. Using the value for β of -70.0 kcal., the corrected hyperconjugation energies for toluene, ethylbenzene and *tert*-butylbenzene are 1.45, 1.24 and 0.79 kcals. respectively, and this is the quite satisfactory order to be expected.

The third-order conjugation energies listed in Table III are appreciably less than the M. R. B., Roberts and Skinner[14] and even than the Coulson and Crawford[2a] values. This might be ascribed to including the corrected Coulomb integrals in Eqs. (9) and (10) but not including in the reference (2a)[15].

V. Charge Distributions and Bond Orders

It was already mentioned in Sec. II that when overlap is included the definitions for the charge and the bond order must be changed. Following Chirgwin and Coulson[16], the total π-electron density q_μ on atom μ and the mobile bond order $p_{\mu\nu}$ between adjacent atoms μ, ν are given by

$$q_\mu=\sum_{j=1}^{m} n_j x_{j\mu} y_{j\mu} \qquad (12)$$

$$p_{\mu\nu}=\frac{1}{2}\sum_{j=1}^{m} n_j\,(x_{j\mu}y_{j\nu}+x_{j\nu}\,y_{j\mu}) \qquad (13)$$

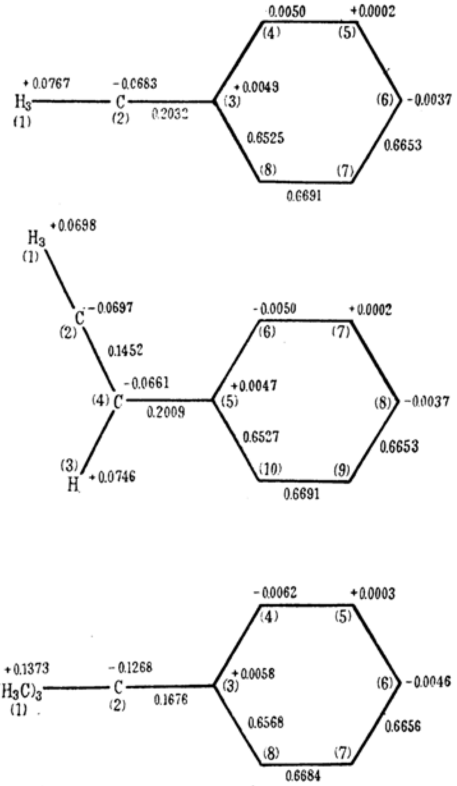
where $y_{j\mu}$ is the "covariant" coefficients associated with ψ_j in contrast with the "contravariant" ones $x_{j\mu}$, and defined by the relation

$$y_{j\mu}=\sum_{\nu=1}^{n} S_{\mu\nu}\,x_{j\nu}$$

with the normalization condition

$$\sum_{\nu=1}^{n} x_{j\nu}\,y_{j\nu}=1 \quad (j=1,\ 2,\cdots\cdots n).$$

In Eqs. (12) and (13), the summation is carried over all the occupied molecular orbitals j, and n_j is the number of electrons in the j'th MO. The computed values of the total π-electron charge densities and mobile bond orders thus obtained are shown in the following diagram.



The numberings of the atoms and the π-electron charge distribution and mobile bond order diagrams in toluene, ethylbenzene, and *tert*-butylbenzene, omitting bond orders between C and H_2 or H_3 group in toluene and ethylbenzene and between C and $(CH_3)_3$ in *tert*-butylbenzene.

The dipole moment due to the migration of electrons from alkyl group to benzene ring can be evaluated from the calculated charge densities and the bond lengths predicted from the bond orders (see column 2 of Table IV). Assumption of a resonance moment only is taken here as in Sec. IV of Part I. The results recorded in Table V show considerable agreements with the observed values.

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[13] Coulson and Crawford give the value -71.6 kcal. for β.

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

[15] The third-order conjugation energies computed in the present study were somewhat rescrutinized; Y. I'Haya, to be published.

[16] B.H. Chirgwin and C.A. Coulson, *Proc. Roy, Soc.* (London), **A201**, 196 (1950).

TABLE IV

CONJUGATION ENERGIES OF ALKYLBENZENES, IN UNITS OF β

	r(C–C), Å	E_1(CJ)	E_3(CJ)*	Deduction**	$\varDelta$+C
Benzene	1.39	1.073526	0.012690	0.015387	1.070829
Toluene	1.39	1.095352	0.014086	0.017921	1.091517
	(2–3) 1.51	(0.021826)			
Ethylbenzene	1.39	1.093538	0.015394	0.020455	1.088477
	(2–4) 1.53	(0.020012)			
	(4–5) 1.51				
t-Butyl-benzene	1.39	1.086034	0.014040	0.017921	1.082153
	(2–3) 1.52	(0.012508)			

* $\sum_r \varepsilon(r) N_{C-C}(r)$

** $2\varepsilon(1.54) N_{C-C} + \varepsilon(1.33) N_{C=C}$.

TABLE V

DIPOLE MOMENTS, ABSORPTION FREQUENCIES AND OSCILLATOR STRENGTHS IN ALKYLBENZENES

		Benzene	Toluene	Ethylbenzene	t-Butylbenzene
μ (D)	calcd.	—	0.372	0.491	0.746
	obsd.*	—	0.37	0.58	0.70
Vapor λ, (Å)	calcd.	(2625)	2666	2665	2649
	obsd.**	2625	2668	2664	2655
Solution λ, (Å)	calcd.	(2640)	2681	2680	2664
	obsd.♯	2640	2692	2680	2672
$f \times 10^{-4}$	calcd.	—	16.1	11.0	8.2
	obsd.♯	—	15	9	5

* J. W. Baker and L. G. Groves, *J. Chem. Soc.*, **1939,** 1144.

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

♯ Y. I'Haya, the preceding Paper.

VI. The Near Ultraviolet Absorption Spectra

The Red Shifts Resulting from Alkyl Substitution.—The general features have already been explained in Sec. V of Part I and it has been shown that the substitution of the hydrogen atoms of resonating molecules by alkyl groups cause the shift of the whole absorption curve to a longer wave-length (cf. Fig. 4 of Part I). We have also seen that this may result undoubtedly from a raising of the highest occupied level and a lowering of the lowest unoccupied level, and this lowering may be a characteristic feature of hyperconjugation. The simple LCAO MO calculations of π-electron transitions are also used here as done in Part I, and are compared with the observed values in Table V. In spite of using such a simple method instead of a more accurate method of antisymmetrized molecular orbitals[17], the agreement between them is fairly satisfactory.

Intensities of Spectra.—The oscillator strength f is computed for each of a series of alkyl benzens using the same equations as Eqs. (16) and (20) of Part I, and listed in Table V. Also in this case, therefore, the difficulty which was mentioned in foot note 41) of Part I is inevitable. However, the agreement between the computed and observed values shows that the omission of resulting errors from it is probably not too serious.

Although more detailed reasons for these wave-length shifts and intensities of the absorption spectra are not yet clear, a question which has long been unexplained seems to be semi-quantitatively solved; that is the absorption spectra representing π-electronic transitions allowed by the lower symmetries than benzene due to charge migrations from alkyl groups into benzene ring shift to longer wave-length and become stronger on passing from *tert*-butylbenzene to toluene. This result can also be explained by the computed hyperconjugation energies mentioned in the last paragraph of Sec. IV, for it is ascribed to increasing of hyperconjugation in a series of alkylbenzenes from *tert*-butylbenzene to toluene.

VII. Critical Discussion

It has long been a question why the absorption spectra of a series of alkylbenzenes should become stronger and shift to longer wave-length but on the other hand the dipole moments should become smaller on passing from *tert*-butylbenzene to toluene. The re-

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17) Sec A.L. Sklar, *J. Chem. Phys.*, 7, 984 (1939).

sults of computations obtained in the present study can explain this difficulty for the first time in spite of taking the simple LCAO MO method including overlap and choosing some unjustified empirical parameters.

However, here remains another difficulty to be settled; that is the inoization potential. That hyperconjugation plays a more important role here than any other alkyl-substituted resonating systems is indicated by the smaller lowering in ionization potentials on passing from *tert*-butylbenzene to toluene compared with the lowering in other systems[18]. In this connection, if more elaborated computations should be made as non-empirically as possible, an improvement would be made concerning this problem.

Attention should also be called to neglecting the inductive effect. The inductive effect has usually been regarded as being one of short range and is therefore unlikely to be of greater importance in large molecules such as alkylbenzenes than small ones[19]. However, Muller, Pickett and Mulliken[20] have recently stressed in the study of the benzenium ion that a joint inductive-hyperconjugative effect gives a considerably greater additional stabilization than the hyperconjugative effect only. This is likely to occur. Computations together with the inductive effect are in progress, and the result of both, including alkylbenzenes, will be presented before long.

Summary

The theory of hyperconjugation has been rescrutinized for a series of alkylbenzenes using the empirical LCAO MO method including overlap integrals for neighboring atoms. A detailed comparison of the theoretically computed and empirically determined conjugation energies of benzene gives a value of -70.0 kcal. for β, the reasonance integral for benzene C–C. Using this value, hyperconjugation energies for toluene, ethylbenzene and *tert*-butylbenzene are 1.45, 1.24 and 0.79 kcals. respectively. The third-order conjugation energies are found to be considerably less than any previous evaluations. Comparison of the predicted and observed dipole moments, absorption frequencies and oscillator strengths show fairly satisfactory agreements between them.

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[18] See ref. 9).

[19] Daub and Vandenbelt have concluded that the red-shifts of the absorption spectra are chiefly due to a resonance effect and that they are very insensitive to an inductive effect; *J. Am. Chem. Soc.*, 69, 2714 (1947); ibid., 71, 2414 (1949), and in ref. 2b) Crawford has obtained very satisfactory agreement with experimental data in computations of methyl-substituted benzenes using the same method without induction.

[20] N. Muller, L.W. Pickett and R.S. Mulliken, *J. Am. Chem. Soc.*, 76, 4770 (1954).