

393. *The Effect of Deuteration on Electron Distribution and Energy of Conjugated Molecules. Part I. LCAO-MO Treatment of Toluene.*

By R. PAUNCZ and E. A. HALEVI.

The LCAO-MO treatment of toluene is reconsidered, with inclusion of inductive effects, preliminary to a consideration of the effect of deuteration in the side chain on energy and electron distribution (Part II). It is shown that the two approximations commonly employed yield substantially the same trends. The net charge migration into the ring depends only on the relative electronegativity assumed between the methyl-carbon and the hydrogen atoms, whereas the charge distribution within the ring depends only on the inductive transmission coefficient (ϵ). Increasing either of these quantities increases the dipole moment, raises the total π -electron energy (destabilisation), but increases the delocalisation energy (stabilisation), so that a more precise definition of "hyperconjugative stabilisation," as generally correlated with hyperconjugative electron release, is called for.

THE object of this series of papers is to discuss the effect of deuteration on the properties of conjugated molecules in the ground state. The need for such an investigation arose from consideration of recent work on secondary isotope effects. These effects, first demonstrated in kinetic studies of solvolysis,^{1,2} have been interpreted in terms of zero-point energy differences arising from configurational changes between the ground and the transition state. On the other hand it has been shown that polarity differences between isotopic species of the same molecule can be correlated with the slightly different configurations *in the ground state* that arise because of the anharmonicity of the lowest vibrational levels.^{3,4} Differences in the acid dissociation constants of methyl- and methylene-deuterated aliphatic acids, which strongly suggest differential inductive effects, are most simply explained on this basis.⁵

In attempting to discuss these effects from a theoretical point of view, it seemed advisable to begin with a study of side-chain deuteration in aromatic systems, since the theoretical methods of LCAO-MO are particularly well adapted to investigations of the properties of conjugated molecules in the ground state and to the study of reactivity, also since experimental work on secondary isotope effects in aromatic substitution is now under way in several laboratories.^{6,7}

Since it is expected that the predicted effects will be very small, it is necessary to ascertain that such calculated differences are not inherent in the approximations made in the particular method of calculation; so the present paper is devoted to a reconsideration of the toluene problem including the inductive effect of the methyl group. The specific effects of isotopic substitution in the toluene side chain are taken up in the following paper.

Method of Calculation.—Previous investigations of toluene^{8,9} have been related to the general study of hyperconjugation on the basis of the LCAO-MO method. In these treatments the H₃ "pseudo-heteroatom" is assigned a group orbital of p_z symmetry strongly overlapping with the p_z orbital of the methyl-carbon atom which is obtained by resolving the three sp^3 orbitals directed towards the hydrogen atoms into components symmetric and antisymmetric with regard to the plane of the aromatic ring. Factors that have been taken into account differently by various investigators are overlap and the electropositivity

¹ Lewis *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 6306, and later papers.

² Shiner *et al.*, *ibid.*, 1953, **75**, 2925 and later papers.

³ Bell and Coop, *Trans. Faraday Soc.*, 1938, **34**, 1209.

⁴ Halevi, *ibid.*, 1958, **54**, 1441.

⁵ Halevi and Nussim, *Bull. Res. Council, Israel*, 1956, **5**, A, 263; results presented before the 16th Internat. Congr. Pure Appl. Chem., Paris, July, 1957; Halevi, *Tetrahedron*, 1957, **1**, 174.

⁶ Swain, Knee, and Kresge, *J. Amer. Chem. Soc.*, 1957, **79**, 505.

⁷ Halevi and Ron, unpublished work.

⁸ Coulson and Crawford, *J.*, 1953, 2052; Crawford, *ibid.*, p. 2058.

⁹ I'Haya, *Bull. Chem. Soc. Japan*, 1955, **28**, 369, 376.

and retaining (4) and (5), we put the secular equations into the form:

$$x_i(\tau + \delta_i) + \sum_{j \neq i} x_j \rho_{ij} \{1 + S_o(\tau + \frac{1}{2}[\delta_i + \delta_j])\} = 0 \quad \dots \quad (6a)$$

Equation (6a) cannot be reduced to a form analogous to (9) unless the coulomb integrals for all atoms are assumed to be equal, in which case the two approximations are identical.

This is essentially the method employed by I'Haya⁹ in his treatment of toluene. He used the same values of ρ_{ij} as Coulson and Crawford did, but on the basis of theoretical considerations¹² took:

$$\delta_1 = -0.3 \quad \delta_2 = -0.1 \quad \delta_3 = \dots \delta_6 = 0$$

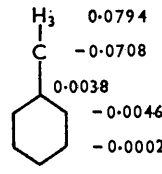
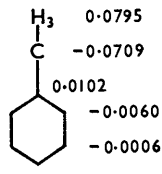
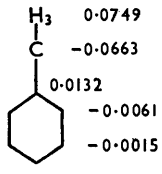
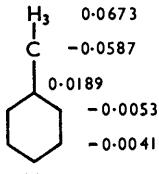
It will be noted that neither of these approximations allows explicitly for the transmission of an inductive effect beyond atom 3. The ability to deal with an inductive effect is essential for our purposes, so we introduce the parameter ϵ (< 1) defined as:

$$\delta_i = \epsilon \delta_{i-1}$$

which expresses the damping of induced electropositivity through a chain of carbon atoms¹³ and prescribes all the values of δ_i once δ_1 and ϵ have been fixed.

The effect of varying the essential parameters and of using alternative methods of approximation will now be discussed. This will be done separately for the electron distribution and for the energy.

FIG. 1. ($\delta_1 = -0.5$.)

				
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
	(Coulson-Crawford)	$\epsilon = 1/5$	$\epsilon = 1/4$	$\epsilon = 1/3$
Dipole moment (D)...	0.276	0.328	0.353	0.415
Net charge migration to ring	0.0085	0.0084	0.0085	0.0085

Electron Distribution. The Rôle of ϵ and δ_1 .—Let us first consider the effect on electron distribution of varying the coefficient of inductive transmission, ϵ . Coulson and Crawford assumed ϵ to be zero within the ring. Using their method and the value $\delta_1 = -0.5$ we have calculated the charge distribution for $\epsilon = \frac{1}{5}$, $\frac{1}{4}$, and $\frac{1}{3}$. To simplify the calculations the inductive effect was assumed to be carried as far as atom 5 (the *meta*-position) so that $\delta_5 = \delta_6 = 0$. As will appear below, it was necessary to take $\delta_4 \neq 0$, but the further refinement $\delta_5 \neq 0$ is of minor importance.

The results are shown in Fig. 1*a-d*. We can see that although the dipole moment increases with increasing ϵ , this is due entirely to increasing charge separation in the benzene ring as there is no net increase in charge transmitted from the methyl group. Thus if the value of δ_1 is fixed, the correct value of ϵ depends on what we take to be the correct values for the dipole moment and charge distribution in the ring. On the other hand, if we compare the results of calculations made by using the same inductive transmission but different values of the electropositivities (δ_1) (Fig. 2) we see that, although the dipole moment and net charge migration differ appreciably, the *o* : *m* : *p* net charge ratios

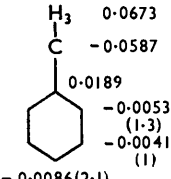
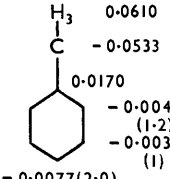
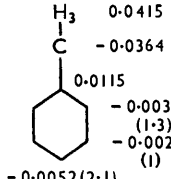
¹² I'Haya, *J. Chem. Phys.*, 1955, **23**, 1165.

¹³ (a) Branch and Calvin, "The Theory of Organic Chemistry," p. 203, Prentice Hall, New York, 1941; (b) Dewar, *J.*, 1949, **463**; (c) Jaffe, *J. Chem. Phys.*, 1952, **20**, 279, 778; 1953, **21**, 415.

(given in parentheses in Fig. 2) are substantially the same. This means that the correct choice of ϵ depends solely on what we consider to be a reasonable charge distribution among the ring positions.

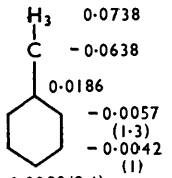
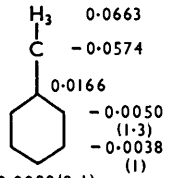
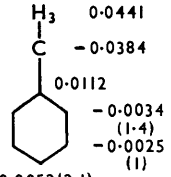
The net activation of the *meta*-position in toluene relative to benzene is well established. If this can be taken as an indication of net charge migration to the position in the *ground state* it requires that ϵ be not equal to zero. (It also requires, as noted above, that the difference of δ_4 from zero be not neglected.) A choice between the alternative values of ϵ requires a quantitative estimate of ground-state electron distribution which is not directly derivable from the chemical evidence. The ratio of the "partial rate factors" of the *para*- (or *ortho*) to the *meta*-position depends strongly on the electronic requirements of the transition state. Thus for example, the ratio is much less for bromination with a charged bromine cation than for that with a neutral bromine molecule.¹⁴ Even reactions with

FIG. 2. ($\epsilon = 1/3$.)

			
	<i>a</i>	<i>b</i>	<i>c</i>
	$\delta_1 = -0.5$	-0.45	-0.3
Dipole moment (D)	0.415	0.372	0.252
Net charge migration to ring	0.0085	0.0077	0.0051

positively charged reagents, which should be better indicators of relative charge distribution, depend considerably on polarisability effects. For example, stabilisation of triphenylmethyl cations by a methyl group is more effective from the *para*- than from the *meta*-positions, but comparatively less so than in nitration or Br^+ bromination.¹⁵ Even here some contribution to stabilisation of the carbonium ion, perhaps the major one, from the *para*-position must come from delocalisation arising from the strong electron demand of the positive centre, and would tend to exaggerate the differences in ground-state distribution in the neutral toluene molecule. The question of the *o* : *p* net charge ratio is complicated by steric effects in one direction and possible contributions of polarisability directly through space (direct field effects) in the other.

FIG. 3. ($\epsilon = 1/3$.)

			
	<i>a</i>	<i>b</i>	<i>c</i>
	$\delta_1 = -0.5$	-0.45	-0.3
Dipole moment (D)	0.444	0.399	0.263
Net charge migration	0.0100	0.0090	0.0057

All in all it seems that any choice of ϵ between say $\frac{1}{5}$ and $\frac{1}{3}$ would be equally acceptable. In what follows we have arbitrarily adopted a value of $\epsilon = \frac{1}{3}$, as originally suggested and confirmed on the basis of evidence from other systems.¹³

¹⁴ de la Mare and Harvey, *J.*, 1956, 36.

¹⁵ Lichtin and Bartlett, *J. Amer. Chem. Soc.*, 1951, **73**, 5530.

Comparison of the Methods.—In order to see to what extent conclusions regarding the electron distribution, dipole moment, and net charge migration depend on the method of calculation adopted, we can compare the results previously obtained with $\epsilon = \frac{1}{3}$ by Wheland's approximation with the results of calculations based on Mulliken's approximation with the same values of the parameters (Fig. 3). It will be noted that the $o : m : p$ ratio is virtually unaltered in all cases, so that apparently the choice of ϵ does not depend on the method. Moreover a comparison of the two sets (Figs. 2 and 3) shows that quite good agreement is obtained in the values of the charge distribution, net charge migration, and dipole moment obtained by the two methods for the various values of δ_1 .^{*} It appears therefore that any conclusions drawn about the variation of these quantities with the essential parameters would not depend upon the particular method employed.

There finally remains at our disposal a choice of a reasonable value for δ_1 , the electro-positivity parameter of the H_3 group. It has generally been chosen to yield a value of the dipole moment in the neighbourhood of 0.4 D, the experimental value. Most of the values given above approximate to this. It should be remembered that the total dipole moment of toluene is not necessarily a purely π -electron moment. First, polarisation of the σ -bonds, implicitly taken into consideration in assuming non-zero values of the various δ_i 's, is ignored in calculating the total dipole moment. Secondly, corrections for self-consistency have not been made. Thirdly, it is implicitly assumed that the resultant of the *para*-C-H bond moment and the "bond moments" of the two remaining "bonds" for the H_3 pseudo-atom with the group orbital ($a + b + c$) cancel exactly. Since the C-H bond moments are assumed to be of the order of 0.4 D and to vary with bond type, this too may introduce an error. It appears, therefore, that exact agreement with the experimental value of the dipole moment should not be taken too seriously as a criterion for the proper choice of the parameters, particularly δ_1 .

In what follows we have adopted the value -0.45 for δ_1 , a value which seems reasonable on the basis of the considerations given above.

Energetic Relations.—General considerations. The essential energetic quantities that are generally calculated directly from a given set of parameters are: The total π -electron energy (E_{mob}); the localised π -electron energy (E_{loc}), calculated with the same parameters but by assuming localised bonds; the delocalisation energy ($E_{\text{del}} = E_{\text{mob}} - E_{\text{loc}}$). The usual measure of the additional stabilisation afforded by the methyl group is the hyperconjugation energy [$E_{\text{hyp}} = E_{\text{del}}^{\text{(toluene)}} - E_{\text{del}}^{\text{(benzene)}}$]. In order to bring these quantities into relation with thermochemically measured energy differences, additional quantities have had to be taken into consideration. First, differences in the σ -electron energy resulting from the lengthening or shortening of the bonds compared with the standard double and single bonds were accounted for in terms of compression energy (C). Secondly, since even the aliphatic reference molecules are not ideal, in the sense that they undergo some delocalisation, account must also be taken of third-order conjugation energy.

The present investigation is not concerned with choosing the best parameters to fit thermochemical data, but rather with the effect of varying these parameters on the energetic relations. Moreover, compression energies and third-order conjugation energies depend essentially on bond length, and in our calculations bond lengths have been kept constant, so that these quantities also remain constant throughout. (We shall be considering explicitly the effect of variation of the C-H bond length in the following paper but this is irrelevant to the present discussion.)

Even when account is taken of the slight changes in bond lengths that occur when the bond lengths initially assumed are corrected to correspond to the calculated bond orders, the widest variation of bond length encountered in this series of calculations is of the order of 0.002 Å and the corresponding energetic corrections differ by no more than 0.001 β_0 per

^{*} *E.g.*, the decrease of δ_1 from -0.45 to -0.3 decreases the dipole moment and the net charge migration in about the same ratio of 1 to 1.5.

bond, and, summed over the molecule, are negligible in comparison with the other energetic differences. This means that in what follows we can safely restrict ourselves to the variation of the directly calculable quantities, E_{mob} and E_{loc} , and to their difference E_{del} . (E_{hyp} will of course differ from E_{del} by the delocalisation energy of benzene.)

The Rôle of ϵ and δ .—The relevant energetic quantities calculated by using Wheland's approximation are given in Table I (in units of β_0). It can be seen that increasing the electropositivity of the H_3 pseudo-atom ($-\delta_1$) leads to a very great reduction in the absolute values of both the total and localised π -electron energies, but to a smaller *increase* in the delocalisation energy. Thus increasing the charge migration to the ring ($-\delta_1$) leads, as one might expect, to an increase in the hyperconjugation energy, but at the same time raises the total π -electron energy to a very much greater extent.

It can also be seen that increasing the value of ϵ , which is related to charge separation *within* the ring, while holding δ_1 constant, operates in the same direction. However, as Coulson has pointed out,¹⁶ this procedure amounts to altering the average coulomb integral and hence the net attraction of the nuclei for electrons. A comparison of columns 3 ($\delta_1 = -0.5$; $\epsilon = \frac{1}{3}$) and 5 ($\delta_1 = -0.45$; $\epsilon = \frac{1}{3}$), in which the mean coulomb term is approximately the same, shows that the effect of varying ϵ while keeping the mean coulomb term constant is very much smaller.

TABLE I.

	$\delta_1 = -0.5$ $\delta_2 = -0.1$ $\delta_3 = \delta_4 = 0$	$\delta_1 = -0.5$		$\delta_1 = -0.45$	$\delta_1 = -0.3$	
		$\epsilon = 1/5$	$\epsilon = 1/4$	$\epsilon = 1/3$		
$E_{\text{mob}} = 8\alpha + \dots\dots\dots$	8.6103	8.5894	8.5584	8.4963	8.5418	8.6816
$E_{\text{loc}} = 8\alpha + \dots\dots\dots$	7.5226	7.5003	7.4680	7.4032	7.4492	7.5904
$E_{\text{del}} \dots\dots\dots$	1.0877	1.0891	1.0904	1.0931	1.0926	1.0912
$E_{\text{hyp}} \uparrow \dots\dots\dots$	0.0211	0.0224	0.0237	0.0264	0.0260	0.0246
	(1)*	(2)	(3)	(4)	(5)	(6)

* Coulson and Crawford.⁸ † $E_{\text{del}}^{\text{(benzene)}} = 1.0666\beta_0$.

Since ϵ , whatever its true value, is a fixed parameter of the system that will not change with deuteration, the effect of its variation upon the energy will not concern us further. However, hyperconjugative electron-release from alkyl groups to an aromatic ring must arise from an electronegativity difference between the α -carbon atom and the hydrogen atoms bonded to it. The effective electronegativity of the carbon atom can be altered by substitution on it, and that of the hydrogen atoms by isotopic substitution, so that the effect of varying their difference acquires real significance. "Hyperconjugative stabilisation" is generally thought to parallel hyperconjugative electron release. It is now clear that this parallelism depends on just how "hyperconjugative stabilisation" is defined.

In principle the changes in σ -bond energies due to alteration of the electronegativity parameters should also be taken into account, as should have been the σ -dipole moments in the previous discussion.¹⁷ This neglect is particularly unfortunate, since induction presumably operates through the σ -skeleton. However, we see no simple way of dealing with these factors.

TABLE 2.

	$\epsilon = 1/3$	$\delta_1 = -0.5$	-0.45	-0.30	0
$E_{\text{mob}} = 8\alpha + \dots\dots\dots$		8.2207	8.2934	8.5158	8.9665
$E_{\text{loc}} = 8\alpha + \dots\dots\dots$		7.1292	7.2022	7.4256	7.8769
$E_{\text{del}} \dots\dots\dots$		1.0915	1.0912	1.0902	1.0896
$E_{\text{hyp}} \dots\dots\dots$		0.0249	0.0245	0.0236	0.0229

Comparison of the Methods.—In Table 2, we have the energetic quantities derived on the basis of Mulliken's approximation, at each of three values of the parameter δ_1 and

¹⁶ Coulson, personal communication.

¹⁷ Craig, personal communication.

fixed value of ϵ ($\frac{1}{3}$). They are to be compared with columns (4), (5), and (6) of Table 1. The limiting case $\delta_1 = 0$ (in which case the two methods become equivalent) is given too. From the comparison we see that the same trends are obtained with both methods with regard to all the energetic quantities. The values themselves are all somewhat larger when derived from a given value of δ_1 by Wheland's method than by Mulliken's approximation. (The differences, of course, decrease with decreasing δ_1 to zero at $\delta_1 = 0$.) This can be contrasted with what we have seen regarding the charge distribution where the state of affairs was reversed, a greater value of net charge being always predicted on the basis of Mulliken's approximation (other things being equal) than on the basis of Wheland's method.

Excitation Energies.—In view of the common correlation of the electron-donating power of substituents with shifts in the electronic absorption spectra of aromatic molecules, it was of interest to investigate the effect of varying the inductive parameters, particularly δ_1 , on the energies of the various transitions. We restricted our considerations to the 2600 Å region. Four transitions yield values in this region. These are * 4 \longrightarrow 5 and 3 \longrightarrow 6 both polarised along the long axis, and 4 \longrightarrow 6 and 3 \longrightarrow 5 both polarised transversely to this axis.

In Table 3, values of the corresponding transition energies are given (in units of β_0) for both methods, a constant value of ϵ ($\epsilon = \frac{1}{3}$) and varying values of δ_1 being used.

TABLE 3.

Transition	Polarisation	$\delta_1 = -0.5$	Wheland			Mulliken		
			-0.45	-0.3	-0.5	-0.45	-0.3	0
4 \longrightarrow 5	Long.	2.0774	2.0763	2.0724	2.0539	2.0557	2.0595	2.0619
3 \longrightarrow 6	„	2.1383	2.1379	2.1364	2.1334	2.1334	2.1334	2.1333
4 \longrightarrow 6	Transv.	2.0926	2.0852	2.1020	2.0761	2.0811	2.0938	2.1142
3 \longrightarrow 5	„	2.1231	2.1190	2.1068	2.1112	2.1080	2.0996	2.0811

The 2600 Å absorption has been sometimes regarded as corresponding simply to the lowest transition 4 \longrightarrow 5. We can see that the energy of this transition depends on δ_1 , but this dependence is different in the two approximations, approaching the value for $\delta_1 = 0$ in one case from above and in the other from below. Moreover, if the two *transverse* transitions are considered, they are seen to lie quite close together. Their spacing depends on δ_1 , both methods predicting that they should cross at a value of $-\delta_1$ somewhat below 0.3. Clearly we must expect very strong interaction between these levels, perhaps strong enough to depress the lower-lying component below the energy of the 4 \longrightarrow 5 transition. Since transitions 4 \longrightarrow 5 and 3 \longrightarrow 6 are not as close together as 4 \longrightarrow 6 and 3 \longrightarrow 5 they would be assumed to interact to a smaller extent.

All these considerations tend to render any conclusions based on spectral shifts in this system very doubtful.

General Conclusions.—It should first be noted that the interplay between hyperconjugative and inductive effects, represented here by the parameters δ and ϵ , are rather more subtle than generally realised. The concept of "hyperconjugative stabilisation" requires careful definition, particularly when it is correlated with "hyperconjugative electron release" as is often done in kinetic discussions.

The introduction of the parameter ϵ into the calculations was essential in order to obtain a reasonable charge distribution among the ring-carbon atoms. However, since the true ground-state charge distribution in toluene is still in some doubt, the correct value to assume for ϵ must also remain open. However, it is clear that any choice of ϵ in the range $\frac{1}{5}$ — $\frac{1}{3}$ would not affect any of our conclusions significantly.

In the following paper we shall be concerned with the effects of small changes in some of the molecular parameters on the electron distribution and the various energetic

* The molecular orbitals are numbered in order of increasing energy. This numbering should not be confused with the numbering of the atoms.

quantities. From the comparison of the results obtained with alternative method of calculation, it appears that the predictions regarding these effects will be essentially independent of the method used.

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DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY,
HAIFA, ISRAEL.

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