394. *The Effect of Deuteration on Electron Distribution and Energy of Conjugated Molecules. Part II.* LCAO–MO Treatment of* [α-$^2H_3$]-*Toluene.*

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The LCAO–MO treatment of toluene (Part I) is extended to [α-$^2H_3$]toluene, which is assumed to differ from the parent molecule by virtue of a slightly different mean configuration of the methyl group. Increased H_3–C overlap in the deuterated molecule lowers the total π-electron energy, but very slightly decreases the hyperconjugation energy and electron-release to the ring. Increased H · · · H non-bonding interactions have the opposite effect, the changes in the energetic quantities being of the same order of magnitude but the increased electron-release considerably greater. The change in hybridisation of the methyl-carbon atom appears to have a smaller effect in the same direction.

THE object of this paper is to consider possible differences in ground-state properties between [α-$^2H_3$]toluene and the normal toluene molecule on the basis of the LCAO–MO treatment, as discussed in Part I.* Our premise is that dissimilarities between these two molecules can only arise by virtue of a difference in the *mean* configuration of the methyl group. This, in turn, is assumed to result from the anharmonicity of the " zero-point " vibrational levels in the symmetrical stretching and bending modes.

The effect of these configurational differences on the ground-state properties calculated according to the above scheme can be reflected in the following three ways: (1) There is a difference in the overlap integral S_{12},† which depends on both bond length and bond angle. (2) The change in H · · · H distance alters the non-bonding interactions and so affects the effective electropositivity of the H_3 group. (3) The change in bond angle results in a corresponding hybridisation change.

The configurational differences will be discussed first, and their effects on the parameters and through them on the molecular properties will then be taken up.

Configurational Differences.—In order to get the best fit between the rotational constants and molecular dimensions of several isotopic species of the methyl halides, it was necessary to assume that the C–H bond length is 0·005—0·009 Å shorter, and the HCH angle is 12—15′ larger in the trideuterated species than in the normal molecules.[1,2] Since these differences are similar throughout the series CH_3F—CH_3I, they must be relatively insensitive to the size and electronegativity of the atom bonded to the central carbon atom, so that similar configurational differences may be expected in the methyl group of toluene.

Values of the parameters derived from rotational data are not quite the same as the corresponding *mean* values, but it is possible to arrive at an independent estimate of the differences in mean bond length and bond angle on the basis of the harmonic frequencies

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* Part I, preceding paper.

† For the definition of this and other symbols, see Part I.

[1] Miller, Aamodt, Dousmanis, Townes, and Kraitchman, *J. Chem. Phys.*, 1952, **20**, 1112.

[2] Andersen, Bak, and Brodersen, *ibid.*, 1956, **24**, 989.

and anharmonicity constants of the symmetrical stretching and bending modes which are treated as if they were completely independent.[3]

By using Hansen and Dennison's data[4] for ethane, as representative of a methyl group bonded to carbon, the following values are obtained:

$$\bar{r}_{\mathrm{CH}} - \bar{r}_{\mathrm{CD}} = 0{\cdot}0027\ \text{Å}$$

$$\chi_{\mathrm{HCH}} - \chi_{\mathrm{DCD}} = 17{\cdot}4' = 0{\cdot}0051 \text{ radian}$$

It is evident from the shape of the Morse curve that the mean length of a C–D bond is less than that of a C–H bond. Since the approximate method employed has been shown in the case of diatomic molecules to yield mean-bond-length differences that are consistently about two-thirds of the accurate value,[3] it is reasonable to take $(\bar{r}_{\mathrm{CH}} - \bar{r}_{\mathrm{CD}}) = 0{\cdot}004$ Å, in fair agreement with the rotational value. The absolute value of the mean-bond-angle difference calculated is also in reasonable agreement with the spectroscopic results. In order to achieve agreement with experiment in sign as well $(\chi_{\mathrm{DCD}} > \chi_{\mathrm{HCH}})$, it must be assumed that bringing the three hydrogen atoms closer to each other raises the potential energy less steeply than moving them towards the adjacent carbon atom by a similar change in angle.*

On the basis of these considerations we shall in what follows assume the variation to be in the range:

$$(\bar{r}_{\mathrm{CH}} - \bar{r}_{\mathrm{CD}}) = 0{\cdot}004\text{—}0{\cdot}009\ \text{Å}$$

$$(\chi_{\mathrm{DCD}} - \chi_{\mathrm{HCH}}) = 0{\cdot}003_5\text{—}0{\cdot}005 \text{ radian}$$

Change in Overlap.—The numbering scheme of Part I, which begins with the H_3 pseudo-atom, will be used. The overlap integral between the H_3 group orbital possessing $2p_z$ symmetry and the $2p_z$ orbital of the methyl-carbon atom is given by:[5]

$$S_{12} = \sqrt{2}\left(\sin\frac{\chi}{2}\right) S \frac{1}{\sqrt{1-s}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $S \equiv S(1s, 2p\sigma)$; $s \equiv s(1s, 1s)$.

Denoting r_{CH} by r and $r_{\mathrm{H}\cdots\mathrm{H}}$ by $l(= 2r \sin \chi/2)$ we get for a differential change in S_{12} with bond length and angle:

$$\frac{\mathrm{d}S_{12}}{S_{12}} = \left(\frac{1}{S}\frac{\mathrm{d}S}{\mathrm{d}r} + f \sin\frac{\chi}{2}\right)\mathrm{d}r + \frac{\cos\frac{\chi}{2}}{2}\left(\operatorname{cosec}\frac{\chi}{2} + fr\right)\mathrm{d}\chi \quad . \quad . \quad . \quad (2)$$

where $f \equiv \dfrac{1}{1-s} \cdot \dfrac{\mathrm{d}s}{\mathrm{d}l}$.

The $1s$–$1s$ and $1s$–$2p\sigma$ overlap integrals are standard integrals.[6] They are, in their explicit forms (in atomic units)

$$s = \tfrac{1}{3} \exp(-l)(l^2 - 3l + 3) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$S = \frac{8z^{5/2}}{r^2 w^4}\{4z \exp(-r)[wr^2 - 6r - 6] + \exp(-zr)[w^2r^3 + 8z(wr^2 + 3zr + 3)]\} \quad (4)$$

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* Professor C. A. Coulson, in a personal communication, has questioned the applicability to toluene of bond-angle changes taken from methyl groups in aliphatic compounds. A better model would certainly be a molecule in which the methyl group is bonded to an unsaturated carbon atom. The available rotational data (see Table IV in Laurie, *J. Chem. Phys.*, 1958, **28**, 706) indicate that here too $\Delta\chi$ is positive and of the same order of magnitude as in the methyl halides, but whether larger ($CH_3{\cdot}C{\equiv}CCl$) or smaller ($CH_3{\cdot}CN$; $CH_3{\cdot}C{\equiv}CH$) is not certain.

[3] Halevi, *Trans. Faraday Soc.*, 1958, **54**, 1441.

[4] Hansen and Dennison, *J. Chem. Phys.*, 1952, **20**, 313.

[5] See, *e.g.*, Lofthus, *J. Amer. Chem. Soc.*, 1957, **79**, 24.

[6] See, *e.g.*, Preuss, "Integraltafeln zur Quantenchemie," Vol. I, Springer, Berlin, 1956.

where z is one-half the Slater effective nuclear charge (for the carbon $2p$ orbital, $z = 1{\cdot}625$, and $w \equiv (z^2 - 1)$.

The expression for $\mathrm{d}S_{12}/S_{12}$, calculated for toluene with the parameters, $\chi = 109° \, 28'$ (tetrahedral), and $r_{\mathrm{CH}} = 1{\cdot}10$ Å, is, with r in Å and χ in radians:

$$\frac{\mathrm{d}S_{12}}{S_{12}} = -\,0{\cdot}50\,\mathrm{d}r + 0{\cdot}34\,\mathrm{d}\chi \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (5)$$

Substituting the estimated differential changes in mean-bond-length and angle in (5), we note first that the two effects reinforce each other, tending to increase the overlap. The relative change in overlap is found to be in the range:

$$\frac{\Delta S_{12}}{S_{12}} = \frac{S_{\mathrm{CD_3}} - S_{\mathrm{CH_3}}}{S_{12}} = 0{\cdot}003\text{—}0{\cdot}006$$

Taking a rounded value of $S_{12} = 0{\cdot}625$, we obtain:

$$\Delta S_{12} = 0{\cdot}002\text{—}0{\cdot}004, \text{ and } \Delta\rho_{12} = \frac{\Delta S_{12}}{S_0} = 0{\cdot}008\text{—}0{\cdot}016$$

Effect of Change in Overlap on Energy and Charge Distribution.—On the basis of the above, we may take $\Delta\rho_{12}$ to be of the order of 0·01, and determine to what extent such a change in overlap will affect the energy and charge distribution. In Table 1 are given the differences in the energetic quantities when ρ_{12} is increased or decreased by 0·01 from the reference value of 2·50. In these calculations, carried out according to both Wheland's and Mulliken's approximations, the parameters used are $\varepsilon = 1/3$ and $\delta_1 = -\,0{\cdot}45$. The absolute values of the energies for $\rho_{12} = 2{\cdot}50$ are given in Tables 1 and 2 respectively of Part I. The energy is in units of β_0.

TABLE 1.

	Wheland		Mulliken	
	$E^{2.51} - E^{2.50}$	$E^{2.50} - E^{2.49}$	$E^{2.51} - E^{2.50}$	$E^{2.50} - E^{2.49}$
ΔE_{mob}	+0·00794	+0·00795	+0·00736	+0·00739
ΔE_{loc}	+0·00810	+0·00812	+0·00753	+0·00755
ΔE_{del} (= ΔE_{hyp})	−0·00016	−0·00017	−0·00017	−0·00016

Both approximations show a strong *increase* of both E_{mob} and E_{loc} with overlap in such a way that the delocalisation energy *decreases* to a very slight extent. This apparently paradoxical decrease in hyperconjugation energy with increasing $\mathrm{C{\equiv}H_3}$ overlap is in fact quite reasonable in terms of considerations given by Mulliken, Rieke, and Brown.[7] It should also be noted that this slight decrease is not completely negligible from the point of view of secondary isotope effects. Taking $|\,\beta_0\,|$ to be approximately equal to 80 kcal./mole,[8] E_{del} of [α-$^2\mathrm{H_3}$]toluene is seen to be some 13 cal./mole lower than that of toluene, which would account for a change of 2—3% in a rate or equilibrium constant at ordinary temperatures. To the extent that a given isotope effect is determined by the difference in *total* π-electron energy, its magnitude would be very much greater.

The energy changes are largely independent not only of the approximation used and the precise value of ρ_{12} assumed in the reference molecules, but also of the inductive parameter, ε. Even assuming the low value of $\varepsilon = 1/5$, we obtain with Wheland's approximation, $\Delta E_{\mathrm{mob}} = 0{\cdot}00787$, $\Delta E_{\mathrm{loc}} = 0{\cdot}00802$, and $\Delta E_{\mathrm{del}} = -0{\cdot}00015$, in good agreement with the values based on $\varepsilon = 1/3$.

The changes in net charge distribution are given in Table 2. Here too, the results are substantially independent of the approximation used and the value of ε, and are insensitive to the precise value of ρ_{12} taken as reference. Although, by virtue of increased overlap,

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[7] Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41.

[8] Coulson and Crawford, *J.*, 1953, 2052.

TABLE 2.

	Wheland			Mulliken	
	$\varepsilon = 1/5$	$\varepsilon = 1/3$		$\varepsilon = 1/3$	
Atom no.	$q^{2.51} - q^{2.50}$	$q^{2.51} - q^{2.50}$	$q^{2.50} - q^{2.49}$	$q^{2.51} - q^{2.50}$	$q^{2.50} - q^{2.49}$
1	−0·00031	−0·00026	−0·00027	−0·00029	−0·00029
2	+0·00024	+0·00020	+0·00021	+0·00021	+0·00022
3	−0·00001	−0·00001	−0·00001	−0·00001	−0·00001
4	+0·00003	+0·00003	+0·00002	+0·00003	+0·00002
5	0·00000	0·00000	0·00000	0·00000	0·00000
6	+0·00002	+0·00002	+0·00002	+0·00002	+0·00003

hyperconjugative electron release from a D_3 pseudoatom is less effective than from H_3, this release effectively goes only as far as the adjacent atom, the changes in charge density on the ring atoms being very small indeed. However, toluene in its ground state represents a system with only weak electron-demand, so that the possibility that overlap differences may be of greater importance in carbonium ions, where electron demand is maximal and hyperconjugation is of the " isovalent " type,[9] cannot be excluded. This question is now under investigation.

Effect of Change in Non-bonding Interaction.—Although the polarity of an isolated CH bond of sp^3 hybridisation is a matter of debate [10] there seems to be general agreement that H_3, acting as a group in CH_3, is more electropositive than the carbon atom to which it is bound. The greater electropositivity of the H_3 group is assumed by Mulliken and his co-workers [11] to be due to non-bonding interaction among the hydrogen atoms. Mulliken gave a first estimate of this difference, and his arguments were made the basis of a more quantitative treatment by I'Haya,[12] who found $\delta_1 = -0{\cdot}3$ for the methylene group and assumed the same value for the methyl group.

Although the expressions for the H_2 and H_3 non-bonding energy are formally identical, the effective Hamiltonian is different in the two cases. The solution of the H_3 problem involves a number of difficulties, but from the form of the Hamiltonian we can infer that in this case electron-release must be greater than from H_2, resulting in a larger value of $-\delta_1$.

Any change in the configuration of the methyl group will change the H · · · H distance, which in turn will affect δ_1. This distance ($l = 2r \sin \chi/2$) will be affected by changing the bond length and bond angle as follows:

$$dl = 2 \sin \chi/2 dr + r \cos \chi/2 d\chi \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

In the range we have assumed for isotopic variation, and with the direction of change as assumed above, the decrease in bond length (r) leads to a decrease in l of the order of:

$$\Delta l_r = (l_{\mathrm{D}} - l_{\mathrm{H}}) = -0{\cdot}011 \pm 0{\cdot}004\ \text{Å}$$

and the increase in angle to an increase in l:

$$\Delta l_\chi = +0{\cdot}0025 \pm 0{\cdot}0005\ \text{Å}$$

the net change being a decrease:

$$\Delta l = -0{\cdot}0085 \pm 0{\cdot}0045\ \text{Å}.$$

Clearly, the H · · · H non-bonding interactions in CD_3 will be greater than in CH_3, and this, on the basis of Mulliken's arguments, would lead to an increase in the absolute value of δ_1, *i.e.*, greater electropositivity of D_3 than of H_3, for which experimental support can be found in the effect of deuteration on the acid dissociation of aliphatic acids.[13]

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[9] Muller and Mulliken, *J. Amer. Chem. Soc.*, 1958, **80**, 3489.

[10] See, *e.g.*, Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, 1955, pp. 240—243.

[11] Muller, Pickett, and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 4770.

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

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

Some measure of the change in δ_1 may be had on the basis of I'Haya's treatment. It is found that in the neighbourhood of the normal configuration of the methyl group, decreasing the H · · · H distance (l) to the extent noted above, results in increasing the absolute value of δ_1 by about 2%. In our scheme of computation, if δ_1 is taken as $-0{\cdot}45$ in toluene it becomes $-0{\cdot}46$ in [α-$^2H_3$]toluene.

Interpolating in the results presented in Table 3 of Part I ($\varepsilon = \frac{1}{3}$; $\delta_1 = -0{\cdot}45$ to $-0{\cdot}50$), we obtain for a change to $\delta_1 = -0{\cdot}46$ the results given in Table 3.

TABLE 3.

	Wheland	Mulliken
ΔE_{mob}	−0·00910	−0·01454
ΔE_{loc}	−0·00919	−0·01461
ΔE_{del} (= ΔE_{hyp})	+0·00009	+0·00007

TABLE 4. ($q^{-0{\cdot}46} - q^{-0{\cdot}45}$).

Atom	Wheland	Mulliken	Atom	Wheland	Mulliken
1	+0·00126	+0·00149	4	−0·00013	−0·00015
2	−0·00109	−0·00127	5	−0·00006	−0·00007
3	+0·00039	+0·00039	6	−0·00017	−0·00018

Comparing the results of Tables 1 and 3, we see that the effect on the energetic quantities of methyl deuteration through its effect on electronegativity is opposite in direction and of the same order of magnitude as its effect through the change in overlap.

The effects of variation in δ_1 on charge distribution were discussed extensively an Part I. Since q varies quite linearly with δ_1 in this range, the net charges to be expected in [α-$^2H_3$]-toluene can also be obtained by interpolation. The results for a change from $\delta_1 = -0{\cdot}45$ to $0{\cdot}46$ ($\rho_{12} = 2{\cdot}50$) are given in Table 4.

Comparing Tables 2 and 4 we see that in charge distribution, as in energy, the two effects of deuteration oppose each other. However, with regard to charge distribution, particularly in the ring, the change in electronegativity is about five times as powerful as the change in overlap, and amounts to about 2—3% of the original net charge, which may be an effect of some significance.

Change in Hybridisation.—Another consequence of varying bond angles (but not bond lengths) is a change in the hybridisation parameter, θ, which appears in the expression for the hybrid orbital:

$$t_i = s\cos\theta + p_i\sin\theta \qquad (7)$$

Here t_i is the hybrid orbital and p_i a carbon p-orbital, both directed towards the ith hydrogen (or carbon) atom, and θ is determined by the orthogonality condition ($\int t_i t_k \, d\tau = \delta_{ik}$). Having taken as our reference state a tetrahedral configuration of the methyl group, the hybridisation is pure sp^3, and for each of the four equivalent orbitals $\theta = 60°$.

Now if the DCD angle (χ) is assumed to be slightly greater than tetrahedral, the three orbitals towards the deuterium atoms (t_i^{D}) remain equivalent to each other, but not to the fourth orbital (t^{C}). If account is taken of the dependence of θ on χ and on ξ (the DCC angle) their forms become:

$$t_i^{\text{D}} = s\sqrt{\left(\frac{-\cos\chi}{-\cos\chi + 1}\right)} + p\frac{1}{\sqrt{(-\cos\chi + 1)}} \qquad (8)$$

$$t^{\text{C}} = s\frac{\cos\xi}{\sqrt{(\cos^2\xi - \cos\chi)}} + p\frac{\sqrt{-\cos\chi}}{\sqrt{(\cos^2\xi - \cos\chi)}}$$

In dealing with hyperconjugative effects, we use the orthonormal transformation from the three t_i^D (t_a, t_b, t_c) to the following orbitals, the fourth orbital (t^C) remaining unchanged.

$$\left.\begin{aligned} u_1 &= \frac{1}{\sqrt{3}}(t_a + t_b + t_c) \\ u_2 &= \frac{1}{\sqrt{2}}(t_b - t_c) \\ u_3 &= \sqrt{\frac{2}{3}}\left[t_a - \frac{1}{2}(t_b + t_c)\right] \\ u_4 &= t^C \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

Of these, the first has σ-type symmetry, and the second and third have π_y and π_z symmetry respectively. Now it follows from (8) and (9) that a symmetric change in HCH angle can affect only u_1 and u_4. In particular, u_3, the orbital entering into conjugation with the ring, remains unaltered.

For the tetrahedral configuration, u_1 and u_4 are given by:

$$\left.\begin{aligned} u_1 &= \frac{\sqrt{3}}{2}s - \frac{1}{2}p_x \\ u_4 &= \frac{1}{2}s + \frac{\sqrt{3}}{2}p_x \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

Assuming a maximum angle change of $\Delta\chi = -\Delta\xi = 17'$ (0·005 radian) we obtain:

$$\begin{aligned} u_1' &= 0{\cdot}8706s - 0{\cdot}4922p_x \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11) \\ u_4' &= 0{\cdot}4922s + 0{\cdot}8706p_x \end{aligned}$$

The electronegativity of a carbon atom in a hybrid orbital may be assumed to increase linearly with $\cos^2\theta$.[14] Thus in u_1', the carbon atom is more electronegative than in u_1 ($\cos^2\theta' = 0{\cdot}7579$; $\cos^2\theta = 0{\cdot}75$), the change being about 9% of the electronegativity difference between pure sp^3- and sp^2-orbitals. On the other hand, the electronegativity of the carbon atom in the u_4 orbital decreases to the same extent. The net effect is thus a charge migration in the σ-orbitals from the hydrogen atoms in the direction of the ring.

In the tetrahedral configuration there is an electronegativity difference between the σ group-orbital of the hydrogen atoms and u_1, the former being more electropositive.[11] The electronegativity difference between u_4 and the sp^2-orbital of the adjacent ring atom can be split into two parts: (*a*) the intrinsically greater electronegativity of sp^2 than of sp^3; and (*b*) the difference induced, in the same direction, by the hydrogen group. Increasing the HCH angle enhances both effects.

Implicit in our treatment, in which a constant parameter, ε, determines the relative electronegativities of the π-orbitals on adjacent atoms, and does not differentiate between neighbours of the same and different hybridisation of the corresponding σ-orbitals, is that the primary factor is induction, the intrinsic electronegativity difference being assigned relatively minor importance. Having found that increasing the HCH angle increases the $C_{(2)}$–$C_{(3)}$ electronegativity difference by no more than 9% of the *intrinsic* sp^3–sp^2 electronegativity difference, we see that its effect relative to the total difference must be considerably smaller. We must note, moreover, that this effect of angle change appears in the σ-*skeleton*. What we require, and what is in effect represented by the various $(\delta_1 - \delta_k)$'s, are the induced π-electronegativity differences, which result from induction in the σ-skeleton, and may be presumed smaller than the σ-electronegativity differences themselves. This gives us reason to believe that the effect of changing the HCH angle, and hence hybridisation, on $(\delta_2 - \delta_3)$ will be even smaller than its presumed effect on σ-electronegativity differences.

With regard to $(\delta_1 - \delta_2)$, it has been noted that there is no effect of hybridisation change

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[14] Moffitt, *Proc. Roy. Soc.*, 1950, *A*, **202**, 534, 548.

on the π-electronegativity difference. Such an effect could only arise indirectly through the change in σ-electronegativity, which we have shown to be small.

All in all, it seems safe to neglect the effect of hybridisation change on electronegativity relative to the primary factor, which we take to be non-bonding interactions. In any event, in passing from toluene to [α-$^2H_3$]toluene the direction of the two effects is the same, and both can be accommodated by an increase in the absolute value of δ_1.

Conclusions.—It appears that of the two configurational differences considered, the shortening of the CH bond in [α-$^2H_3$]toluene is the more important. The increased H_3–C overlap and the increased electropositivity of the H_3 pseudoatom lead to roughly equal and opposite energetic effects. The latter factor is predominant in determining the change in electron distribution, so that electron release to the ring may be sufficiently greater in [α-$^2H_3$]toluene than in toluene for experimental verification.

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