

HMO STUDY OF TOLUENE  
AND XYLENES USING INDUCTION  
AND HETEROATOM MODELS

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In the present paper a selected set of physical properties of toluene and xylenes and anions thereof is interpreted with the aid of simple HMO method, using the induction model<sup>1</sup> and the heteroatom model<sup>2</sup> for methyl group. We aimed at finding the best parameters for both models, with respect to both each single quantity for individual compounds studied and the whole set of quantities for this group of compounds. The interpretation of the dipole moment of toluene, the energy of the lowest singlet transition in toluene and in xylenes, and the hyperfine proton splitting in the anion of *m*-xylene is presented.

METHOD OF CALCULATION

Calculations were carried out using the simple MO LCAO method. The values of parameter  $\delta_c$ , (induction model), were taken from the interval  $\langle 0 \text{ to } -0.6 \rangle$  with the step 0.05. The parameters  $\delta_x$  and  $\gamma_{cx}$  (heteroatom model) were changed over the interval  $\langle 1.6 \text{ to } 2.4 \rangle$  with the step 0.2 and over the interval  $\langle 0.3 \text{ to } 0.9 \rangle$  with the step 0.05, respectively.

For Coulomb integral of all the carbon atom (except for the atoms  $C'$  in the induction model, to which the methyl group is attached) we used the value of  $\alpha$ . Similarly, the value of  $\beta$  was used for all resonance integrals between neighbouring carbon atoms. The Hamiltonian matrix was diagonalized on a Minsk 22 digital computer. Spin densities,  $\rho_i$ , on the atoms of  $\pi$ -electron

TABLE I  
Calculated and Experimental Values of Quantities Studied

Compound	$\zeta$	$\zeta_{1M}$	$\zeta_{MH}$	$\zeta_{exp}$ (ref:)
Benzene	$\Delta E$ , eV	—	—	4.72 (6)
Toluene	$\Delta E$ , eV	4.53	4.48	4.64 (6)
	$\mu$ , D	0.39	0.40	0.40 (7)
<i>o</i> -Xylene	$\Delta E$ , eV	4.57	4.38	4.62 (8)
<i>p</i> -Xylene	$\Delta E$ , eV	4.44	4.26	4.55 (9)
<i>m</i> -Xylene	$\Delta E$ , eV	4.58	4.43	4.58 (8)
	$a_2^H$ , gauss	6.55	6.69	6.85 (10)
	$a_4^H$ , gauss	2.05	2.01	1.46 (10)
	$a_5^H$ , gauss	7.80	7.72	7.72 (10)

system of anions and  $\pi$ -components of dipole moment were calculated from the components of eigenvectors in the usual way. The  $\sigma$ -component of dipole moment, the magnitude of which was estimated<sup>3</sup> as 0.03–0.06 D, was neglected. In order to calculate the energy of the lowest singlet transition,  $\Delta E$ , one has to know the value of the resonance integral  $\beta$ . As we were interested in the contribution provided by the use of both models for the selected set of quantities, we first determined the value of  $\beta$  using the value of energy for the lowest singlet transition of benzene. Resulting value of  $\beta$  was  $-2.36$  eV. The excitation energies  $\Delta E$  correspond to 0–0 transitions of  $\alpha(L_b)$  bands. The absorption spectra of benzene and toluene were measured in cyclohexane; in the case of xylenes the vapour-phase absorption spectra were used. The survey of the experimental values for each of the selected calculated quantities is given in Table I.

For each value of parameter  $\delta_c$ , and of the couple of parameters  $\delta_x$  and  $\gamma_{cx}$  we determined the value of dipole moment for toluene and of the  $\Delta E$  for all the compounds studied. The hyperfine proton splitting constants were calculated only in the anion of *m*-xylene. In the case of toluene and *p*-xylene the values of orbital coefficients are determined by the symmetry only and thus they are not influenced by both models employed in the calculations. We first determined the best values of parameters  $\delta_c$ ,  $\delta_x$ , and  $\gamma_{cx}$  for each single quantity for each of the compounds studied. In the case of dipole moment and of the energies of the lowest singlet transition we took as the criterion the agreement between the calculated and the experimental values. For the hyperfine splitting constants the best parameters were determined according to the work<sup>4</sup>. The determination of the best parameters is based on the validity of a linear relationship between hyperfine proton splitting constant,  $a_H$ , for the proton of a ring, and  $\pi$ -electron spin density,  $\rho$ , on a trigonal carbon atom to which the proton is attached<sup>5</sup>:

$$a_H = Q^H \rho, \quad (1)$$

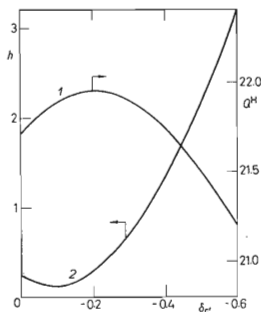


FIG. 1

Induction Model. Dependence of Parameter  $|Q^H|$  and Quantity  $h$  for Ring Protons of *m*-Xylene on Parameter  $\delta_c$ .

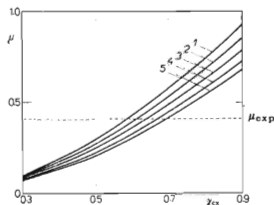


FIG. 2

Heteroatom Model. Dependence of Calculated Value of Dipole Moment of Toluene on Parameter  $\gamma_{cx}$

where  $Q^H$  is the negative constant with the same value for all the protons, regardless their position. According to the theory of errors, the most probable  $Q^H$  is given as

$$Q^H = \frac{\sum_{i=1}^n a_i q_i}{\sum_{i=1}^n a_i^2} \quad (2)$$

and the mean error of a single measurement,  $h$ , corresponding to the  $Q^H$  given by Eq. (2), is then

$$h = [1/(n-1)] \sum_{i=1}^n [(a_{Hi})_i - Q^H a_i]^2 \quad (3)$$

The criterion for the proton splitting constants is following: the best values of parameters  $\delta_{c'}$ , resp.  $\delta_x$  and  $\gamma_{cx}$  are those that yield the minimal value of  $h$  for the  $Q^H$  determined according to Eq. (2).

We further obtained the best parameter  $\delta_{c'}$ , and the best couple of parameters  $\delta_x$  and  $\gamma_{cx}$  relating to the set of eight selected quantities. For each quantity  $\xi$  we determined for each  $\delta_{c'}$ , resp.  $\delta_x$  and  $\gamma_{cx}$  the absolute value of the deviation ( $d$ ) of the calculated value  $\xi_i$  from the experimental value,  $\xi_{exp}$ , which was related to the value of  $\xi_{exp}$ .

$$d = |(\xi_i - \xi_{exp})/\xi_{exp}| \quad (4)$$

From the values of  $d_k$  for individual quantities we calculated the average deviation  $\bar{d}$

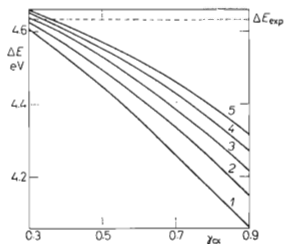


FIG. 3

Heteroatom Model. Values of the Lowest Singlet Transition Energies in Toluene as a Function of Parameter  $\gamma_{cx}$

1  $\delta_x = 1.6$ ; 2  $\delta_x = 1.8$ ; 3  $\delta_x = 2.0$ ; 4  $\delta_x = 2.2$ ; 5  $\delta_x = 2.4$ .

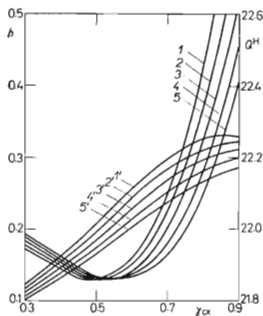


FIG. 4

Heteroatom Model. Dependence of Parameter  $|Q^H|$  and Quantity  $h$  for Ring Protons of Toluene on Parameter  $\gamma_{cx}$

1 and 1'  $\delta_x = 1.6$ ; 2 and 2'  $\delta_x = 1.8$ ; 3 and 3'  $\delta_x = 2.0$ ; 4 and 4'  $\delta_x = 2.2$ ; 5 and 5'  $\delta_x = 2.4$ .

$$\bar{d} = (1/n) \sum_{k=1}^n d_k, \quad (5)$$

for  $n = 8$ . As best values of parameters  $\delta_{c'}$ ,  $\delta_x$  and  $\gamma_{cx}$  we took that value for which the deviation  $\bar{d}$  attains minimal value.

#### RESULTS AND DISCUSSION

**Induction model.** The values of quantities  $\mu$ ,  $\Delta E$ ,  $Q^H$  and  $h$  are changing smoothly with parameter  $\delta_{c'}$ . From the dependence of  $\mu$  on  $\delta_{c'}$  for toluene it follows that  $\mu_{\text{calcd}} = \mu_{\text{exp}}$  for  $\delta_{c'} = -0.18$ . Similarly, from the plot of  $\Delta E$  versus  $\delta_{c'}$  for toluene we obtain that  $\Delta E_{\text{calcd}} = \Delta E_{\text{exp}}$  for  $\delta_{c'} = -0.08$ . The shape of the dependence of  $\Delta E$  on  $\delta_{c'}$  for *o*-, *m*- and *p*-xylene is similar to the dependence obtained for toluene. The corresponding best values of parameters  $\delta_{c'}$  are summarized in Table II. The dependence of quantities  $|Q^H|$  and  $h$  on  $\delta_{c'}$  is shown in Fig. 1, curve 1 representing the plot of  $|Q^H|$  on  $\delta_{c'}$ , and curve 2 that of  $h$  on  $\delta_{c'}$ . From Fig. 1 it follows that for the group of three hyperfine splitting constants for the protons of a ring in *m*-xylene the best value of parameter  $\delta_{c'}$  is  $-0.11$ . For the whole set we calculated the value of  $\bar{d}$  in dependence on parameter  $\delta_{c'}$ . The obtained dependence  $\bar{d}(\delta_{c'})$  can be well approximated by two straight lines, the point of intersection of which determines the best value of parameter  $\delta_{c'}$  relating to the whole set. With regard to the chosen step in parameter  $\delta_{c'}$ , the best value  $\delta_{c'} = -0.17$  is determined with the accuracy of  $\pm 0.025$ . The values of individual quantities calculated using the above value of parameter  $\delta_{c'}$  are given in Table I and are denoted by index IM.

**Heteroatom Model.** The values of quantities  $\mu$ ,  $\Delta E$ ,  $Q^H$ , and  $h$  calculated for each couple of parameters  $\delta_x$  and  $\gamma_{cx}$  were plotted against  $\gamma_{cx}$  for single values of  $\delta_x$ . The curves  $\mu(\gamma_{cx})$  and  $\Delta E(\gamma_{cx})$  for toluene are shown in Figs 2 and 3, resp. The shape of the curves  $\Delta E(\gamma_{cx})$  for *o*-, *m*- and *p*-xylene resemble that for toluene (see Fig. 3). The dependence of  $|Q^H|$  on  $\gamma_{cx}$  and  $h$  on  $\gamma_{cx}$  for *m*-xylene are shown in Fig. 4. From Figs 2–4 and from the curves  $\Delta E(\gamma_{cx})$  for xylenes, not shown in the picture, we obtained the best values of  $\gamma_{cx}$  (for each value of  $\delta_x$ ) for each individual quantity studied. These are given in Table II. For the whole of quantities we calculated the value of  $\bar{d}$  for each couple of parameters  $\delta_x$  and  $\gamma_{cx}$ . Similarly to induction model, the curves  $\bar{d}(\gamma_{cx})$

TABLE II  
Best Values of Parameters  $\delta_{c'}$  and  $\gamma_{cx}$  for Single Quantities and Whole Set

Quantity	$\delta_{c'}$	$\gamma_{cx}$				
		$\delta_x = 1.6$	$\delta_x = 1.8$	$\delta_x = 2.0$	$\delta_x = 2.2$	$\delta_x = 2.4$
$\mu$ of toluene	-0.18	0.59	0.61	0.64	0.67	0.70
$\Delta E$ of toluene	-0.08	—	—	0.30	0.33	0.36
$\Delta E$ of <i>o</i> -xylene	-0.12	—	—	0.31	0.33	0.36
$\Delta E$ of <i>p</i> -xylene	-0.11	—	0.30	0.33	0.36	0.38
$\Delta E$ of <i>m</i> -xylene	-0.18	—	0.33	0.38	0.42	0.44
$a_2^H, a_4^H, a_5^H$ of <i>m</i> -xylene	-0.11 <sup>a</sup>	0.47 <sup>b</sup>	0.50 <sup>c</sup>	0.52 <sup>d</sup>	0.55 <sup>e</sup>	0.57 <sup>f</sup>
Whole set	-0.17	0.58	0.61	0.64	0.67	0.69

<sup>a</sup>  $Q^H = -21.90$  gauss; <sup>b</sup>  $Q^H = -21.99$  gauss; <sup>c</sup>  $Q^H = -22.02$  gauss; <sup>d</sup>  $Q^H = -22.05$  gauss; <sup>e</sup>  $Q^H = -22.07$  gauss; <sup>f</sup>  $Q^H = -22.09$  gauss.

can be well approximated by couples of straight lines, the points of intersection of which yield the best value of parameter  $\gamma_{cx}$  for each value of parameter  $\delta_x$ . The form of the dependence of  $\bar{d}$  on  $\gamma_{cx}$  is represented in Fig. 5. The obtained best values of  $\gamma_{cx}$  are given in Table II. With regard to the chosen step in  $\gamma_{cx}$  these values are laden with the error  $\pm 0.025$ . In these calculations we used the couple of parameters (2.4; 0.69) since it has the lowest value of average deviation  $\bar{d}$ . The values of individual quantities calculated for this couple of parameters are given in Table I and are denoted by index MH.

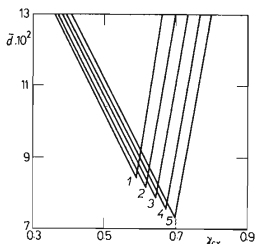


FIG. 5

Heteroatom Model. Plot of Quantity  $\bar{d}$  against Parameter  $\gamma_{cx}$

1  $\delta_x = 1.6$ ; 2  $\delta_x = 1.8$ ; 3  $\delta_x = 2.0$ ; 4  $\delta_x = 2.2$ ;  
5  $\delta_x = 2.4$ .

From the calculation it follows that for induction model the best parameters  $\delta_c$  lie within a narrow interval ( $-0.08$  to  $-0.18$ ), the best value for the whole set of quantities being  $-0.17$ . In examining the applicability of heteroatom model we were looking for the best  $\gamma_{cx}$  for each value of parameter  $\delta_x$ . For  $\delta_x = 1.6$  and  $1.8$  we found that not all of the individual best values of  $\gamma_{cx}$  lie in the studied interval of  $\gamma_{cx}$ . The best values of parameter  $\gamma_{cx}$  for the remaining values of  $\delta_x$  ( $2.0, 2.2, 2.4$ ) lie in the intervals with length  $0.34$ ; these are  $\langle 0.30$  to  $0.64 \rangle$ ,  $\langle 0.33$  to  $0.67 \rangle$ , and  $\langle 0.36$  to  $0.70 \rangle$ . As for induction model, the best values of parameter  $\gamma_{cx}$  lie at upper boundary of the above intervals.

The present calculation was performed for three kinds of quantities in a given group of compounds with the special selection of the value of integral  $\beta$ . The calculation clearly shows that the interpretation of both the single quantities for each of the compounds studied and the whole set of the quantities for the given group of compounds is improved by the inclusion of methyl group into calculation.

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