

Estimation of Inductive Effect of Methyl Group in Methylbenzenes from Charge-transfer Spectra of Their Molecular Complexes with Some π -Electron Acceptors

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Coulson-Longuet-Higgins perturbation theory has been used to obtain expressions for energies of methylbenzenes from those of benzene. After correlating these energy expressions with the charge-transfer transition energies of the complexes of the methylbenzenes with a number of π -electron acceptors, a suitable inductive effect Hückel parameter for the methyl group has been derived in a straightforward way.

The energy of electronic charge-transfer (CT) transition in molecular complexes between electron donors and electron acceptors is given by the well known relation^{1,2},

$$h\bar{\nu}_{CT} = I_D - E_A - C \quad \dots (1)$$

where $\bar{\nu}_{CT}$ is the wavenumber (cm^{-1}) of the CT absorption, I_D is the vertical ionisation potential of the donor, E_A the electron affinity of the acceptor and C is a term summing the contributions from non-bonding species, polarisation and solvation. The main part of C comes from the electrostatic attraction between the negatively charged acceptor and the positively charged donor in the excited state³. Working with a common acceptor and a common solvent for a series of structurally similar donors one may take both E_A and C to be constant. Thus one may correlate $h\bar{\nu}_{CT}$ with I_D , which can, in turn, be correlated with the Hückel energy of the highest occupied molecular orbital (HOMO) of the donor. In the present work we use a correlation of the type

$$h\bar{\nu}_{CT} = -E_D + b \quad \dots (2)$$

where E_D is the energy of the HOMO of the donor in a series of donors with a common acceptor and solvent.

Materials and Methods

The donors chosen are benzene and various methylbenzenes such as toluene, *o*-, *m*- and *p*-xylenes, 1,2,4-trimethylbenzene, mesitylene, durene, penta-methylbenzene and hexamethylbenzene. These were of extra pure quality. Three acceptors considered separately are: (i) pyromellitic dianhydride (PMDA); (ii) 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ); and (iii) 2,3-dicyano-*p*-benzoquinone (DCNQ).

Method of Calculation

According to Coulson-Longuet-Higgins⁴ perturbation theory, the change in coulomb integral of a carbon atom carrying a methyl substituent alters the energy of the j th Hückel molecular orbital by the amount

$$\Delta E = E_j - E_j^0 = \delta\alpha_r \sum_r C_{rj}^2 \quad \dots (3)$$

where $\delta\alpha_r$ is the change in coulomb integral of the r th atom from the standard value of the coulomb integral of carbon in benzene, C_{rj} is the atomic orbital coefficient of the r th atom in the j th MO and E_j^0 is the energy of the j th MO in the unperturbed system, i.e. benzene.

To take into account the equivalence of many locations of substituents which are possible for a particular methylbenzene the Eq. (3) is modified to the form (4)

$$E_j = E_j^0 + h_{Me} \frac{1}{n} \sum_n \sum_r C_{rj}^2 \quad \dots (4)$$

where $\delta\alpha_r$ for a methyl group has been put equal to h_{Me} (β being the standard C-C resonance integral in benzene), r refers to the location of methyl groups, and n is the number of equivalent structures of the methylbenzene under consideration.

Combining Eqs (2) and (4), we get

$$h\bar{\nu}_{CT} = -h_{Me} \frac{1}{n} \sum_n \sum_r C_{rj}^2 + \text{constant} \quad \dots (5)$$

where the j th MO now means the HOMO of the methylbenzene donor. A plot of $h\bar{\nu}_{CT}$ against $\frac{1}{n} \sum_n \sum_r C_{rj}^2$ is, therefore, expected to be linear from the slope of which h_{Me} can be obtained.

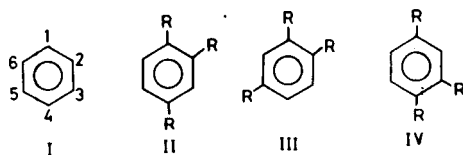
The HOMO of benzene is one of the following degenerate molecular orbitals:

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$$\Psi_1 = \frac{1}{12} (2\varphi_1 + \varphi_2 - \varphi_3 - 2\varphi_4 - \varphi_5 + \varphi_6)$$

$$\Psi_2 = \frac{1}{2} (\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6)$$

where φ_s are the π -type atomic orbitals of benzene carbon atoms numbered as shown in structure (I)



Substitution at position-1 does not perturb Ψ_2 but raises the energy of Ψ_1 , making it the HOMO for toluene. Hence for toluene the coulombic perturbation coefficient is calculated from Ψ_1 . For methylbenzenes having more than one methyl substituent the mean of C_{rj}^2 ($r \neq 1$ or 4) obtained from Ψ_1 and Ψ_2 is added to C_1^2 of Ψ_1 to get $\sum_r C_{rj}^2$ and the average of these over the n equivalent structures of such alkylbenzenes under consideration is taken as the coulombic perturbation coefficient⁵.

The case of 1, 2, 4-trimethylbenzene will serve as an example. If the numbering with position-1 in structure (I) is used, three structures (II), (III) and (IV) are obtained by choosing each substituent in turn at the 1-position and maintaining a minimum in summing the location numbers. (A mirror image set of three additional structures may also be obtained but these are not distinct for the present argument). As $C_{1j}^2 = C_{4j}^2$ and $C_{2j}^2 = C_{3j}^2 = C_{5j}^2 = C_{6j}^2$ for both Ψ_1 and Ψ_2 , the value of $\sum_r C_{rj}^2$ for 1, 2, 4-trimethylbenzene is computed as

$$2C_1^2 (\text{from } \Psi_1) + \frac{1}{2} (C_2^2 \text{ from } \Psi_1 + C_2^2 \text{ from } \Psi_2) \text{ (for II and IV)}$$

and

$$C_1^2 (\text{from } \Psi_1) + 2 \cdot \frac{1}{2} (C_2^2 \text{ from } \Psi_1 + C_2^2 \text{ from } \Psi_2) \text{ (for III)}$$

However, the molecule behaves as if it had only one structure which is composite of II, III and IV. The calculated mean value $\frac{1}{n} \sum_n \sum_r C_{rj}^2$, therefore is a linear combination of all these structures normalised to one active structure.

Results and Discussion

Experimental data for CT transition energies for the systems studied have been taken from literature^{6,7} and are given in Table 1 together with the calculated perturbation coefficients.

Table 1—Charge-Transfer Transition Energies and Calculated Perturbation Coefficients

Donor	$h\nu_{CT}$ (cm^{-1})			$\frac{1}{n} \sum_n \sum_r C_{rj}^2$
	PMDA ^a	DDQ ^b	DCNQ ^b	
Benzene	33,600	24,600	25,700	0
Toluene	30,300	22,700	23,800	0.333
<i>o</i> -Xylene	28,900	21,100	22,200	0.500
<i>m</i> -Xylene	28,600	21,100	22,200	0.500
<i>p</i> -Xylene	28,100	19,600	20,700	0.667
1,2,4-Trimethylbenzene	27,000	—	—	0.777
Mesitylene	27,300	19,600	21,000	0.667
Durene	25,600	17,200	18,500	1.000
Pentamethylbenzene	24,400	16,800	18,200	1.133
Hexamethylbenzene	23,000	16,000	17,200	1.333

(a) Data collected from reference 6; (b) data collected from ref. 7.

The two-fold degeneracy of the HOMO of benzene is lifted slightly when it is substituted and as a consequence multiple CT bands are expected with alkylbenzenes as donors. This was first predicted by Orgel^{7a} and subsequently verified by many workers^{7b}.

A list of references for works on multiple CT bands may be found in Foster's book^{7c}. As the perturbation formula used in this paper refers to the HOMO of the donor, the longest wavelength CT band must be used for correlation. The bands for complexes with PMDA as acceptor are well resolved and the data in Table 1 correspond to the longest wavelength ones. As regards the other two acceptors the CT energies shown in Table 1 are results of unpublished work of P.H. Emslie and have been collected from Foster's book (loc. cit.). However, the linear plots obtained for complexes with these two acceptors by applying the perturbation technique used in this paper are parallel to the one

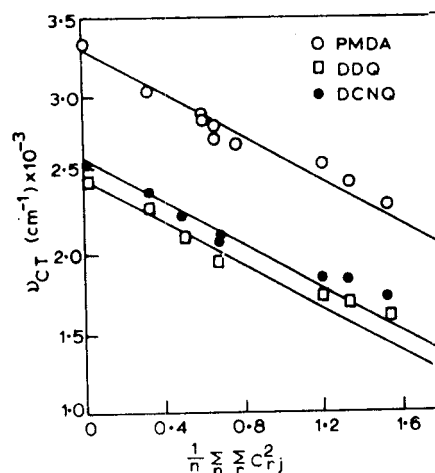


Fig. 1—Plots of $h\nu_{CT}$ against perturbation coefficients for three acceptors: pyromellitic dianhydride (PMDA); 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ); and 2,3-dicyano-*p*-benzoquinone (DCNQ)

obtained for the PMDA-alkylbenzenes complexes and therefore the bands reported for these complexes may be regarded as closely corresponding to the longest wavelength bands.

Figure 1 shows that the plots of $h\nu_{CT}$ against the perturbation coefficients are linear for all the three acceptors studied, with almost the same slope, as expected from Eq. (5). The slope ($= -7833.333 \text{ cm}^{-1}$) when used in Eq. (5), yields a value of $h_{Me} = -0.3136$, with $\beta = -3.1 \text{ eV}$ as obtained from the first four singlet-singlet transition energies of benzene. This value of h_{Me} is in excellent agreement with that (-0.3) obtained by Kysel⁸ while it is at least comparable to Streitwieser's⁹ recommended value of -0.5 . Lepley⁵ has reported a value of -0.21 for the inductive effect parameter for the methyl group which is close to the present value.

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