Determination of the gas-phase value of the inductive effect parameter of the methyl group from solvatochromic study of the charge-transfer band maxima of complexes of tetracyanoethylene with methylbenzenes

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Abstract. From solvatochromicity of CT-band maxima of complexes of TCNE with methylbenzenes in several apolar and polar solvents the inductive effect parameter, h_{Me}, of the methyl group has been calculated by the Coulson–Longuet-Higgins perturbation theory. From the measured solvent dependence of h_{Me}, the gas-phase value of the same has been determined to be -0.38 which is comparable with Streitwieser's recommended value of $h_{Me} = -0.50$. The higher value of h_{Me} in the gas phase than in solution has been explained.

Keywords. Solvatochromicity of CT-band maxima; complexes of TCNE with methylbenzenes; $-CH_3$ group inductive-effect parameter.

1. Introduction

A survey of literature concerning determination of the inductive effect parameter of the methyl group (h_{Me}) from CT-transition energies of various types of organic EDA complexes having progressive methyl substitution either in the donor or in the acceptor moiety reveals a wide variation in the value of h_{Me} (-0.20 to -0.40) as reported by different investigators (Lepley 1964; Kysel 1974; Seal and Mukherjee 1984; Mukherjee and Seal 1986). One of the probable reasons for this variation in h_{Me} may be a solvent effect since CT-transitions from which h_{Me} is ultimately evaluated often exhibit solvatochromicity because dipole moments of CT-complexes are different in their ground and excited states, the latter being virtually ionic (Davis 1975). In view of the solvatochromic effect on the CT-band maxima from which h_{Me} is evaluated, a study of the effect, if any, of the medium on the inductive effect parameter of the methyl group is most natural and expected. With this objective in view CT-complexes of some weakly polar or non-polar benzenoid hydrocarbons with TCNE, a non-polar acceptor, have been studied in several apolar and polar solvents. The results of our investigations are reported in the present communication.

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2. Theory and method

The energy (hv_{CT}) of CT-transition observed in molecular complexes is expressed by the well-known equation (McConnell *et al* 1953; Mulliken and Person 1961)

$$hv_{CT} = I_D - E_A - C, \tag{1}$$

where I_D is the vertical ionisation potential of the donor, E_A is the electron affinity of the acceptor and the term C sums the contributions from non-bonding interactions, solvation etc. The electrostatic interaction between the negatively charged acceptor and the positively charged donor in the excited state contributes mainly to C (Mulliken and Person 1969). Working with a common acceptor and a series of structurally similar donors in a given solvent, E_A and C may be taken as constants. Since I_D is equal to the negative of the energy of HOMO of the donor (E_D), one may use (1) in the form,

$$hv_{CT} = -E_D + \text{constant}. \tag{2}$$

For a π-donor in which a $-CH_3$ group is attached to a conjugated carbon atom, the coulomb integral of the latter changes by the amount

$$\delta\alpha = \alpha - \alpha_0 = h_{Me}\beta, \tag{3}$$

where α_0 is the standard coulomb integral of carbon atom in benzene and β is the standard C–C resonance integral in benzene. Consequently, in a series of methylated donors E_D changes with a change in the position or number of $-CH_3$ groups. Such a variation in energy can be followed by expressing E_D as a function of h_{Me} by applying the CLH perturbation theory (Coulson and Longuet-Higgins 1947) according to which the π-energy of the HOMO of any alkyl-benzene is given by

$$E_j = E_j^0 + \delta\alpha_r \sum_r C_{rj}^2, \tag{4}$$

where C_{rj} is the atomic orbital coefficient of the rth conjugated C-atom of benzene (to which the $-CH_3$ group is attached) in the jth MO in the LCAO wave function of the HOMO of benzene. Taking into consideration the equivalence of many locations of substituents which are possible for a particular methylbenzene, (4) is modified to the following form

$$E_j = E_j^0 + h_{Me}\beta(1/n)\sum_n \sum_r C_{rj}^2, \tag{5}$$

where $\delta\alpha_r$ for the $-CH_3$ group has been taken as equal to $h_{Me}\beta$, r refers to the location of methyl groups, and n is the number of equivalent structures of the methylbenzene under consideration.

Combining (2) and (5) one obtains a linear correlation

$$hv_{CT} = -h_{Me}\beta(1/n)\sum_n \sum_r C_{rj}^2 + \text{constant}, \tag{6}$$

from the slope of which the inductive effect PMO parameter h_{Me} can be evaluated.

3. Results and discussion

Complexes of TCNE with several methyl-substituted benzenes, viz toluene, *o*-xylene, mesitylene and hexamethylbenzene (HMB) have been studied in several polar and non-polar solvents. The donors chosen are either weakly polar or non-polar. Data for the frequency maxima of the CT-bands expressed as CT-transition energies (in eV) are shown in table 1 which contains the values of dielectric constants and refractive indices of solvents also. These data have been taken from the work of Rosenberg and Hale (1965). The method of computation of the perturbational co-efficient $(1/n)\Sigma_n\Sigma_r C_{rj}^2$, taking into consideration the degeneracy of the HOMO of benzene, can be found in Seal and Mukherjee (1984). The computed values for the donors are recorded in table 1.

For each solvent, a plot of hv_{CT} vs $(1/n)\Sigma_n\Sigma_r C_{rj}^2$ is fairly linear, verifying thereby the validity of (6). An LS fitting of the data for each solvent gives a fairly good linear correlation with a significant correlation coefficient, 0·98. The slopes of the plots shown in figure 1 evaluated graphically agree closely with those obtained by the LS method. From the LS slopes, h_{Me} values have been calculated using $\beta = -3.1$ eV as obtained from the first four singlet–singlet transitions of benzene. The values of h_{Me} in different solvents are shown in table 2 and they show a clear solvent-dependence.

An attempt has been made to determine the gas-phase value of h_{Me} from the observed solvent shift of the CT-band maxima. An inspection of hv_{CT} values in table 1 shows clearly that no linear correlation exists between solvent dielectric constant and the position of v_{max}. The stabilising interactions between donor–acceptor pairs in these solvents must be attributed to the polarisability of the solvent molecules because hv_{CT} values increase with decreasing values of the refractive index function (table 1) for each complex. The gas-phase value of hv_{CT} for each complex has been calculated by an LS curve fitting of the data $hv_{CT(soln)}$ and the polarizability function, $(n_D^2 - 1)/(2n_D^2 + 1)$, of the solvents. The values of $hv_{CT(g)}$ for the complexes of TCNE with toluene, *o*-xylene, mesitylene and hexamethylbenzene, which are shown in table 1, exhibit a fair correlation with $(1/n)\Sigma_n\Sigma_r C_{rj}^2$, the correlation coefficient being 0·94. As $(P_N/r| \leqslant 0.9) = 90\%$ for $N = 4$, the number of data points (Taylor 1982), the statistical reliability of h_{Me} values in different solvents as well as in the gas phase is greater than 90%. The slope of the plot *F* in figure 1 yields a value -0.38 for h_{Me}, which is substantially

Table 1. Transition energies of CT-complexes between TCNE and alkylbenzenes in different solvents and in the gas-phase at 20°C.

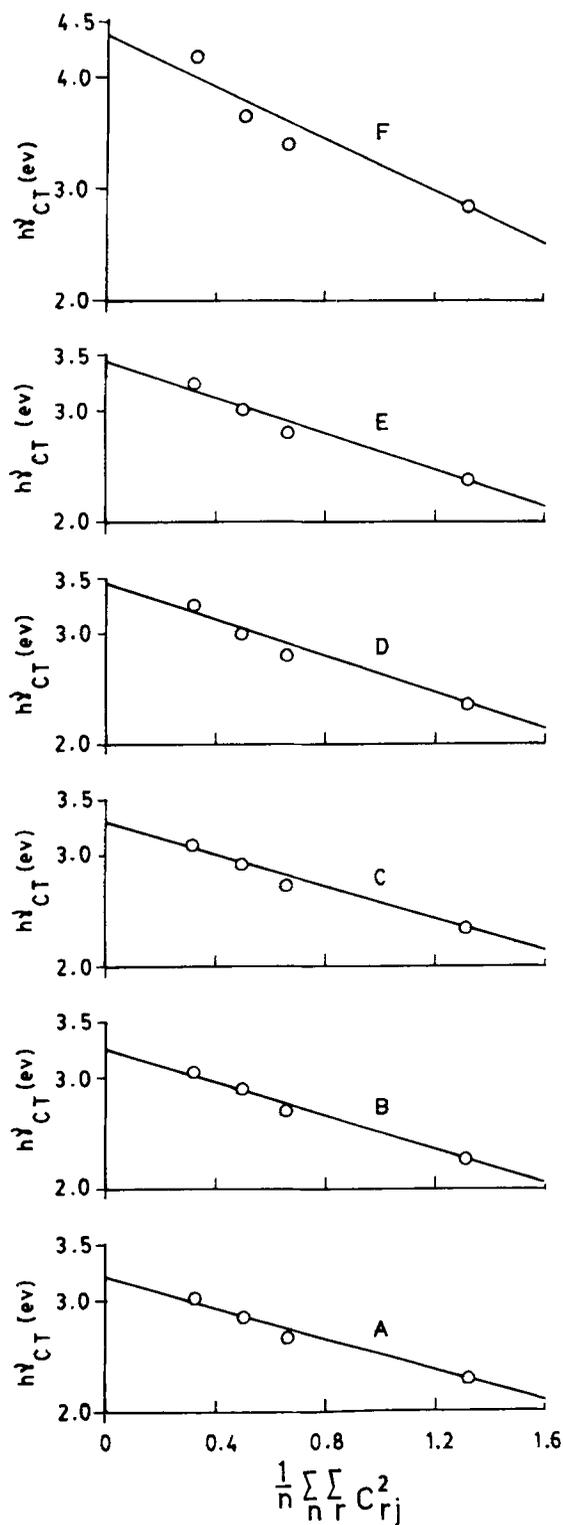|	Solvent						
	CCl_4	CH_2Cl_2	$n\text{-}C_6H_{14}$	CH_3CN	CH_3OH	Gas-phase	$\frac{1}{n}\sum_n\sum_r C_{rj}^2$
Dielectric constant	2·2	9·1	1·9	37·5	33·6	1	
Refractive index (n_D)	1·463	1·424	1·375	1·344	1·331	1	
$n_D^2 - 1/2n_D^2 + 1$	0·2159	0·2033	0·1863	0·1748	0·1698	0	
Donor/hv_{CT}(eV)							
Toluene	3·0250	3·0498	3·1118	3·2482	3·2606	4·1867	0·333
o-Xylene	2·8639	2·8887	2·9259	3·0126	3·0250	3·6400	0·500
Mesitylene	2·6779	2·6903	2·7275	2·8143	2·8268	3·4000	0·667
Hexamethylbenzene	2·2936	2·2812	2·3556	2·3804	2·4052	2·8533	1·333

Figure 1. Plot of $h\nu_{CT}$(eV) vs $(1/n)\Sigma_n\Sigma_r C_{rj}^2$ for complexes of TCNE with aromatic hydrocarbons in apolar and polar solvents. A – carbontetrachloride; B – dichloromethane; C – n-hexane; D – acetonitrile; E – methanol and F – gas phase.

Table 2. Inductive effect parameter of the methyl group in different solvents and in the gas-phase at 20°C along with correlation coefficient and statistical reliability.

Medium	h_{Me}	r	Statistical reliability
CCl_4	-0.2289	0.9885	90%
CH_2Cl_2	-0.2417	0.9896	90%
$n\text{-}C_6H_{14}$	-0.2339	0.9820	90%
CH_3CN	-0.2660	0.9825	90%
CH_3OH	-0.2617	0.9809	90%
Gas-phase	-0.3845	0.9438	90%

higher than those reported (Mukherjee and Seal 1986; Roy *et al* 1989) earlier and is comparable with Streitwieser's (1961) recommended value -0.50 for h_{Me}. The probable reason for a higher value of h_{Me} in the gas phase than in the liquid state may be due to a greater bond interaction between the methyl group and the benzene ring than is possible in a solvent where the solute–solvent interaction is more predominant than the intramolecular interaction between the methyl function and the aromatic loop (Brown 1959).

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