Determination of inductive effect parameter of methyl group from trends in fluorescence maxima of some charge-transfer complexes of N-ethyltetrachlorophthalimide with methylbenzenes and methoxybenzenes using graph theoretical technique

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From trends in fluorescence maxima \( (h\nu_{CT}) \) of charge transfer complexes of N-ethyltetrachlorophthalimide with methylbenzenes and methoxybenzenes the inductive effect PMO parameter of the methyl group has been calculated using Coulson-Longuet-Higgins perturbation theory. For complexes of methylbenzenes \( h_{Me} \) is found to be \(-0.175\) while for methoxybenzenes a value of \(-0.2855\) has been estimated for the same. The agreement with literature data is good. The necessary perturbational coefficients and eigenvalues have been calculated using some recently developed graph theoretical techniques which reduce the entire computation to a paper-and-pencil work.

The charge-transfer (CT) transition energies \( (h\nu_{CT}) \) of electron donor-acceptor (EDA) complexes of a given acceptor with a series of structurally similar donors vary linearly with the energy of the highest occupied molecular orbitals (HOMO) of the donors \(^1\) as expected from Mulliken's theory. For \( \pi \)-electron donors with progressive alkyl or heteroatom substitution, the HOMO energies of the donors can be expressed as functions of the heteroatom parameter or inductive effect parameter of the alkyl group using Coulson-Longuet-Higgins perturbation theory within the Hückel formalism. When such expressions are correlated with \( h\nu_{CT} \) in accordance with Mulliken's theory, values of the heteroatom parameter or the inductive effect parameter of the alkyl group can be evaluated as shown by Lepley, Kyssel and recently by Seal and Mukherjee. Since fluorescence bands are almost mirror images of the absorption spectra, trends in CT fluorescence maxima, \( h\nu_{CT(f)} \) of the CT complexes can also be similarly treated.

Phthalimide and its derivatives are known to act as weak \( \pi \)-electron acceptors in the formation of CT complexes. Presently we have investigated the trends in \( h\nu_{CT(f)} \) of several complexes of \( N \)-ethyltetrachlorophthalimide with a series of (i) methylbenzenes and (ii) methoxybenzenes and the inductive effect PMO parameter of methyl group has been estimated from the trends. For methylbenzenes the unperturbed system is benzene the Hückel MOs of which are well known. For methoxybenzenes the unperturbed system are the corresponding phenols (as the object is to obtain the inductive effect PMO parameter of the methyl group only). To get the necessary perturbational quantities related to their HOMOs, graph theoretical techniques have been used since the method is easier to apply and by its use one can avoid calculation of all the MO wavefunctions which are unnecessary for use by the present perturbational technique.

Principle and Method

The \( h\nu_{CT} \) of EDA complexes is expressed by the well known equation

\[
h\nu_{CT} = I_D - E_A - C \quad \ldots (1)
\]

where \( I_D \) is the vertical ionisation potential of the donor, \( E_A \) is the electron affinity of the acceptor and \( C \) is a term which sums the contributions from non-bonding factors, polarisation and solvation. The main part of \( C \) comes from the electrostatic attraction between the negatively charged acceptor and positively charged donor in the excited state. In the case of a common acceptor and a series of structurally similar donors in a given solvent Eq. (1) may be rewritten as in the form

\[
h\nu_{CT} = -E_D + b \quad \ldots (2)
\]

where \( E_D \) is the energy of the HOMO of the donor and \( b \) is a constant. As pointed out earlier \( h\nu_{CT(f)} \) of CT complexes can also be similarly
treated. Hence, one may write Eq (2) in the form (3),

$$\hbar V_{CT(\phi)} = -E_D + b'$$  \hspace{1cm} (3)

where $b'$ is a new constant. Now, if the donors form a series of progressively alkyl substituted aromatic compounds, $E_D$ can be expressed in terms of the PMO parameter of the alkyl group using Coulson-Longuet-Higgins perturbation theory. Then using Eq. (3) one can estimate the PMO parameter of the alkyl group from the experimentally observed trends in $\hbar V_{CT(\phi)}$.

According to Coulson-Longuet-Higgins perturbation theory as applied to Hückel formalism, the $\pi$-energy of the HOMO of an alkyl benzene is given by

$$E_D = E_{HOMO} = E_0^0 + h_R \beta \sum_{n} \sum_{r} C^2_{n,r}$$  \hspace{1cm} (4)

where $E_0^0$ is the energy of the HOMO of benzene (the unperturbed system), $n$ is the number of equivalent structures of the alkylbenzene and $C_{n,r}$ is the atomic orbital coefficient of the $r$th conjugated atom of benzene (to which the alkyl group $R$ is attached) in its HOMO. The method of calculation of the perturbational coefficient $\frac{1}{n} \sum_{r} C^2_{n,r}$ taking into consideration the degeneracy of the HOMO of benzene, can be found in reference 8. In Eq. (4) $\beta$ is the standard resonance integral between two bonded carbon atoms in benzene and $h_R$, the PMO parameter of the alkyl group ($R$) is given by Eq. (5)

$$\delta \alpha = h_R \beta$$  \hspace{1cm} (5)

where $\delta \alpha$ is the change in Coulomb integral ($\alpha$) of a benzene carbon atom due to the inductive effect of the group $R$ attached to this atom. Writing $\chi_{n,r}^0 \beta$ for $E_0^0$ and putting Eq. (4) in Eq. (3) one obtains

$$\hbar V_{CT(\phi)} + \chi_{n,r}^0 \beta = -h_R \beta \sum_{n} \sum_{r} C^2_{n,r} + \text{constant}$$  \hspace{1cm} (6)

Thus, a plot of $\hbar V_{CT(\phi)} + \chi_{n,r}^0 \beta$ against the perturbational coefficient should be linear with a slope equal to $-h_R \beta$ from which $h_R$ can be calculated.

For the series of methoxybenzenes considered in the present study, phenol and $p$-quinol have been taken as the unperturbed systems. As the HOMO's of these systems are non-degenerate equation analogous to Eq. (6) is

$$\hbar V_{CT(\phi)} + \chi_{n,r}^0 \beta = -h_R \beta \sum_{n} \sum_{r} C^2_{n,r} + \text{constant}$$  \hspace{1cm} (7)

The $\pi$-MO energies and necessary coefficients related to HOMOs of phenol and $p$-quinol were calculated graph theoretically. The characteristic polynomial (CP) of phenol whose graph $G_1$ is shown in Fig. 1 can be written as

$$(-1)^7 \{A - X\} = -[\{h_0 - X\}C_6 - k_{C-O}L_5]$$  \hspace{1cm} (8)

where $A$ is the adjacency matrix of the graph, $I$ is the unit matrix of the size of $A$, $h_0$ and $k_{C-O}$ are the perturbational parameters for oxygen atom in phenol. The latter two parameters are given by Eq. (9)

$$\alpha_0 = \alpha + h_0 \beta \text{ and } \beta_{C-O} = k_{C-O} \beta$$  \hspace{1cm} (9)

$C_6$ and $L_5$ are respectively the characteristic polynomials of benzene and a linear chain of 5 conjugated atoms. With $h_0 = 2$ and $k_{C-O} = 0.8$ as recommended by Streitwieser 12, one has for phenol the CP,

$$P(G_1; X) = (-1)^7 \{A - X\} = x^7 - 2x^6 - 6.64x^5 + 12x^4 + 11.56x^3 - 18x^2 - 5.92x + 8$$  \hspace{1cm} (10)

where zeros are at $x = 1, -1, 1.80904, 2.462208, -2.0286414, 0.8274095, -1.0700509$ which are the energies of the $\pi$-MOs of phenol in $\hbar$ unit and have been calculated by Newton-Raphson method. The perturbational coefficient $C^2_{n,r}$ corresponding to HOMO (of energy $\chi_{n,r}^0$) is obtained by Ulam subgraph method (Eq. 11)

$$C^2_{n,r} = \left| \frac{P(G_1 - v_r; \chi_{n,r}^0)}{P'(G_1; \chi_{n,r}^0)} \right|$$  \hspace{1cm} (11)

where $G_1 - v_r$ is the subgraph obtained by deletion of the $r$th vertex from $G_1$ and $P'$ stands for the first derivative of the CP. For phenol with the heteroatom and hetero-bond parameters given above, HOMO energy, $\chi_{n,r}^0 = 0.8274095$. For $p$-quinol the graph $G_2$ is shown in Fig. 1. To avoid complication in the construction of CP, this graph was factorised according to recently developed algorithms 14,15. The factorisation scheme is shown in Fig. 2. According to this scheme one has for $p$-quinol,
Table 1 - Charge-transfer fluorescence maxima of complexes of N-ethyltetrachlorophthalimide with methylbenzenes as donors and the necessary perturbational coefficients

<table>
<thead>
<tr>
<th>Donor</th>
<th>$h\nu_{CT}(eV)$</th>
<th>$h\nu_{CT} + \chi_0^0\beta(eV)$</th>
<th>$\sum E_n^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesitylene</td>
<td>2.8887</td>
<td>-0.2113</td>
<td>0.667</td>
</tr>
<tr>
<td>Durene</td>
<td>2.6531</td>
<td>-0.4469</td>
<td>1.000</td>
</tr>
<tr>
<td>Pentamethylbenzene</td>
<td>2.6159</td>
<td>-0.4841</td>
<td>1.133</td>
</tr>
<tr>
<td>Hexamethylbenzene</td>
<td>2.5291</td>
<td>-0.5709</td>
<td>1.333</td>
</tr>
</tbody>
</table>

Table 2 - Charge-transfer fluorescence maxima of complexes of N-ethyltetrachlorophthalimide with methoxybenzenes and the necessary perturbational coefficients

<table>
<thead>
<tr>
<th>Donor</th>
<th>$h\nu_{CT}(eV)$</th>
<th>$h\nu_{CT} + \chi_0^0\beta(eV)$</th>
<th>$\sum E_n^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxybenzene</td>
<td>2.6159</td>
<td>0.0509</td>
<td>0.1450</td>
</tr>
<tr>
<td>1,4-Dimethoxybenzene</td>
<td>2.1324</td>
<td>-0.0139</td>
<td>0.1772</td>
</tr>
<tr>
<td>p-Methylmethoxybenzene</td>
<td>2.4299</td>
<td>-0.1351</td>
<td>0.3395</td>
</tr>
</tbody>
</table>

Results and Discussion

Experimental values of $h\nu_{CT}$ collected from the works of Borkent et al. are listed in Tables 1 and 2 together with the computed quantities required for Eqs (6) and (7). The relevant graphical plots are shown in Figs 3 and 4 respectively. The plots are fairly linear, verifying thereby the validity of the Eqs. (6) and (7). With $\beta = -3.1$ eV (as obtained from the first four singlet-singlet transitions of benzene) a least-square fitting of data leads to the linear correlation (13)

$$h\nu_{CT} + \chi_0^0\beta = -0.5408 + \sum_n \sum_r E_n^0 + 0.1305 \ldots (13)$$

for the methylbenzene series (Table 1) with a significant correlation coefficient, 0.9852. The slope of this linear plot gives $h_{Me} = -0.175$. For the series of methoxybenzenes (Table 2) the correlation is given by Eq. (14),

$$h\nu_{CT} + \chi_0^0\beta = -0.8850 + \sum_r E_n^0 + 0.1625 \ldots (14)$$
with a very good correlation coefficient of 0.982. The slope in this case gives $h_{\text{Me}} = -0.2855$. The present values are close to those obtained by Kyse1 $(-0.3)$, Lepley $(-0.21)$ and Seal and Mukherjee $(-0.27$ to $-0.42)$ from CT absorption maxima of some molecular complexes other than the ones dealt with in this paper.

The difference in the intercepts of the correlations (13) and (14) is noteworthy. Since the terms $E_A$ and $C$ of Mulliken equation (1) have been absorbed in these intercepts, they should depend not only on the acceptors but also on the donors. The acceptor is the same in the two series of complexes and the difference in the intercepts is presumably due to the difference in the $C$-term caused by the use of two different kinds of donors.

The present analysis has brought out the fact that systematic shift of $\nu_{\text{CT}(f)}$ towards lower energy with progressive methyl substitution in benzene or phenol is due to an increase in their donor ability caused by the inductive effect of methyl group. Moreover, some applications of graph theory (in HMO formalism) in which interest is growing in recent years, have been demonstrated. If one tries to obtain the required eigenvalues and eigenvectors by the usual HMO procedure, one has to diagonalise two matrices of size $7 \times 7$ and $8 \times 8$ for phenol and $p$-quinol respectively. This is almost impossible without a digital computer. One can adopt group-theoretical method to block-diagonalise the matrices but this requires use of character tables, construction of symmetry-adopted linear combinations etc. Graph theoretical techniques, on the other hand, are much easier to apply, particularly when there is a plane of symmetry. Wherever possible, such techniques lead to resolution of the graph into factors involving isolated vertices whose weights are directly some eigenvalues. Thus, as shown in Fig. 2, we find two isolated vertices with weights 1 and $-1$ from the graph $G_2$. The same will be obtained if we apply the process to $G_1$. Factors other than the isolated vertices are small linear chains with weighted vertices and edges whose CPs can be easily calculated. However, if the graph is small and has a pendant vertex, then factorisation is not required and one can compute the CP directly as we have done for $G_1$ (phenol). The graph theoretical techniques have another important advantage: squares of the eigen-coefficients can be expressed in terms of the eigenvalues (Eq. 11). The present perturbational method requires the wavefunction of HOMO only. Hence using Eq. (11) one can avoid computation of other MO wavefunctions which are unnecessary for the present purpose.

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