EXCITED STATE DIPOLE MOMENTS FROM
SOLVATOCHROMIC DATA

This Chapter is organised in two sections. The first section is devoted to studies on some 7-nitrobenz-2-oxa-1,3-diazol-4-yl (NBD) derivatives in which we first attempt to find out the correct Onsager cavity radii required for the analysis of solvatochromic data to measure the change in the dipole moment on excitation using the Lippert-Mataga equation. Then we focus on two other model compounds containing the NBD chromophore to determine the nature of the emitting state and possible role of rotary decay mechanism using AMI calculations. The second section of the Chapter is concerned with estimation of the excited state dipole moments of a set of coumarin derivatives using a recently developed modified Lippert-Mataga equation in which the Stokes shift between the absorption and fluorescence wavenumbers is correlated with the microscopic solvent polarity parameter, $E_1^n$.1

6.1. Studies on NBD derivatives

6.1.1. Selection of Onsager cavity radius

Even though a number of direct methods such as fluorescence polarisation,2 electric dichroism,3 stark splitting of rotational levels4 and microwave conductivity or absorption5 are available and considered to be fairly accurate for the estimation of the excited state dipole moment, the most common ones are based on the analysis of the solvatochromism of the absorption and fluorescence maxima6,7 In the method suggested by Lippert and
Mataga, the Stokes shift between the absorption and fluorescence maxima is related to the dipole moment change on excitation and solvent polarity function involving the dielectric constant and refractive index (eqn. 3.3).\textsuperscript{6,7} The main difficulty associated with quantitative measurement of the change in dipole moment on excitation using the above method is the choice of the Onsager cavity radius. In fact, it has been reported that the values obtained for \( \Delta \mu \) of a fluorophore from the above equation may differ from the actual values by as much as 50\% depending on the choice of the cavity radius.\textsuperscript{8} In the absence of any clear guidelines for the selection of the cavity radius of a particular system, the choice is often arbitrary\textsuperscript{8-11} and hence the determined Aji values are far from accurate. We address to this Onsager radius problem by considering some NBD derivatives in which the length of the molecules is varied keeping the basic chromophore unchanged (Chart 6.1).

1. \( X \text{ and } Y = H \)
2. \( X = CH_3 \text{ and } Y = H \)
3. \( X = CH_2-CH_3 \text{ and } Y = H \)
4. \( X = CH_2-(CH_2)_4-COOH \text{ and } Y = H \)
5. \( X = CH_2CH_2CH_3 \text{ and } Y = H \)
6. \( X \text{ and } Y = CH_2CH_3 \)
7. \( X \text{ and } Y = CH_3 \)

**CHART 6.1**

\[ \text{CHART 6.1} \]
NBD molecules are extensively used as fluorescence probes to follow a variety of processes such as membrane fusion, lipid motion, organisation of lipids and proteins in membranes etc. The fluorescence properties of NBD derivatives are quite similar to those of aminophthalimides discussed earlier. The fluorescence quantum yield of the NBD derivatives is reasonably high in aprotic solvents ($\approx 0.5$) and extremely low in water ($\approx 10^{-2}$). This property is ideally suited for its application as fluorescence probe. Labelling biological compounds with the NBD chromophore is fairly easy to achieve as the NBD halides react readily with thiols and amino groups. Amino NBD derivatives also find application in nonlinear optics. The applications of NBD derivatives have been reviewed recently.

We have estimated theoretically the charge densities at different atoms (Chart 6.2) of the fully optimised structures of 1-3 and then calculated their dipole moments in the ground and excited state. It can be seen from the data presented in Table 6.1 that for 1 the difference between the ground and excited state dipole moment amounts to 3.5. When one of the hydrogens is replaced by a methyl group to form 2, both the ground and excited state dipole moments increase by 0.5 D (so that the change in the dipole moment remains constant). This behaviour is consistent with the inductive effect of the alkyl group which favours increased charge separation. On replacement of the methyl group by an ethyl group as in 3, the dipole moment remains more or less constant. It is interesting to observe that although the longest molecular axis in NBD derivatives 1-3 vary significantly, it does not have any effect on the calculated value of $\Delta \mu$. 

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CHAR1 6.2
The invariance of the $\Delta \mu$ values on the length of the alkyl chain suggests that for even longer derivatives such as 4, which is actually used in fluorescence applications, one should not consider, for the purpose of the selection of the Onsager radius, the length of the long axis of the molecule; instead, the cavity radius should be measured from the maximum distance across which the charge separation takes place. If it were not so, $\Delta \mu$ for the compound 3, based on its longest molecular axis (as calculated theoretically) and solvatochromic data for 4 (as solvatochromism of the absorption and fluorescence bands of these compounds do not differ significantly) would have been 5.5 D which is nearly 55% more than the estimated value of 3.5 D. The theoretically calculated distance between the average coordinates of the oxygen atoms in the nitro group and the nitrogen atom of the amino group (which remains practically the same in all these derivatives), where charge separation could occur is 6.38 Å. Half of this, i.e. 3.19 Å when used for the analysis of the solvatochromic data of 4, $\Delta \mu$ value is obtained as 3.9 D which is in line with the $\Delta \mu$ values for the other compounds.

Table 6.1. Dipole Moments (in D) of NBD Derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_e$</th>
<th>$\Delta \mu$</th>
<th>Method used</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.1</td>
<td>12.6</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>9.6</td>
<td>13.2</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>9.5</td>
<td>13.2</td>
<td>3.5</td>
</tr>
<tr>
<td>4$^a$</td>
<td>-</td>
<td>-</td>
<td>3.9</td>
</tr>
</tbody>
</table>

$^a$assuming an Onsager cavity radius of 3.19 Å
6.1.2. Nature of the emitting state and the role of rotary decay mechanism: A theoretical analysis

Recently, nonfluorescent TICT state has been proposed for one of the two NBD derivatives, 5 and 6 (Chart 6.1) to account for the polarity dependence of the fluorescence properties. In order to get insight into the Photophysical behaviour of NBD derivatives we have carried out calculations, similar to those performed on DMABN and aminophthalimides, on two simpler compounds, 1 and 7 whose application encompasses large areas of interest. We highlight only the salient features of the results which are relevant to the rotary decay process.

6.1.2.1. Ground state properties

The ground state profiles of the two molecules in the gas phase, shown as a function of the twist angles in figs 6.1 and 6.2, are quite similar to those obtained for other compounds reported in the thesis. The planar conformation is the most stable form (energy minimum observed for dihedral angle of 0-10 deg). The planar form is significantly stabilised with respect to the twisted form on solvation. The twisted forms are high enough in energy compared with the respective planar forms so as not to expect any twisting in the ground state either in the gas phase or in presence of any solvent. The ground state dipole moments at the planar conformation are 9.1 and 9.76 D for 1 and 7 respectively.
Fig. 6.1. Variation of the ground state energy of 1 as a function of the twist angle in the gas phase (●), dioxane (○), and Acetonitrile (▲).
Fig. 6.2. Variation of the ground state energy of 7 as a function of the twist angle in the gas phase (○), dioxane (●), and Acetonitrile (●).
6.1.2.2. Excited state properties

The variation of the lowest excited singlet state energy as a function of the twist angle of the amino group in the gas phase as well as in two solvents is shown in fig. 6.3 for 1. The calculated energy profiles in dioxane and acetonitrile suggest that for 1 twisting is not possible because of high barrier involved (0.41 eV in acetonitrile). Therefore, the emitting state of 1 can only be an LE state whose dipole moment is estimated as 12.6 D. For 7, the energy profiles are shown in fig. 6.4. It can be seen that \( \text{LZ} \rightarrow \text{TICT} \) process is almost barrier-less in polar media such as in acetonitrile. Therefore, one expects the TICT state to be populated for this compound. However, it is interesting to note that in this particular case the solvent stabilisation of the excited TICT state leads to lowering of its energy below the ground state in this particular conformation. In other words, crossing of the \( \text{UOC} \) ground and excited states results in a situation such that on excitation, 7 is expected to slide down the surface to a twisted conformation without emission of photons. Thus the TICT state in N-alkylated derivatives of NBD should be nonfluorescent.
Fig. 6.3. Variation of the first excited state energy of 1 as a function of the twist angle in the gas phase (•), dioxane (●), and Acetonitrile (▲).
Fig. 6.4. Variation of the first excited state energy of 7 as a function of the twist angle in the gas phase (△), dioxane (●), and Acetonitrile (○).
6.2. **Studies on coumarin derivatives**

It is well documented in the literature that solvatochromic shifts of dipolar species correlate much better with the microscopic solvent polarity parameters such as $E_T(30)$ or $E_T^{N18}$ than with traditionally used bulk solvent polarity functions, $A_f$ (as defined in Chapter III) or $F_2(D,n)^7$ (as defined below) involving dielectric constant ($D$) and refractive index ($n$).$^{19}$

$$F_2(D,n) = \left[\frac{(D-1)}{(D+2)}\right] - \left[\frac{(n^2-1)}{(n^2+1)}\right] \frac{2n^2+1}{n^2+2}$$  

This has also been demonstrated by us in Chapter V using the solvatochromic data for AP and DAP. The theoretical basis for the correlation of the Stokes shift with $E_T^N$ has been published recently$^1$ (discussed in detail in Chapter III). According to this formulation

$$\Delta \tilde{v} = 11307.6 \left\{ \frac{a_{//}}{a_{//}} \right\}^2 \frac{a}{a}^3 \frac{E_T^N}{\text{constant.}}$$  

$\Delta \tilde{v}$ can be determined from the slope of the plot of the Stokes shift vs $E_T^N$ using the reported $\Delta \mu_D$ of 9 D of the betaine dye and its Onsager radius, $\delta_D$ of 6.2 $\AA$.$^{13}$

In view of better correlation observed in plots of $\Delta \tilde{v}$ against $E_T^N$, the slope from which the $\Delta \mu$ values are evaluated is expected to be more accurate. In addition, the above equation provides a number of practical advantages. First, the formulation used in this method provides a partial cancellation of the problems associated with Onsager radius in the original Lippert-Mataga equation$^6$, because ratios of two Onsager radii are involved. Second, the method
provides definite advantage for studies with binary solvent mixtures. Since the use of a mixture of just two solvents, one polar and the other nonpolar, provides systematic variation of the polarity with any desired number of data points and the polarity of various compositions are experimentally determined simply by measuring $E_T^*$, the experimental procedure is simplified and statistical analysis is more reliable than that using different solvents. In view of this we apply the method to determine the excited state dipole moments of a set of coumarin dyes (Chart 6.3) extensively used in laser applications.\textsuperscript{20}

CHART 6.3
The excited state dipole moments of these molecules control the tunability range of their emission energy as a function of the solvent polarity. Further, since some of these systems may possess low-lying TICT state, the fluorescence can originate from either an LE state or a TICT state. Since it is possible to differentiate these two states on the basis of their dipole moments, our measurements should provide insight to the nature of the emitting state.

The absorption and emission maxima of the dyes in various solvents are compiled in Table 6.2. The solvents where strong specific interactions (e.g. 11-bonding) with the dyes are possible were excluded. As can be seen from the Table, the shift of emission peaks with solvent polarity changes is more pronounced than the same for the absorption peaks. This indicates that $\Delta \mu$ ($\mu_e - \mu_g$) is positive. The correlation coefficients of the Stokes shifts of the six dyes with the solvent polarity functions $F_2$ (D, n), recommended by Koutek on the basis of a detailed statistical analysis, as well as $E^T_i$, are presented in Table 6.3. As seen from the Table, the correlation of experimental Stokes shifts of the coumarins with $E^T_i$ is far superior to that with the $F_2$ (D,n) function. Fig. 6.5 and 6.6 show typical plots of Stokes shifts versus $F_2$ (D,n) and $E^T_i$ respectively for C102 as an illustrative example.
Table 6.2. Wave numbers (cm\(^{-1}\)) of the absorption and emission (within parenthesis) maxima of the six coumarin dyes in the different solvents.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CCl(_4)</th>
<th>Toluene</th>
<th>1,4-Dioxane</th>
<th>THF</th>
<th>Ethyl acetate</th>
<th>Acetone</th>
<th>AcOH nitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>28011 (24863)</td>
<td>27855 (24449)</td>
<td>27777 (24271)</td>
<td>27624 (24178)</td>
<td>27739 (24026)</td>
<td>27247 (23618)</td>
<td>27137 (23694)</td>
</tr>
<tr>
<td>C102</td>
<td>27027 (24260)</td>
<td>26882 (23923)</td>
<td>23667 (23641)</td>
<td>26525 (23343)</td>
<td>26738 (23063)</td>
<td>26247 (22624)</td>
<td>26110 (22302)</td>
</tr>
<tr>
<td>C120</td>
<td>30030 (25893)</td>
<td>29762 (25562)</td>
<td>29498 (25240)</td>
<td>29070 (24975)</td>
<td>29498 (24950)</td>
<td>29070 (24643)</td>
<td>29325 (24486)</td>
</tr>
<tr>
<td>C151</td>
<td>28490 (24108)</td>
<td>27933 (23288)</td>
<td>27624 (22748)</td>
<td>26810 (22371)</td>
<td>27472 (22492)</td>
<td>27027 (21949)</td>
<td>27322 (21844)</td>
</tr>
<tr>
<td>C152</td>
<td>26596 (22810)</td>
<td>26042 (22212)</td>
<td>26110 (21720)</td>
<td>25840 (21249)</td>
<td>25740 (21258)</td>
<td>25510 (20483)</td>
<td>25381 (20317)</td>
</tr>
<tr>
<td>C153</td>
<td>25000 (22371)</td>
<td>24630 (21386)</td>
<td>24510 (29790)</td>
<td>24331 (20492)</td>
<td>24450 (20358)</td>
<td>24038 (19717)</td>
<td>23923 (19470)</td>
</tr>
</tbody>
</table>
Table 6.3. Correlation coefficients for the fit of the Stokes shifts of the coumarin dyes against the solvent polarity functions $E_1^N$ and $F_2$ (D,n).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Using polarity functions</th>
<th>Using $E_1^N$ of binary mixture$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F_2$ (D,n)</td>
<td>$E_1^N$</td>
</tr>
<tr>
<td>C1</td>
<td>0.780</td>
<td>0.945</td>
</tr>
<tr>
<td>C102</td>
<td>0.899</td>
<td>0.968</td>
</tr>
<tr>
<td>C120</td>
<td>0.693</td>
<td>0.887</td>
</tr>
<tr>
<td>C151</td>
<td>0.676</td>
<td>0.892</td>
</tr>
<tr>
<td>C152</td>
<td>0.924</td>
<td>0.948</td>
</tr>
<tr>
<td>C153</td>
<td>0.863</td>
<td>0.931</td>
</tr>
</tbody>
</table>

$^a$Acetonitrile:benzene mixture; 9 compositions used in the correlation.
Fig. 6.5. Plot of Stokes shifts of C102 versus the solvent polarity function, $F_2$ (D,n) of the seven solvents shown in Table 6.2.
Fig. 6.6. Plot of Stokes shifts of C102 versus the solvent polarity function, $E_T^N$, of the seven solvents shown in Table 6.2.
Table 6.3 also provides the correlation coefficients for the plot of the Stokes shift versus the $E_T^*$ obtained in a separate experiment employing the binary solvent mixtures of benzene and acetonitrile. Nine compositions ranging from 20% to 100% acetonitrile were used and the $E_T^*$ values experimentally determined. We have examined the reproducibility of these experimentally determined $E_T^*$ values using the empirical equation for $E_T^*$ suggested by Langhals. The agreement between the theoretical and experimental $E_T^*$ values of the mixtures is excellent at the compositions used. As seen in Table 6.3, the correlation of Stokes shifts of the six dyes is at its best with $E_T^*$ values of the solvent mixtures. Since the number of data points used here are more, the statistical relevance of this fit is also enhanced over that using the different solvents. The plot of Stokes shifts versus the $E_T^*$ parameter employing the acetonitrile-benzene binary mixture, for C$^{102}$ is shown in fig 6.7. Though the $E_T^*$ values and the Stokes shifts span a slightly smaller range here, the number of data points is larger and the superiority of the fit is clearly seen.
Fig. 6.7. Plot of Stokes shifts of the molecule C102 versus $E_T^N$ values of the acetonitrile-benzene mixture of nine different compositions.

The Onsager radius, the ground and excited state dipole moments and $\Delta \mu$ values of six dyes are given in Table 6.4. The ground state dipole moments of the dyes C1, C102 and C120 are those evaluated using the AM1 procedure of McCarthy and Blanchard.\textsuperscript{23} The last three compounds (C151, C152 and C153) contain fluorine atoms for which the AM1 parametrisation is known to be
inadequate, especially for the computation of the heats of formation and geometry. Therefore, we have carried out the geometry optimisation for these molecules using the PM3 parametrisation.\textsuperscript{24} Using these geometries, the $\mu_g$ and $\mu_e$ were calculated using the AM1 procedure. It is seen that between every pair of dyes related by a CH$_3$/CF$_3$ substitution, the latter has a slightly lower dipole moment. Examination of the atomic charges on the amino group, carbonyl oxygen, CH$_3$ and CF$_3$ groups provides an insight into the reason for this. The decrease in $\mu_g$ is caused by the fact that the CH$_3$→O dipole component that adds to the principal N→O vectors in the methyl-substituted compound is replaced by the much smaller CF$_3$→O component in the trifluoromethyl-substituted molecules. The experimental $\Delta\mu$ values obtained (using eqn 6.2) from the slopes of the plots against $E_T$ values of the different solvents as well as of the binary mixtures are found to be similar, except for some variation in the case of Cl. However, it appears from the Table that $\Delta\mu$ values for the dyes as determined by this method are slightly lower than the reported values.\textsuperscript{23,25} This suggests that there is a need for the Onsager radius used for the betaine dye to be scaled to slightly larger value. However, it would be probably appropriate that scaling of Onsager radius, if necessary, be undertaken only when the excited state dipole moment of the compounds are available from one of the direct methods such as microwave absorption or conductivity measurements which produces more accurate values and does not depend on the Onsager cavity radius. The last column of Table 6.4 provides the $\mu_e$ calculated using theoretical $\mu_g$ and the $\Delta\mu$ determined experimentally using the binary mixture.
Table 6.4. Comparison of $\Delta \mu$ values obtained from the present analysis in various solvents and binary mixture with the computed values.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$a$ (Å)</th>
<th>$\Delta \mu/D$</th>
<th>$\mu_c/D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(theory)</td>
<td>Various solvents</td>
<td>Binary mixture</td>
</tr>
<tr>
<td>C1</td>
<td>3.48</td>
<td>1.45</td>
<td>2.25</td>
</tr>
<tr>
<td>C102</td>
<td>3.46</td>
<td>1.84</td>
<td>2.11</td>
</tr>
<tr>
<td>C120</td>
<td>3.46</td>
<td>1.43</td>
<td>1.44</td>
</tr>
<tr>
<td>C151</td>
<td>3.46</td>
<td>1.72</td>
<td>1.58</td>
</tr>
<tr>
<td>C152</td>
<td>3.45</td>
<td>1.92</td>
<td>2.16</td>
</tr>
<tr>
<td>C153</td>
<td>3.46</td>
<td>2.27</td>
<td>2.22</td>
</tr>
</tbody>
</table>

The values for C1, C102 and C120 are from ref 23. The values for C151, C152 and C153 are those calculated in the present study using PM3 optimised geometries. Calculated using the experimental $\mu_u$ and the theoretical $\mu_e$ values.

As seen from Table 6.4, the change of dipole moment on electronic excitation is rather small for all the molecules studied. This suggests that the emission of these dyes originate from a state, which although more polar than the ground state, is probably an LE state. Further, it may be noted that the compounds C102 and C153 are fairly rigid and incapable of showing a twist around the C-N bond. The close similarity of the $\mu_e$ of these molecules with their respective counterparts capable of twisting, implies that the emitting states of all these systems are ICT in nature. ICT states if present, appear to be non-emissive.
6.3. References


