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## Excited State Dipole Moment Of New Indole Derivatives By Solvatochromic Shift Method


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**ABSTRACT**

The electronic absorption and fluorescence spectra of newly synthesized indole derivatives viz., 1) 5-methyl-3-phenyl-2-[4'-amino-s-triazolo-3'-yl] indole-5'-hydrazide, (MPATH) 2) 3-[5'-methyl-3'-phenylindol-2'-yl] -s-triazolo[3,4-b][1,3,4] thiadiazol-6(5H) -thione (MPITTT) and 3) 5-methyl-3-phenyl-2- [s-oxadiazol-2'-thione-5'-yl] indole (MPOTT) have been measured at  $1 \times 10^{-5}$  M concentration in various solvents at room temperature. The ground state dipole moment ( $\mu_g$ ) and first excited singlet state dipole moment ( $\mu_e$ ) have been estimated from solvatochromic shifts of absorption and fluorescence spectra as a function of the dielectric constant (D) and refractive index (n), and also by utilizing the microscopic solvent polarity parameter ( $E_T^N$ ). These indole derivatives have shown greater dipole moment in the excited state than the ground state. The results indicate that the observed band in these compounds may be attributed to  $\pi \rightarrow \pi^*$  transition. © 2007 Trade Science Inc. - INDIA

**KEYWORDS**

Indole;  
 Dipole moment;  
 Solvatochromic shift;  
 Absorption;  
 Fluorescence.

**INTRODUCTION**

Dipole moments of organic molecules in their ground and excited singlet states are of great interest because they can be used as a tool to study their configuration and /or conformations. Moreover, the

values of excited state dipole moments provide information about the changes of electronic distribution occurring upon electronic excitation. A prior knowledge of the excited state dipole moment helps to assess the efficacies of quantum chemical derivations of wave functions and electron correlation treat-

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ments. Recent studies have indicated that excited state dipole moment can be used in the design of nonlinear optical materials, which have large hyperpolarizabilities and in membrane research<sup>[1-3]</sup>.

Even though the more equipment intensive methods like fluorescence polarization, electric dichroism, and microwave conductivity are considered to be more accurate, the popular method for experimental determination of excited state dipole moments is based on the analysis of the solvatochromism of absorption and/or fluorescence maxima<sup>[4,5]</sup>. It is known that electronic spectra of the molecules are influenced by their immediate environment. Among the major environmental factors influencing the electronic spectra, solvent effects are of particular importance. A change of solvent is accompanied by a change in polarity, dielectric constant and change in polarizability of the surrounding medium. Thus, the change of solvent affects the ground state and excited state differently<sup>[5]</sup>. The changes produced by the solvent on the  $\pi$ -electron system of the molecule can be accounted in terms of the overall effect of the interaction forces (which are mainly of Vander-Walls type). It is also known that as the  $\pi$ -electron system becomes less localized, the transition energy becomes smaller and this results a bathochromic shift (red shift) and its opposite effect gives rise to a hypsochromic shift (blue shift). In order to assign the electronic transitions as  $n \rightarrow \pi$  or  $\pi \rightarrow \pi^*$ , solvatochromic technique is found to be quite informative.

Based on quantum mechanical perturbation theory<sup>[5-7]</sup> of absorption and fluorescence, band shifts of a spherical solute in different solvents of varying permittivity and refractive index, the following equations are obtained:

According to Bakhshiev:

$$\bar{\nu}_a - \bar{\nu}_f = S_1 F_1(D, n) + C_1 \quad (1)$$

According to Chamma-viallet:

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -S_2 F_2(D, n) + C_2 \quad (2)$$

Where  $\bar{\nu}_a$  and  $\bar{\nu}_f$  are the wave number of absorption and fluorescence maxima; D and n are the dielectric constant and refractive index of the solvent respectively.  $F_1(D, n)$  and  $F_2(D, n)$  are the solvent polarities and can be expressed as<sup>[7]</sup>

$$F_1(D, n) = \left\{ \frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right\} \frac{2n^2+1}{n^2+2} \quad (3)$$

$$F_2(D, n) = F_1(D, n) + \frac{3(n^4-1)}{2(n^2+2)^2} \quad (4)$$

and further  $S_1$  and  $S_2$  are expressed as

$$S_1 = \frac{2(\mu_e - \mu_g)^2}{a^3 hc} \quad (5)$$

$$S_2 = \frac{2(\mu_e^2 - \mu_g^2)}{a^3 hc} \quad (6)$$

Where  $\mu_g$  and  $\mu_e$  are the ground and excited state dipole moments of the molecule, 'a' is the Onsager cavity radius, h is the Planck's constant and c is the velocity of light. The values of  $S_1$  and  $S_2$  can be determined by plotting the solvent dependent Stokes shift  $(\bar{\nu}_a - \bar{\nu}_f)$  and  $(\bar{\nu}_a + \bar{\nu}_f)/2$  versus the solvent polarity functions  $F_1(D, n)$  and  $F_2(D, n)$  respectively for different solvents in accordance to the equations (1) and (2). The Onsager cavity of radius 'a' of the solute can be determined by using atomic increment method according to Edward's theory<sup>[8]</sup>.

If the ground and excited states are parallel and the cavity radius 'a' is same in both ground and excited states, the ground state dipole moment ( $\mu_g$ ) and excited state dipole moment ( $\mu_e$ ) can be calculated by combining the equation (5) and (6)<sup>[3,7,9,10]</sup>, i.e.

$$\mu_g = \frac{1}{2} \left( \frac{\alpha^3 hc S_1}{2} \right)^{1/2} \left( \frac{S_2}{S_1} - 1 \right) \quad (7)$$

$$\mu_e = \frac{1}{2} \left( \frac{\alpha^3 hc S_1}{2} \right)^{1/2} \left( \frac{S_2}{S_1} + 1 \right) \quad (8)$$

or

$$\mu_e = \left( \frac{S_2 + S_1}{S_2 - S_1} \right) \mu_g; S_2 > S_1 \quad (9)$$

The excited state dipole moment ( $\mu_e$ ) can also be determined by using the expression

$$\mu_e = \Delta\mu + \mu_g \quad (10)$$

Where  $\Delta\mu$  is called the change in the dipole moment between the ground and excited state, and can be estimated using the expression<sup>[11]</sup>

$$\bar{\nu}_a - \bar{\nu}_f = S_3 E_T^N + \text{Constant} \quad (11)$$

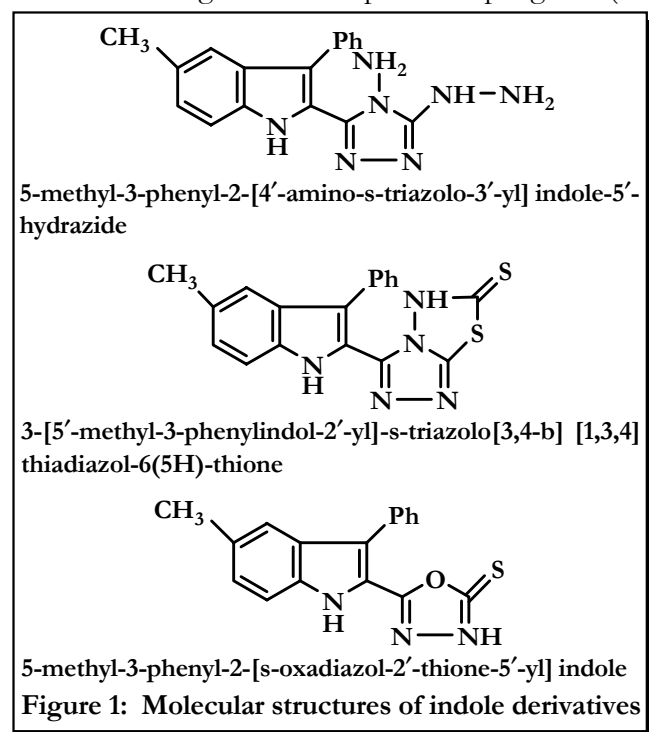
$$\text{where } S_3 = 11307.6 \left[ \left( \frac{\Delta\mu}{\Delta\mu_D} \right)^2 \left( \frac{\alpha_D}{\alpha} \right)^3 \right]$$

$E_T^N$  is the solvent polarity function proposed by Reichardt based on absorption wave number of a standard Betaine dye in the solvent,  $\Delta\mu_D$  and  $\alpha_D$  are the change of dipole moment and Onsager radius respectively of Betaine dye;  $\Delta\mu$  and 'a' are the corresponding quantities of the molecule of interest.

As a part of our ongoing research on indole, we report the determination of ground and excited state dipole moment of newly synthesized derivatives namely 1) 5-methyl-3-phenyl-2-[4'-amino-s-triazolo-3'-yl] indole-5'-hydrazide, (MPATIH), 2) 3-[5'-methyl-3'-phenylindol-2'-yl]-s-triazolo[3,4-b][1,3,4] thiadiazol-6(5H)-thione (MPITTT) and 3) 5-methyl-3-phenyl-2-[s-oxadiazol-2'-thione-5'-yl] indole (MPOTT) by solvent perturbation method based on absorption and fluorescence shifts in various solvents.

## EXPERIMENTAL

The solutes MPATIH, MPITTT and MPOTT were synthesized in our laboratory using standard methods and the purity was checked by HPLC method. The molecular structures of these solutes are shown in figure 1. The spectroscopic grade (s.d.



finest chemical ltd.) solvents viz., cyclohexane, dioxane, benzene, toluene, propanol, butanol, methanol and acetonitrile were used to prepare the solution. The absorption spectra of the solutes at the concentration of  $1 \times 10^{-5}$  mol dm<sup>-3</sup> in different solvents were recorded using UV-visible Absorption spectrophotometer (Hitachi 150-20 Model). For the same concentration, the steady state fluorescence intensities were recorded by exciting the solutes corresponding to a longer wavelength absorption band using Fluorescence spectrophotometer (Hitachi F-2000 Model) in different solvents.

## RESULTS AND DISCUSSION

The fluorescence spectra were measured by exciting the sample corresponding to the longer absorption band. The wavenumbers of absorption and fluorescence maxima of the indole derivatives in various solvents are summarized in TABLE 1. It is observed that no significant shifts in the absorption band maxima were recorded for all the solutes, when varying the polarity of the solvents. In contrast, they exhibited a red shift (bathochromic) in the fluorescence spectra with an increase in solvent polarity, indicating  $\pi \rightarrow \pi^*$  transition<sup>[22]</sup>. The shift of the fluorescence wavelengths would be caused, if the excited state charge distribution in the solute is markedly different from the ground state charge distribution, it makes the excited dipole moment greater than the ground state dipole moment.

The plots, the Stokes shift values ( $\bar{\nu}_a - \bar{\nu}_f$ ) against  $F_1(D,n)$ ;  $(\bar{\nu}_a + \bar{\nu}_f)/2$  against  $F_2(D,n)$  and Stokes shift ( $\bar{\nu}_a - \bar{\nu}_f$ ) versus solvent polarity  $E_T^N$  in accordance with the equations (1), (2) and (11) were drawn and shown in figures. 2-4. The characteristics of the correlations, i.e. the slopes, intercepts and correlation co-efficient have been calculated by least-squares fit method and are collected in TABLE 2. It can be seen that for the most of cases, correlation co-efficients are larger than 0.85, indicating that, the equations (1), (2) and (11) are quite linear. As can be seen from the plots, some solvents (ex: dioxane, acetonitrile) do not fit the correlations. This may be due to the approximation made in the solvatochromic shift method and/or to solute-

## Full Paper

TABLE 1: Solvent shift data for different indole derivatives

## Compound MPATIH

Solvent	$\bar{\nu}_a$ cm <sup>-1</sup>	$\bar{\nu}_f$ cm <sup>-1</sup>	$\bar{\nu}_a - \bar{\nu}_f$ cm <sup>-1</sup>	$\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ cm <sup>-1</sup>
Cyclohexane	32467	25773	6694	29210
Dioxane	32154	25316	6838	28735
Benzene	31646	25381	6265	28514
Toluene	31847	25316	6531	28582
Butanol	31526	24510	7016	28018
Propanol	32092	24272	7702	28241
Methanol	31766	24096	7494	28019
Acetonitrile	32258	25253	7005	28756

## Compound MPITTT

Cyclohexane	Not dissolved	-	-	-
Dioxane	32154	25445	6709	28799
Benzene	28653	24938	3715	26795
Toluene	28490	25000	3490	26745
Butanol	28280	22727	5553	25503
Propanol	28029	22624	5465	25356
Methanol	28329	22779	5550	25554
Acetonitrile	28736	22422	6314	25579

## Compound MPOTI

Cyclohexane	Not dissolved	-	-	-
Dioxane	30864	25445	5419	28154
Benzene	30395	25381	5014	27888
Toluene	31056	25316	5740	28186
Butanol	30303	23148	7155	26724
Propanol	30769	23250	7519	27009
Methanol	30864	23585	7279	27224
Acetonitrile	30581	25789	5114	27746

solvent specific interactions. However, the dioxane solvent has shown much deviation from linearity for the solute MPITTT, which makes it appear as pseudo polar. Such an anomalous solvent effect has already been found for other molecules, but it has not been clearly explained<sup>[13]</sup>. The linear  $E_T^N$  dependence of Stokes shift indicates the existence of general type of solute - solvent interaction.

From the slopes  $S_1$ ,  $S_2$  and Onsager radius  $a$ ; the ground state and the excited state dipole moments have been calculated by using the equations (7) and (8). The values of  $a$ ,  $\mu_g$  and  $\mu_e$  are collected in TABLE 3. It is to be noted that the excited state dipole moment  $\mu_e$  has also been determined for all the mol-

ecules by the equation (10) using ground state dipole moment values. Where,  $\Delta\mu$  has been evaluated from the slope  $S_3$  of the plot of Stokes shift versus  $E_T^N$  using the reported values of  $\Delta\mu_D = 9D$  of the Betaine dye and its Onsager radius  $a_D = 6.2 \text{ \AA}$ <sup>[14]</sup>. Note that, since the ratio  $a/a_D$  is involved; errors involved in the estimation of the Onsager radius may be cancelled to some extent. The calculated dipole moment values are comparable with the other indole derivatives. It is to be noted that from the equation (9), the excited state dipole moment  $\mu_e$  can also be determined by the pre-knowledge of  $\mu_g$  without estimation of Onsager radius  $a$ . According to equations (7) and (8),  $\mu_g$  and  $\mu_e$  depend not only on the

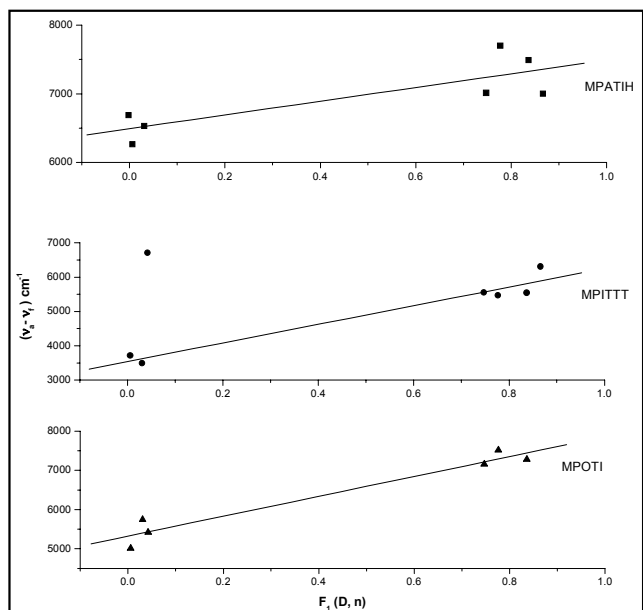


Figure 2: Plot of stokes shift  $\bar{\nu}_a - \bar{\nu}_f$  versus  $F_1$  (D, n) according to bakhshiev's relation

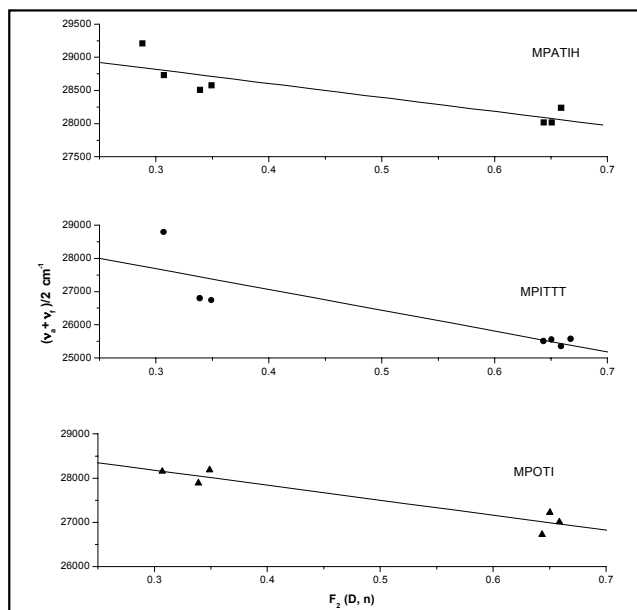


Figure 3: Plot of stokes shift  $(\bar{\nu}_a + \bar{\nu}_f)/2$  versus  $F_2$  (D, n) according to chamma and viallet relation

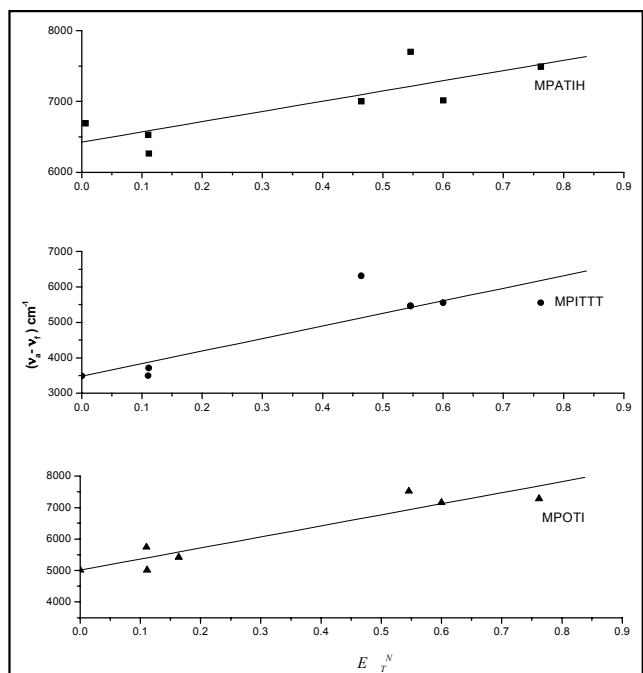


Figure 4: Plot of stokes shift  $\bar{\nu}_a - \bar{\nu}_f$  versus  $E_T^N$

slopes  $S_1$  and  $S_2$  but also on Onsager radius 'a' of the dyes. Further, they depend on the position and nature of the substituents. From the TABLE 3, it is observed that,  $\mu_e > \mu_g$  for all the molecules.

These molecules are non-planar because of the bulkier substituents, which are attached to the indole molecule. When these molecules get excited, further loss in the planarity probably would occur

TABLE 2: Statistical treatment of the correlations of solvent spectral shifts

Solute	Slope	Intercept	correlation co-efficient	Number of data
MPATIH	$S_1=999$	6492	0.85	07
	$S_2=2112$	29450	0.88	07
	$S_3=1451$	6419	0.85	07
MPITTT	$S_1=2711$	3540	0.97	07
	$S_2=4078$	28170	0.99	07
	$S_3=3543$	3483	0.84	07
MPOTI	$S_1=2533$	5324	0.98	06
	$S_2=3387$	29194	0.95	06
	$S_3=3507$	5014	0.92	06

TABLE 3: Values of onsager radius, ground state and excited state dipole moments

Solute	Onsager radius 'a' Å	$\mu_g$ D	$\mu_e^* \text{ D}$	$\mu_e^{\#} \text{ D}$
MPATIH	4.13	1.30	3.82	2.88
MPITTT	4.21	1.12	5.58	3.93
MPOTI	3.94	0.66	4.59	3.19

\*  $\mu_e$  determined by the equation (8)

#  $\mu_e$  determined by the equation (10)

and also a large intramolecular charge transfer (ICT) in the excited state renders the molecule more polar in this state as compared to ground state. Hence  $\mu_e$  is greater than  $\mu_g$  for all the molecules. Also, the change of dipole moment ( $\Delta\mu = \mu_e - \mu_g$ ) on electronic excitation is rather small, for all the dyes. This sug-

## Full Paper

gests that the emission of these dyes originates from a state, which, although more polar than the ground state, is probably a locally excited one.

It is worthwhile to stress that the use of  $E_T^N$  as the solvent polarity function for solvatochromism studies of Stokes shifts can be an efficient procedure to determine the  $\mu_c$  of organic molecules compared to the traditionally used bulk solvent polarity function involving relative primitivities and refractive index (Bakhshiev, and Chamma-Viallet equations). In polar solvents, the dependence of Stokes shift on solvent polarity in bakhshiev, and chamma-viallet expressions seems to be less regular due to the number of assumptions and simplifications made concerning the validity of their use and the errors associated in the estimation of the onsager radius.

On the other hand,  $E_T^N$  can be easily measured experimentally using absorption of the dye. It can also be noted that extra precautions to purify the solvents can be relaxed, since the solvent polarity function is being experimentally determined and used. It is also significant to note that since a ratio of  $a/a_D$  is involved, hence, the errors involved in the estimation of onsager radius may be obviated to some extent.

## CONCLUSIONS

In this study, it is observed that corresponding to cyclohexane solution, all other solutions exhibited red shift in fluorescence maxima indicating a  $\pi - \pi^*$  transition. The linear  $E_T^N$  dependence of Stokes shift indicated the existence of general type solute-solvent interactions. All these indole derivatives studies here; show higher dipole moments in the excited state than the ground state. The fairly large excited state dipole moments are indicative of an intramolecular charge separation for these indole derivatives. Also, the present study using equation (9) permits one to estimate the values of excited state dipole moment by the pre-knowledge of ground state dipole moment without the necessity of knowing the radius of the solute.

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