IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 8, Issue 6 Ver. III (Nov. - Dec. 2016), PP 102-108
www.iosrjournals.org

Dipole Moments of Some Fluororescent Molecules

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Abstract: *The ground state (μ_g) and the excited state (μ_e) dipole moments of three fluorescent molecules namely 5-chloro-2-phenylindole (CPI), 5-methyl-2-phenylindole (MPI) and 1, 3-diphenyl benzene (MT) were studied at room temperature in various solvents. The ground state dipole moments (μ_g) of all the three fluorescent molecules were determined experimentally by Guggenheim method. The excited state dipole moments (μ_e) were estimated from Lippert's, Bakshiev's and Chamma Viallet's equations by using the variation of the Stokes shift with the solvent dielectric constant and refractive index. Ground and excited state dipole moments were evaluated by means of solvatochromic shift method and also the excited state dipole moments are determined in combination with ground state dipole moments. It was observed that dipole moment values of excited states (μ_e) were higher than corresponding ground state values (μ_g), indicating a substantial redistribution of the π-electron densities in a more polar excited state for all the dyes investigated.*

Keywords: *Fluorescent molecules; Ground state dipole moments; Excited state dipole moments; Solvatochromic shift method*

I. Introduction

Determination of the ground and excited state dipole moments of dye molecules is important, because the values so obtained provide information about the change in electronic distribution upon excitation. Fluorescent molecules have several applications such as anticoagulants, fluorescence indicator and possess anthelmintic and optical brightness properties [1]. In the present paper we report the ground (μ_g) and excited state (μ_e) dipole moments of some fluorescent molecules. The investigation of excited state dipole moments of CPI, MPI and MT provide rich information on the electronic and geometrical structure of the molecule in the short lived state. Knowledge of this would be helpful in designing nonlinear optical materials, in elucidation of the nature of the excited states and also it would reflect the charge distribution in the molecule and allows one to judge the site of attack by electrophilic and nucleophilic reagents in some photochemical reactions.

The ground state dipole moment of a chemical system can be measured using different techniques [2–7], not many techniques are available for the estimation of the dipole moment in short lived state. Among the different methods available so far for the estimation of dipole moment of short lived species such as electronically excited state of a molecule are based on the spectral shift caused either externally or internally. Among the different methods like electric polarization of fluorescence [8], electric dichroism [9] and microwave conductivity [10], which are considered to be very accurate but their use is limited because of equipment intensive and restriction to relatively small molecules. The experimental determination of excited state dipole moment based on the analysis of the solvatochromism of absorption and fluorescence maxima is quite popular. The solvatochromic method is based on a linear correlation between the wave numbers of the absorption and fluorescence maxima and a solvent polarity function which involves both dielectric constant (e) and refractive index (n) of the medium [11–15].

Several workers [16–34] have made extensive experimental and theoretical studies on ground (μ_g) and excited state (μ_e) dipole moments using different techniques in variety of organic fluorescent compounds. However, there are no reports available in literature on the ground (μ_g) and excited state (μ_e) dipole moments of the three fluorescent molecules which we have considered here for the present investigation.

II. Experimental

Chemicals used and spectroscopic measurements

The fluorescent molecules CPI, MPI and MT were generous gift from one of our collegues. The molecular structures of these dyes are given in Fig. 1. The solvents benzene, toluene, ethyl acetate, propanol, methanol and acetonitrile (MeCN) are of spectroscopic grade and were obtained from S-D Fine Chemicals Ltd., India and used without any further purification. The required solutions were prepared at fixed solute concentration in all the solvents. The solute concentration of CPI was 1x 10^{-5} M and in case of MPI and MT it was 1x 10^{-4} M. The concentrations of the solutes were kept sufficiently low in order to minimize the effects of self absorption. The electronic absorption spectra were recorded on a Hitachi 150-20 UV–VIS spectrophotometer and fluorescence spectra on a Hitachi F-2000 spectrofluorometer.

The dielectric constants of the dilute solutions were measured in a suitably fabricated cell of usually small capacitance where the accurate determination of small changes in the capacitance would be possible. The small capacitance can be measured with the help of FT 6421 LCR data bridge at 10 KHz frequency. The refractive indices of various dilute solutions of the solute for sodium D line were determined by using Abbe's refractometer. All the measurements were carried out at room temperature.

Experimental ground state dipole moment

To calculate ground state (μ_g) dipole moment from the static dielectric measurements in dilute solutions, several methods are available [2–7]. The ground state (μ_g) dipole moments of the dye molecules CPI, MPI and MT were calculated by the Guggenheim method [6], given by

$$\mu_g^2 = \left[\frac{27kT}{4\pi N(\varepsilon_1 + 2)(n_1^2 + 2)} \right] \Delta \qquad (1)$$

$$\text{Where } \Delta = \left[\left(\frac{\varepsilon_{12} - \varepsilon_1}{C} \right)_{c \to 0} - \left(\frac{n_{12}^2 - n_1^2}{C} \right)_{c \to 0} \right] \qquad (2)$$

Where Δ

where Δ is the difference between the extrapolated intercepts of the plots $(\varepsilon_{12} - \varepsilon_1)/C$ versus C and $(n_{12}^2 - n_1^2)/C$ versus C with respect to infinite dilution (C →0). The symbols k, T, N, ε, n and C are Boltzmann's constant, absolute temperature, Avagadro's number, dielectric constant, refractive index and concentration, respectively. The suffixes 1, 2 and 12 refer to the solvent, solute and solution, respectively.

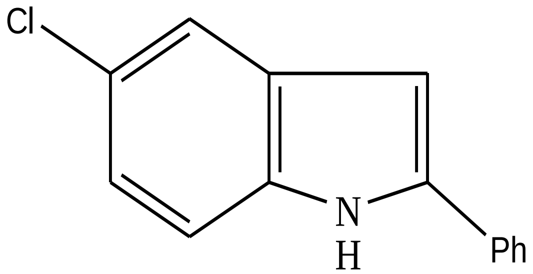
The dielectric constants of the dilute solutions are determined by measuring the capacitance of the solution, connecting leads and air. By measuring the capacitance of different concentration of the dyes in toluene, the dielectric constant of the solution (ε_{12}) was calculated using the equation

$$\varepsilon_{12} = \left(\frac{c_{12} - c_1}{c_a - c_1} \right) \qquad (3)$$

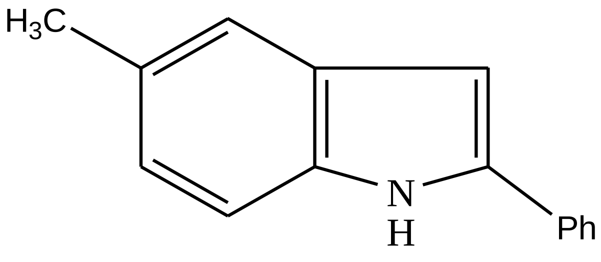
where the symbols c_{12} and c_a represents the capacitance of cylindrical cell with the solution and air, respectively. The symbol c1 represents the capacitance of the connecting leads.

Excited state dipole moments

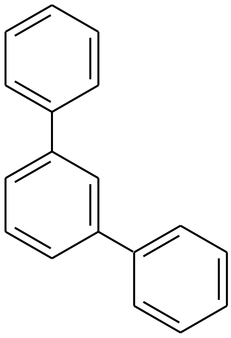
The three independent equations used for the estimation of excited state dipole moments of fluorescent molecules are as follows:



5-chloro-2-phenylindole (CPI)



5-methyl-2-phenylindole (MPI)



1, 3-diphenyl benzene (MT)

Fig. 1. Molecular structure of solute molecules along with IUPAC names.

Lippert's equation [11] $\bar{\nu}_a - \bar{\nu}_f = mF(\varepsilon, n)$ + constant (4)

Bakshiev's equation [12] $\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\varepsilon, n)$ + constant (5)

Chamma Viallet's equation [13] $\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = m_2 F_2(\varepsilon, n)$ + constant (6)

The expressions for [Lippert's polarity function] F(ε, n), [Bakshiev's polarity function] F1(ε, n) and [Chamma Viallet's polarity function] F2(ε, n) are given as

$$F(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \tag{7}$$

$$F_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \tag{8}$$

$$F_2(\varepsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2}\right] \tag{9}$$

Where $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maxima wave numbers in cm^{-1}, respectively. The other symbols ε and n are dielectric constant and refractive index of the solvents, respectively. From Eqs. (4) – (6) it follows that ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F(ε, n), ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F1(ε, n) and ½($\bar{\nu}_a$ + $\bar{\nu}_f$) versus F2 (ε, n) should give linear graphs with slopes m, m_1, and m_2, respectively, and are given as

$$m = \frac{2(\mu_e - \mu_g)^2}{hca^3}, \tag{10}$$

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{11}$$

$$\text{and } m_2 = \frac{2(\mu_e{}^2 - \mu_g{}^2)}{hca^3} \tag{12}$$

where μ_g and μ_e are the ground and excited state dipole moments of the solute molecules. The symbols h and c are Planck's constant and the velocity of light in vacuum, respectively, 'a' is the Onsager radius of the solute molecule and the values of which were calculated from the molecular volume of dye molecules according to the Suppan's equation [19]. If the ground state and excited states are parallel, the following expressions are obtained on the basis of Eqs. (11) and (12) [32, 35]

$$\mu_g = \frac{m_2 - m_1}{2}\left[\frac{hca^3}{2m_1}\right]^{\frac{1}{2}} \qquad (13)$$

$$\mu_e = \frac{m_1 + m_2}{2}\left[\frac{hca^3}{2m_1}\right]^{\frac{1}{2}} \qquad (14)$$

$$\mu_e = \left[\frac{m_1 + m_2}{m_2 - m_1}\right]\mu_g \text{ for } (m_2>m_1) \qquad (15)$$

III. Results And Discussion

The ground state dipole moments of the fluorescent molecules were estimated by using Guggenheim method [6]. The values obtained from this method are 4.52 D, 4.56 D and 3.78 D for CPI, MPI and MT, respectively. The ground state (μ_g) dipole moment values obtained from Eq. (13) are presented in Table 3.

The spectral shifts ($\bar{\nu}_a$ - $\bar{\nu}_f$) and ½($\bar{\nu}_a$ + $\bar{\nu}_f$) of all the three fluorescent molecules and solvent polarity function values F(ε, n), F1(ε, n)and F2(ε, n) for various solvents are presented in Table 1. We have used six solvents with dielectric constants varying from 2 to 37. Figs. 2– 4 show the graph of ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F (ε, n), ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F1(ε, n) and ½(($\bar{\nu}_a$ + $\bar{\nu}_f$) versus F2(ε, n), respectively. A linear progression was done and the data was fit to a straight line, corresponding values of the slopes are given in Table 2. In most cases ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F(ε, n) and ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F1(ε, n) correlation is established for a larger number of solvents than ½($\bar{\nu}_a$ + $\bar{\nu}_f$) versus F2(ε, n) correlation. In most cases the correlation coefficients are larger than 0.92 and indicate a good linearity for m, m_1, and m_2 with selected number of Stokes shift data points. In the case of m_2 for MPI and MT some of the same solvents do not participate in the correlation. Generally this deviation from linearity may be due to specific solute solvent interactions. The literature survey shows that m2 is usually negative but for our chemical systems it is positive which is in agreement with findings of several other workers [2, 22, 34].

The excited state (μ_e) dipole moments of the three fluorescent molecules, estimated by computing the values of ground state (μ_g) dipole moments obtained from Guggenheim method, in Eqs. (10)–(12) are presented in Table 3. Also the μ_e values obtained from Eq. (14) and the ratio μ_e / μ_g obtained from Eq. (15) are presented in Table 3. It may be noted that the measured values of μ_g and μ_e for MPI, MT and CPI differ from each other. The higher values of μ_e in the case of MPI may be attributed to the structural difference between the molecules. It may be noted that, the discrepancies occur between the estimated values of μ_e, for all the three fluorescent molecules. These differences between the values of μ_e may be in part, due to the various assumptions and simplifications made in the use of Lippert's, Bakshiev's and Chamma Viallet's correlations [36–38]. The dipole moment of CPI increases almost twice on excitation as compared to MPI and MT, this change in dipole moment on excitation can be explained in terms of nature of emitting state or intramolecular charge transfer. Further a large change in dipole moment on excitation suggests that excited state is twisted intramolecular charge transfer (TICT) in nature. Thus, presence of a large TICT and increase in planarity on excitation render the molecule more polar (as compared to ground state) giving rise to a large change in the dipole moment on excitation.

IV. Conclusion

It can be seen that the dipole moments of CPI, MPI and MT are significantly higher in excited singlet state than in ground state. The increase in dipole moments in the excited singlet states range between about 1 to 6.5 D depending on compounds. This demonstrates that the fluorescent molecules are more polar in excited states than in ground states for all the solvents studied. It may be noted that the difference in the ground state and excited state dipole moment estimated from Eqs. (13) and (14) and from Guggenheim method and Bakshiev method yields nearly equal values but the absolute ground and excited state values estimated are different. It is worth while to stress that the discrepancies observed may be due to approximations made in both methods to estimate ground state and excited singlet state dipole moments for the three fluorescent molecules. Also, Eq. (15) can be used to estimate the value of excited state dipole moment by pre-knowledge of the value of ground state dipole moment, without the necessity of knowing the Onsager radius of the solute.

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Tables and Figures

Table 1 Solvatochromic data of CPI (I), MPI (II) and MT (III) along with the calculated values of polarity functions

Solvent		$\overline{V}_a$ (cm^{-1})	$\overline{V}_f$ (cm^{-1})	$\overline{V}_a - \overline{V}_f$ (cm^{-1})	½($\overline{V}_a$ + $\overline{V}_f$) (cm^{-1})	F(ε, n)	F$_1$(ε, n)	F$_2$(ε, n)
Benzene	I	35620	29154	6106	32207	0.0031	0.0066	0.3413
	II	37037	30769	6268	33903			
	III	36166	30030	6136	33098			
Toluene	I	35587	29325	6262	32456	0.0131	0.0271	0.3489
	II	37735	31250	6485	34492			
	III	36101	29850	6251	32975			
Ethyl acetate	I	36127	29325	6802	32726	0.1977	0.4892	0.4977
	II	36900	30395	6505	33547			
	III	37174	30864	6310	34019			
Propanol	I	36363	29411	6952	32887	0.2734	0.7772	0.6511
	II	38167	31446	6721	34806			
	III	36630	30303	6327	33466			
Methanol	I	36549	29498	7051	33023	0.3088	0.8547	0.6508
	II	39215	32258	6957	35736			
	III	37593	31250	6343	34421			
MeCN	I	36764	29673	7091	33128	0.3055	0.8630	0.6657
	II	39840	32786	7054	36313			
	III	37037	30674	6363	33855			

Table 2: Statistical treatment of the correlations of solvent spectral shifts of CPI, MPI and MT

Compound	Slope	Correlation Coefficient	Number of data
Lippert correlations			
CPI	3038	0.99	6
MPI	1962	0.89	6
MT	549	0.90	6
Bakshiev correlations			
CPI	1041	0.98	6
MPI	677	0.89	6
MT	186	0.89	6

Table 3: Ground state and excited state dipole moments of CPI, MPI and MT

Molecule	Radius ‘a” (Å)	(D)[a]	(D)[b]	(D)[c]	(D)[d]	(D)[e]	(D)[g]	$(\mu_e/\mu_g)^g$
CPI	3.66	4.52	1.36	8.36	6.77	7.87	3.62	2.648
MPI	3.98	4.56	9.94	8.06	6.62	11.28	12.00	1.207
MT	3.81	3.78	8.89	5.51	4.79	8.14	9.90	1.113

[a] The experimental ground state dipole moments calculated from the Guggenheim method.
[b] The ground state dipole moments calculated using Eq. (13).
[c] The experimental excited state dipole moments calculated from Lippert’s equation.
[d] The experimental excited state dipole moments calculated from Bakshiev’s equation.
[e] The experimental excited state dipole moments calculated from Chamma Viallet’s equation.
[f] The excited state dipole moments calculated using Eq. (14).
[g] The ratio of excited state and ground state dipole moment values calculated using Eq. (15).

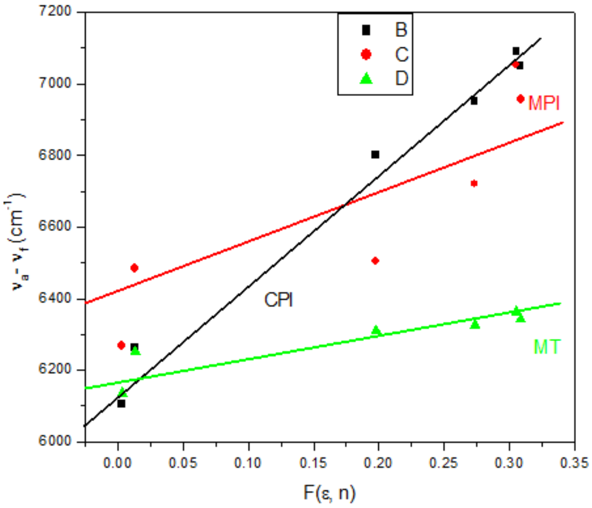

Fig. 2. The variation of Stokes shift with F by using Lippert’s equation.

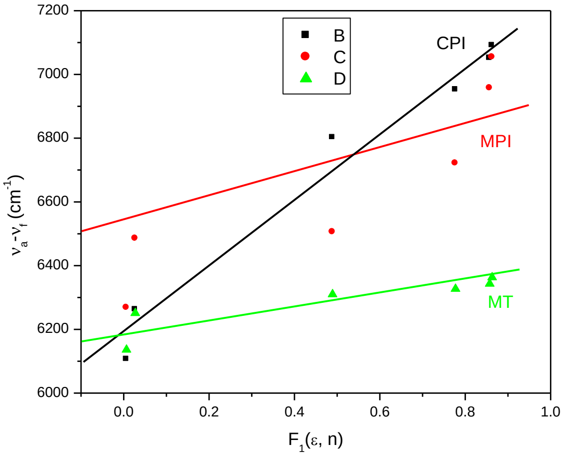

Fig. 3. The variation of Stokes shift with $F_1$by using Bakshiev’s equation.

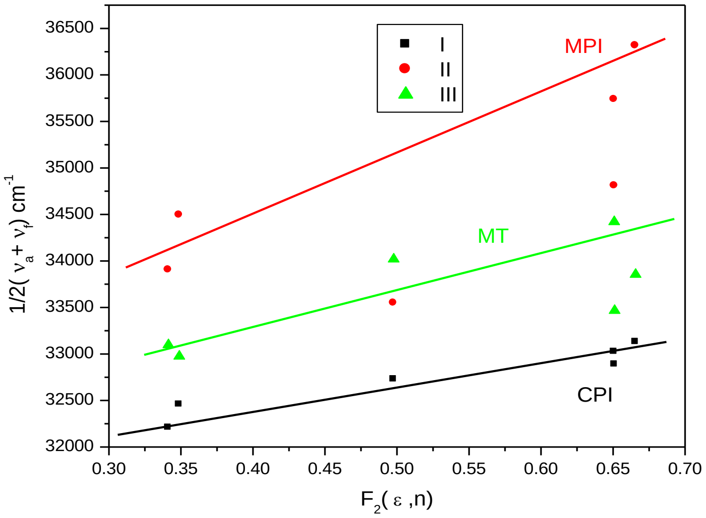

Fig. 4. The variation of arithmetic mean of Stokes shift with F_2 by using Chamma Viallet’s equation