Study of Solvent Effect in 2, 5-DPAPMC Dye Using Different Solvent Polarity Parameters and Estimation of Dipole Moments

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Abstract

The solvent effect on absorption and fluorescence spectra of a ketocyanine dye 2,5-di[(E)-1-(4-dipropylaminophenyl) methylidine]-1-cyclopentanone (2,5-DPAPMC) is analysed using Lippert-Mataga bulk polarity function, Reichardt's microscopic solvent polarity parameter and Kamlet's multiple linear regression approach. The spectral properties better follows Reichardt's microscopic solvent polarity parameter than Lippert-Mataga bulk polarity parameter. This indicates the presence of both general solute – solvent interactions and specific interactions. Kamlet's multiple linear regression approach indicates the major role of polarizability/dipolarity solvent influence than HBD and HBA. The spectral data in different solvents is used to estimate excited state dipole moment using theoretically determined ground state dipole moment. The excited state dipole moment of dye is found to be larger than its corresponding ground state dipole moment and, ground and excited state dipole moments are not parallel, but subtends an angle of 29°.

Keywords: Ketocyanine dye, Solvent polarity, Dipole moment, Solvatochromism, Intramolecular charge transfer.

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1. Introduction

The investigation on solvatochrimism in organic fluorophores has been a subject of interesting study in recent years [1-6]. These investigations have significant importance in the field of photophysics and photochemistry. Accordingly, photophysical properties like absorption and fluorescence spectral shifts, fluorescence quantum yield (Φ_f), fluorescence life time (τ_f), etc., have been a subject of several investigations [7, 8]. The data from solvatochromism can be used to determine the electric dipole moment of molecules in the excited states. The knowledge of dipole moment of electronically excited molecules is useful in designing nonlinear optical materials [9], in elucidation of the nature of the excited states and also it reflects the charge distribution in the molecule.

The spectral properties of ketocyanine dyes have been the subject of intensive investigations in previous years [10–25]. The pronounced solvent effects in both absorption and emission spectra of these dyes make them promising probes for monitoring micro-polarity, hydrogen-bond donating interaction, metal ion sensing, investigation of the cell membrane structures, evaluating the micro-environmental characteristics of biochemical and biological systems and many others [26-31]. Even though many investigations have been carried out on spectral properties of ketocyanine dyes in general and 2,5-di[(E)-1-(4-dipropylaminophenyl) methylidine]-1-cyclopentanone (2,5-DPAPMC) in particular, there is a lack of information on the analysis of spectral properties in terms of different solvent polarity parameters and, estimation of ground and excited state dipole moments to the best of present knowledge. This motivated to carry out the present work. The aim of the present work is to systemically analyse solvent effects on absorption transition energy, fluorescence transition energy and stoke's shift using different solvent polarity parameters and estimate ground and excited-state dipole moments of 2,5-DPAPMC. The molecular structure of 2,5-DPAPMC is given in Figure 1.
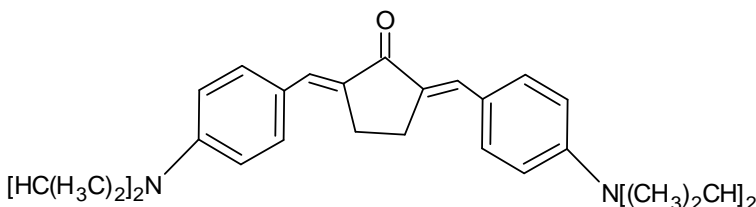
Fig. 1. Molecular structure of 2,5-DPAPMC

2. Theoretical Background

The Lipper-Mataga bulk solvent polarity parameter (F(ε,n)) values of solvents used in the present study were calculated using equation (1) [32, 33],

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

where ε and n are respectively dielectric constant and refractive index of respective solvents.

The microscopic solvent polarity parameter (E_N^T) values of solvents were taken from literature [27].

The multiple linear regression method proposed by Kamlet and co-workers [34-36] has also been used to correlate absorption transition energy($\overline{V}_a$), fluorescence transition energy ($\overline{V}_f$) and stoke's shift($\Delta \overline{v}$) with an index of the solvents dipolarity/polarizability which is a measure of the solvent's ability to stabilize a charge or dipole through nonspecific dielectric interactions (π*), and indices of the solvent's hydrogen-bond donor (HBD) strength (α) and hydrogen-bond acceptor (HBA) strength (β), according to the equation (2);

$$y = y_0 + a\alpha + b\beta + c\pi* \tag{2}$$

where y is the spectroscopic property under consideration, y_0 is respective spectroscopic property in gas phase, a, b, and c are respectively measures of solvents HBD, HBA and

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dipolarity/polarisability. The theoretical ground state dipole moment (μ_g) of the dye was obtained by quantum chemical calculations. The B3LYP model which is based on density functional theory was used. The 6-31G(d) basis set was employed in the calculation. All the computations were carried out using Gaussian 09 program [37] on a Pentium – 4 PC.

Solvent dependence of absorption and fluorescence band maxima was used to estimate the excited-state dipole moment and is determined according to Bakshiev's and Kawski-Chamma-Viallet's [38-44] equations (3) and (4) as given below:

$$\overline{v}_a - \overline{v}_f = m_1 F_1(\varepsilon, n) + \text{constant} \tag{3}$$

$$\frac{\overline{v}_a + \overline{v}_f}{2} = -m_2 F_2(\varepsilon, n) + \text{constant} \tag{4}$$

where $\overline{v}_a$ and $\overline{v}_f$ are the absorption and fluorescence maxima wavenumbers in cm^{-1} respectively, and

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \frac{(2n^2 + 1)}{(n^2 + 2)} \tag{5}$$

$$F_2(\varepsilon, n) = \left[\frac{(2n^2 + 1)}{2(n^2 + 2)} \left(\frac{\varepsilon - 1}{\varepsilon + 1} - \frac{n^2 - 1}{n^2 + 1} \right) + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \right] \tag{6}$$

From equations (3) & (4), the plots of $(\overline{v}_a - \overline{v}_f)$ versus $F_1(\varepsilon, n)$, and $(\overline{v}_a + \overline{v}_f)/2$ versus $F_2(\varepsilon, n)$ are linear with slopes m_1 and m_2 respectively and are given below:

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{7}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{8}$$

where μ_g and μ_e are ground and excited dipole moments of a molecule respectively, h is Planck's constant, c is the velocity of

light and a is Onsager cavity radius of a molecule respectively. The Onsager cavity radius of 2,5-DPAPMC was estimated using the method suggested by J. T. Edward [45].

If the ground and excited states are parallel, the following expressions can be obtained on the basis of above equations [46]

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2} \tag{9}$$

$$\mu_e = \frac{m_1 + m_2}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2} \tag{10}$$

If dipole moments μ_e and μ_g are not parallel to each other but form an angle ϕ, then ϕ can be calculated using equation (9).

$$\cos\phi = \frac{1}{2\mu_g\mu_e}\left[(\mu_g^2 + \mu_e^2) - \frac{m_2}{m_1}(\mu_e^2 - \mu_g^2)\right] \tag{11}$$

We have also used another method based on empirical solvent polarity parameter E_T^N to estimate excited state dipole moment. This method correlates the spectral shift better than the traditionally used bulk solvent polarity functions. In this method the problem associated with the estimation of Onsager cavity radius is minimized. Also, this polarity scale includes intermolecular solute/solvent hydrogen bond donor/acceptor interactions along with solvent polarity. The theoretical basis for the correlation of the spectral band shift with E_T^N is according to the equation (10) [47]

$$\overline{v}_a - \overline{v}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_B}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + \text{constant} \tag{12}$$

where $\Delta\mu_B$ and a_B are the change in dipole moment and Onsager cavity radius respectively of the Betaine dye, and $\Delta\mu$ and a are the corresponding quantities of the molecule of interest. The change in dipole moment $\Delta\mu$ can be extracted from the slope of the plot of (

$\bar{\nu}_a - \bar{\nu}_f$) versus E_T^N using the reported values of $\Delta\mu_B$ = 9D and a_B = 6.2Å.

3. Results and Discussion

3.1. Analysis of solvatochromism

Solvent polarity function values $F(\varepsilon, n)$, $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$ and E_T^N for various solvents used in the present study are collected in Table 1. The absorption and emission maxima, respective wave numbers, stokes shift and arithmetic mean of stokes shift values (in cm⁻¹) for 2,5-DPAPMC dye in different solvents are given in Table 2. Absorption and emission maxima were taken from reference [22]. From Table 2, it is observed that when solvent is changed from non-polar toluene to acetonitrile which is a polar aprotic solvent, there is a   spectral band shift of 11nm in the absorption spectrum, whereas it is 35 nm for methanol which is a polar protic solvent. Also, when solvent is changed from non-polar toluene to a polar aprotic solvent acetonitrile, there is a spectral band shift of 92 nm in the fluorescence spectrum, whereas it is 153 nm for a polar protic solvent methanol. This implies that the ground state energy distribution is less affected by change in polarity and hydrogen bonding characteristics of solvent compared to excited state. The stokes' shift values increases with increase in solvent polarity. The stokes' shift of 4540 cm⁻¹ is observed in polar protic solvent methanol and 3880 cm⁻¹ in case of polar aprotic solvent acetonitrile. These observations indicate the sensing ability of 2,5-DPAPMC to the polarity and hydrogen bonding characters of the solvents. The observed solvatochromic behavior could be due to the presence of two tautomeric forms of 2,5-DPAPMC (keto and charged enol forms, Figure 2).

The contribution of both tautomers in solution is governed by the nature and polarity of the used solvents. The less polar keto form contributes mainly in non- and less polar solvents. In contrast the highly polar enol form predominates in polar and strong hydrogen bonding donor solvents, thus, causing larger spectral shifts [1]. Further, both absorption and fluorescence band maxima undergoes pronounced red shifts with increase in solvent polarity. The

observed solvent sensitivity is understandable in terms of $\pi \rightarrow \pi^*$ with intramolecular charge transfer (ICT) from dipropyl amino group to the carbonyl oxygen.

Table 1. The Values of Solvent Polarity Functions

Solvents[a]	F[b]	F_1[c]	F_2[d]	E_T^N [e]
Toluene	0.0131	0.0288	0.3498	0.0990
Dioxane	0.0205	0.0415	0.3074	0.1640
Butyl Acetate	0.1729	0.4156	0.4723	0.2410
DMF	0.2745	0.8357	0.7096	0.3860
Acetonitrile	0.3060	0.8627	0.6643	0.4600
Isopropanol	0.2743	0.7701	0.6412	0.5460
Ethanol	0.2893	0.8138	0.6521	0.6540
Methanol	0.3087	0.8545	0.6507	0.7620

[a] Solvents are listed in the order of increasing E_T^N

[b] Lippert-Mataga solvent polarity function

[c] Bakhshiev's solvent polarity function

[d] Kawaski-Chamma-Vialet solvent polarity function

[e] E_T^N values taken from Ref. [27]

Table 2. Solvatochromic Data of 2,5-DPAPMC in Different Solvents

Solvents	λ_a (nm)	ν_a (cm^{-1})	λ_f (nm)	ν_f (cm^{-1})	$(\nu_a - \nu_f)$ (cm^{-1})	$(\nu_a + \nu_f)/2$ (cm^{-1})
Toluene	464	21560	491	20360	1200	20960
Dioxane	463	21580	533	18760	2820	20170
Butyl Acetate	460	21740	536	18660	3080	20200
DMF	482	20760	581	17220	3540	18990
Acetonitrile	475	21040	583	17160	3880	19100
Isopropanol	486	20580	599	16700	3880	18640
Ethanol	492	20320	625	16000	4320	18160
Methanol	499	20060	644	15520	4540	17790

To get further insight on the solvatochromic behavior of 2,5-DPAPMC, spectroscopic properties are correlated with relevant solvent polarity scales. The spectroscopic properties $\overline{\nu}_a$, $\overline{\nu}_f$ and $\Delta\overline{\nu}$ are plotted as a function of Lipper-Mataga solvent polarity parameter (or orientation polarizability) $F(\varepsilon, n)$. The least square correlation analysis gave a better correlation in case of

fluorescence(r = 0.89) and stokes' shift (r = 0.89) as compared to absorption (r = 0.78). The relatively poor correlation in case of absorption implies that Lippert-Mataga solvent polarity parameter is not a complete valid polarity scale to explain solvent effects in the present case. This could be due to the reason that this method not consider specific solute – solvent interactions such as hydrogen bonding effect, complex formation and also ignore molecular aspects of solvation. The poor correlation of absorption transition energies with $F(\varepsilon, n)$ indicates the role of hydrogen bonding effect in the present case, as is evident from very large spectral shifts in polar protic solvents. Therefore, an attempt has been made to explain spectroscopic properties by solvent polarity parameter E_T^N.
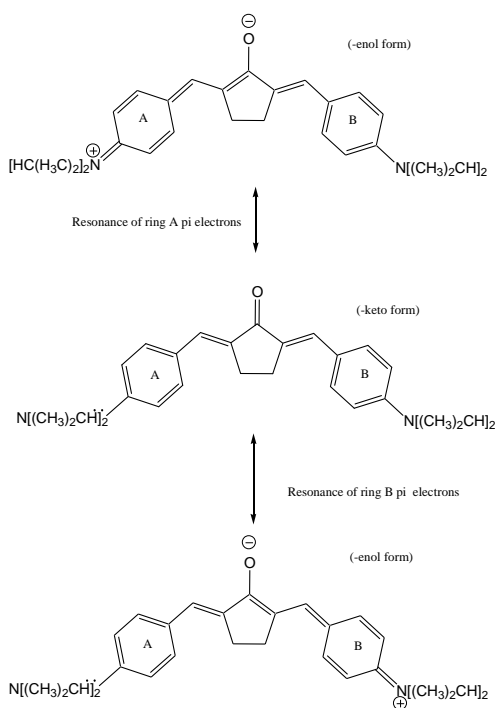

Fig. 2. Keto and charge-separated enol resonating structures of 2,5-DPAPMC.

The $\bar{\nu}_a, \bar{\nu}_f$ and $\Delta\bar{\nu}$ are correlated with the microscopic solvent polarity parameter E_T^N. The least square correlation analysis gave a

better correlation for all the three spectral properties $\bar{v}_a$ (r = 0.95), $\bar{v}_f$ (r = 0.97) and $\Delta\bar{v}$ (r = 0.91). This implies that spectroscopic properties $\bar{v}_a$, $\bar{v}_f$ and $\Delta\bar{v}$ of 2,5-DPAPMC have better dependence on E_T^N compared to $F(\varepsilon, n)$. The better correlation of $\Delta\bar{v}$ with E_T^N also confirms the presence of a general solute-solvent interactions as well as hydrogen bonding interactions.

In order to get information about the individual contributions of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities of the solvents on the spectroscopic properties, $\bar{v}_a$, $\bar{v}_f$ and $\Delta\bar{v}$ are correlated with solvatochromic parameters α, β and π* using multiple regression. The multiple regression analysis data along with correlation coefficients is given in equation (13).

$$\left.\begin{array}{l} \bar{v}_a\,(cm^{-1}) = 22891 - 1209\alpha - 48\beta - 1695\pi^*\,; r = 0.99 \\ \bar{v}_f\,(cm^{-1}) = 23090 - 1608\alpha - 1130\beta - 2203\pi^*\,; r = 0.93 \\ \Delta\bar{v}\,(cm^{-1}) = 1846 + 1923\alpha + 3747\beta + 3856\pi^*\,; r = 0.78 \end{array}\right\} \quad (13)$$

From above equations it is clear that non-specific dielectric interaction (π*) has the major solvent influence. However, the contribution of HBD and HBA parameters cannot be neglected. It is clear from multiple regression analyses of $\bar{v}_a$ and $\bar{v}_f$ with better correlation coefficients, HBD(α) influence is more than HBA (β).

3.2. Estimation of ground and excited state dipole moments

The ground state dipole moment of 2,5-DPAPMC was obtained using quantum chemical calculation following geometry optimisation and is found to be 5.16 D. The optimized molecular geometry with the direction of dipole moment is shown in Figure 3.
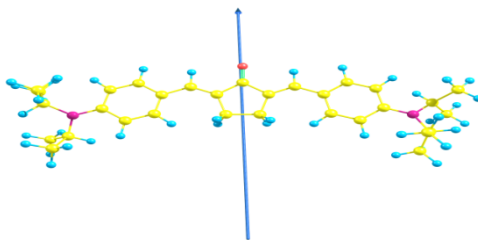
Fig.3. Optimized molecular geometry of 2,5-DPAPMC

Figure (4) shows the plots of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\varepsilon, n)$ (Figure 4(a)) and $(\bar{\nu}_a + \bar{\nu}_f)/2$ versus $F_2(\varepsilon, n)$ (Figure 4(b)). The linear analysis was done and the data was fit to a straight line. The corresponding values of slopes, intercepts and correlation coefficients are collected in Table 3. In both the cases the correlation coefficients are more than 0.90 with selected number of data points. The excited state dipole moment (μ_e) is calculated from the slopes of respective plots and are given in Table 4.

From Table 4, it is clear that calculated excited state dipole moments from Bakshiev's ($\mu_e{}^b$) and Kawski-Chamma-Viallet's ($\mu_e{}^c$) equations are fairly in good agreement with each other. The excited state dipole moment is also calculated using polarity parameter E_T^N according to equation (12) and Figure 4(c). The value of excited state dipole moment calculated from this method is represented as $\mu_e{}^d$ and is also collected in Table 4. This value is less than $\mu_e{}^b$ and $\mu_e{}^c$ which are calculated from Bakshiev's and Kawski-Chamma-Viallet's equations. This could be due to the fact that, methods based on Bakshiev's and Kawski-Chamma-Viallet's equations not consider specific solute–solvent interactions such as hydrogen bonding effect, complex formation and also ignore molecular aspects of solvation, whereas these aspects are included in the method based on E_T^N [27].
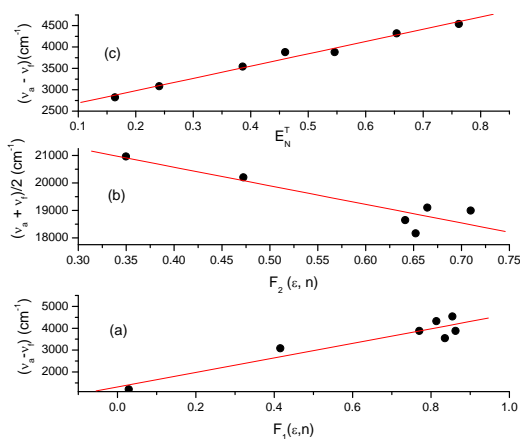
Fig.4. Plots of (a) $(\bar{\nu}_a - \bar{\nu}_f)(cm^{-1})$ versus F1(ε,n) (b) plot of $(\bar{\nu}_a + \bar{\nu}_f)/2(cm^{-1})$ versus F2(ε,n) and (c) Plot of $(\bar{\nu}_a - \bar{\nu}_f)(cm^{-1})$ versus E_N^T

Table 3. Slope (m), Intercept (C), Correlation Coefficient (r) and No. of Data Points (n) Corresponding to Statistical Treatment of Spectral Shifts with F_1, F_2 and E_T^N

Radius (Å)	$\mu_g{}^a$	$\mu_e{}^b$	$\mu_e{}^c$	$\mu_e{}^d$
4.88	5.16	11.27	10.01	8.30

Table 4.The Onsager Cavity Radius and, Ground-state and Singlet Excited State Dipole Moments (in Debye, D)

Function	m	C	r	n
F_1	3327	1313	0.94	7
F_2	6765	23275	0.91	6
E_T^N	2876	2402	0.99	7

[a]Ground state dipole moment calculated by Gaussian software.

[b] Excited – state dipole moment calculated from Bakhshiev's equation.

[c] Excited – state dipole moment calculated from Kawski-Chamma-Viallet's equation.

[d] Excited – state dipole moment calculated with Δμ from equation (12)

The ground and excited state dipole moments of 2,5-DPAPMC were also estimated assuming that they are parallel using equations (9) and (10). The estimated values are μ_g = 3.15D and μ_e = 9.26D. The difference in values of μ_g and μ_e compared to respective values from other methods (Table 4) suggest that μ_g and μ_e are not parallel. This prompted to estimate the angle between μ_g and μ_e according to equation (11) and the value is found to be 29°. It means that μ_g and μ_e are not parallel.

From Table 4, it is clear that the dipole moment of 2,5-DPAPMC is higher in the first excited-state as compared to the ground-state. The dipole moment increases almost two times on excitation. This indicates the existence of a more relaxed excited state, due to ICT favoured by the cooperative effects of the dipropyl aniline moieties as donors and the carbonyl group as an acceptor, and suggests that the present dye can serve as a good candidate component of non-linear optical materials [1].

4. Conclusions

The solvent effect on spectral properties of 2,5-DPAPMC has been analysed using different polarity parameters. The spectral properties of this dye are influenced more by dipolarity/polarizability of solvents. However, the contributions from solvents HBD and HBA cannot be ignored. HBD influences are more than HBA. The dye has higher dipole moment in the excited state than in the ground state. This clearly indicates that dye has more relaxed excited state due to ICT and suggests that it can serve as good candidate component of nonlinear optical materials. To the present day knowledge this is the first report on detailed analysis of effect of solvents and estimation of dipole moments of 2,5-DPAPMC, and would be of great help in many fields.

Acknowledgements

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