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ANALYSIS OF SOLVATOCHROMISM OF A BIOLOGICALLY ACTIVE KETOCYANINE DYE USING DIFFERENT SOLVENT POLARITY SCALES AND ESTIMATION OF DIPOLE MOMENTS

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ABSTRACT

The effect of solvents on photophysical properties namely absorption transition energy, fluorescence transition energy and stoke's shift of a ketocyanine dye 2,5-di[(E)-1-(4 - aminophenyl) methylidine]-1-cyclopentanone (2,5-APMC) is analyzed using Lippert-Mataga bulk polarity function, Reichardt's microscopic solvent polarity parameter and Kamlet's multiple linear regression approach. The spectral properties better follow Reichardt's microscopic solvent polarity parameter than Lippert-Mataga bulk polarity function. This indicates that both general solute – solvent interactions and specific interactions are operative. Kamlet's multiple linear regression approach indicates that polarizability/dipolarity solvent influences are more compare to HBD and HBA solvent influences. The solvatochromic correlations are 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 state dipole moment and excited state dipole moments are not parallel, but makes an angle of 57^0.

Keywords: Ketocyanine dye, Solvent polarity, Dipole moment, Solvatochromism

1. INTRODUCTION

The investigation on effect of solvents on photophysical properties of organic fluorophores has been a subject of interesting investigation in recent years (Katarzyna G et al. 2005; Sonia P O et al. 2008; Evale B G et al. 2009; Patil N R et al. 2011; Deepa H R et al. 2013; Tarek et al. 2013). These investigations have considerable importance in the field of photophysics and photochemistry. Accordingly, photophysical properties like fluorescence quantum yield (Φ_f), fluorescence life time (τ_f), absorption and fluorescence spectral shift, etc., have been a subject of several investigations (Porter C and Suppan P, 1965; Ghazy R et al. 2004). The data from effect of solvents on absorption and fluorescence spectra can be used to estimate the electric dipole moment of the molecules in the excited states. The knowledge of dipole moment of electronically excited molecules is quite useful in designing nonlinear optical materials (Chemla D S and Zyss J, 1987), in elucidation of the nature of excited states and also it reflects the charge distribution in the molecule.

Photophysical properties of ketocyanine dyes have been the subject of intensive investigations during previous few decades (Kessler M A and Wolfbeis O S, 1991; Banerjee D et al. 1995a; Banerjee D et al. 1995b; Banerjee D et al. 1995c, Banerjee D et al. 1996, Banerjee D and Bagchi S, 1996; Pramanik R, et al. 1999; Das P K, et al. 2000; Marcotte N and Fery-Forgues S, 2000; Pivovarenko V G et al. 2000; Pramanik R, et al. 2000; Pramanik R ,et al. 2001; Doroshenko A O and Pivovarenko V G, 2003; Shannigrahi M et al. 2003; Doroshenko A O et al. 2004; Jahur A M et al.2008). 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 (Kessler M A and Wolfbeis O S, 1991; Barnabas M V et al. 1992; Reichardt C. 1994; Banerjee D et al. 1995a; Banerjee D et al. 1995b; Banerjee D et al. 1995c, Banerjee D et al. 1996, Banerjee D and Bagchi S, 1996; Lobnik A and Wolfbeis O S, 1998; Doroshenko A O et al. 1999; Pramanik R et al. 1999; Rurack K et al. 1999; Das P K et al. 2000; Marcotte N and Fery-Forgues S, 2000; Pivovarenko V G et al. 2000; Pramanik R et al. 2000; Pramanik R et al. 2001; Doroshenko A O et al. 2002; Doroshenko A O and Pivovarenko V G, 2003; Shannigrahi M et al. 2003; Doroshenko A O et al. 2004; Jahur A M et al.2008). Even though intensive investigations have been carried out on photophysics and photochemistry of ketocyanine dyes in general and 2,5-di[(E)-1-(4 - aminophenyl) methylidine]-1-cyclopentanone (2,5-APMC) 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 prompted me 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 scales and, estimate ground and excited-state dipole moments of 2,5-APMC. The molecular structure of 2,5-APMC is given in Figure 1. The spectral properties are analyzed using Lippert and Mataga bulk solvent polarity parameter, Reichardt's microscopic solvent polarity parameter and solvatochromic parameters proposed by Kamlet et al. The ground state dipole moment is determined by quantum chemical method. program. The excited state dipole moment is estimated using Bakhshiev's, Kawaski-Chamma-Viallet equations and Richardt's microscopic solvent polarity parameter E_N^T .

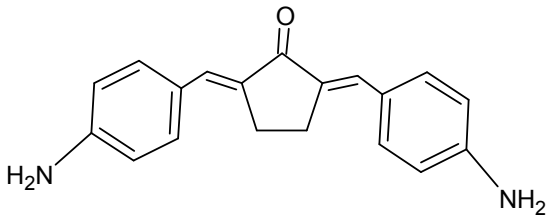

Figure 1
Molecular structure of 2, 5-APMC

2. THEORETICAL BACKGROUND

The values of Lipper-Mataga bulk solvent polarity parameter (F(ε,n)) for solvents used in the present study were calculated using equation (1) (Mataga et al. 1956; Lakowicz J R. 2006),

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

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 (Reichardt C. 1994). The multiple linear regression method proposed by Kamlet and co-workers (Kamlet J M et al. 1977; Kamlet J M et al. 1981; Kamlet et al. 1983) has also been used to correlate absorption transition energy($\bar{\nu}_a$), fluorescence transition energy ($\bar{\nu}_f$) and stoke's shift($\Delta\bar{\nu}$) 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 equation (2);

$$y = y_0 + a\alpha + b\beta + c\pi^* \qquad (2)$$

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 dipolarity/polarisability.

The theoretical ground state dipole moment (μ_g) of 2,5-APMC 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 (Frisch M J et al. 2010) 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 (Bakshiev N G. 1964; Kawski A. 1964; Kawski A. 1965; Kawski A and Stefanowska U, 1965; Kawski A and Kołakowski W, 1966; Kawski A and Pasztor B,1966;Chamma A and Viallet P, 1970) equations (3) and (4) as given below:

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\varepsilon, n) + \text{ constant} \quad (3)$$

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_2 F_2(\varepsilon, n) + \text{ constant} \quad (4)$$

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

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

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

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

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

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

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. The Onsager cavity radius of 2, 5-APMC was estimated using the method suggested by J. T. Edward (Edward J T. 1970).

If the ground and excited states are parallel, the following expressions can be obtained on the basis of above equations (Kawski A. 2002)

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

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

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 (11).

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

We have also used another method based on the 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 (12) (Ravi M et al. 1995)

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

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

3. RESULTS AND DISCUSSION

3.1. Analysis of solvent effect on photophysical properties

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 for 2,5-APMC dye in different solvents are given in Table 2. The spectral data used was taken from Ref. (Doroshenko A O and Pivovarenko V G, 2003). From Table 2, it is observed that when solvent is changed from non-polar toluene to polar aprotic solvent acetonitrile, there is a spectral band shift of 17nm in the absorption spectrum, whereas it is 36nm for methanol which is 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 64nm in the fluorescence spectrum, whereas it is 109nm for 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 value increases with increase in solvent polarity. The stokes' shift of 5180cm^{-1} is observed in polar protic solvent methanol and 4800cm^{-1} in case of polar aprotic solvent acetonitrile. These observations indicates the sensing ability of 2,5-APMC 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-APMC (keto and charged enol forms, figure 2).

The degree of 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 (Tarek F et al. 2013). Further, both absorption and fluorescence band maxima undergoes pronounced red shift with an increase in the solvent polarity. The observed solvent sensitivity is understandable in terms of $\pi \rightarrow \pi^*$ with intramolecular charge transfer (ICT) from amino group to the carbonyl oxygen.

Table 1
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] ***Microscopic solvent polarity parameter*** E_T^N

Table 2
Solvatochromic data[a] of 2,5-APMC in different solvents

Solvents	λ_a (nm)	ν_a (cm^{-1})	λ_f (nm)	ν_f (cm^{-1})	(ν_a -ν_f) (cm^{-1})	(1/2) (ν_a +ν_f) (cm^{-1})
Toluene	418	23920	485	20600	3320	22260
Dioxane	418	23880	518	19300	4580	21590
Butyl Acetate	421	23780	514	19460	4320	21620
DMF	454	22040	556	17980	4060	20010
Acetonitrile	435	23000	549	18200	4800	20600
Isopropanol	453	22060	574	17420	4640	19740
Ethanol	455	21960	588	17020	4940	19490
Methanol	454	22020	594	16840	5180	19430

[a] ***Taken from Ref. (Doroshenko A O and Pivovarenko V G, 2003).***

To get further insight on the solvatochromic behavior of 2,5-APMC, spectroscopic properties are correlated with relevant solvent polarity scales. The spectroscopic properties $\bar{\nu}_a, \bar{\nu}_f$ and $\Delta\bar{\nu}$ were 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 absorption(r = 0.85) and fluorescence (r = 0.88) as compared to stokes' shift (r = 0.65). The average correlation in case of stokes' shift 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 fact 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 stoke's shift 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 another solvent polarity parameter E_T^N.

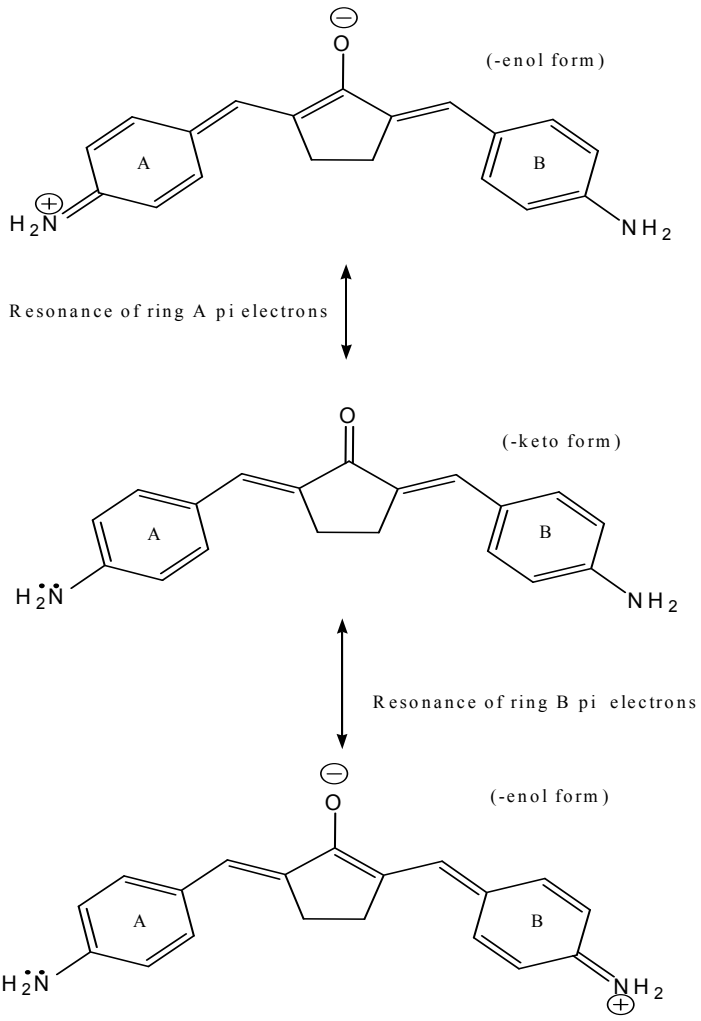

Figure 2
Keto and charge-separated enol resonating structures of 2, 5-APMC

The $\bar{\nu}_a, \bar{\nu}_f$ and $\Delta\bar{\nu}$ are correlated with E_T^N. The least square correlation analysis gave a better correlation for all the three spectral properties $\bar{\nu}_a$ (r = 0.88), $\bar{\nu}_f$ (r = 0.96) and $\Delta\bar{\nu}$ (r = 0.80). This implies that spectroscopic properties $\bar{\nu}_a, \bar{\nu}_f$ and $\Delta\bar{\nu}$ of 2,5-APMC have better dependence on E_T^N compared to $F(\varepsilon, n)$. The better correlation of $\Delta\bar{\nu}$ with E_T^N also confirms the presence of a general solute-solvent interactions as well as hydrogen bonding interactions.

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

$$\left.\begin{aligned} \bar{\nu}_a(\mathrm{cm}^{-1}) &= 26197 - 781\alpha - 1420\beta - 2059\pi^* \quad r = 0.97 \\ \bar{\nu}_f(\mathrm{cm}^{-1}) &= 22679 - 1396\alpha - 1645\beta - 2049\pi^* \quad r = 0.96 \\ \Delta\bar{\nu}(\mathrm{cm}^{-1}) &= 4673 + 1478\alpha + 1733\beta + 1884\pi^* \quad r = 0.60 \end{aligned}\right\} \quad (13)$$

From equation (13) 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 that HBA (β) influence is more than HBD (α).

3.2. Estimation of ground and excited state dipole moments

The ground state dipole moment of 2,5-APMC was obtained using quantum chemical calculation following geometry optimisation and is found to be 4.52 D. The optimized molecular geometry with the direction of dipole moment is shown in Figure 3.

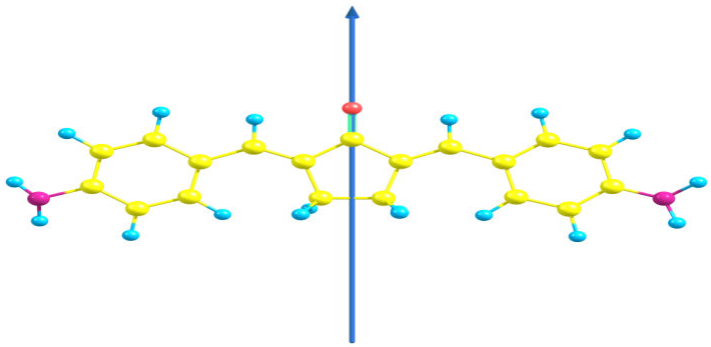

Figure 3
Optimized molecular geometry of 2, 5-APMC

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

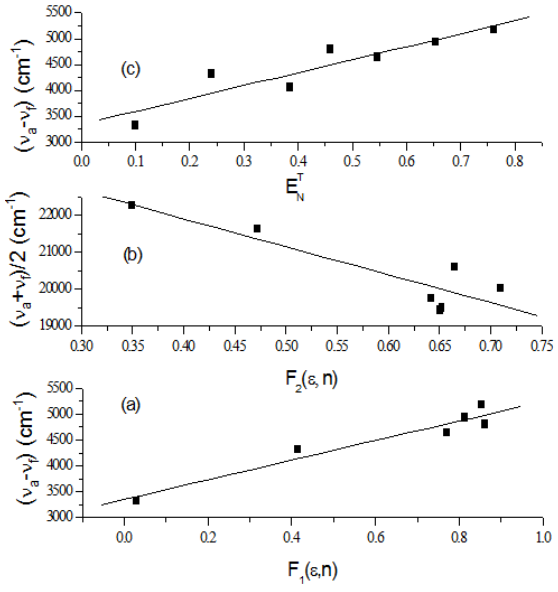

Figure 4
(a) Plot of $(\overline{\nu}_a - \overline{\nu}_f)(\mathrm{cm}^{-1})$ ***versus F₁(ε,n)***
(b) plot of $(\overline{\nu}_a + \overline{\nu}_f)/2(\mathrm{cm}^{-1})$ ***versus F₂(ε,n) and***
(c) Plot of $(\overline{\nu}_a - \overline{\nu}_f)(\mathrm{cm}^{-1})$ ***versus*** E_N^T

Table 3
Statistical treatment of the correlations of the spectral shifts

Correlation	Slope	Correlation coefficient	Data points
Bakhshiev correlation	1896	0.96	6
Kawaski-Chamma-Vialet correlation	-7602	0.90	7
E_T^N correlation	2500	0.92	7

Table 4
The Onsager cavity radius and, Ground-state and singlet excited state dipole moments (in Debye, D)

Radius (Å)	μ_g[a]	μ_e[b]	μ_e[c]	μ_e[d]
4.02	4.52	8.02	8.33	6.73

[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 momens calculated from* E_T^N.

From Table 4, it is clear that calculated excited state dipole moments from Bakshiev's (μ_e^b) and Kawski-Chamma-Viallet's (μ_e^c) equations are fairly in good agreement with each other. The excited state dipole moment was 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 μ_e^d and is also collected in Table 4. This value is slightly smaller than one 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 (Reichardt C. 1994).

The ground and excited state dipole moments of 2,5-APMC were also estimated assuming that they are parallel using equations (9) and (10). The estimated values are μ_g = 5.26D and μ_e = 8.80D. The slightly higher 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 us to estimate the angle between μ_g and μ_e according to equation (11) and the value is found to be 57^0. From Table (4) it is clear that the dipole moment of 2, 5-APMC 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 aniline moieties as donors and the carbonyl group as an acceptor, and suggests that the present dye can serve as good candidate component of non-linear optical materials [Tarek F et al. 2013].

4. CONCLUSION

The solvent effect on photophysical properties of 2,5-APMC 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. HBA influences are more than HBD. 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 solvatochromism and estimation of dipole moments of 2,5-APMC, and would be of great help in many fields as mentioned in the introduction.

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