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ANALYSIS OF TWO FLUORESCENT MOLECULES PROPERTIES USING SOLVATOCHROMIC SHIFT METHOD

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ABSTARCT

The absorption and emission spectra of two fluorescent coumarins molecules coumarins namely 5BAMC and 4DHMC have been recorded at room temperature in solvents of different polarities. The ground state dipole moments (μ_g) of two coumarins were determined experimentally by Guggenheim method. The exited state (μ_e) dipole moments were estimated from Lippert's, Bakhshiev's and Kawski-Chamma-Viallet's equations using the variation of Stoke's shift with the solvent dielectric constant and refractive index. The geometry of the molecule was fully optimized and the μ_g were also calculated theoretically by Gaussian 03 software using B3LYP/6-31g* level of theory. Further, $\Delta\mu$ were calculated both from solvatochromic shift method on the basis of microscopic solvent polarity parameter (E_T^N) and the values are compared. The μ_g and μ_e were calculated by means of solvatochromic shift method and μ_e was determined in combination with μ_g. It was observed that μ_e were higher than those of the μ_g, indicating a substantial redistribution of the π-electron densities in a more polar excited state for two coumarins.

Keywords: Solvatochromic shift method, ground state and excited state dipole moments, coumarins and DFT.

1. INTRODUCTION

The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of interesting investigation [1-5]. Excitation of a molecule by photon causes a redistribution of charges leading to conformational changes in the excited state. This can result in an increase or decrease of dipole moment of the excited sate as compared to ground state. The dipole moment of an electronically excited state of a molecule is an important property that provides information on the electronic and geometrical structure of the molecule in the short-lived state. All the methods available so far for the determination of singlet excited-state dipole moment are based on the spectral shift caused either externally by electrochromism or internally by solvatochromism. The solvatochromic method is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. Several workers have made extensive experimental and theoretical studies on ground state (μ_g) and excited-state (μ_e) dipole moments using different techniques in variety of organic fluorescent compounds like coumarins, indoles, purines, and fluorescein and in some laser dyes [6-19] etc.

Coumarins and their derivatives establish a family of dyes which are applicable in different fields of science and technology [6-7]. They exhibit strong fluorescence in the UV and VISIBLE region which makes them suitable for used as colorants, dye laser media and as nonlinear optical chromospheres. In this paper, we report the effects of solvent on absorption and emission spectra, and estimation of ground and excited-state dipole moments of two coumarins namely 5BAMC and 4DHMC by solvatochromic shift method and theoretical studies on ground state (μ_g) dipole moments using DFT(B3LYP/6-31g* method)[20]. However, there are no reports available in literature on the determination of μ_g and μ_e values of these molecules investigated.

2. EXPERIMENTAL

2.1. Chemicals used

The solutes of two fluorescent coumarins molecules namely 5BAMC and 4DHMC were synthesized in our laboratory using standard methods [21-24]. The molecular structures of these molecules are given in Fig.1. The solvents used in the present study namely methanol, propanol, dmso, trichloroethane, ethyl acetate, diethyl ether, dichloromethane, tetrahydrofuran, dimethylformamide, ethanol,benzene, toluene, acetonitrile, acetone, carbon tetrachloride,1,4 dioxane, ether and butanol are used for 5BAMC whereas, acetonitrile, butanol, diethylether (dee), dichloroethane (dce), dimethylformamide (dmf), dimethylsulphoxide (dmso), n-heptane, isopropanol and toluene solvents are used for 4DHMC. All the solvents were obtained from S-D-Fine Chemicals Ltd., India, and they were of spectroscopic grade. The required solutions were prepared at fixed concentration of solutes 1×10^{-4} M in each solvent.

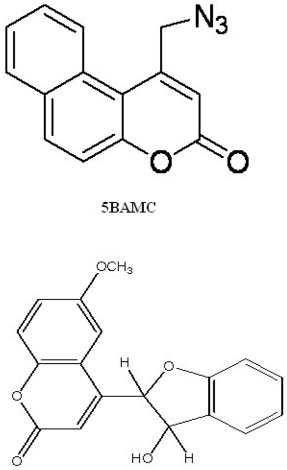

Figure 1: ***The molecular structures of [5BAMC] & [4DHMC]***

2.2. Spectroscopic measurements

The absorption spectra were recorded using Hitachi 50–20 UV–Vis spectrophotometer. Fluorescence intensities of the solutions were measured on Hitachi F-2000 Spectrofluorimeter at room temperature with perpendicular geometry. 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 Forbes Tinsley (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 these measurements were carried out at room temperature (300 K).

2.3 Determination of the dielectric constant and refractive index.

The capacitance of air, the solvent and the solution have been used to measure dielectric constant. By measuring the capacitance of different concentrations of the solute in toluene the dielectric constant of the solution (ε_{12}) was calculated using the expression

$$\varepsilon_{12} = \frac{C_2 - C_X}{C_1 - C_X} \qquad (1)$$

where C_2, C_X and C_1, represent the capacitances due to leads, solution, and air respectively. The values of dielectric constants thus determined for 5BAMC and 4DHMC using toluene. The values of refractive indices (n_{12}) of solutions were determined for 5BAMC and 4DHMC using toluene respectively.

3. Theory

3.1 Theoretical calculations of ground-state dipole moments

The ground-state dipole moments (μ_g) of these two molecules were calculated by quantum chemical calculations. All the computations were carried out using the Gaussian 03 program [20] on a Pentium-4 PC. The basis sets at the levels of theory B3LYP/ 6-31 g* were used for calculations and corresponding optimized molecular geometries are shown in Fig.2. The values of ground-state dipole moments obtained from *ab initio* calculations using DFT.

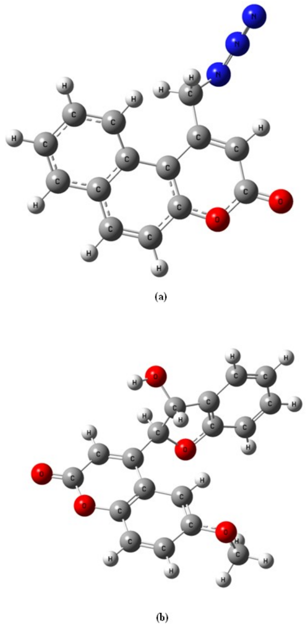

Figure 2 : ***Optimized geometries of (a) 5BAMC and (b) 4DHMC***

Ground state optimized molecular geometries of (a) 5BAMC and (b) 4DHMC are shown in Fig. 3. The arrow indicates the direction of the dipole moment.

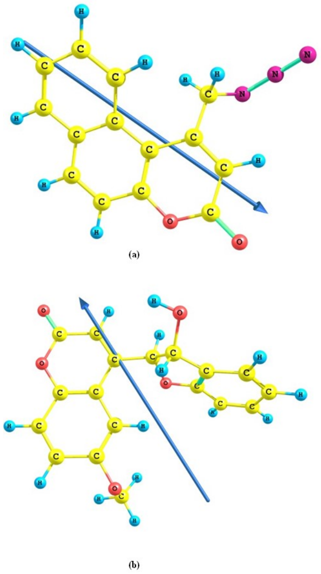

Figure 3 : ***Ground state optimized molecular geometries of (a) 5BAMC and (b) 4DHMC. The arrow indicates the direction of the dipole moment.***

3.2 Experimental calculations of ground-state dipole moments

The ground-state dipole moments (μ_g) of these two dyes were estimated experimentally using Guggenheim's method [25]. According to this the expression for ground-state dipole moment is given by

$$\mu_g^2 = \left[\frac{27KT}{4\pi N(\varepsilon_1 + 2)(n_1^{\ 2} + 2)} X \frac{\Delta}{C} \right] \tag{2}$$

where

$$\Delta = (\varepsilon_{12} - n_{12}^2) - (\varepsilon_1 - n_1^{\ 2})$$

where K the Boltzmann constant, T the absolute temperature in Kelvin, 'N' the Avogadro's number, ε_{12} the dielectric constant and n_{12} refractive index of the solution, ε_1 and n_1 are the dielectric constant and refractive index of the pure solvent and *C* the concentration of the solute in given solvent. The estimated values of the ground-state dipole moments (μ_g) using Eq.2 for 5BAMC and 4DHMC respectively.

3.3 Experimental calculations of excited state dipole moments

The three independent equations used for the estimation of excited state dipole moments of two dyes are as follows

Lippert's equation [26]

$$\bar{\nu}_a - \bar{\nu}_f = \mathrm{m}_1 \mathrm{F}_1(\varepsilon, \mathrm{n}) + \text{Constant} \tag{3}$$

Bakshiev's equation [27]

$$\bar{\nu}_a - \bar{\mathrm{v}}_\mathrm{f} = -\mathrm{m}_2 \mathrm{F}_2(\varepsilon, \mathrm{n}) + \text{Constant} \tag{4}$$

Kawski-Chamma-Viallet's equation [28]

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = \mathrm{m}_3 \mathrm{F}_3(\varepsilon, \mathrm{n}) + \text{Constant} \tag{5}$$

The expressions for $\mathrm{F}_1(\varepsilon,\mathrm{n})$ [Lippert's polarity function], $\mathrm{F}_2(\varepsilon,\mathrm{n})$ [Bakshiev's polarity equation] and $\mathrm{F}_3(\varepsilon,\mathrm{n})$ [Kawski-Chamma-Viallet's polarity equation] are given as

$$\mathrm{F}_1(\varepsilon,n)=\left[\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1}\right] \tag{6}$$

$$\mathrm{F}_2(\varepsilon,n)=\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right]\frac{(2n^2+1)}{(n^2+2)} \tag{7}$$

$$\mathrm{F}_3(\varepsilon,n)=\frac{2n^2+1}{2(n^2+2)}\left[\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right]+\frac{3(n^4-1)}{2(n^2+2)^2} \tag{8}$$

Where $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maxima wavelength in cm^{-1} respectively. The other symbols ε and n are dielectric constant and refractive index respectively. From Eqs.6-8 it follows that $(\bar{\nu}_a-\bar{\nu}_f)$ versus $\mathrm{F}_1(\varepsilon, n)$, $(\bar{\nu}_a-\bar{\nu}_f)$ versus $\mathrm{F}_2(\varepsilon, n)$ and $\frac{\bar{\nu}_a+\bar{\nu}_f}{2}$ versus $\mathrm{F}_3(\varepsilon, n)$ should give linear graphs with slopes m_1, m_2 and m_3 respectively and are given as

$$\mathrm{m}_1=\frac{2(\mu_e-\mu_g)^2}{hca^3} \tag{9}$$

$$\mathrm{m}_2=\frac{2(\mu_e-\mu_g)^2}{hca^3} \tag{10}$$

$$\mathrm{m}_3=\frac{2(\mu^2{}_e-\mu^2{}_g)}{hca^3} \tag{11}$$

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 velocity of light in vacuum respectively; 'a' is the Onsager radius of the solute molecule. If the ground state and excited states are parallel, the following expressions are obtained on the basis of Eq.10-11.

$$\mu_g=\frac{m_3-m_2}{2}\left[\frac{hca^3}{2m_2}\right]^{1/2} \tag{12}$$

$$\mu_e=\frac{m_3+m_2}{2}\left[\frac{hca^3}{2m_2}\right]^{1/2} \tag{13}$$

And $$\mu_e=\left[\frac{m_2+m_3}{m_3-m_2}\right]\mu_g \qquad \text{for } (\mathrm{m}_3>\mathrm{m}_2) \tag{14}$$

3.4 MOLECULAR-MICROSCOPIC SOLVENT POLARITY PARAMETER (E_T^N)

The empirical polarity parameter E_T^N proposed by Richards [3] gave towering results with solvetochromic shift of dipolar molecules. The results correlate better with microscopic solvent polarity E_T^N rather than the traditionally used bulk solvent polarity functions involving dielectric constant (ε) and refractive index (n) as in the later error estimation of Onsager cavity radius 'a' has been minimized. In E_T^N the error estimation of the Onsager cavity radius has been minimized, it also 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 was proposed by Reichardt and developed by Ravi et al. [29], according to Eq. (2.15)

$$\bar{\nu}_a-\bar{\nu}_f=11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_b}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N+constant \tag{15}$$

where $\Delta\mu_b$= 9D and $a_B = 6.2\ A^0$ are the change in dipole moment on excitation and Onsager cavity radius respectively of molecule and $\Delta\mu$ and $'a'$ are the corresponding quantities for the solute molecule of interest. A dimensionless normalized scale E_T^N was introduced in order to avoid the use of non SI unit kal/mol in $E_T(30)$ solvent polarity scale and is defined by Eq. (2.16), using water (E_T^N=1) and tetramethylsilane (TMS = E_T^N = 0) as extreme reference solvents [3].

$$E_T^N = \frac{E_T(Solvent) - E_T(TMS)}{E_T(Water) - E_T(TMS)} = \frac{E_T(Solvent) - 30.7}{32.4} \qquad (16)$$

The change in dipole moment $(\Delta\mu)$ can be evaluated from the slope of the stokes shift versus E_T^N plot and is given by Eq. (2.17)

$$\Delta\mu = (\mu_e - \mu_g) = \sqrt{\frac{m\ X\ 81}{\left(6.2/a\right)^3 11307.6}} \qquad (17)$$

Where 'm' is the slope obtained from the plot of Stokes shift $(\bar{\nu}_a - \bar{\nu}_f)$ versus microscopic solvent polarity (E_T^N) using Eq. (2.17). The Onsager radius of the molecule can be calculated by the method suggested by Edward [30].

3. RESULTS AND DISCUSSION

The spectral shifts $\bar{\nu}_a - \bar{\nu}_f$ and $\bar{\nu}_a + \bar{\nu}_f$ of two fluorescent molecules and solvent polarity function values $F_1(\varepsilon,n)$, $F_2(\varepsilon,n)$ and $F_3(\varepsilon,n)$ for various solvents are presented in Table 1& 2 and Table 3 &4 respectively. We have used seventeen solvents for 5BAMC and nine solvents for 4DHMC with dielectric constants varying from 2.200 to 47.240 for 5BAMC and 2.380 TO 47.240 for 4DHMC. Figs. 4-6 show the graph of ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F_1 (ε, n), ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F_2 (ε, n) and ($\bar{\nu}_a$ + $\bar{\nu}_f$) versus F_3 (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 5. In most cases ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F_1 (ε, n), ($\bar{\nu}_a$ - $\bar{\nu}_f$) versus F_2 (ε, n) and ($\bar{\nu}_a$ + $\bar{\nu}_f$) versus F_3 (ε, n) correlation is established for a larger number of solvents. In most cases the correlation coefficients are larger than 0.984 which indicate a good linearity for m_1, m_2 and m_3 with selected number of Stokes shift data points. Generally, the deviation from linearity may be due to specific solute solvent interactions.

Table 1: *Solvatochromic data of 5BAMC in different solvents*

Solvents	λ_a nm	λ_f nm	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\Delta\bar{\nu} = \bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a + \bar{\nu}_f$ (cm^{-1})
methanol	353.7	424.4	28272.547	23562,676	4665.871	51835.223
propanol	355.0	424.8	28169.014	23540.490	4628.524	51709.504
dmso	356.9	427.1	28019.053	23413.720	4605.333	51432.773
tce	355.3	419.1	28155.229	23860.654	4510.575	52015.883
ea	351.7	417.6	28433.324	23946.360	4486.964	52379.684
ethylalcohol	355.2	425.8	28153.153	23485.204	4667.949	51638.357
dee	350.1	414.4	28563.268	24131.274	4476.994	52694.542
dcm	353.3	420.5	28304.557	23781.213	4523.344	52085.77
thf	354.2	421.5	28232.637	23724.792	4507.845	52130.429
dmf	355.0	425.7	28169.014	23490.721	4650.293	51659.735
benzene	351	413.0	28490.000	24213.100	4276.900	52893.100
toluene	350.3	412.3	28546.960	24254.184	4292.776	52801.114
acetonitrile	352.7	422.5	28352.708	23668.639	4684.069	51779.347
acetone	355	425.5	28169.014	23501.763	4667.251	51670.777
CCl_4	348.5	410.0	28694.404	24390.244	4304.16	53084.648
dioxane	349.2	410.6	28636.884	24354.603	4282.281	52991.487
butanol	353.7	421.3	28272.547	23736.055	4487.492	52008.602

Table 2: *Solvatochromic data of 4DHMC in different solvents*

Solvents	λ_a nm	λ_f nm	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\Delta\bar{\nu} = \bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a + \bar{\nu}_f$ (cm^{-1})
acetonitrile	343.6	467.0	29103.609	21413.276	7690.333	50516.885
butanol	341.0	454.8	29325.513	21987.687	7337.826	51313.200
dce	344.0	453.9	29069.767	22031.284	7038.483	51101.051
dee	332.4	425.7	30084.236	23490.721	6593.515	53574.957
dmf	347.3	470.6	28793.550	21249.469	7544.081	50043.019
dmso	349.7	472.2	28595.939	21177.467	7418.472	49773.406
n-heptane	329.5	404.2	30349.014	24740.228	5608.786	55089.242
isopropanol	341.6	457.7	29274.005	21848.372	7425.633	51122.377
toluene	332.9	408.5	30039.051	24479.804	5559.247	54518.855

Table 3*:* *Calculated values of polarity functions 5BAMC*

Solvents	ε	n	F$_1$(ε,n)	F$_2$(ε,n)	F$_3$(ε,n)	E_T^N
methanol	33.000	1.374	0.302	0.856	0.651	0.762
propanol	18.000	1.385	0.264	0.782	0.654	0.617
dmso	47.240	1.478	0.264	0.843	0.745	0.444
tce	2.500	1.494	0.194	0.548	0.601	0.160
ea	6.081	1.372	0.174	0.493	0.499	0.228
ethylalcohol	24.550	1.360	0.281	0.817	0.654	0.654
dee	4.2660	1.352	0.167	0.377	0.429	0.210
dcm	9.100	1.424	0.218	0.59	0.586	0.321
thf	7.500	1.404	0.210	0.550	0.552	0.207
dmf	38.500	1.430	0.276	0.841	0.722	0.404
benzene	2.300	1.501	0.032	0.006	0.341	0.111
toluene	2.380	1.496	0.015	0.033	0.352	0.099
acetonitrile	37.500	1.346	0.305	0.863	0.666	0.460
acetone	21.00	1.360	0.284	0.839	0.641	0.355
CCl$_4$	2.200	1.460	0.024	0.023	0.323	0.052
dioxane	2.300	1.421	0.019	0.039	0.3065	0.164
butanol	17.800	1.416	0.162	0.753	0.6482	0.602

Table 4: *Calculated values of polarity functions 4DHMC*

Solvents	ε	n	F$_1$(ε,n)	F$_2$(ε,n)	F$_3$(ε,n)	E_T^N
acetonitrile	37.500	1.346	0.280	0.797	0.633	0.460
butanol	17.800	1.416	0.215	0.561	0.552	0.602
dce	47.240	1.478	0.132	0.371	0.425	0.194
dee	4.2660	1.352	0.132	0.371	0.425	0.210
dmf	38.500	1.430	0.276	0.8356	0.712	0.404
dmso	47.240	1.478	0.259	0.842	0.744	0.444
n-heptane	4.266	1.352	0.165	0.371	0.425	0.012
isopropanol	8.930	1.424	0.217	0.590	0.584	0.617
toluene	2.380	1.496	0.022	0.029	0.350	0.099

Table 5: ***Statistical treatment of the correlations of solvents spectral shifts of 5BAMC and 4DHMC***

Parameters		Compounds	
		5BAMC	4DHMC
Slopes 'm'	A	1388.951	7212.608
	B	451.725	2374.309
	C	3598.888	5778.873
	D	551.374	3176.685
Correlation coefficient 'r'	A	0.992	0.991
	B	0.988	0.995
	C	0.984	0.995
	D	0.829	0.863
Number of data	A	17	9
	B	17	9
	C	17	9
	D	17	9

A-Lippert Correlation; B- Bakshiev Correlation
C- Chamma Viallet Correlation; D- dependence of Stoke's shift

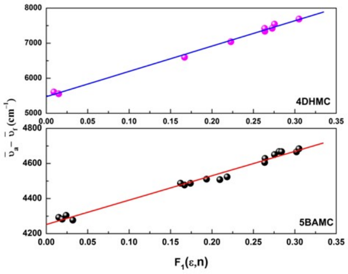

Figure 4 : ***The variation of Stoke's shift with F_1 (ε, n) using Lippert equation for 5BAMC and 4DHMC***

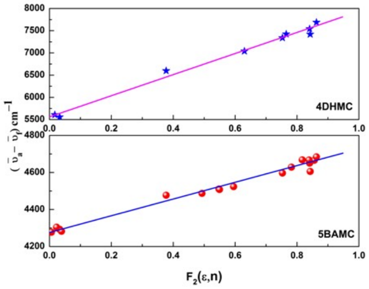

Figure 5: ***The variation of Stoke's shift with F_2 (ε, n) using Bakshiev's equation for 5BAMC and 4DHMC***

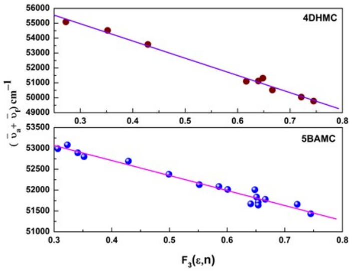

Figure 6: ***The variation of arithmetic means of Stoke's shift with F_3(ε, n) using Kawski-Chamma-Viallet's equation for 5BAMC and 4DHMC***

The ground state dipole moments of two coumarins were estimated by using Guggenheim method [25]. The values obtained from this method are 6.450D and 4.492D for 5BAMC and 4DHMC respectively and also ground state (μ_g) dipole moment values obtained from Eq.12 are presented in Table 6. The values of Onsager cavity radii of 5BAMC and 4DHMC molecules were calculated by molecular volumes and the Parachor [30] and are listed in Table 6.

Table 6: ***Ground and excited state dipole moments of 5BAMC and 4DHMC***

Compound	Radius 'a' (A°)	$\mu_g{}^a$ (D)	$\mu_g{}^b$ (D)	$\mu_g{}^c$ (D)	$\mu_e{}^d$ (D)	$\mu_e{}^e$ (D)	$\mu_e{}^f$ (D)	$\mu_e{}^g$ (D)	$\Delta\mu^h$ (D)	$\Delta\mu^i$ (D)	$(\mu_e/\mu_g)^j$
5BAMC	3.771	6.450	6.129	5.505	9.171	8.002	7.796	6.956	1.451	0.943	1.264
4DHMC	3.917	4.492	4.212	2.670	6.471	11.055	8.258	7.396	4.726	2.395	2.770

Debye (D) = 3.33564X10-30cm = 10-18 esu cm.

a Calculated by Gaussian Software.

b The experimental ground states dipole moments calculated from Guggenheim method.

c The ground states dipole moments calculated using Eq. 12.

d The experimental excited state dipole moments calculated from Lippert's equation.

e The experimental excited state dipole moments calculated from Bakhshiev's equation.

f The experimental excited state dipole moments calculated from Chamma-Viallet's equation.

g The excited states dipole moments calculated using Eq. 13.

h The change in dipole moments for μeg and μgc

i The change in dipole moments calculated from Eq. 17

j The ratio of excited state and ground state dipole moments values calculated using Eq.14.

The excited state (μ_e) dipole moments of the two fluorescent molecules, estimated by computing the values of ground state (μ_g) dipole moments obtained from Guggenheim method, in Eq. 9-11 are presented in Table 6. Also the (μ_g) and (μ_e) values were obtained from Eq. 12 and 13. The ratio of (μ_g) and (μ_e) obtained from Eq.14 are presented in Table 6. The experimental (from Eq. 2) and theoretically calculated (*ab initio* calculations using DFT) values are presented in Table 6. The experimental and theoretical ground state (μ_g) dipole moment results are good in agreement for our used chemical systems as shown in Table 6 [4, 12 and 26]. The difference in the ground state dipole moment is due to the necessity of knowing the radius of the solute molecule in Eq. 12 as compared to experimental and theoretical values obtained from Eq. 2 and *ab initio* calculations using DFT. It may be noted that the measured values of (μ_g) and (μ_e) for $C_1$and C_2 differ from each other. The higher values of (μ_e) in the case of C_2 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 the two coumarins. 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 Kawski-Chamma-Viallet's correlations [26-28]. The large magnitude of Stoke's shift indicates that the excited state geometry could be different from that of the ground state. The general observation is that there is an increase in Stoke's shift with increase in solvent polarity which shows that there is an increase in the dipole moment on excitation.

The linear E_T^N dependence of Stoke's shift indicates the existence of general type of solute-solvent interaction in which the Stoke's shift depends on the dielectric constant and refractive index of the solvents. The Fig. 7 shows the variation of Stoke's shift with E_T^N for 5BAMC and 4DHMC. With increasing solvent polarity, both absorption and emission bands undergo a bathochromic shift. This indicates that ICT (intermolecular charge transfer) absorption of the less dipolar ground state molecule with dominant mesomeric structure, leading to highly dipolar excited state and with the prominent structures of molecules.

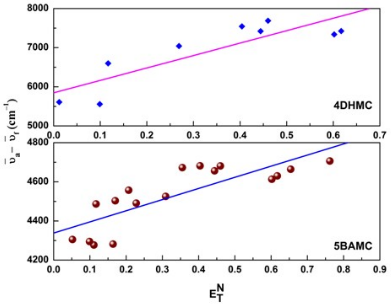

Figure 7 : ***The variation of Stoke's shift with E_T^N for 5BAMC and 4DHMC***

The Solvatochromic data can be used to identify the spectra, namely π- π*, n-π*, etc. It can be noticed from Table1 that, with increase in the solvent polarity, the fluorescence emission peak undergoes a bathochromic shift, confirming a π- π* transition. The shift of the fluorescence wavelengths towards longer wavelengths could be caused, if the excited state charge distribution in the solute is markedly different from the ground state charge distribution, and is such as to give a stronger interaction with polar solvents in the excited state. . The observed variations in the dipole moment values can also be understood in terms of their possible resonance structures as shown in Fig 8.

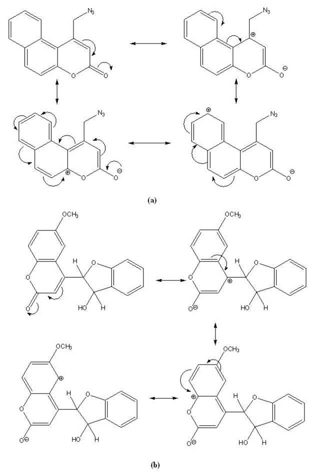

Figure. 8: ***Possible resonance structure of (a) 5BAMC and (b) 4DHMC***

4. CONCLUSION

We have studied the photophysical properties of $C_1$and C_2. It has been found that excited state dipole moment (μ_e) is greater than ground state dipole moment (μ_g) for both the coumarins. The increase in dipole moment in the excited singlet states range between about 2.5 to 3 D. This demonstrates these two coumarins are more polar in excited states than in ground states for all the solvents studied. The ground state dipole moments results are correlated (experimental and theoretical) in our used chemical systems. It may be noted that there is a difference in the ground state and excited state dipole moments. It is worthwhile to stress that the discrepancies observed may due to approximations made in both methods to estimate ground state and excited singlet state dipole moments for two coumarins. Also Eq. 14 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 solutes.

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