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PHOTO PHYSICAL PROPERTIES OF TWO COUMARIN DERIVATIVES USING SOLVATOCHROMIC SHIFT METHOD

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ABSTRACT

The ground state (μ_g) and excited state (μ_e) dipole moments of two coumarin derivatives namely MDTC and BDTC were estimated in various solvents. The dipole moments were estimated from Lippert, Bakhshiev and Kawaski-Chamma-Viallet equations by using the variation of stokes shift with the solvent dielectric constant and refractive index. Ground state dipole moments were also calculated theoretically by DFT studies using Gaussian 03 software. It was observed that the excited state dipole moments calculated by solvatochromic shift method were greater than the ground state dipole moments indicating a substantial redistribution of the π-electron densities in a more polar excited state for both the coumarin derivatives.

Key words: Coumarin derivatives, Solvatochromic shift method, Ground state and excited state dipole moments and DFT studies.

1. INTRODUCTION

Photophysics of fluorescent organic compounds gives a better knowledge of excited state properties which in turn will help in the designing of newer molecules and understanding their performance in specific applications. Determination of ground state and excited state dipole moments of dye molecules is important because the values of dipole moments provide information about the change in electronic distribution after excitation, charge distribution in the molecule and to judge the site of attack by nucleophilic and electrophilic reagents in some photochemical reactions. The excited state dipole moments of some fluorescent molecules such as studied here also determine the tunability range of the emission energy as a function of the polarity of the medium. Coumarins are well known laser dyes for the blue – green spectral region. Coumarins and their derivatives are finding lot of applications in different fields of Science and technology [1-2]. They exhibit a strong fluorescence in UV and VISIBLE region. Hence they are more suitable for the use as colorants, dye laser media and also as NLO chromospheres. In medicine, coumarins are used as fluorescent probes to determine the rigidity and fluidity of living cells and its surrounding medium. They also possess distinct biological activity and have been described as potential agents for anticancer. Several workers have made both experimental and theoretical studies on ground state and excited state dipole moments by using solvatochromic shift method and

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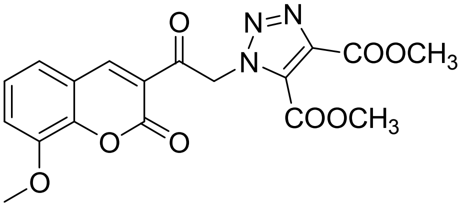
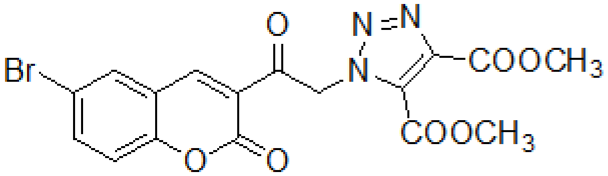
other methods on fluorescent organic molecules like coumarins, thiophene, imidazoles, indoles, purins etc. [3-21]. In our present work we report the effect of both polar and non-polar solvents on the absorption spectra and emission spectra of both the coumarins molecules. We have estimated the ground state and excited state dipole moments using solvatochromic shift method. Theoretical calculations were carried out by using Gaussian 03 program [22, 23] to supplement the experimental results. However, there are no reports available in literature on the determination of μ_g and μ_e values for these molecules investigated.

2. MATERIALS AND METHODS

The fluorescent coumarin molecules namely MDTC and BDTC were synthesized in our laboratory using standard methods [24].The molecular structure of these molecules are given in Fig.1. The solvents used in the present study namely toluene(TL) and 1,4dioxane(DX) trichloroehtane(TCE), tetrahydrofuran(THF), dichloromethane(DCM), dichloroethane(DCE), dimethylsulphoxide(DMSO) and acetonitrile(AN) 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. The absorption and emission spectra were recorded using Perkin Elmer UV–Vis spectrophotometer and Perkin Elmer fluorescence spectrophotometer. All these measurements were carried out at room temperature.



8-Methoxy-3-[1-(4,5-dicarbomethoxy-1,2,3-triazoloacetyl)]coumarin [MDTC]



6-Bromo-3-[1-(4,5-dicarbomethoxy-1,2,3-triazoloacetyl)]coumarin [BDTC]

Figure 1
The molecular structure of MDTC and BDTC

3. THEORY

3.1 Computational calculations.

The ground state dipole moments of these two molecules were calculated by quantum chemical calculations. All the computations were carried out using Gaussian 03 program on a Pentium- 4 PC and the basis set level used is B3LYP/6-31 g*. Corresponding optimized molecular geometries of MDTC and BDTC are as shown in Fig.2 and the ground state optimized molecular geometries of MDTC and BDTC are shown in Fig.3. The arrow mark indicates the direction of the dipole moment.

3.2 Experimental calculation of excited state dipole moments.

The three independent equations for the calculation of the excited state dipole moments of the solute molecules are as follows.

Lippert equation [27]

$$\overline{\vartheta_a} - \overline{\vartheta_f} = m_1 F_1(D.n) + const \tag{1}$$

Bakshiev equation[28]

$$\overline{\vartheta_a} - \overline{\vartheta_f} = m_2 F_2(D.n) + const \tag{2}$$

Kawaski-Chamma-Viallet equation [29]

$$\frac{\overline{\vartheta_a} + \overline{\vartheta_f}}{2} = m_3 F_3(D.n) + const \tag{3}$$

Here $F_1(D,n)$, $F_2(D,n)$ and $F_3(D,n)$, are Lippert polarity function, Bakshiev polarity function and Kawaski-Chamma-Viallet polarity function respectively. They are given in terms of dielectric constant (D) and refractive index (n) of the solvents as follows.

$$F_1(D.n) = \left[\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1}\right] \tag{4}$$

$$F_2(D.n) = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right]\left(\frac{2n^2+1}{n^2+2}\right) \tag{5}$$

$$F_3(D.n) = \left(\frac{2n^2+1}{2(n^2+2)}\right)\left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right] + \frac{3(n^4-1)}{2(n^2+2)^2} \tag{6}$$

A plot of $\overline{\vartheta_a} - \overline{\vartheta_f}$ v/s $F_1(D.n)$, $\overline{\vartheta_a} - \overline{\vartheta_f}$ v/s $F_2(D.n)$ and $\frac{\overline{\vartheta_a} + \overline{\vartheta_f}}{2}$ v/s $F_3(D.n)$ gives a linear plot with respective slopes m_1, m_2 and m_3. These slopes are given by

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

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

$$m_3 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{9}$$

Where μ_g and μ_e are ground state and excited state dipole moments, h is the Planck constant, c is the speed of light and ‘a’ is Onsager’s cavity radius [30]. By assuming ground state and excited state dipole moments are parallel following equations are obtained from equation (8) and (9).

$$\mu_g = \frac{(m_3 - m_2)}{2}\left[\frac{hca^3}{2m_2}\right]^{1/2} \qquad (10)$$

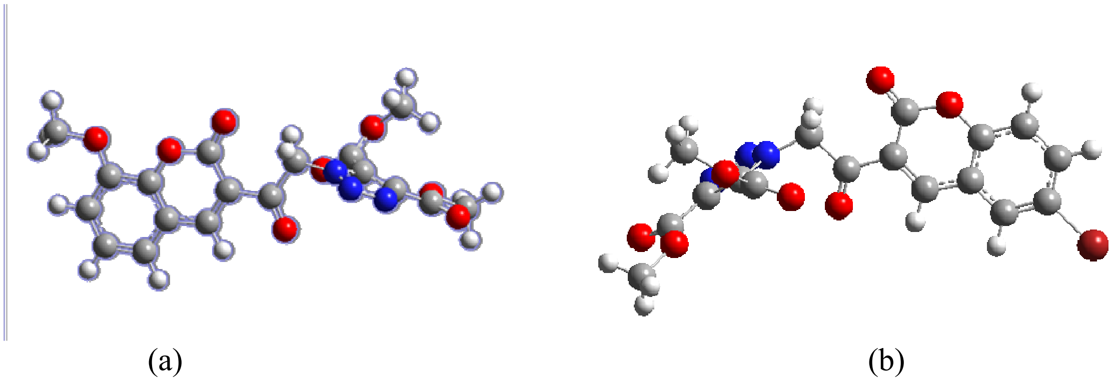
$$\mu_e = \frac{(m_3 + m_2)}{2}\left[\frac{hca^3}{2m_2}\right]^{1/2} \qquad (11)$$

$$\mu_e = \frac{(m_3 + m_2)}{(m_3 - m_2)} \times \mu_g \quad \text{For } m_3 \text{ greater than } m_2 \qquad (12)$$

4. RESULTS AND DISCUSSIONS

Stokes shifts were calculated from $\lambda_{f\ max}$ rather than 0 – 0 emission transition and are presented in Table.1 and Table.2 along with the solvent polarity functions of solvents used in our present work. The possible resonance structures for the solute molecules are given in Fig.4 (a) and Fig 4 (b). The absorption and emission spectra of both the molecules are given in Fig.5.and Fig.6. We have used eight solvents whose dielectric constants vary from 2.4 to 48. Lippert plot, Bakhshiev plot and Kawaski-Chamma-Viallet plots are constructed for normal fluorescence spectrum of MDTC and BDTC. These plots are linear with an excellent correlation co efficient and represented in Fig.7 to Fig.9. The small deviation from the linearity may be attributed to specific solute solvent interactions. With the increase in solvent polarity the emission peak shifts towards red by nearly 30nm in case of MDTC and 6 nm in case of BDTC. This red shift also indicates strong host guest interactions. The slopes and corresponding correlation coefficients are presented in Table.3. Ground state dipole moments were calculated using equation (10). Excited state dipole moments were calculated using Lippert equation, Bakhsiev equation and Kawaski-Chamma-Viallet equations. Ground state dipole moments were also calculated theoretically using Gaussian 03 program and the basis set level used is B3LYP/6-31 g*. All these values are given in Table.5. It may be noted that the excited state dipole moments calculated from Lippert equation, Bakshiev equation and Kawaski-Chamma-Viallet equations were greater than the ground state dipole moments. The small discrepancies in the values of excited state dipole moments may be in part, due to the various assumptions and simplifications made in the use of above mentioned equations.

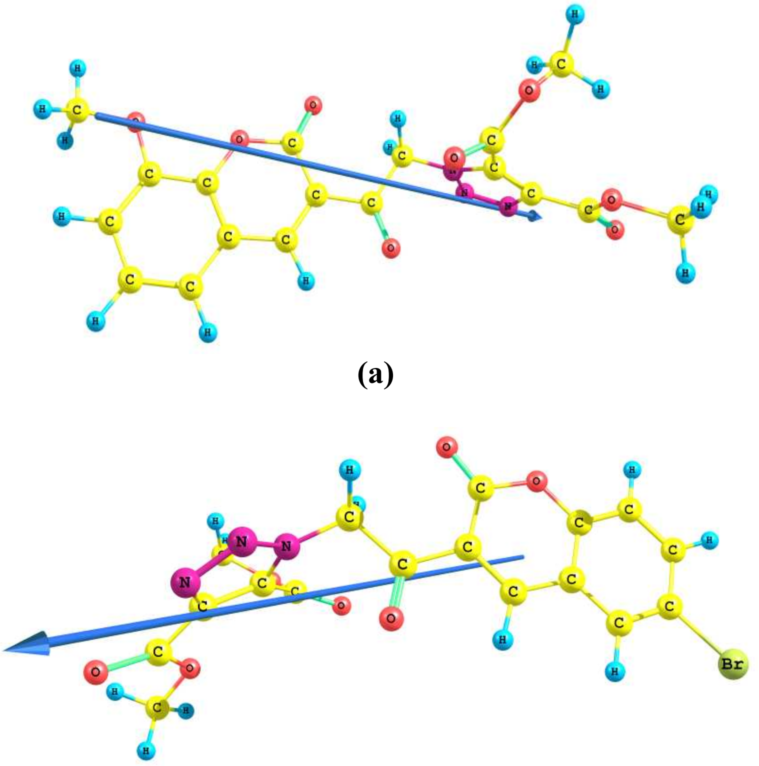
FIGURES GRAPHS AND TABLES



(a) (b)

Figure2

Optimized molecular geometry of MDTC (a) and BDTC (b)



(a)

(b)

Figure 3

The ground state optimized molecular geometries of MDTC (a) and BDTC (b)

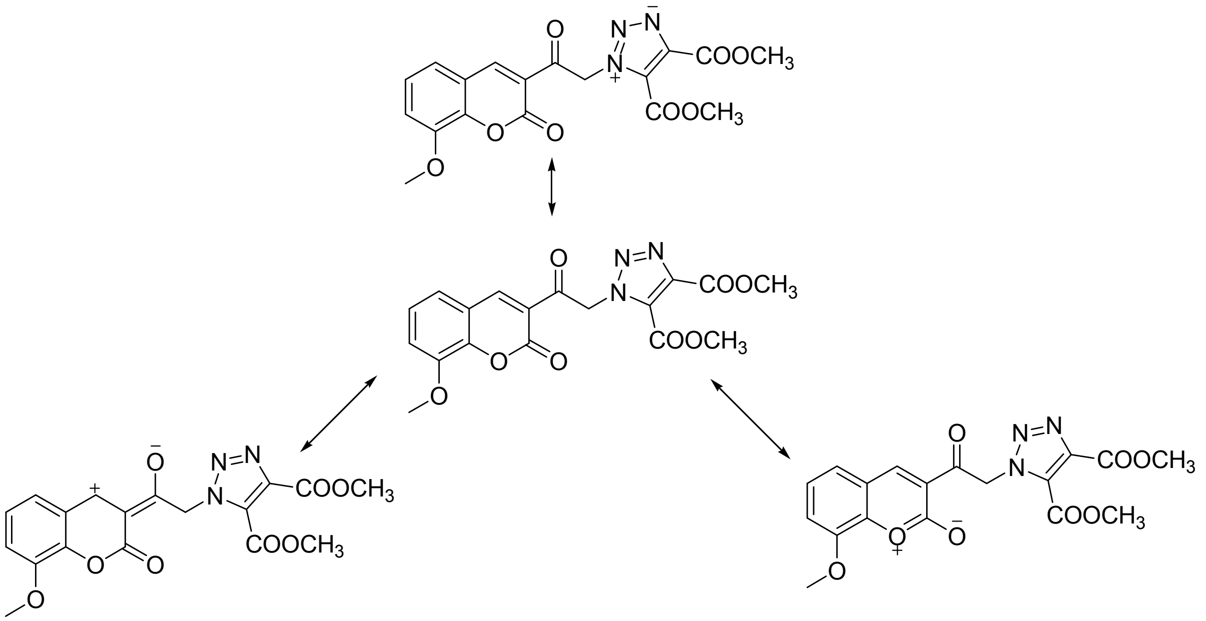


Figure 4 ***(a): Resonance structure of MDTC***

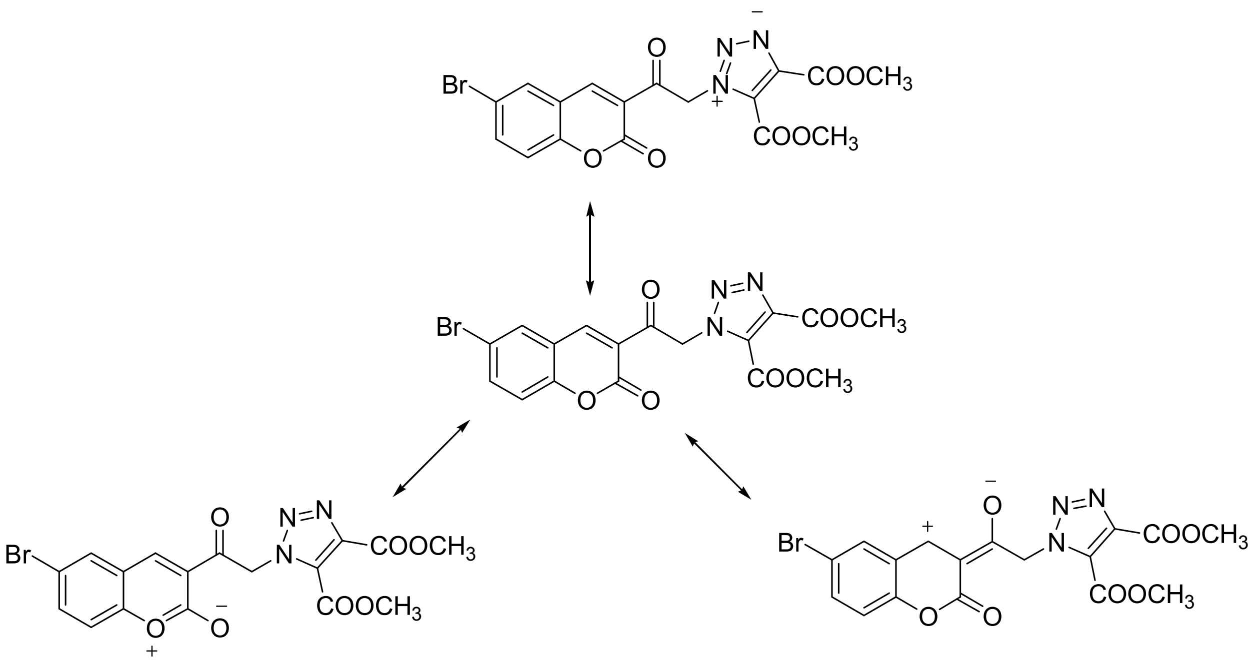


Figure 4 ***(b): Resonance structure of BDTC***

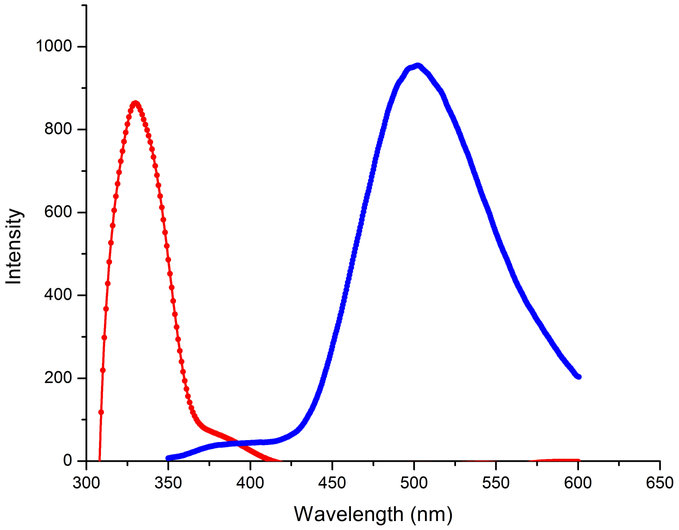


Figure 5
Absorption emission spectra of MDTC in DCE.

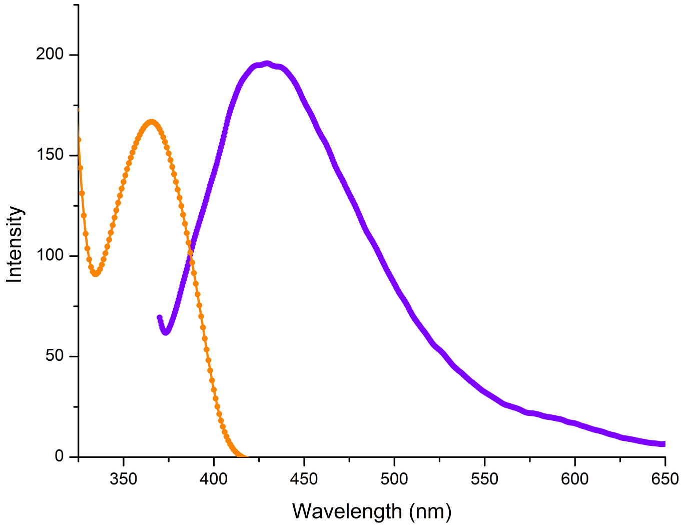


Figure 6
Absorption emission spectra of BDTC in DMSO

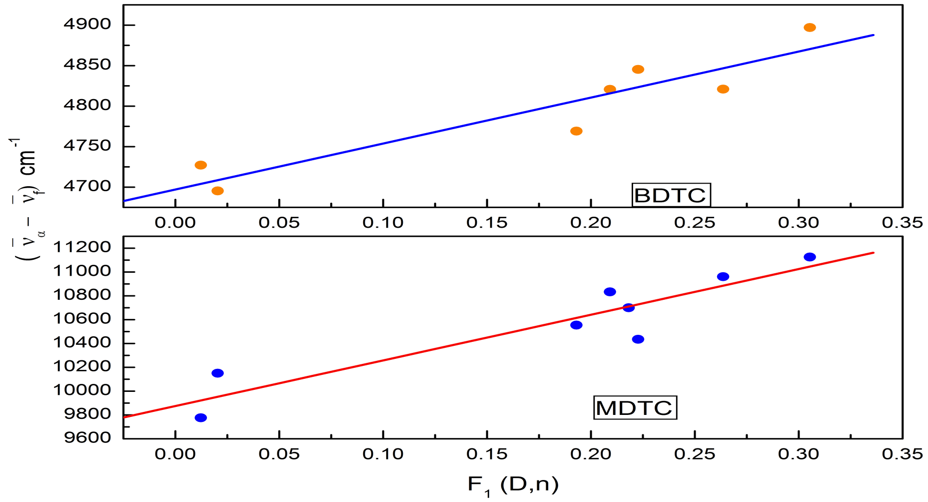


Figure 7
The variation of stoke shift with F_1(D, n) using Lippert equation for MDTC and BDTC

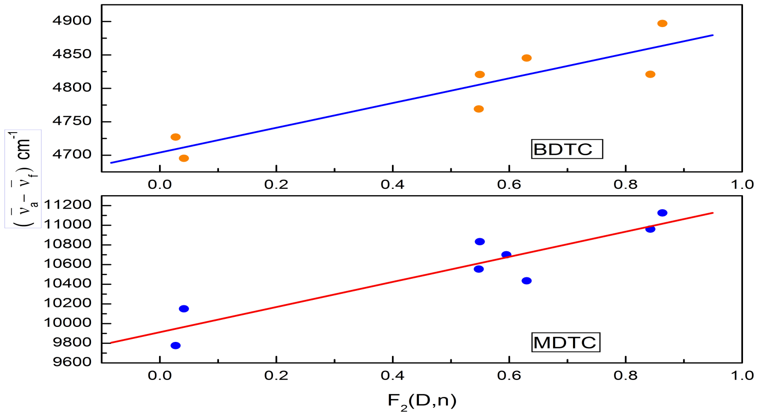


Figure 8

The variation of stoke shift with $F_2(D, n)$ using Baksheiv equation for MDTC and BDTC

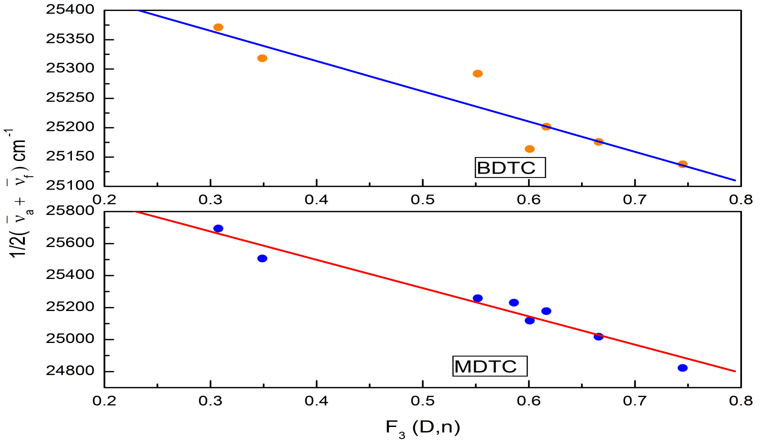


Figure 9

The variation of stoke shift with F_3 (D,n) using Kawaski-Chamma-Viallet equation for MDTC and BDTC.

Table.1

Solvatochromic data of MDTC in different solvents and solvent polarity functions.

Solvent	F_1 (D,n)	F_2 (D,n)	F_3 (D,n)	λ_a (nm)	λ_f (nm)	$\Delta\bar{\vartheta} - \overline{\vartheta_a} - \overline{\vartheta_f}$	$\frac{\overline{\vartheta_a} + \overline{\vartheta_f}}{2}$
TOL	0.0123	0.027	0.3488	329	485	9776.58	25506.84
1,4DX	0.0204	0.0414	0.3074	325	485	10150.68	25693.89
TCE	0.193	0.5478	0.6009	329	504	10553.87	25118.19
THF	0.2092	0.5495	0.5519	326	504	10833.58	25258.05
DCM	0.2182	0.5952	0.5859	327	503	10700.32	25230.87
DCE	0.2227	0.63	0.6165	329	501	10435.06	25177.60
DMSO	0.2636	0.8425	0.745	330	517	10960.68	24822.69
AN	0.3054	0.863	0.6658	327	514	11125.78	25018.14

F_1(D,n): Lippert polarity function, F_2(D, n): Bakshiev polarity function, F_3(D,n): Kawaski-Chamma-viallet polarity function.

Table.2

Solvatochromic data of BDTC in different solvents and solvent polarity functions.

Solvent	F_1 (D,n)	F_2 (D,n)	F_3 (D,n)	λ_a (nm)	λ_f (nm)	$\Delta\bar{\vartheta} = \bar{\vartheta}_a - \bar{\vartheta}_f$	$\frac{\bar{\vartheta}_a + \bar{\vartheta}_f}{2}$
TOL	0.0123	0.027	0.3488	361	436	4765.06	25318.36
1,4DX	0.0204	0.0414	0.3074	361	434	4659.36	25371.15
TCE	0.193	0.5478	0.6009	363	439	4769.16	25163.62
THF	0.2092	0.5495	0.5519	361	437	4820.61	25292.06
DCE	0.2227	0.63	0.6165	362	439	4845.26	25201.67
DMSO	0.2636	0.8425	0.745	363	440	4820.93	25137.73
AN	0.3054	0.863	0.6658	362	440	4897.03	25175.78

F_1(D,n): Lippert polarity function, F_2(D,n): Bakshiev polarity function, F_3(D,n): Kawaski-Chamma-viallet polarity function.

Table.3

Slopes, Correlation coefficients and Number of data for MDTC and BDTC.

Correlations	Compound	Slope	Correlation coefficient	No of data
Lippert Correlation	MDTC	3833.88	0.9294	8
	BDTC	567.93	0.9300	7
Bakshiev Correlation	MDTC	1277.71	0.9209	8
	BDTC	184.89	0.9043	7
Kawaski-Chamma-Viallet Correlation	MDTC	-1768.71	0.9793	8
	BDTC	-515.50	0.9358	7

Table.5

Ground and excited state dipole moments of MDTC and BDTC

Compound	Radius 'a' (A^0)	$\mu_g{}^a$ (D)	$\mu_g{}^b$ (D)	$\mu_e{}^c$ (D)	$\mu_e{}^d$ (D)	$\mu_e{}^e$ (D)	$\mu_e{}^f$ (D)
MDTC	4.2863	8.0471	0.6073	3.7681	6.0827	3.7682	3.7683
BDTC	4.2500	5.4999	1.0035	2.2014	3.0615	2.2014	2.2018

Debye(D) = 3.33564 × 10^{-30}Cm = 10^{-18}esu cm.

[a] Calculated by Gaussian Software.

[b] The ground states dipole moments calculated using Eq. 10.

[c] The excited states dipole moments calculated using Eq. 11.

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

[e] The experimental excited state dipole moments calculated from Bakshiev equation.

[f] The experimental excited state dipole moments calculated from Kawaski-Chamma-viallet equation.

5. CONCLUSIONS

We have studied the photo physical properties of two coumarin derivatives namely MDTC and BDTC using solvatochromic shift method. Both polar and non-polar solvents were employed in our study. With the increase in the solvent polarity we have noticed a red shift of 30 nm in case of MDTC and 6 nm in case of BDTC. This indicates a strong interaction between solvent and solute molecules and $\pi \rightarrow \pi^*$ transition. The excited state dipole moment ranges from 3.7771D to 6.1390D for MDTC and 2.2014D to 3.0615D in case of BDTC. There is a considerable increase in the excited state dipole moments when compared to ground state dipole moments indicating a substantial redistribution of π- electron densities in a more polar excited state for both Coumarins. To the best of our knowledge this is the first report on the dipole moments of these two coumarin derivatives and this should be of great practical importance in many fields as mentioned in the introduction.

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