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SPECTROSCOPIC PROPERTIES AND ESTIMATION OF GROUND AND EXCITED STATE DIPOLE MOMENTS OF BIOLOGICALLY ACTIVE FLUORESCENT MOLECULE FROM ABSORPTION AND EMISSION SPECTRA

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ABSTARCT

The absorption and emission spectra of fluorescent molecule namely 6-Methyl-3-[1-(4, 5-dicarbomethoxy-1, 2, 3-triazoloacetyl)] coumarin (6MDTC) has been recorded at room temperature in solvents of different polarities. The exited state (μ_e) dipole moment was estimated from Lippert's, Bakhshiev's and Kawski-Chamma-Viallet's equations using the variation of Stoke's shift with the solvents of different polarities using dielectric constant and refractive index. The geometry of the molecule was fully optimized and the ground state dipole moment (μ_g) was also calculated theoretically by Gaussian 03 software using B3LYP/6-31g* level of theory. The μ_g and μ_e were calculated by solvatochromic shift method and μ_e was also determined in combination with μ_g. It was observed that μ_e was greater than that of the μ_g, indicating a substantial redistribution of the π-electron densities in a more polar excited state for this coumarin. Further, the changes in dipole moment ($\Delta\mu$) was calculated both from solvatochromic shift method and on the basis of microscopic empirical solvent polarity (E_T^N) and the values are compared.

Keywords: Solvatochromic shift method, ground state and excited state dipole moments, 6MDTC and DFT.

1. INTRODUCTION

Solvatocromism is subject of interesting investigation for organic compounds [1-5]. If a molecule is excited by photon, it causes redistribution of charges leading to conformational changes in the excited state. Due to this there may be change in dipole moments of ground and excited state. Of which excited state dipole moment is important parameter in short lived state. There are several methods to determine excited state dipole moment experimentally. Spectral shift may be caused by either electrochromism (External) or solvatochromism (Internal). In the present study solvatochromism is used which 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 - 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 6-Methyl-3[1-(4,5 dicarbomethoxy 1,2,3-triazoloace tyl)] coumarin (6MDTC) 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 the literature on determination of μ_g and μ_e values of this molecule investigated.

2. EXPERIMENTAL

2.1. Chemicals used

The solutes of fluorescent molecule namely 6-Methyl-3-[1-(4, 5-dicarbomethoxy-1, 2, 3-triazoloacetyl)] coumarin (6MDTC) was synthesized in our laboratory using standard methods [21-24]. The molecular structure of this molecule is given in Fig.1. The solvents used in the present study namely tetrahydrofuran, acetonitrile, dichloromethane, 1,4 dioxane, dimethyl sulphoxide, toluene and diethyl ether are used for (6MDTC). All the solvents were obtained from S-D-Fine Chemicals Ltd., India, and they were of spectroscopic grade. The required solutions were prepared at a fixed concentration of solutes 1X 10^{-4} M in each solvent.

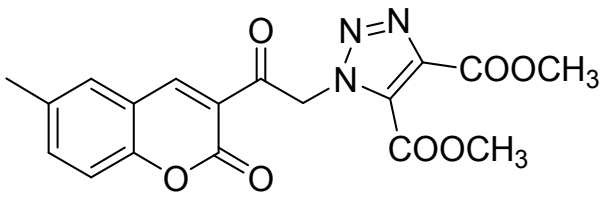

Figure 1
The molecular structures of (6MDTC)

2.2. Spectroscopic measurements

The absorption spectra were recorded using Hitachi 50–20 UV–VISIBLE spectrophotometer and fluorescence intensities of the solutions were measured on Hitachi F-2700 Spectrofluorimeter Dept. of Physics MSRIT Bangalore-54 at room temperature with perpendicular geometry.

3. Theory

3.1 Theoretical calculations of ground-state dipole moments

The ground-state dipole moment (μ_g) of this molecule was 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 geometry is shown in Fig.2. The value of ground-state dipole moment obtained from *ab initio* calculations using DFT. Ground state optimized molecular geometry of (6MDTC) is shown in Fig. 3. The arrow indicates the direction of the dipole moment.

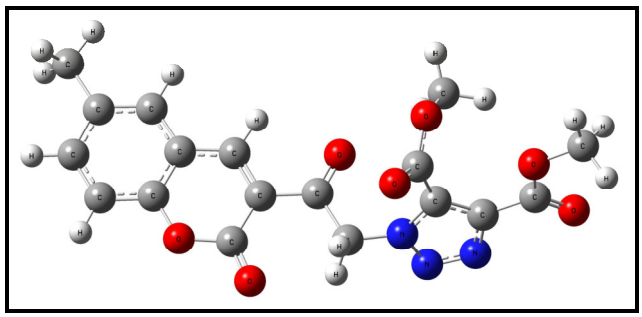

Figure 2
Optimized geometries of (6MDTC)

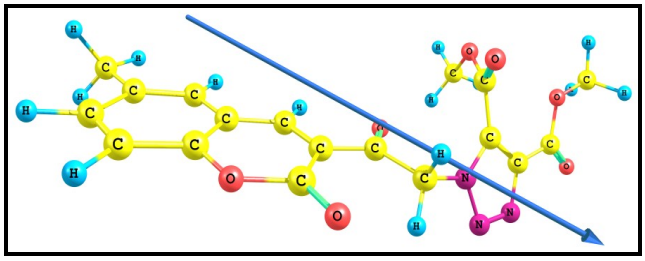

Figure 3
Ground state optimized molecular geometries of (6MDTC).
The arrow indicates the direction of the dipole moment.

3.2 Experimental calculations of excited state dipole moments

The independent equations used for the estimation of excited state dipole moment of dye are as follows

Lippert's equation [26]

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\varepsilon, n) + \text{Constant} \quad (1)$$

Bakshiev's equation [27]

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

Kawski-Chamma-Viallet's equation [28]

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = m_3 F_3(\varepsilon, n) + \text{Constant} \quad (3)$$

The expressions for $F_1(\varepsilon, n)$ [Lippert's polarity function], $F_2(\varepsilon, n)$ [Bakshiev's polarity equation] and $F_3(\varepsilon, n)$ [Kawski-Chamma-Viallet's polarity equation] are given as

$$F_1(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \quad (4)$$

$$F_2(\varepsilon, n) = \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right]\frac{(2n^2 + 1)}{(n^2 + 2)} \quad (5)$$

$$F_3(\varepsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \quad (6)$$

Where $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and fluorescence maximum 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 $F_1(\varepsilon, n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_2(\varepsilon, n)$ and $\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ versus $F_3(\varepsilon, n)$ should give linear graphs with slopes m_1, m_2 and m_3 respectively and are given as

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

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

$$m_3 = \frac{2(\mu^2_e - \mu^2_g)}{hca^3} \quad (9)$$

Where μ_g and μ_e are the ground and excited state dipole moments of the solute molecule. 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.

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

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

and

$$\mu_e = \left[\frac{m_2 + m_3}{m_3 - m_2}\right]\mu_g \qquad \text{for } (m_3 > m_2) \quad (12)$$

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

The empirical polarity parameter E_T^N proposed by Richards [3] gave towering results with solvatochromic 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 Richards and developed by Ravi et al. [29], according to Eq. (2.15)

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_b}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + constant \quad (13)$$

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].

$$E_T^N = \frac{E_T(Solvent) - E_T(TMS)}{E_T(Water) - E_T(TMS)} = \frac{E_T(Solvent) - 30.7}{32.4} \quad (14)$$

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)

$$\Delta\mu = (\mu_e - \mu_g) = \sqrt{\frac{m\ X\ 81}{(6.2/a)^3\ 11307.6}} \quad (15)$$

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].

4. RESULTS AND DISCUSSION

4.1 Solvent effect on Absorption and Fluorescence Spectra

The typical absorption and fluorescence spectrum of (6MDTC) in Toluene solvent is shown in the Fig. 4

and 5 respectively. The observed absorption and emission spectrum of coumarin are broad which shifts depending on the solvents. The large spectral shift is observed in the emission spectra as compared to the absorption spectra. The less pronounced shift in the absorption spectra observed in all the solvents studied implies that the ground state energy distribution is not affected to a greater extent possibly due to the less polar nature of the coumarin in the ground state. The pronounced shift in the emission clearly indicates that the dipole moment of the excited state is higher compared to the ground state. In such cases, the relaxed exited state S_1 will be energetically stabilized relative to the ground state S_0 and a significant red shift of the fluorescence will be observed.

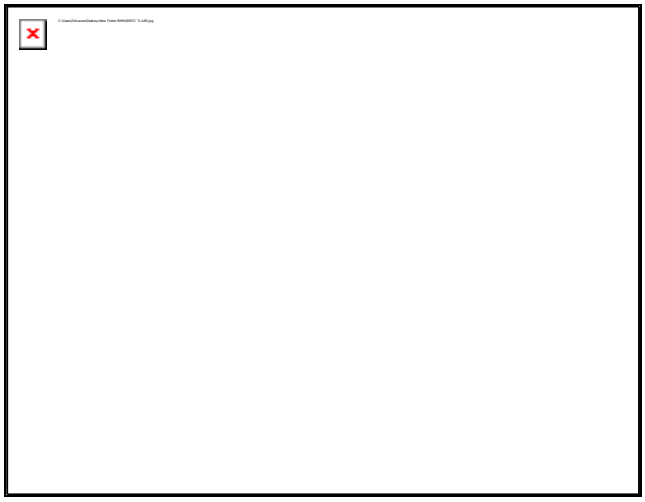

Figure 4
Absorption Graph (6MDTC) in Toluene

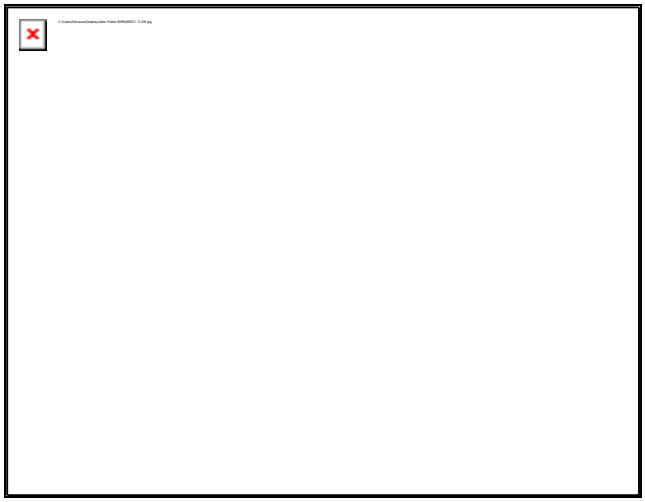

Figure 5
Emission Graph (6MDTC) in Toluene

4. 2 Estimation of Ground state and Excited state Dipole moments

In order to estimate the ground state and excited state dipole moments of the solute molecule, the calculated values of spectral shifts $\bar{\nu}_a - \bar{\nu}_f$ and $(\bar{\nu}_a + \bar{\nu}_f)/2$ of fluorescent molecule along with solvent polarity function values $F_1(\varepsilon, n)$, $F_2(\varepsilon, n)$, $F_3(\varepsilon, n)$ and E_T^N for various solvents are presented in Table 1. We have used seven solvents for (6MDTC) with dielectric constants varying from 2.300 to 47.240. Fig. 6-8 show the graph of (ν_a - $\bar{\nu}_f$) versus, F_1 (ε, n), (ν_a - $\bar{\nu}_f$) versus F_2 (ε, n) and (ν_a + $\bar{\nu}_f$)/2 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 2. In most cases (ν_a

- $\bar{\nu}_f$) versus F_1 (ε, n), (ν_a - $\bar{\nu}_f$) versus F_2 (ε, n) and (ν_a + $\bar{\nu}_f$)/2 versus F_3 (ε, n) correlation is established for all the solvents used for this study. In most cases the correlation coefficients are larger than 0.9715 which indicate a good linearity for m_1, m_2 and m_3 with all Stokes shift data points. Generally, the deviation from linearity may be due to specific solute solvent interactions. For polar solute molecule like (6MDTC) the interaction with non polar depends on the dipole –induced-dipole forces, the solute solvent interaction depends on the stronger dipole-dipole forces. It is therefore useful as pointed out by others also [31, 32] to use E_T^{30} function which is the empirical measure of the solvent polarity [33] for understanding the polarization dependence of spectral characteristics. Unfortunately (E_T^{30}) values have by dimension of kcal/mol, a unit which should be abandoned in the framework of SI units [34]. Therefore the use of the so-called normalized E_T^N values have been recommended, which are defined in Eq. 14. 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 solvent polarity. Figure 9 shows that the plot of Stoke's shift as a function of E_T^Nin all solvents for (6MDTC). With increasing in the solvent polarity, both absorption and emission bands undergoes 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 structure of molecule. Ground state (μ_g) dipole moment values obtained from Eq.10 are presented in Table 3. The value of Onsager cavity radii of (6MDTC) molecule was calculated by molecular volumes and the Parachor and is listed in Table 3.

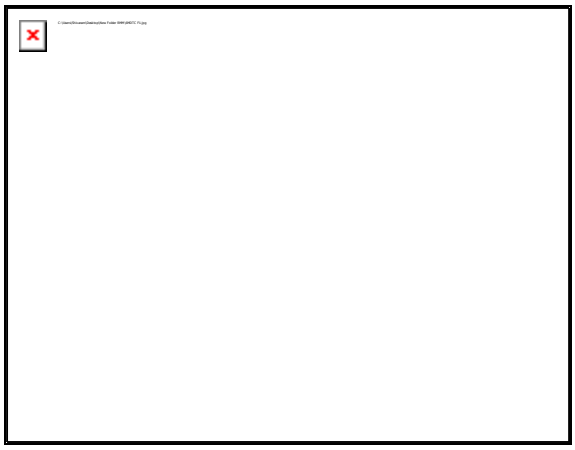

Figure 6

The variation of Stoke's shift with F_1 (ε, n) using Lippert equation for (6MDTC)

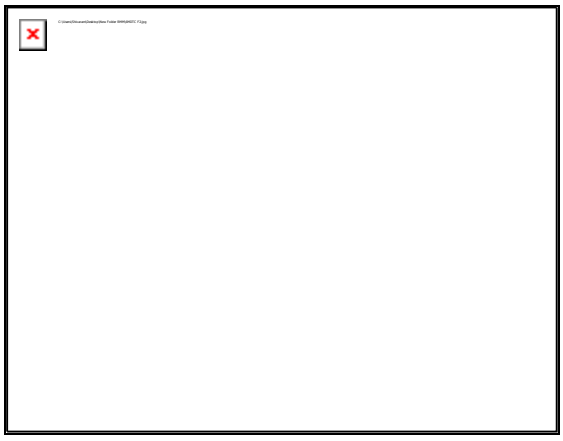

Figure 7

The variation of Stoke's shift with F_2 (ε, n) using Bakshiev's equation for (6MDTC)

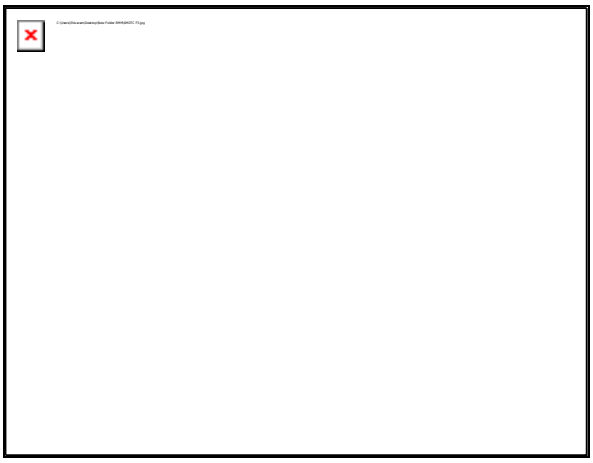

Figure 8
The variation of arithmetic means of Stoke's shift with $F_3(\varepsilon, n)$ using Kawski-Chamma-Viallet's equation for (6MDTC)

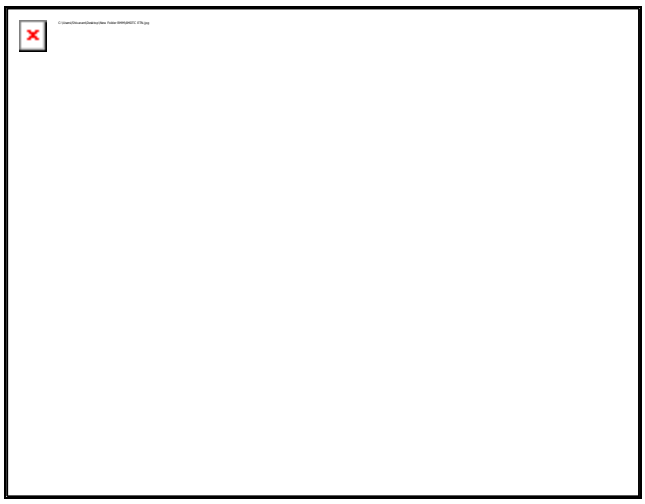

Figure 9
The variation of Stoke's shift with E_T^N for (6MDTC)

Table 1
Calculated values of polarity functions Solvatochromic data of (6MDTC) in different solvents

Solvents	$F_1(\varepsilon,n)$	$F_2(\varepsilon,n)$	$F_3(\varepsilon,n)$	E_T^N	λ_a (nm)	λ_f (nm)	$\bar{\vartheta}_a$ (cm^{-1})	$\bar{\vartheta}_f$ (cm^{-1})	$\bar{\vartheta}_a - \bar{\vartheta}_f$ (cm^{-1})	$(\vartheta_a + \vartheta_f)/2$ (cm^{-1})
Tetrahydrofuran	0.2097	0.5472	0.5481	0.207	360.46	441.97	27742.70	22625.86	5116.84	25184.28
Acetonitrile	0.3047	0.8625	0.6669	0.460	361.57	449.57	27657.02	22243.25	5413.77	24950.13
Dichloromethane	0.2186	0.5957	0.5856	0.321	361.47	443.83	27664.46	22531.37	5133.09	25097.91
1,4-Dioxan	0.0299	0.0611	0.3163	0.164	358.76	430.17	27873.45	23246.79	4626.66	25560.12
Dimethyl Sulphoxide	0.2637	0.8417	0.7440	0.444	363.29	451.76	27526.09	22135.58	5390.51	24830.83
Toluene	0.0135	0.0297	0.3496	0.099	359.69	430.90	27801.67	23207.23	4594.44	25504.45
Diethyl ether	0.1668	0.3772	0.4289	0.210	359.10	436.70	27847.45	22898.97	4948.48	25373.21

Table 2

Statistical treatment of the correlations of solvents spectral shifts of (6MDTC)

Parameter1			Parameter2			Parameter3		
Slope	A	2919.44	Correlation coefficient 'r'	A	0.9715	Number of data	A	7
	B	910.43		B	0.9993		B	7
	C	2273.38		C	0.9977		C	7
	D	2201.27		D	0.8395		D	7

A-Lippert Correlation; B- Bakshiev Correlation; C- Chamma Viallet Correlation; D- E_T^N

Table 3

Ground and excited state dipole moments of (6MDTC)

Compound	Radius 'a' (A^o)	μ_g^a (D)	μ_g^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	μ_e^f (D)	$\Delta\mu^g$ (D)	$\Delta\mu^h$ (D)	$(\mu_e/\mu_g)^i$
(6MDTC)	4.302	10.6351	1.1914	5.9975	3.8753	10.9150	3.9267	2.7354	2.2952	3.2528

Debye (D) = $3.33564X10^{-30}$cm = 10^{-18} esu cm.

[a] Calculated by Gaussian Software.

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

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

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

[e] The experimental excited state dipole moments calculated from Chamma-Viallet's equation.

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

[g] The change in dipole moments for μ_e^f and μ_g^b

[h] The change in dipole moments calculated from Eq.15

[i] The ratio of excited state and ground state dipole moments values calculated using Eq.13.

The excited state (μ_e) dipole moments of the fluorescent molecule, estimated by computing the values of ground state (μ_g) dipole moment obtained from Eq. 10 is presented in Table 3. Also the excited state dipole moment (μ_e) value is obtained from Eq. 11. The ratio of (μ_e) and (μ_g) obtained from Eq.12 is presented in Table 3. Theoretically calculated *ab initio* calculations using DFT value is presented in Table 3. The calculated and theoretical ground state (μ_g) dipole moment result is good in agreement for our used chemical systems as shown in Table 3. Numerically higher theoretical values may be resulting from constrained use of basis set and quantum chemical methods due to limited computational facility [4, 12, 25 and 26]. It may be noted that the measured value of (μ_g) and (μ_e) for (6MDTC) differ from each other. It may be noted that the discrepancies occur between the estimated values of (μ_e) for the coumarin from different methods. 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 Solvatochromic data can be used to identify the spectra, namely π-π^*, n-π^*, etc. It can be noticed from Table1 that, with an 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 10.

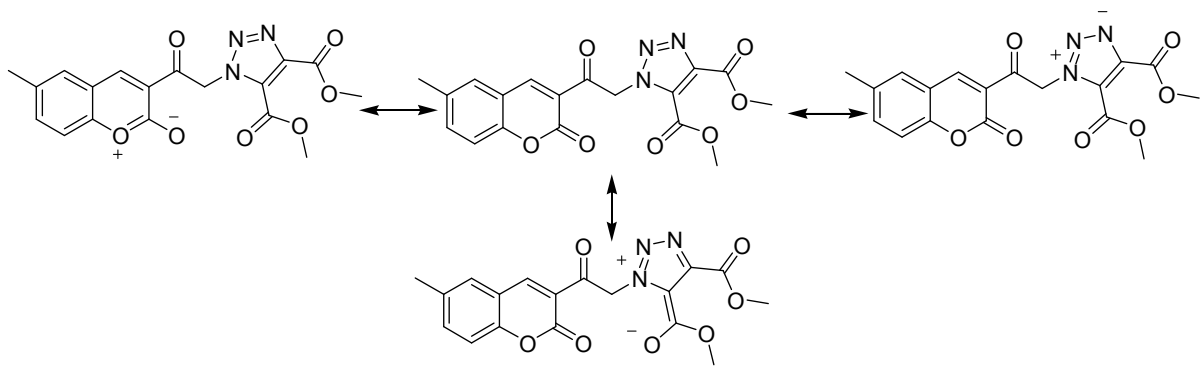

Figure 10
Possible resonance structure of (6MDTC)

5. CONCLUSION

We have estimated and compared dipole moment of the molecule (6MDTC) in electronic ground state by theoretical method and calculated ground state dipole moment by using equation 10. We have also estimated excited state dipole moment by experimental method. We found the coumarin possesses higher dipole moment value in excited state than in ground state by 2.7354 D. The considerable increase in dipole moment upon excitation suggests that excited state is ICT in nature which is expected to increase the planarity of Coumarin upon excitation and make the molecule more polar than ground state. Numerically higher theoretical value may be resulting from constrained use of basis set and quantum chemical methods due to limited computational facility. Also Eq. 11 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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