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Solvent Effect on the Fluorescence Properties of Two Biologically Active Thiophene Carboxamido Molecules

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Abstract

The absorption and fluorescence spectra of two thiophene carboxamido molecules namely 2-(3',4',5'- trimethoxy phenyl) imino-3-N-ethylcarboxamido-4, 5, tetramethylene thiophene (X) and 2-(4'-N, N-dimethylaminophenyl) imino-3-(N-2' methylphenyl carboxamido)-4, 5, tetramethylene thiophene (Y) have been recorded at room temperature. The ground (μ_g) and excited (μ_e) state dipole moments are estimated from Lippert, Bakhshiev, Kawski-Chamma-

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Viallet equations by using the variation of Stokes shift with microscopic solvent dielectric constant (ϵ) and refractive index (n). The excited dipole moments were also estimated by using the variation of Stokes shift with microscopic empirical solvent polarity parameter (E_T^N) and the values are compared. It was estimated that dipole moments of the excited state were higher than those of the ground state of both the molecules. Further, the change in dipole moment ($\Delta\mu$) were calculated both from solvatochromic shift method and on the basis of microscopic empirical solvent polarity parameter (E_T^N).

Keywords: Solvatochromic shift method, Ground state dipole moments, Excited state dipole moments, Thiophene carboxamido.

1. Introduction

In the last few years, thiophene-based materials which are semiconductor and fluorescent compounds have become a highly interdisciplinary field of research with diverse studies ranging from fabrication of electronic and optoelectronic devices to the selective detection of biosensors. These organic molecules are recognized to be important materials having novel electronic and photonic properties suitable for many technological applications [1-5]. It is also evident from the literature survey that thiophene such as substituted thiophene and condensed thiophene are interesting compounds being studied in medicine and they are reported to possess an array of useful biological and pharmacological activities like antibacterial, antifungal, antiviral, anticancerous, analgesic and anti-inflammatory activities. The synthesis, reactivity and conformational analysis of substituted and condensed thiophene have been extensively studied in recent years. They are important both as interesting models for structural investigation and also for biological screening. The effect of solvent on the absorption and fluorescence characteristics of organic compounds has been a subject of interesting investigation. 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 state 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.

Knowledge of the excited state dipole moment of electronically excited molecules is quite useful in designing nonlinear materials, elucidating the nature of the excited states and in determining the course of a photochemical transformation. The electro optic methods such as electronic polarization of fluorescence, electric-dichroism, microwave conductivity and stark splitting are generally considered to be very accurate, but their use is limited because they are considered equipment sensitive and the studies have been restricted to relatively very simple molecules. The solvatochromic method is based on the shift of absorption and fluorescence maxima in different solvents of varying polarity. Koutek has shown that under suitable conditions, the solvatochromic method yields fairly satisfactory results. Similar works were also reported by others [6-17]. In the present work, we report different solvent effect on the Photophysical properties such as Stokes shift which is useful for estimation of the ground and excited state dipole moments of two thiophene Carboxamidos by solvatochromic method based on absorption and fluorescence shift in various solvents. However, there are no reports available in literature on the determination of μ_g and μ_e values of these two biologically active thiophene Carboxamidos investigated. The theoretical ground state (μ_g) dipole moments were estimated by Gaussian software using B3LYP/6-31g* method [18].

2. Materials and Methods

The solute molecules namely 2-(3',4',5'-trimethoxyphenyl) imino-3-N-thylcarboxamido-4,5,-tetramethylenethiophene (**X**) and 2(4'-N,N dimethylaminophenyl)imino 3(N-2'-methylphenylcarboxamido) 4,5,tetramethylenethiophene (**Y**) were synthesized in our laboratory using standard methods [19-20]. The molecular structures of this thiophene Carboxamido are given in Fig. 1. The solvents used in the recent study namely acetonitrile (AN), dichloro ethane (DCE), Diethylether (DEE), Dimethylformamide (DMF), dimethylsulphoxi

de (DMSO), heptane, hexane, isopropyl alcohol (IPA) and toluene (TL) for X and acetonitrile (AN), cyclohexane (CH), diethyl ether (DEE),

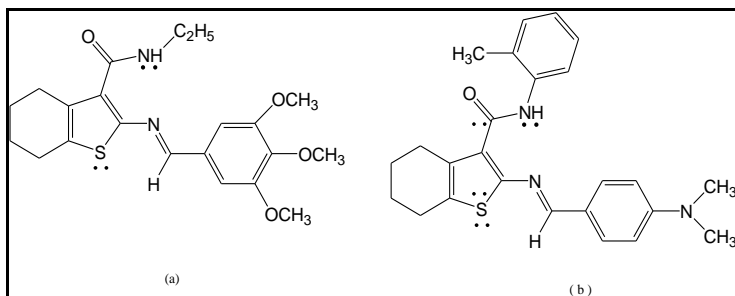


Fig. 1. The molecular structures of (a) X and (b) Y.

1,4-dioxane (DX), heptane, hexane, isopropyl alcohol-(IPA), tetrahydrofuran (THF) and toluene (TL) for Y 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^{-5} M in each solvent. The absorption spectra were recorded using Hitachi 50-20 UV-Vis spectrophotometer. The fluorescence spectra were recorded using Hitachi F-2000 fluorescence spectrophotometer. All these measurements were carried out at room temperature.

3. Theory

3.1 Determination of excited-state dipole moments

The five independent equations were used for the estimation of excited state dipole moments of two thiophene carboxamido. They are as follows

Lippert's equation [21]:

$$\overline{\vartheta}_a - \overline{\vartheta}_f = m_1 F_1(\epsilon, n) + \text{constant} \quad (1)$$

Bakhshiev's equation [22]:

$$\overline{\vartheta}_a - \overline{\vartheta}_f = m_2 F_2(\epsilon, n) + \text{constant} \quad (2)$$

Kawski-Chamma-Viallet's equation [23]:

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

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

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

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

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

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. (1)-(3) it follows that $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_2(\epsilon, n)$

and $\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ versus $F_3(\epsilon, n)$ should give linear graphs with slopes m_1 , m_2 and m_3 respectively and are given as

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

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

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

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 Eqs. (8) and (9)

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

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

and

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

3.2 Molecular-microscopic solvent polarity parameter (E_T^N)

The empirical polarity parameter (E_T^N) proposed by Richards [7] gave towering results with solvatochromic shift of dipolar molecules. The results correlate better with microscopic solvent polarity parameter (E_T^N) rather than the traditionally used bulk solvent polarity functions involving dielectric constant (ϵ) and refractive index (n). 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.* [24], according to Eq. (13):

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

where $\Delta\mu_B = 9D$ and $a_B = 6.2 \text{ \AA}$ are the change in dipole moment on excitation and Onsager cavity radius respectively of a betaine dye, $\Delta\mu$ 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 kcal/mol in $E_T^{(30)}$ solvent polarity scale and is defined by Eq. (14), using water

$[(E_T^N)=1]$ and tetramethylsilane (TMS = $(E_T^N) = 0$) as extreme reference solvents.

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

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. (15)

$$\Delta\mu = (\mu_e - \mu_g) = \sqrt{\frac{m \times 81}{(6.2/\alpha)^2 \times 11307.6}} \quad (15)$$

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. (13). For the computation, Gaussian software is used to calculate theoretical μ_g using DFT.

4. Results and discussion

4.1 Experimental determination of excited state (μ_e) dipole moments of the molecules

The typical absorption and fluorescence spectra of X and Y in isopropanol are as shown in Fig. 2 and Fig. 3 respectively. Solvent polarity function values $F_1(\epsilon, n)$, $F_2(\epsilon, n)$, $F_3(\epsilon, n)$ and microscopic solvent function (E_T^N) for various solvents used in this report are presented in Table 1 and Table 2. The absorption and emission maxima wave numbers, Stokes shift and arithmetic mean of Stokes shift values (in cm^{-1}) for both the molecules in different solvents are given in Table 1 and Table 2. Absorption and emission maxima wave numbers are calculated from wavelength maxima values. The large magnitude of Stokes 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 the Stokes shift values with increasing solvent polarity which shows there is an increase in the dipole moment on excitation.

The Solvatochromic data can be used to identify the spectra, namely $\pi \rightarrow \pi^*$, $n \rightarrow n^*$, etc. The fluorescence emission peak

undergoes a red shift, confirming a $\pi \rightarrow \pi^*$ transition. The shift of the fluorescence wavelengths towards longer wavelengths could be due to the marked difference between the excited state charge distribution in the solute and the ground state charge distribution resulting in a stronger interaction with polar solvents in the excited state.

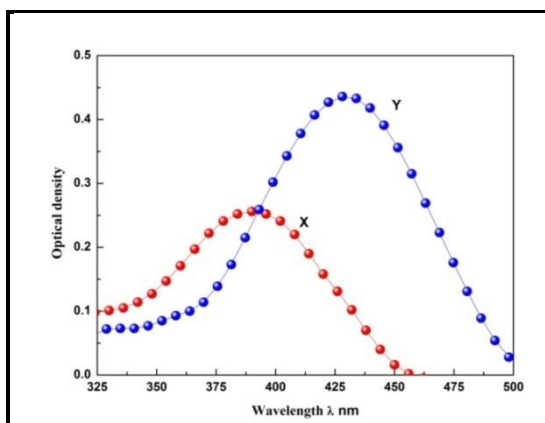


Fig. 2. Typical absorption spectra of X and Y in Isopropanol

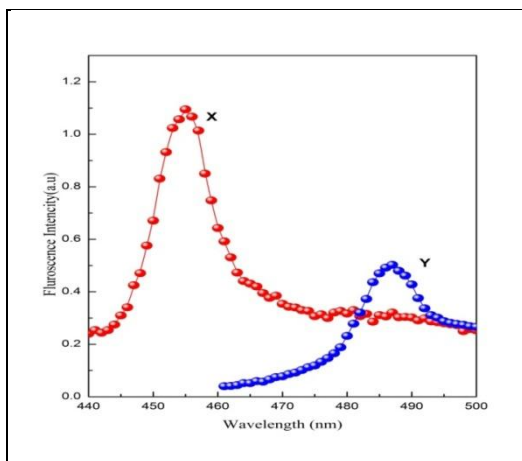


Fig. 3. Typical fluorescence spectra of X and Y in Isopropanol.

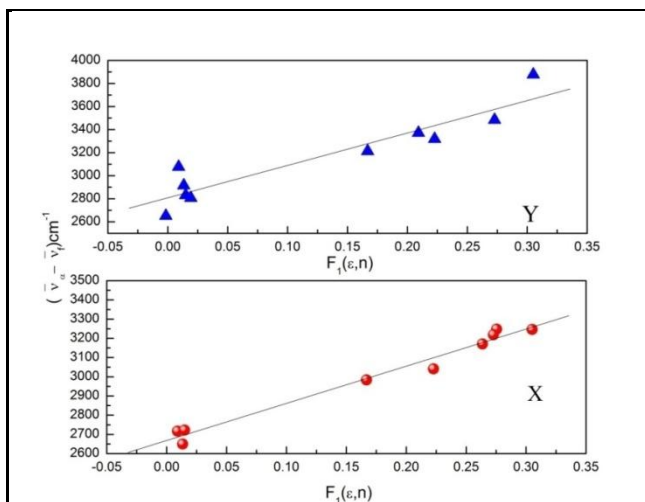


Fig. 4. The plots of $(\bar{\nu}_a - \bar{\nu}_f)$ vs $F_1(\epsilon, n)$ for X and Y.

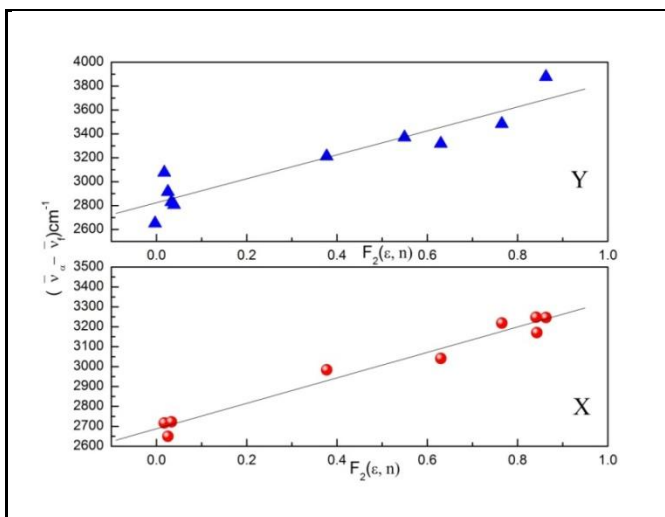


Fig. 5. The plots of $(\bar{\nu}_a - \bar{\nu}_f)$ vs $F_2(\epsilon, n)$ for X and Y.

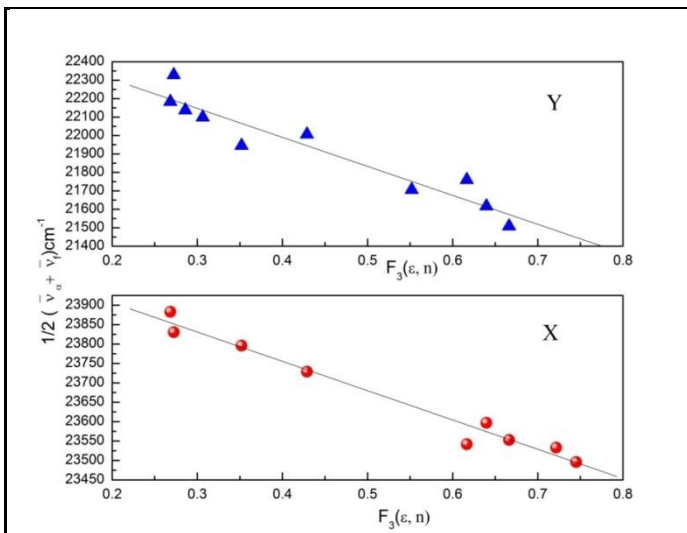


Fig. 6. The plots of $1/2(\bar{v}_a + \bar{v}_f)$ vs $F_3(\epsilon, n)$ for X and Y.

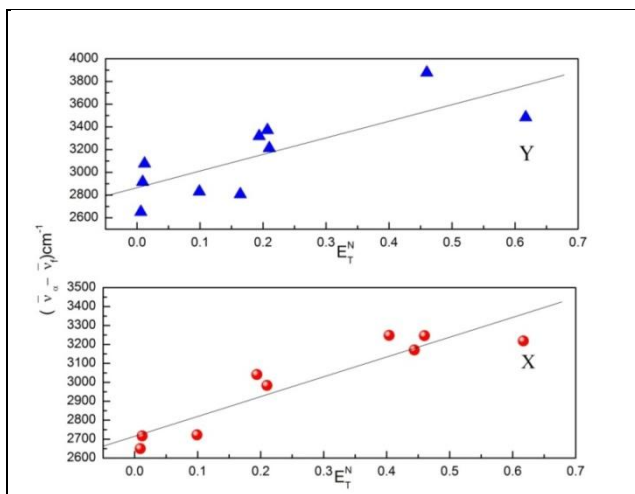


Fig. 7. The plots of $(\bar{v}_a - \bar{v}_f)$ vs molecular- microscopic solvent polarity parameter (E_T^N) for X and Y.

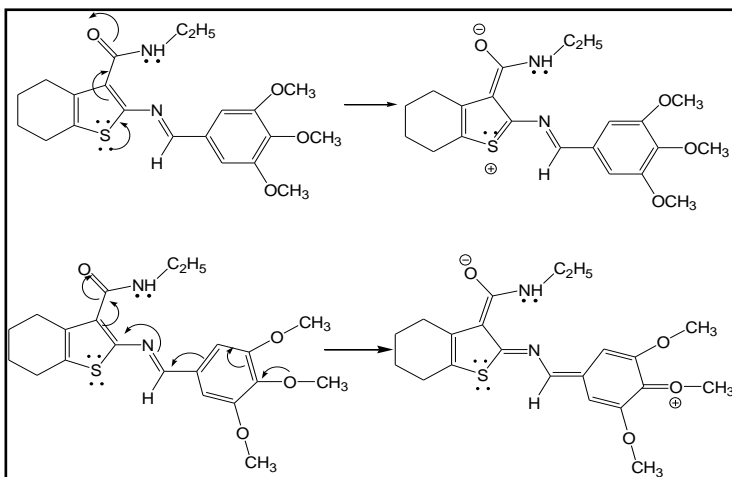


Fig. 8. Possible resonance structures of X.

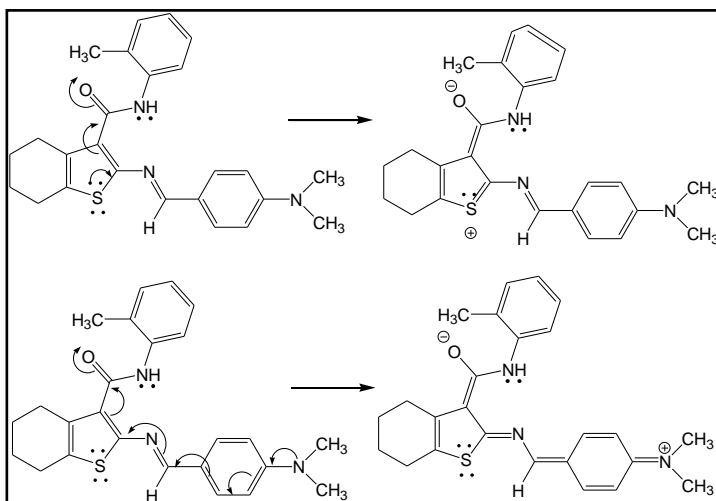


Fig. 9. Possible resonance structures of Y

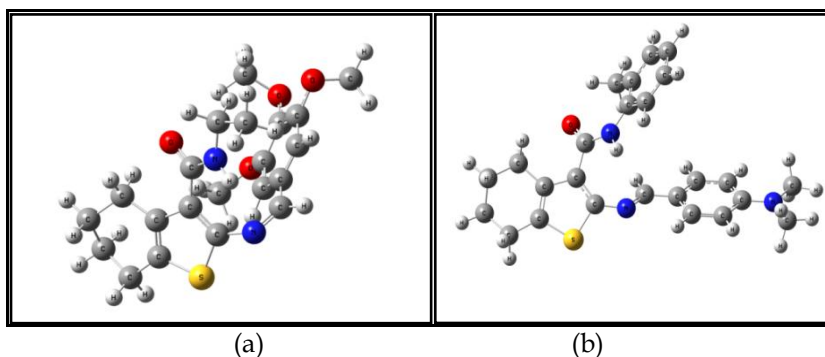


Fig. 10. Optimized geometry of (a) X and (b) Y

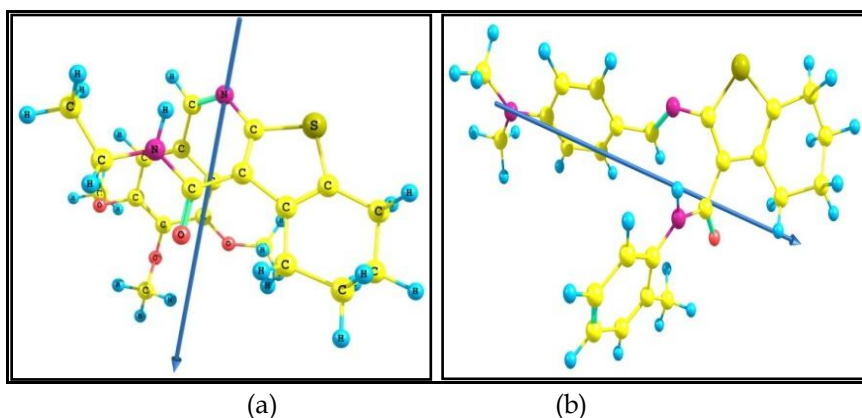


Fig. 11. Ground state optimized geometry of (a) X and (b) Y. The arrow indicates the direction of the dipole moment.

Fig. 4 to Fig. 7 show the graph of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$, $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_2(\epsilon, n)$ and $\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ versus $F_3(\epsilon, n)$ from which slopes m_1 , m_2

and m_3 are obtained respectively. The plot of $(\bar{\nu}_a - \bar{\nu}_f)$ versus (E_T^N) will give the slope m . The correlation co-efficient, slopes and number of data of the fitted lines are given in Table 3. Good correlation coefficient is obtained for all both the solutes. In most of the cases the correlation coefficients are larger than 0.900 and indicate a linearity for m , m_1 , m_2 and m_3 with selected number of Stokes shift data points. The ground state dipole moments (μ_g) of

the two molecules have been estimated by using Eq. (10) and are presented in Table 4. However, no other experimental data on μ_g could be obtained from literature for comparison. The μ_e values obtained from Eqs. (11) and (12) are given in Table 4. The ratio of μ_e and μ_g obtained from Eq. (12) and $\Delta\mu$ obtained from eq. (15) are presented in the Table 4. It may be noted that discrepancies occur between the estimated values of μ_e for both the molecules. These differences in the values of μ_e may be, in part, due to the various assumptions and simplifications made in the use of different Solvatochromic methods.

The values of Onsager cavity radii of the X and Y molecules were calculated by molecular volumes and Parachor [25] and are listed in Table 4. The theoretically calculated (*ab initio* calculations using DFT) values are presented in Table 4. The difference in the ground state dipole moment is due to the necessity of knowing the radius of the solute molecule in Eq. (10) as compared theoretical values obtained from *ab initio* calculations using DFT.

The dipole moments of both the molecules studied here are higher in the excited state compared to ground state. This is explained in terms of possible resonance structures as shown in Fig. 8 and Fig. 9. The dipole moments of X and Y increases twice on excitation. This change in dipole moment on excitation can be explained in terms of nature of emitting state or intermolecular charge transfer. Further large change in dipole moment on excitation suggests that excited state is twisted intermolecular charge transfer

Table 1: Solvatochromic data of X along with the calculated values of polarity functions.

Solvents	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\Delta\nu = (\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})	$\frac{1}{2}(\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})	ϵ	n	$F_1(\epsilon, n)^a$	$F_2(\epsilon, n)^b$	$F_3(\epsilon, n)^c$	$(E_T^N)^d$
Acetonitrile	25176.23	21929.82	3246.40	23553.02	37.50	1.345	0.3050	0.8628	0.6663	0.460
DCE	25062.65	22021.58	3041.07	23542.11	10.70	1.445	0.2227	0.6300	0.6165	0.194
DEE	25220.68	22237.04	2983.63	23728.86	4.34	1.353	0.1668	0.3772	0.4289	0.210
DMF	25157.23	21909.16	3248.06	23533.19	39.00	1.431	0.2753	0.8408	0.7215	0.404
DMSO	25081.51	21910.60	3170.91	23496.05	48.00	1.479	0.2636	0.8425	0.7450	0.444
Heptane	25188.91	22471.91	2717.00	23830.41	2.00	1.388	0.0090	0.0173	0.2724	0.012
Hexane	25207.96	22558.08	2649.87	23883.02	2.00	1.376	0.0133	0.0252	0.2684	0.009
Isopropanol	25201.61	21982.85	3218.75	23597.23	18.30	1.378	0.2727	0.7650	0.6396	0.617
Toluene	25157.23	22434.60	2722.62	23795.91	2.40	1.497	0.0150	0.0330	0.3519	0.099

^a Lippert's polarity function

^b Bakhshiev's polarity function

^c Kawski-Chamma-Viallet's polarity function

^d Microscopic solvent polarity function.

Table 2: Solvatochromic data of Y along with the calculated values of polarity functions

Solvents	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\Delta\nu = (\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})	$1/2 (\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})	ϵ	N	$F_1(\epsilon, n)^a$	$F_2(\epsilon, n)^b$	$F_3(\epsilon, n)^c$	$(E_T^N)^d$
Acetonitrile	23446.65	19569.47	3877.18	21508.06	37.50	1.345	0.3050	0.86280	0.6663	0.460
Cyclohexane	23463.16	20811.65	2651.50	22137.4	2.02	1.426	-0.0015	-0.00313	0.2859	0.006
DCE	23419.20	20100.50	3318.70	21759.85	10.70	1.445	0.2227	0.63000	0.6165	0.194
DEE	23612.75	20399.83	3212.91	22006.29	4.34	1.353	0.1668	0.37720	0.4289	0.210
1,4-Dioxane	23501.76	20695.36	2806.39	22098.56	2.20	1.423	0.0192	0.03890	0.3064	0.164
Heptane	23866.34	20790.02	3076.32	22328.18	2.00	1.388	0.0090	0.01734	0.2724	0.012
Hexane	23640.66	20725.38	2915.27	22183.02	2.00	1.376	0.0133	0.02525	0.2684	0.009
Isopropanol	23364.48	19868.86	3483.77	21616.67	18.30	1.378	0.2727	0.76500	0.6396	0.617
THF	23391.81	20020.00	3371.79	21705.91	7.60	1.408	0.2092	0.54954	0.5519	0.207
Toluene	23364.48	20533.88	2830.60	21944.97	2.40	1.497	0.0150	0.03304	0.3519	0.099

^a Lippert's polarity function

^b Bakhshiev's polarity function

^c Kawski-Chamma-Viallet's polarity function

^d Microscopic solvent polarity function.

Correlations	Compound	Slope	Correlation	Number of data
Lippert Correlation	X	1934.19	0.989	9
	Y	2811.329	0.933	10
Bakhshiev's correlation	X	639.057	0.985	9
	Y	1002.185	0.934	10
Kawski-Chamma-Viallet's correlation	X	754.928	0.986	9
	Y	1571.769	0.954	10
correlation	X	1046.01	0.927	9
	Y	1509.943	0.8	10

Table 3: Statistical treatment of the correlations of the spectral shifts of X and Y

Compound	Radius 'a'(A°)	μ_g^a (D)	μ_g^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	$\Delta\mu^f$ (D)	$\Delta\mu^g$ (D)	$(\mu_e/\mu_g)^h$
X	4.452	0.8571	0.215	2.583	4.334	1.880	2.368	1.665	12.140
Y	4.521	4.736	0.863	3.897	5.946	2.905	3.034	2.042	4.518

Table 4: Ground and excited state dipole moments of X and Y

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

^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 microscopic solvent polarity correlation.

^f The change in dipole moments for μ_e^c and μ_g^b

^g The change in dipole moments calculated from Eq. 15.

^h The ratio of excited state and ground state dipole moments values calculated using Eq.12.

(TICT) in nature. Thus presence of a large TICT and increase in planarity on excitation render the molecule more polar (as compared to ground state) giving rise to a large change in the dipole. In literature one may find that large number of investigators have used solvatochromic shift method to estimate ground and excited state dipole moments. In literature there is a dearth of data on μ_g and μ_e for the molecules used in the present study. Therefore we have not made any comparison.

4.2 Theoretical determination of ground state (μ_g) dipole moments

The primary task for the computational work was to determine the optimized geometry of the compound. The entire calculations were performed at DFT/B3LYP level on a Pentium IV/2.8 GHz personal computer using Gaussian 03W program package, invoking gradient geometry optimization [18]. The input geometry of X and Y molecules has been first optimized without any constraint in the potential energy surfaces at DFT/6-31g* theory/basis set for C, N and H atoms. The molecular structure of the title molecules in the ground state were optimized by a DFT method using B3LYP functional combined with 6-31g* basis set. The optimized geometry of the title molecules is given in Fig. 10.

Dipole moment shows the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as a descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. Dipole moments are strictly determined for neutral molecules. The ground state dipole moments are calculated using DFT/6-31g* theory/basis set and are compared with experimental values. The optimized directions of the dipole moments are shown in Fig. 11.

5. Conclusion

We have estimated and compared the dipole moments of two molecules X and Y in the ground and excited states as a function of the solute-solvent interactions by Solvatochromic shift method. It

can be seen that the dipole moments of X and Y are significantly higher in the excited state than in the ground state. The dipole moments of excited states range between 2.58 to 7.97D depending on the compounds. It may be noted that the measured values of μ_g and μ_e for X and Y differ from each other. This may be attributed to the structural difference between the molecules. Also Eq. (12) can be used to estimate the values of excited state dipole moments by pre knowledge of the value of the ground state dipole moment without the necessity of knowing Onsager radius of the solute. To our knowledge this is the first report on the dipole moments of these molecules and would be of great help in many fields as mentioned in introduction.

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