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ORIGINAL PAPER

Solvent Effect on Absorption and Fluorescence Spectra of Three Biologically Active Carboxamides (C_1, C_2 and C_3). Estimation of Ground and Excited State Dipole Moment from Solvatochromic Method Using Solvent Polarity Parameters

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Abstract The absorption and fluorescence spectra of three Carboxamides namely (E)-2-(4-Chlorobenzylideneamino)-N-(2-chlorophenyl)-4, 5, 6, 7-tetrahydrobenzo[b]thiophene-3-carboxamide (C_1), (E)-N-(3-Chlorophenyl)-2-(3, 4-dimethoxybenzylideneamino)-4, 5, 6, 7-tetrahydrobenzo[b] thiophene-3-carboxamide (C_2) and (E)-N-(3-Chlorophenyl)-2-(3, 4, 5-trimethoxybenzylideneamino)-4, 5, 6, 7-tetrahydrobenzo[b]thiophene-3-carboxamide (C_3) have been recorded at room temperature in solvents of different polarities using dielectric constant (ε) and refractive index (n). Experimental ground (μ_g) and excited (μ_e) state dipole moments are estimated by means of solvatochromic shift method and also the excited dipole moments are estimated in combination with ground state dipole moments. It was estimated that dipole moments of the excited state were higher than those of the ground state of all three molecules. Further, the changes 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) and the values are compared.

Keywords Solvatochromic shift method · Ground state dipole moments · Excited state dipole moments · Carboxamides

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]. Organic molecules have attractive laser gain due to its fortunate combination of properties such as broad tunability, high quantum efficiency and broad spectral band width [2]. It is also evident from the literature survey that thiophenes such as substituted thiophenes and condensed thiophenes are interesting compounds being studied in medicine and they are reported to possess an array of useful biological and pharmacological activities like antibacterial [3], antifungal [4], antiviral [5], anticancerous [6], antiulcerous [7], analgesic and anti-inflammatory activities [8]. The synthesis, reactivity and conformational analysis of substituted and condensed thiophenes 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 [9–13]. Excitation of a

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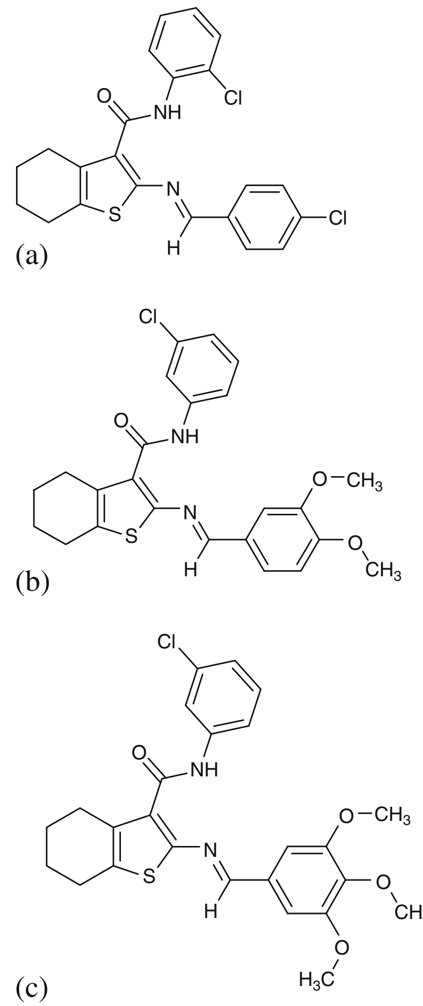


Fig. 1 The molecular structures of (a) $\mathbf{C_1}$, (b) $\mathbf{C_2}$ and (c) $\mathbf{C_3}$

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.

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 excited-state dipole moments of fluorescent molecules such as those studied here also determine the tunability range of the emission energy as a function of the polarity of the medium. 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 electrooptic 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 [14]. The solvent dependence of absorption and fluorescence maxima is used to estimate the excited-state dipole moments of different molecules. Dipole moments of short-lived species are of considerable interest because, they provide information of electronic and geometrical structure of these transient. Knowledge of dipole moment of

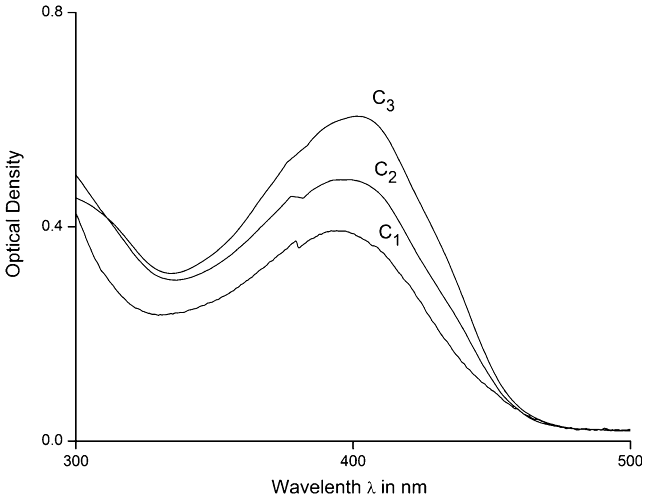


Fig. 2 Typical absorption spectra of C_1, C_2 and C_3 in dichloromethane

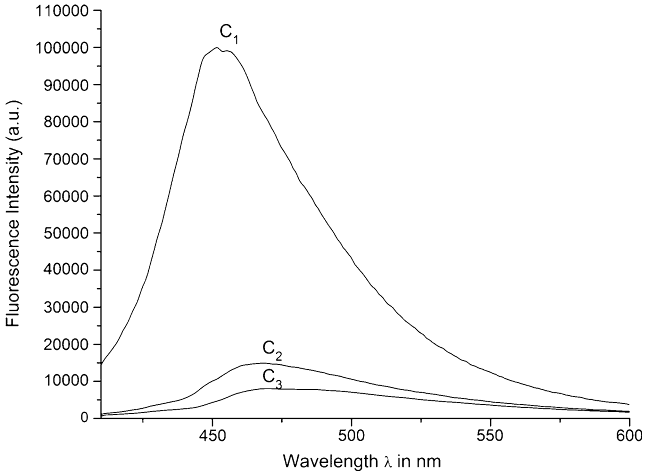


Fig. 3 Typical fluorescence spectra of C_1, C_2 and C_3 in dichloromethane

Table 1 Photophysical parameters of C_1 molecule in different solvents

Solvents	$\overline{\nu}_a$ (cm^{-1})	$\overline{\nu}_f$ (cm^{-1})	$\overline{\nu}_a - \overline{\nu}_f$ (cm^{-1})	$\overline{\nu}_a + \overline{\nu}_f$ (cm^{-1})	ε	n	f(ε, n)	$f(\varepsilon, n) + 2g(n)$	E_T^N
DX	25290.84	22296.54	2994.56	47587.38	2.219	1.4210	0.0440	0.6170	0.164
DCE	25125.63	21551.72	3573.91	46677.35	10.300	1.4448	0.6297	1.2234	0.194
DEE	25322.87	22128.79	3193.81	47451.66	4.266	1.3520	0.3710	0.8510	0.210
EA	25188.92	21997.36	3191.56	47186.28	6.081	1.3720	0.4930	0.9990	0.228
DCM	25393.60	21815.00	3578.60	47208.60	8.930	1.4240	0.5900	1.1660	0.321
DMF	25195.26	21199.92	3995.34	46395.18	38.50	1.4305	0.8356	1.4230	0.404
DMSO	24813.90	21141.65	3672.25	45955.55	47.240	1.4780	0.8427	1.4890	0.444
nBA	25138.26	21459.23	3679.03	46597.49	7.800	1.3990	0.5613	1.2960	0.602
IPA	25207.97	21423.28	3794.69	46621.25	18.300	1.3776	0.7651	1.2786	0.617

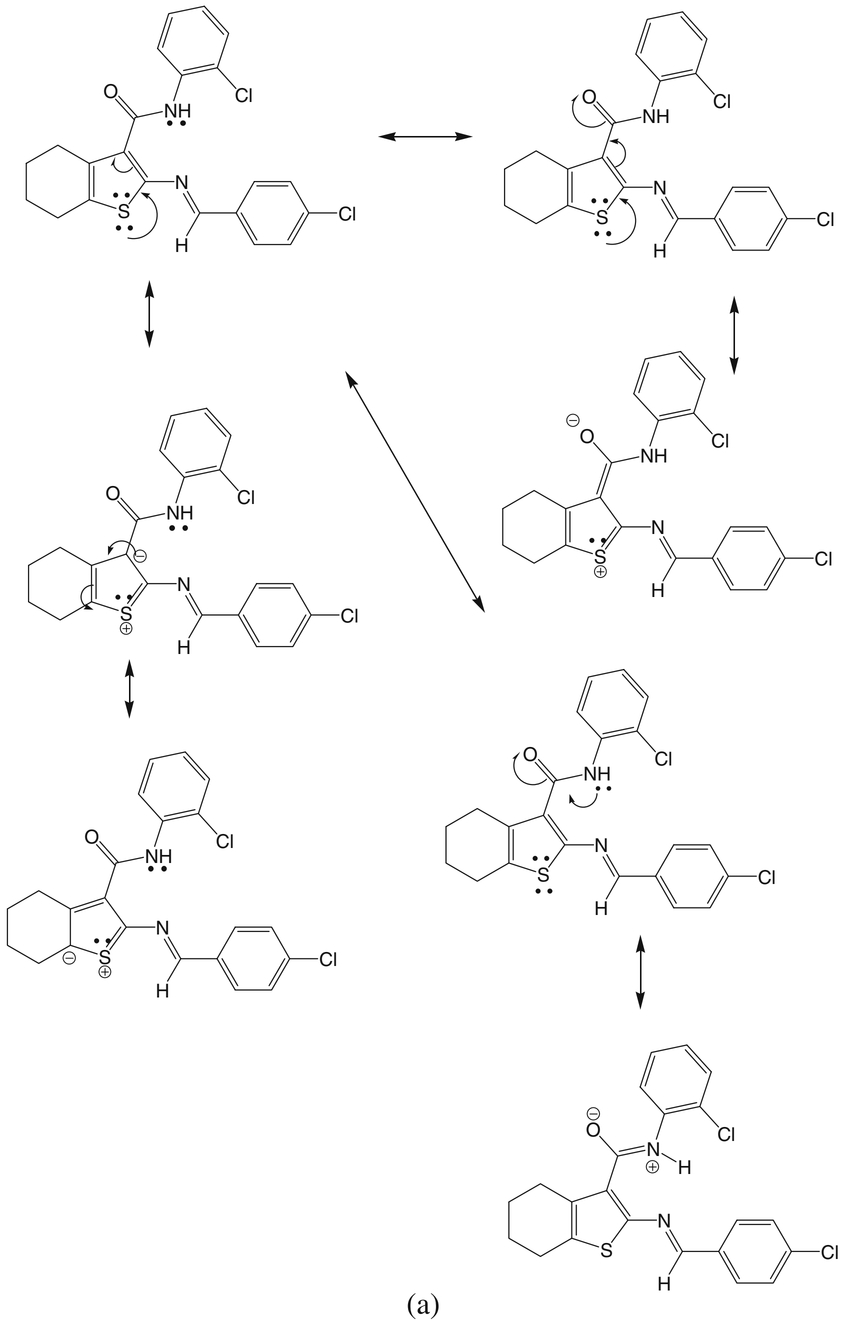
Table 2 Photophysical parameters of C_2 molecule in different solvents

Solvents	$\overline{\nu}_a$ (cm^{-1})	$\overline{\nu}_f$ (cm^{-1})	$\overline{\nu}_a - \overline{\nu}_f$ (cm^{-1})	$\overline{\nu}_a + \overline{\nu}_f$ (cm^{-1})	n	ε	f(ε, n)	$f(\varepsilon, n) + 2g(n)$	E_T^N
DX	25380.71	22573.36	2807.35	47954.07	2.219	1.4210	0.0440	0.6170	0.164
DCE	24937.66	21505.38	3432.28	46443.04	10.300	1.4448	0.6297	1.2234	0.194
DEE	25316.45	22123.89	3192.56	47440.34	4.266	1.3520	0.3710	0.8510	0.210
EA	25316.45	21786.50	3529.95	47102.95	6.0814	1.3720	0.4930	0.9990	0.228
DCM	24875.62	21276.60	3599.02	46152.22	8.9300	1.4240	0.5900	1.1660	0.321
DMF	24038.46	20040.08	3998.38	44078.54	38.500	1.4305	0.8356	1.4230	0.404
DMSO	24096.39	19920.32	4176.07	44016.71	47.240	1.4780	0.8427	1.4890	0.444
nBA	24813.90	21141.65	3672.25	45955.55	7.800	1.3990	0.5613	1.2960	0.602
IPA	24271.85	20202.02	4069.83	44473.87	18.300	1.3776	0.7651	1.2786	0.617

Table 3 Photophysical parameters of C_3 molecule in different solvents

Solvents	$\overline{\nu}_a$ (cm^{-1})	$\overline{\nu}_f$ (cm^{-1})	$\overline{\nu}_a - \overline{\nu}_f$ (cm^{-1})	$\overline{\nu}_a - \overline{\nu}_f$ (cm^{-1})	n	ε	f(ε, n)	$f(\varepsilon, n) + 2g(n)$	E_T^N
DX	25380.71	22321.43	3059.28	47702.14	2.219	1.4210	0.0440	0.6170	0.164
DCE	24875.62	20833.33	4042.29	45708.95	10.300	1.4448	0.6297	1.2234	0.194
DEE	25316.50	21739.13	3577.37	46638.5	4.266	1.3520	0.3710	0.8510	0.210
EA	25316.50	21231.42	4085.08	46547.92	6.0814	1.3720	0.4930	0.9990	0.228
DCM	24937.66	20920.50	4017.16	45858.16	8.9300	1.4240	0.5900	1.1660	0.321
DMF	25316.50	20202,02	5114.48	45518.52	38.500	1.4305	0.8356	1.4230	0.404
DMSO	25125.63	20283.96	4841.67	45409.59	47.240	1.4780	0.8427	1.4890	0.444
nBA	25125.63	20746.89	4378.74	45872.52	7.800	1.3990	0.5613	1.2960	0.602
IPA	25000.00	20703.93	4296.07	45703.93	18.300	1.3776	0.7651	1.2786	0.617

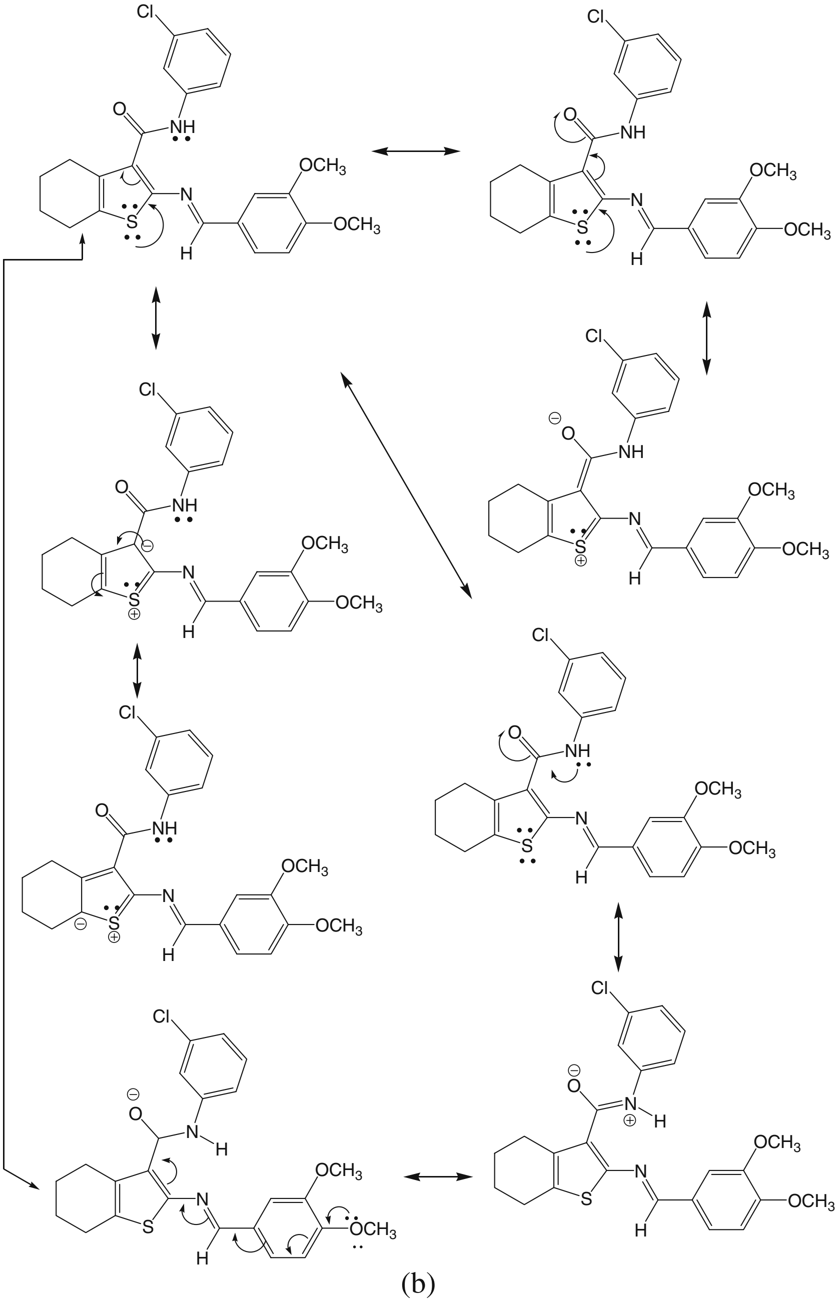
Fig. 4 Possible resonance structures of (a) $\mathbf{C_1}$, (b) $\mathbf{C_2}$ and (c) $\mathbf{C_3}$



electronically excited species is often useful in the design of non-linear optical materials and elucidation of the nature of the excited state, as well as course of any photochemical transformation. Experimental data on excited states are useful in the parameterization of semi-empherical quantum mechanical procedures for these states. Among the techniques available for the determination of excited state dipole moments, the most popular is that based on the Lippert-Mataga equation [15]. In this technique, absorption and fluorescence shift followed using the solvent polarity, described by dielectric constant ε and refractive index. Other methods such as Stark splitting of rotational level [16, 17] and microwave conductivity [18] are considered to be more accurate in determining excited state dipole moments.

The experimental determination of parameter based on the analysis of the solvatochromism of the absorption and fluorescence maxima is quite popular. 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, exalite dyes,

Fig. 4 (continued)



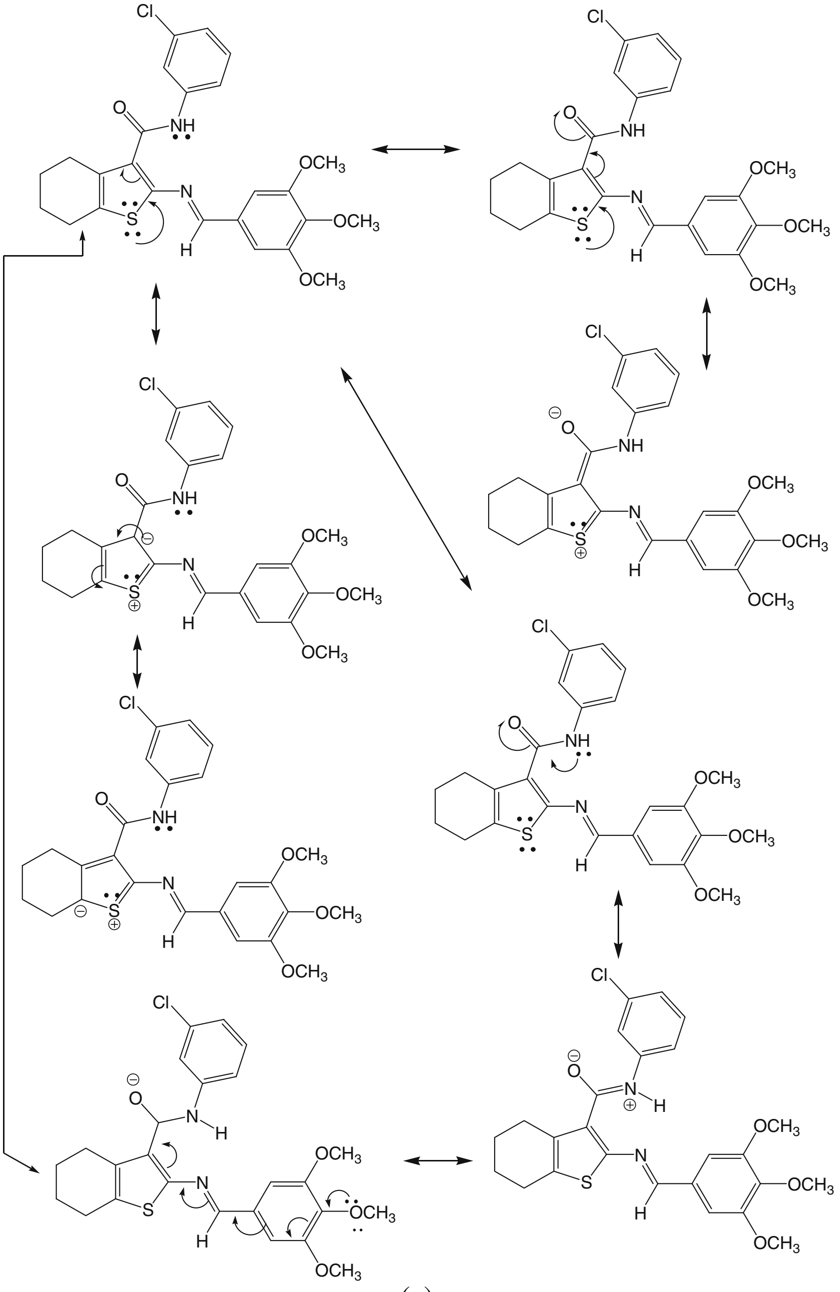
curcuminoid dyes, hemicyanine dyes, coumarin dyes, acridinedione dyes, fluorescein, flavones, PRODAN, BADAN and ACRYLODAN, acridines and phenazines and in some laser dyes [19–26] etc.

In the present work, we report different solvent parameters and spectral parameters such as Stokes shift which is useful for estimation of the ground and excited state dipole moments of three carboxamides by solvent perturbation method [27, 28] 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 carboxamides investigated.

Materials and Methods

The (E)-2-(4-Chlorobenzylideneamino)-N (2-chlorophenyl) 4, 5, 6, 7 tetrahydrobenzo[b]thiophene-3-carboxamide (C_1), (E) N (3-Chlorophenyl)-2(3,4-dimethoxybenzylideneamino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxamide (C_2) and (E)-N-(3-Chloro phenyl)-2-(3,4,5-trimethoxybenzylideneamino)-4,5,6,7-tetrahydrobenzo[b]thiophene-3carb oxamide (C_3) were synthesized in our laboratory using standard methods [29, 30]. The molecular structures of these carboxamides are given in Fig. 1. The solvents used in the present study namely 1,4Dioxane-(DX), 1,2Dichloroeth-

Fig. 4 (continued)



(c)

ane-(DCE), Diethylether-(DEE), Ethyl acetate-(EA), Dichloromethane-(DCM), Dimethylformamide-(DMF), Dimethylsulphoxide-(DMSO), n-Butyl alcohol-(nBA), Isopropyl alcohol-(IPA) 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/L in each solvent. The absorption spectra were recorded using UV–Vis Spectrophotometer (Elico Model). The fluorescence spectra were recorded using Fluorescence Spectrofluorometer (Fluorolog Model). All these measurements were carried out at room temperature (300 K).

Theory

Equations for the Estimation of Dipole Moments

The most commonly used expression in fluorescence spectroscopy is first developed by Mataga et. al. [15, 31] and Lippert [32, 33]. It is based on Onsager's reaction field theory, which assumes that the fluorophore is a point dipole residing in the centre of a spherical cavity (a) with radius in a homogeneous and isotropic dielectric with relative permittivity (ε). The so called Lippert-Mataga equation is

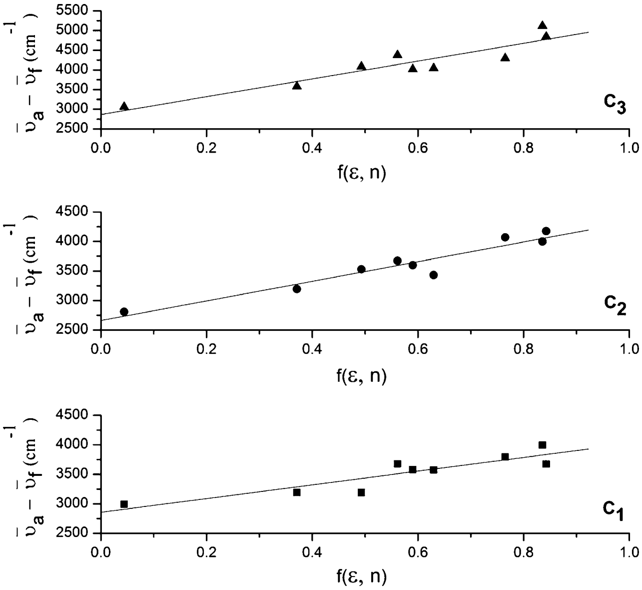


Fig. 5 The plots of $(\overline{\nu}_a - \overline{\nu}_f)$ vs f (ε, n) for C$_1$, C$_2$ and C$_3$

no longer applicable when, in addition to the non-specific interactions, specific fluorophore/solvent interactions such as hydrogen bonding or electron-pair donor/electron-pair acceptor interactions also contribute significantly to the overall solute-solvent interaction. A further limitation results from the cavity radius, which is difficult to estimate for elongated molecules with an ellipsoidal shape [9].

Kawski and co-workers [34–36] obtained a simple quantum mechanical second order perturbation theory of absorption $(\overline{\nu}_a)$ fluorescence $(\overline{\nu}_f)$ band shifts in different solvents of varying permittivity (ε) and refractive index (n) relative to the band position of a solute molecule based on the following equations.

$$\overline{\nu}_a - \overline{\nu}_f = m_1 f(\varepsilon, n) + constant \qquad (1)$$

$$\overline{\nu}_a + \overline{\nu}_f = -m_2[f(\varepsilon, n) + 2g(n)] + constant \qquad (2)$$

where,

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+2}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right] \qquad (3)$$

is the polarity of the solvent [28] and

$$g(n) = \frac{3}{2}\left[\frac{n^4-1}{(n^2+2)^2}\right] \qquad (4)$$

with

$$\mathrm{m}_1 = \frac{2\left(\mu_\mathrm{e} - \mu_\mathrm{g}\right)^2}{\mathrm{hca}^3} \qquad (5)$$

and

$$\mathrm{m}_2 = \frac{2\left(\mu_\mathrm{e}^2 - \mu_\mathrm{g}^2\right)}{\mathrm{hca}^3} \qquad (6)$$

'h' being Planck's constant and 'c' is the velocity of light in vacuum. The parameters 'm_1' and 'm_2' can be determined from absorption and fluorescence band shifts (Eqs. 1 and 2), the values of μ_g and μ_e from Eqs. 5 and 6 can be given as [37].

$$\mu_g = \frac{m_2 - m_1}{2}\left[\frac{hca^3}{2m_1}\right]^{1/2} \qquad (7)$$

$$\mu_e = \frac{m_1 + m_2}{2}\left[\frac{hca^3}{2m_1}\right]^{1/2} \qquad (8)$$

or

$$\frac{\mu_e}{\mu_g} = \frac{m_1 + m_2}{m_2 - m_1}(m_2 > m_1) \qquad (9)$$

The parameters 'm_1' and 'm_2' occurring for the difference $(\overline{\nu}_a - \overline{\nu}_f)$ and the sum $(\overline{\nu}_a + \overline{\nu}_f)$ of the wave-numbers, are linear functions of the solvent polarity parameters f (ε, n) and $[\mathrm{f}(\varepsilon, \mathrm{n}) + 2\mathrm{g}(\mathrm{n})]$ and can be determined from the slopes of the straight lines.

Molecular-Microscopic Solvent Polarity Parameter (E_T^N)

The empirical polarity parameter E_T^N proposed by Reichardt [9] 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

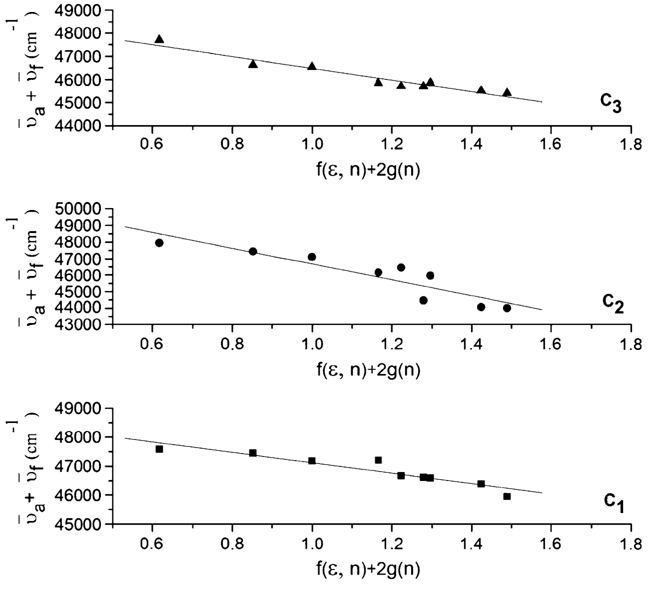


Fig. 6 The plots of $(\overline{\nu}_a + \overline{\nu}_f)$ vs [f (ε, n)+2 g (n)] for C$_1$, C$_2$ and C$_3$

Table 4 Onsager cavity radius (a), calculated values of ground state (μ_g) and excited state (μ_e) dipole moments, slopes (m_1 and m_2) and correlation coefficients (r) for C_1, C_2 and C_3

Solute molecules	Radius 'a' (A°)	μ_g [b] (D [a])	μ_e [c] (D)	Δμ [d] (D)	Δμ [e] (D)	μ_e/μ_g [f]	m_1 (cm^{-1})	m_2 (cm^{-1})	'r' for	
									m_1	m_2
C_1	4.379	0.840	3.949	3.109	1.861	4.701	1160.510	1786.742	0.900	0.935
C_2	4.510	3.639	7.532	3.893	2.162	2.067	1663.914	4773.610	0.956	0.911
C_3	4.601	0.271	4.696	4.425	2.800	17.328	2267.909	2530.149	0.929	0.969

[a] Debye=3.33564×10^{-30} cm=10^{-18} esu cm

[b] The experimental ground-state dipole moments calculated from Eq. 7

[c] The experimental excited-state dipole moments calculated from Eq. 8

[d] The change in dipole moments for μ_e and μ_g

[e] The change in dipole moments calculated from Eq. 12

[f] The ratio of μ_e and μ_g is calculated from Eq. 9

(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. [38], according to Eq. 10:

$$\overline{\nu}_a - \overline{\nu}_f = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_b}\right)^2\left(\frac{a_B}{a}\right)^3\right]E_T^N + constant \qquad (10)$$

where $\Delta\mu_b$=9D and a_B=6.2A^0 are the change in dipole moment on excitation and Onsager cavity radius respectively of a carboxamides (C_1, C_2 and C_3) 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. 11, using water ($E_T^N = 1$) and tetramethylsilane ($TMS = E_T^N = 0$) as extreme reference solvents [9, 39].

$$E_T^N = \frac{E_T(Solvent) - E_T(TMS)}{E_T(Water) - E_T(TMS)} = \frac{E_T(Solvent) - 30.7}{32.4} \qquad (11)$$

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. 12

$$\Delta\mu = \left(\mu_e - \mu_g\right) = \sqrt{\frac{mX81}{\left(\frac{6.2}{a}\right)^3 11307.6}} \qquad (12)$$

Where 'm' is the slope obtained from the plot of Stokes shift $\left(\overline{\nu}_a - \overline{\nu}_f\right)$ versus microscopic solvent polarity (E_T^N) using Eq. 10.

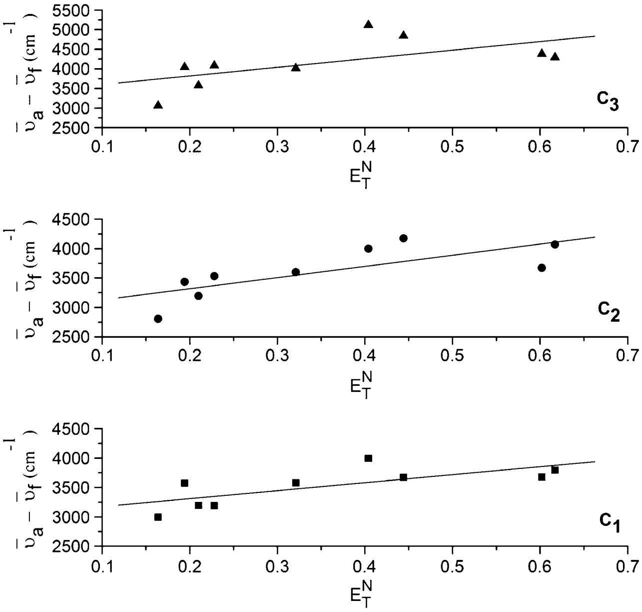


Fig. 7 The plots of $\left(\overline{\nu}_a - \overline{\nu}_f\right)$ vs molecular-microscopic solvent polarity parameter E_T^N for C_1, C_2 and C_3

Results and Discussion

Solvent Effect on Absorption and Fluorescence Spectra

The typical absorption and fluorescence spectra of C_1, C_2 and C_3 in dichloromethane are as shown in Figs. 2 and 3 respectively. The uncertainty in the measured wavelength of absorption and fluorescence maxima is ±0.5 nm and ±1 nm respectively. The observed absorption and emission spectra of these three carboxamides are broad which shift depending on the solvent used. The charge transfer band shows a shift of about 2–10 nm in the absorption spectra on charging the solvent from dioxane to isopropyl alcohol for C_1, 2–22 nm for C_2 and 2–9 nm for C_3 respectively. A 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 carboxamides in the ground state than in the excited state. The pronounced shift in the emission clearly indicates that the dipole moment of the excited state is higher compared to that in the ground state. In such cases, the relaxed excited 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.

Estimation Ground and Excited State Dipole Moments

In order to estimate the ground state and excited state dipole moments of the solute molecules, the solvent polarity f(ε, n), $[f(\varepsilon, n) + 2g(n)]$, wave numbers of absorption and fluorescence emission maxima along with solvent parameters refractive index (n) dielectric constant (ε) and the microscopic polarity scale E_T^N were calculated and are tabulated in Tables 1, 2 and 3. Figures 4 and 5 show that refractive spectral shifts $((\bar{v}_a - \bar{v}_f))$ and $(\bar{v}_a + \bar{v}_f)$ for all carboxamides which are observed in different solvents, against the polarity function f (ε, n) and $[f(\varepsilon, n) + 2g(n)]$ respectively. A linear regression was done and the data were fit to a straight line for all molecules, the plots whose slopes were taken as m_1 and m_2. For polar solute molecules like C_1, C_2 and C_3 the interaction with non polar solvents depend 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 [40, 41] to use E_T^{30} function which is the empirical measure of the solvent polarity [42] 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 [43]. Therefore the use of the so-called normalized E_T^Nvalues have been recommended, which are defined in Eq. 11.

Figure 6 shows that the plot of Stoke's shift as a function of E_T^N in all the solvents for C_1, C_2 and C_3 respectively. 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. With the increasing solvent polarity, both absorption and emission bands undergo a bathochromic shift. This indicates 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 carboxamides. The effect of amino group in case of C_1, C_2 and C_3 is considered where unshared pair of electrons on this group resides in molecular orbitals (largely localized to amino group). Thus due to ICT the electronic charge from these functional groups gets substantially delocalized throughout the system. Hence the energy gap between the highest occupied orbitals of amino substituted molecule is considerably lower than the difference between the highest occupied and the lowest unoccupied orbitals of unsubstituted molecules. The excited state for all the molecules is more polar than the ground state due to intermolecular charge transfer. The Onsager cavity radius is calculated using both Edward's method [44]. The cavity radii of solute molecules are $4.379A^0$, $4.510\ A^0$ and $4.601A^0$ for C_1, C_2 and C_3 respectively. The ground and excited state dipole moments calculated using Eqs. 7 and 8 are summarized in Table 4 along with the slopes 'm_1' and 'm_2'.

The difference in dipole moment calculated from solvent perturbation method and the one calculated using Eq. 12 is fairly in good agreement clearly indicating the excited state dipole moment to be higher compared to ground state. The observed variations in the dipole moment values can also be understood in terms of their possible resonance structures as shown in Fig. 7 (a), (b) and (c) for C_1, C_2 and C_3. In case of C_1, free substituents at aryl amino, carbonyl, and amides are compared C_2 and C_3, there is a free substituent at methoxy but C_3 is has more methoxy groups compared C_2. In the present solute molecules non-bonding electrons on the nitrogen NHC_6H_4Cl and $NCHC_6H_4Cl$ group for $C_{1,}$ NHC_6H_4Cl and $NCHC_6H_3\ (OCH_3)_2$ group for C_2 and NHC_6H_4Cl and $NCHC_6H_2\ (OCH_3)_3$ group for C_3 contribute towards the mobility of π electrons on the aromatic ring. The substituent chloride (C_1, C_2 and C_3) does not produce a considerable change in the π electron mobility. Upon excitation, the carbonyl group becomes strong electron donor. Also, in solute molecule C_2 the nitrogen atom is a part of tertiary amino group. This explains the higher value of dipole moment both in the excited state and ground state for C_2 as compared to C_1 and C_3. During the charge transfer process the—NHC_6H_4Cl group may become more polar relative to the ground state. The charge transfer accompanying excitation to lowest excited singlet-state, usually results in the excited molecule having larger dipole moment than the ground state.

Conclusion

In the present study we have described the solvent effect by examining dipole moments of three biologically active carboxamides namely C_1, C_2 and C_3 in nine solvents. A bathochromic shift is observed upon increasing the polarity of the solvent for all the three carboxamides indicating $\pi \rightarrow \pi^*$ transition which is further confirmed by calculating dipole moments using solvatochromic technique and the one using Eq. 12. We found that probe molecules C_1, C_2 and C_3 possess higher dipole moments in the excited state than the ground state. This clearly indicates the excited state of C_1, C_2 and C_3 is more polar than the ground state. Further, the linear E_T^N dependence on Stoke's shift indicates presence of general type of solute-solvent interaction as well as H-bonding interaction in most of the polar solvents. The ratio of dipole moments (μ_e/μ_g) can also be obtained based on the measurement of Stoke's shift in different solvents as function of dielectric constant and refractive index. To our knowledge, this is the first report on the dipole moments of these biologically active molecules and this should be of great practical importance in many fields as mentioned in the introduction.

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