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Journal of Photochemistry and Photobiology A: Chemistry 139 (2001) 5–16

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Excited state photodynamics of 4-*N*,*N*-dimethylamino cinnamaldehyde: A solvent dependent competition of TICT and intermolecular hydrogen bonding

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Received 9 August 2000; received in revised form 30 October 2000; accepted 22 November 2000

Abstract

This paper describes the dual fluorescence of 4-*N*,*N*-dimethylamino cinnamaldehyde (DMACA) in various solvents. Based on major findings the first fluorescence band has been assigned to be arising out of delocalized excited state (DE) and the anomalous fluorescence band in polar aprotic solvents has been assigned to twisted intramolecular charge transfer (TICT) state whereas, in protic solvent it is arising out due to hydrogen bonding interaction between hydrogen donor part of the solvent and carbonyl group of the probe molecule. This hydrogen bonding being an efficient fluorescence quenching channel trammels the TICT formation and thus an apparent competition exists between TICT and hydrogen bonding formation in protic solvent. The calculated absorption spectrum generated from CNDO calculations follows nicely the experimental absorption band. The AM1 calculations corroborate the large dipole moment change and the charge transfer in orthogonal position as found from experimental observations.

Keywords: 4-*N*,*N*-dimethylamino cinnamaldehyde; Hydrogen bonding interaction; Intramolecular charge transfer

1. Introduction

Since the discovery of dual fluorescence of 4-dimethylamino benzonitrile (DMABN) [1] molecules having donor and acceptor moieties connected by an essential single bond are of great interest for observing intramolecular charge transfer and twisted intramolecular charge transfer (TICT) or conformationally relaxed intramolecular charge transfer (CRICT) depending upon the viscosity and polarity of the solvents. Of the dual fluorescence in these materials the short-axis polarized normal fluorescence band L_b is established to arise from locally excited LE state and the long-axis polarized anomalous L_a band is red shifted and has its origin in highly polar charge transfer state (CT). Myriad of experimental [1–16] and theoretical gas [17–23] and solution phase [24–33] on the nature of ICT in DMABN have already been published. But, still we are away from getting a conclusive mechanism for charge transfer. Three mechanisms for ICT have been proposed so far; viz., TICT [4–8], PICT [9–14] (Pseudo-Jahn-Teller) and RICT [19–21] (Rehybridised ICT). Briefly, in TICT model charge separation in CT state is thought of as a result of complete decoupling between dimethylamino and benzonitrile moieties by twisting the amino group in a perpendicular position. On the other hand, the amino and benzonitrile moieties are strongly coupled in PICT state involving the planarization of initially pyramidalized molecule and the phenyl amino attains partial double bond character. In RICT model, in-plane bending and rehybridizationation of carbon atom is said to occur from sp to sp^2 of the acceptor cyano group. However, the results obtained in some cases show that the contribution of TICT is enough to account for the observed dual fluorescence in both protic polar and aprotic polar solvents when molecules have both donor and acceptor moieties connected by necessary bond [34]. In few cases it was not possible to obtain a relatively good agreement with TICT model where hydrogen bonding came into effect having an impression of dual fluorescence [35]. In this paper we intend to discuss the investigations and analysis of influence of dual fluorescence in different solvents and to perform AM1 and CNDO calculations to understand qualitatively; keeping the idea of TICT in mind and to throw some light in view of mechanistic requirements in forming TICT or CRICT in DMACA vis-a-vis intermolecular hydrogen bonding.

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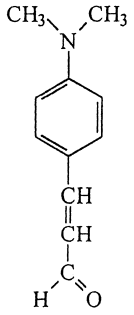
1010-6030/01/$ – see front matter
PII: S1010-6030(00)00423-8

2. Experimental

The compound DMACA was purchased from Aldrich Chemical, and was purified by vacuum sublimation. The solvents ethanol (EtOH), acetonitrile (ACN), tetrahydrofuran (THF), diethyl ether (DEE), chloroform ($CHCl_3$), dioxane, sulfuric acid and triethylamine (TEA) (E. Merck, spectroscopic grade) were used as supplied, but only after checking the purity fluorimetrically in the wavelength range of interest. The methylcyclohexane (MCH), *n*-hexane (CH) and carbon tetrachloride (CCl_4) (E. Merck spectroscopic grade) were used after distillation (dry) and checking of any emission in the required wavelength range. For aqueous solution, we used deionized Milli Pore water.

The absorption spectra at 300 K were recorded with a Shimadzu absorption spectrophotometer model UV-2101PC, and the fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer. For emission measurement, the sample concentration was maintained at 10^{-5} M in each case in order to avoid aggregation. The quantum yields were determined by using the secondary standard method with recrystallized β-napthol in cyclohexane ($\varphi_f = 0.23$) described elsewhere [35]. The fluorescence lifetime was measured by time correlated single photon counting coupled to a micro channel plate photomultiplier (Model 28090, Hamamatsu, Edinburgh Instrument).



4-N, N-dimethyl amino cinnamaldehyde (DMACA)

The degree of polarization of fluorescence at room and low temperatures was obtained by using a modified polarizer accessory with the Hitachi F-4500 spectrophotometer. The degree of polarization *P* is defined as [36,37]

$$P = \frac{I - GI_{\perp}}{I + GI_{\perp}}$$

where I and $I_{\perp}$ are the intensities of the emitted light polarized with electric wave vector perpendicular and parallel, respectively, to the excited light which is polarized with electric vector perpendicular to the plane containing the excited and emitted beam. G is the polarization correction factor of the fluorescence spectrophotometer.

3. Results and discussion

3.1. Absorption spectra

DMACA in some selected solvents shows three distinct absorption peaks (Fig. 1). Of these, two peaks at higher energy side ($S_2 \leftarrow S_0, S_1 \leftarrow S_0$) are of weak solvent dependent nature. In both the cases peaks are slightly shifted towards red with increase of solvent polarity without any significant change of band shape. In hydrocarbon solvent the first higher energy band appears at 241 nm and the second higher energy band at 318 nm, but in polar ethanol/acetonitrile solvent these bands were shifted to 253 and 328 nm, respectively. This observation points only a negligible difference in polarity of ground and first two excited singlet state. The excitation spectrum is practically identical with absorption spectra and the CNDO calculated (CNDU) spectrum broadly follows the absorption spectrum. For both peaks the molar absorption coefficients are indicative of $\pi\pi^*$ in nature. Now comparing the position of these peaks [38] with different benzene derivatives we can assign the bands as ^1L_b and ^1L_a, respectively.

Fig. 1 shows the distinct bathochromic effect of third band, with the increase of solvent polarity. This bathochromic effect is more pronounced in protic solvent rather than aprotic solvent. Acetonitrile is a polar aprotic solvent of higher dielectric constant than ethanol (a protic solvent), but the peak position of third band is more towards red side in ethanol than that of acetonitrile. One cannot correlate the bathochromic effect with any of the solvent polarity parameters that exist in modern photochemistry considering protic and aprotic polar solvents, but the correlation of the bathochromic shift with solvent polarity parameter (e.g. Δf) separately in protic and aprotic solvents could easily be done. Moreover, in protic solvents the bathochromic effect (fluorescence peak position) of this band linearly correlates with hydrogen bonding donating parameter α (a measure of hydrogen bonding donating ability in terms of spectral shift) [39]. In this respect, it is worth mentioning here about the change of band shape in acidic solution. At low concentration of H_2SO_4 in ACN solution, the two higher energy band intensity increase producing negligible amount of red shift of peak positions, whereas the intensity of third long wavelength band decreases with large red shift. With gradual increment of acid concentration in the solution, the absorption spectrum changes decreasing the third band gradually. Finally, at a certain concentration of H_2SO_4, i.e., at pH range (2–3) the absorption spectrum takes its final form with only two bands (Fig. 1), further increase of acid concentration makes no change. Similar effect on absorption spectra was observed on increasing the acidity of protic solution. Hence, two possibilities may be proposed for assigning the third absorption band of DMACA in aprotic and protic solvents. Firstly, the third broad unstructured absorption band may be attributed to a direct transition to the charge transfer (CT)

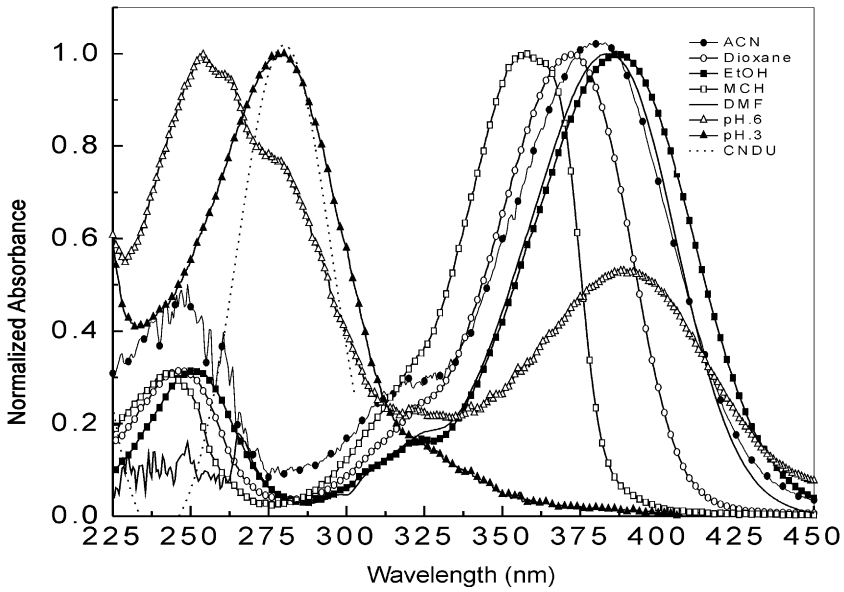
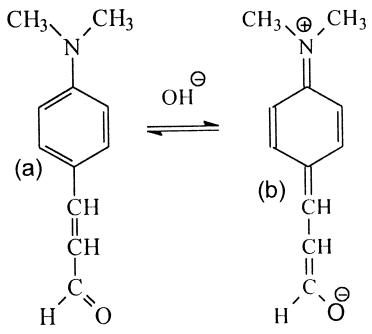


Fig. 1. Electronic absorption spectra of DMACA in different solvents at room temperature and calculated electronic absorption spectra (CNDU).

state in aprotic solvents. The π-electrons in DMACA are delocalized through the long CH chain and the more number of conjugate double bonds make the absorption band more red shifted. So the ^1L_a band and the CT bands are separated due to extra stabilization which is not possible in DMABN. Similar type of evidence was observed in the case of 4-*N*,*N*-dimethylamino cinnamic acid [34]. When an extra phenyl group is added between CN and phenyl group of DMABN a similar absorption band with high molar absorption coefficient was found [40] at the same position. In presence of acid the DMACA is protonated and the lone pair electron of amino group of DMACA is engaged with H^+ ion of acid molecule and the charge transfer possibilities die out resulting in the disappearance of long wavelength absorption band (Scheme 1). Secondly, the extra red shift of the broad band as well as the linearity of the red shift of this band with hydrogen bonding tendency of the solvent may be due to zwitterion formation of DMACA in protic solvents. Hydrogen bond formation (electron donating tendency) of amino nitrogen increases and takes part in resonance structure (b) in Scheme 1. This resonance structure is more polar and zwitterionic in nature which stabilizes the charge transfer (CT) state more, producing more red shifted absorption band. Water has strong hydrogen bonding tendency than ethanol and it stabilizes CT state more and more resulting in larger and larger bathochromic effect (vide infra).



Scheme 1.

3.2. Fluorescence spectra at 300 K

3.2.1. Fluorescence spectra in aprotic solvents

At room temperature DMACA emits distinct dual fluorescence bands which have much stronger dependence on the solvent environment than the absorption spectrum. A summary of the emission maxima and photophysical properties appears in Table 1. The steady state fluorescence spectroscopy presented here in aprotic polar solvents for DMACA does give a simple resolution of two distinct bands (Fig. 2), but for hydrocarbon solution DMACA produces only weak unresolved single fluorescence band at higher energy side. The first one (higher energy band) has very weak normal Stokes shifted emission (F_n) band whose features resembles that of emission of benzene and is comfortably assigned to $^1B_{2u} \rightarrow ^1 A_{1g}$ transition, a delocalized excited (DE) state in phenyl ring [41]. Another important thing to mention here regarding the weakness of F_n band intensity is that DMACA has a strong absorbance due to the third absorption band in the wavelength region of the F_n band which acts as a chopper for that band, i.e., inner filter effect plays a major role to control the fluorescence emission intensity of the first band (DE).

The second band is rather anomalous (A), comparatively stronger in intensity, broad, structureless emission at longer wavelength side which disappears in hydrocarbon solution. Upon increase in polarity of the solvent the emission maximum of structureless band (A) shifts towards longer

Table 1
Absorption and fluorescence data of DMACA at 300 K

Solvent	Absorption data		Fluorescence data									
	λ_{max}^{absl} (nm)	ε_{max} (M)[a]	λ_{max}^{LE} (nm)	λ_{max}^{Al} (nm)	φ_{LE}^{fl}	φ_{A}^{fl}	τ_{LE}^{fl} (ns)	τ_{A}^{fl} (ns)	$k_r^{LE} \times 10^{-6}$ (s^{-1})	$k_{nr}^{LE} \times 10^{-8}$ (s^{-1})	$k_r^{A} \times 10^{-6}$ (s^{-1})	$k_{nr}^{A} \times 10^{-8}$ (s^{-1})
Protic												
MCH	323	12840	370	–	0.021	–	1.5	–	14.0	6.5	–	–
MeOH	310	5879	370	474	0.0012	0.006	1.3	2.2	0.93	7.6	26.3	4.5
EtOH	323	11978	367	472	0.01	0.02	1.2	2.4	8.08	8.2	8	4
BuOH	323	7968	369	469	0.008	0.02	1.2	2.32	6.69	8.6	8.6	4.23
Glycerol	324	10872	372	495	0.001	0.023	1.5	2.8	0.67	6.7	8.2	3.48
Water	330	–	–	484	–	0.002	–	2.0	–	–	1.25	4.9
Aprotic												
ACN	312	10914	355	470	0.008	0.02	1.01	1.4	7.9	9.8	1.4	7
DMF	314	5731	356	471	0.007	0.05	1.02	1.3	6.86	9.7	3.2	7.3
$CHCl_3$	326	12723	–	459	–	0.01	–	1.15	–	–	8.6	8.6
1-Chloro butane	325	8765	354	438	0.008	0.02	1.05	1.2	6.6	9.4	1.6	8.1
DCM	324	14122	355	466	0.006	0.03	1.03	1.3	5.8	9.6	2.3	7.4

[a] $M = dm^3\,mol^{-1}\,s^{-1}$.

wavelength and the intensity of that band decreases. The excitation spectra of both DE and A band do not depend upon the emission wavelength and resemble the absorption spectrum (^1L_b and ^1L_a, bands) when the absorbance of the solution does not exceed 0.3 over the wavelength range studied. These data suggest that the structureless bathochromic emission is due to an intramolecular charge transfer. The most interesting feature of the fluorescence spectra of DMACA in polar aprotic solvents is that it does not follow the Kasha's rule [42], producing no mirror image relationship between them. This gives us a hint that excited state equilibrium geometry and ground state equilibrium geometry is of very different kind. Hence, we could possibly predict the intramolecular charge transfer emission eventually to be due to intramolecular charge transfer emission from different geometry. Quantitative analysis of the red shift [43] indicates that the emitting state possesses a large dipole moment. According to the Lippert–Mataga relation [44], the energy of the emission maximum of the charge transfer band depends in a linear way with the solvent parameter $f(\varepsilon_r, n)$ (in Fig. 3, Δf)

$$\nu_a - \nu_f = \frac{2\mu_e^2}{4\pi\varepsilon_0 hc\rho^3} f(\varepsilon_r, n)$$

where $f(\varepsilon_r, n) = [(\varepsilon_r - 1)/(2\varepsilon_r + 1) - (n^2 - 1)/(2n^2 + 1)]$, ν_f and ν_a correspond to the emission and absorption frequency in a solvent with dielectric constant ε_r, and n

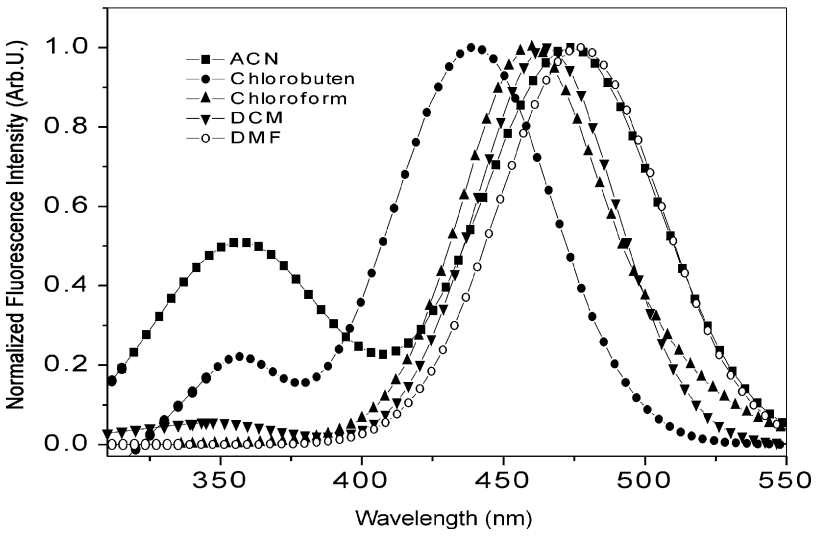


Fig. 2. Corrected fluorescence emission spectra of DMACA in different aprotic solvents at room temperature.

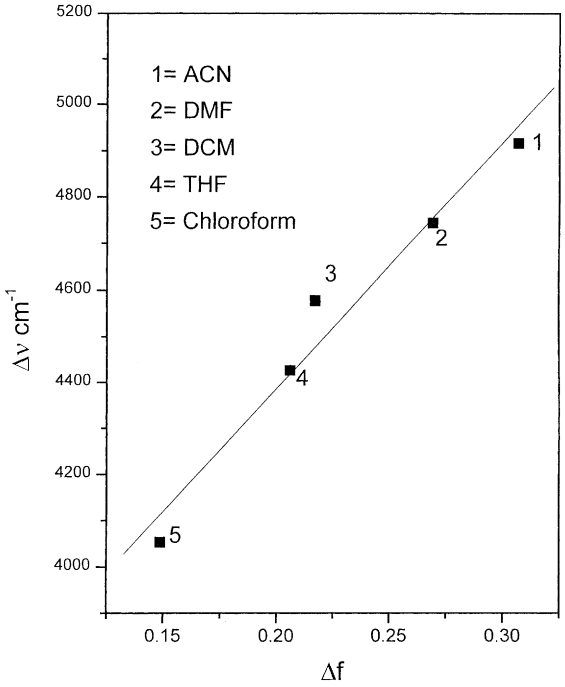


Fig. 3. Lippert–Mataga plot.

corresponds to the refractive index of the medium. h, ε_0, c, ρ corresponds to Plank's constant (6.6×10^{-34} J s), the permittivity of vacuum (8.85×10^{-12} V C^{-1} m^{-1}), the velocity of light in vacuum (3.0×10^{8} m s^{-1}) and the radius of the solvent cavity (in meter), respectively. μ_e (C m^{-1}) is the permanent dipole moment of the molecule in excited state. This relationship is based on the assumption that solvation occurs only by dipolar interaction and that the dipole moment is very weak in ground state. Assuming a value of 4 Å for ρ, the excited state dipole moment of DMACA can be obtained from this ratio of the slope and $2\mu_e^2/4\pi\varepsilon_0 hc\rho^3$ as 5.9 D. This is due to charge transfer from amino group to phenyl ring, a charge displaced by an amount of ∼2 Å. This large change in dipole moment from ground to excited state is caused by the redistribution of atomic charges in excited state, which is only possible due to charge transfer from electron rich donor moiety to acceptor moiety. However, the above said two fluorescence bands have a common excitation spectrum closely resembling the absorption spectrum so that the charge transfer band has an origin in DE band (vide infra).

Thus an intramolecular adiabatic photoreaction occurs prior to the formation of the long wavelength emitting species. The electronic structure of DMACA is closely related to the DMABN in the sense that both the systems possess π donor and acceptor part linked by an essential single bond around which an internal rotation is possible. By this analogy, the long wavelength fluorescence band may preliminarily be assigned to have arisen from a TICT state as in the case of DMABN and other molecules [34,35,49]. This excited state is formed by an intramolecular rotational relaxation towards perpendicular geometry combined with the polar solvent reorientation stabilizing the newly created strong dipole [43]. Of course, the reasoning of TICT band assignment would be firm with quantum chemical calculation. We will simulate the situation of twisted dimethylamino group and the dipole moment computed thereof will be compared with the actual experimental measurement (vide infra).

The solvent reorientation leads to the characteristic solvatochromic red shift observed in this case. The electronic excitation perturbed by the additional effect of dielectric relaxation in polar medium leads to stabilization of a low energy TICT state in a twisted conformation, with unit charge transfer. The room temperature fluorescence observation of TICT state of DMACA is due to the presence of a substituted amino group (N–$(CH_3)_2$) in a solvent of low to moderate polarity and presumably, a medium in which twisting relaxation is not hindered. If the solvent polarity becomes high, then the solvation can strongly polarize the ground state charge distribution as to inhibit the $\lambda \rightarrow a_\pi$ transition or which may precede TICT state formation, resulting in the decrease of the longer wavelength fluorescence and in extreme case no dual fluorescence from this origin could be observed [45].

3.2.2. Fluorescence in protic solvents

DMACA displays distinct dual fluorescence spectra on common excitation (323 nm) peaking around 370 and 460–490 nm. The first fluorescence band (higher energy) has negligible amount of solvatochromic shift on protic solvent polarity favoring the observation of a $^1B_{2u} \rightarrow {}^1A_{1g}$ transition, a characteristic of phenyl ring [41] and the second broad unstructured fluorescence band puts a signature of large solvatochromic shift on solvent polarity, which compels us to guess that the fluorescence spectra to be of a typical ICT transition type as has been done in aprotic solvent before. A few representative spectra of DMACA in protic solvents are shown in Fig. 4, and the fluorescence spectral data of DMACA in homogeneous media are given in Table 1. For comparison, the spectral data of DMACA in protic and aprotic solvents are given in the same table. In protic solvent, an increase in polarity of the medium, both the absorption third band and fluorescence second band maximum of DMACA display a gradual red shift. However, the solvatochromic shifts of the fluorescence maxima are more pronounced than those for the absorption maxima. This behavior is an indicative of an emitting state to be more polar than the ground state. This conclusion is combined with the fact that on electronic excitation the dipole moment of DMACA increases by more than 4 D. Using Lippert–Mataga relation as in the case of aprotic solvent we calculated the change in dipole moment from ground state to the excited state to be of 6 D. In contrast, more attention have been paid to the fact that the Stokes shift towards low energy fluorescence maximum (second fluorescence band) is considerably larger in protic solvents

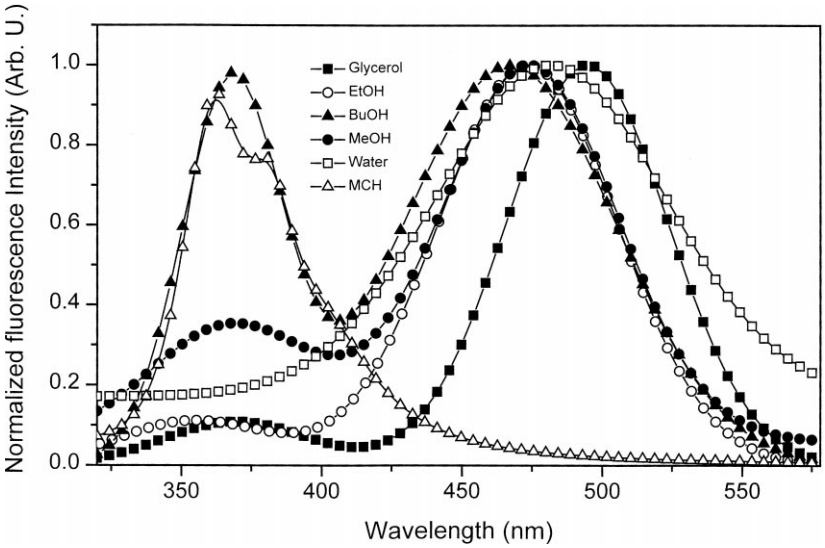


Fig. 4. Corrected fluorescence emission spectra of DMACA in different protic solvents and in MCH at room temperature.

than those expected on the basis of the *solvent polarity* in aprotic solvent alone. This *unusual large Stokes shift of the second fluorescence maximum* of DMACA in protic solvent shows a linear correlation with *hydrogen donating parameter* α [39] of the solvent (Fig. 5), whereas, it does not bear any correlation with *solvent polarity parameter* E_T (30). Therefore, the hydrogen bonding interaction of the carbonyl group of the fluorophore (hydrogen bond acceptor) and the hydroxylated solvents (hydrogen bond donor) must be responsible for this unusual high Stoke shifted fluorescence of the DMACA. The linear correlation of fluorescence quantum yield shows that, fluorescence yield decreases with increase in hydrogen bonding tendency of the solvents which nicely fits with the fact that hydrogen bonding acts as a non-radiative channel proposed by Testa [46]. Possibly this hydrogen bonding causes fluorescence quenching which hinders the TICT formation. In binary mixture of ethanol and water, the fluorescence intensity/yield and solvatochromic shift can be verified continuously as shown in Fig. 6. Addition of small amount of water in ethanol causes a decrease in fluorescence intensity and F_a band shifts toward red. At a certain (15%) concentration of water in ethanol, the fluorescence spectrum takes the form as in pure water solution. Similar type of effect was observed in the case 4-N,N-dimethylamino cinnamic acid [34]. This large effect at low water concentration should be the consequence of ground state clustering or of preferential hydrogen bonding with carbonyl group of DMACA developing zwitterionic form of large dipole of the molecule and solvation of the excited solute dipole by polar water molecules.

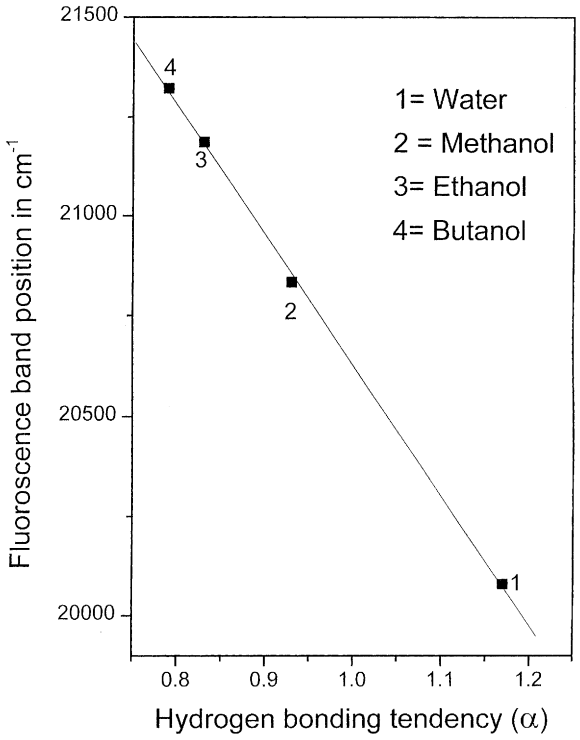


Fig. 5. Plot of hydrogen bonding parameter (α) vs. fluorescence band position of DMACA.

3.2.3. *Viscosity effect on fluorescence spectra*

To study the role of molecular flexibility, if any, in fluorescence spectroscopy in excited DMACA molecule and hopefully to gain better understanding of coupling between the vibrational (umbrella motion) motion of $N(CH_3)_2$ group and solvent stabilization, the fluorescence spectra in ethanol and glycerol mixture have been observed. The basic idea is to control the local viscosity of the solvent without greatly altering the polarity of the solution and it may provide the information about the effect of the change in local viscosity on the dynamics and fluorescence properties as well as charge transfer processes.

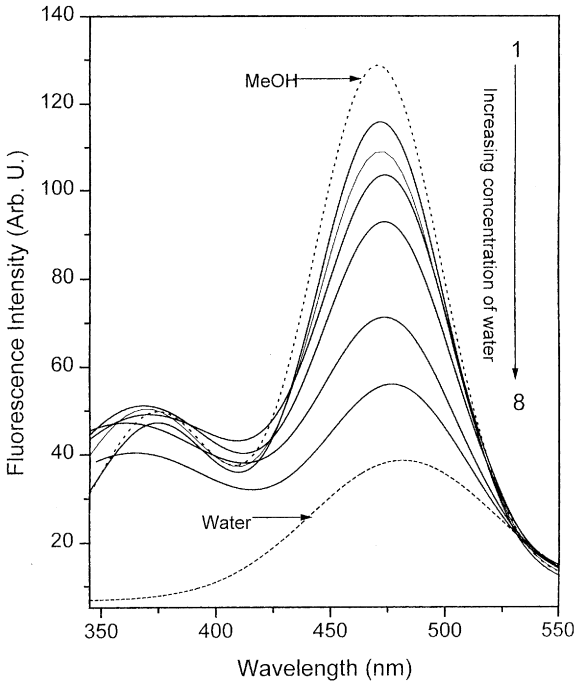


Fig. 6. Corrected fluorescence emission spectra of DMACA in methanol as a function of water concentration: (1) 0% water, (2) 2% water, (3) 4% water, (4) 6% water, (5) 8%water, (6) 12% water, (7) 15% water and (8) pure water.

We have chosen to examine the effect of viscosity, glycerol and methanol because of their nearly similar polarity. Fig. 7 shows fluorescence spectra of DMACA in glycerol as a function of methanol. It clearly shows that the intensity of the F_a emission decreases as the percentage of methanol increases in glycerol solution with blue shift of peak position, whereas, the first band remains constant. Finally, as we go from pure glycerol to 30% glycerol, the fluorescence spectrum of DMACA reaches to the same as in pure methanol. Out of these two effects the blue shift with hypsochromic effect upon increasing methanol in glycerol solution could easily be explained from polarity point of view of the solution. Glycerol (dielectric constant ∼42.50 at 25°C), being more polar than methanol (dielectric constant ∼32.66 at 25°C) stabilizes the hydrogen bonding complex with solvent molecule to a greater extent and hence the red shift of F_a band in pure glycerol solution. Now the fluorescence enhancement (or hyperchromic effect) could well be explained from macroviscosity point of view. The torsional motion of $N(CH_3)_2$ group and other vibrational motion of the molecule might be hindered in viscous glycerol. As methanol concentration increases in the solution the viscosity of the solution decreases resulting in the increase of vibrational freedom decreasing the fluorescence efficiency of the molecule. If we rigidize the solution the fluorescence yield shoots up very high which will be discussed latter.

3.2.4. Fluorescence polarization spectra at room temperature and 77 K

In order to understand the orientation of the transition moment of the two fluorescence bands which appeared in protic solvent polarization studies have been made in viscous medium which might give us better understanding about the origin of anomalous fluorescence band in protic solvents. Fig. 8 depicts the fluorescence polarization spectra of DMACA in glycerol at room temperature, in MCH (non-polar) and ethanol (polar protic) glass at 77 K. In all cases the degree of fluorescence polarization P is positive throughout the fluorescence bands. The positive value of P indicates that both the bands are polarized along the

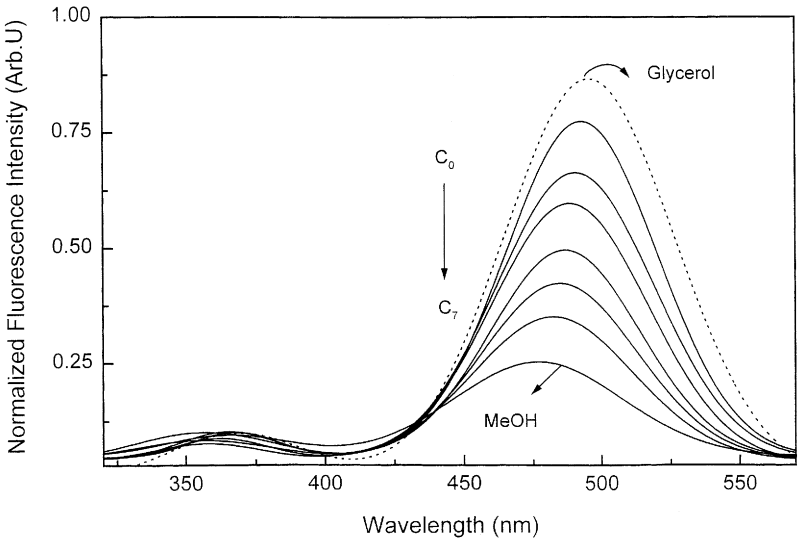


Fig. 7. Corrected fluorescence emission spectra of DMACA in glycerol and methanol mixture. Viscosity dependence emission spectra of DMACA at room temperature with: (C_0) 90% glycerol, (C_1) 72% glycerol, (C_2) 65% glycerol, (C_3) 57% glycerol, (C_4) 50% glycerol, (C_5) 40% glycerol, (C_6) 30% glycerol, and (C_7) pure methanol.

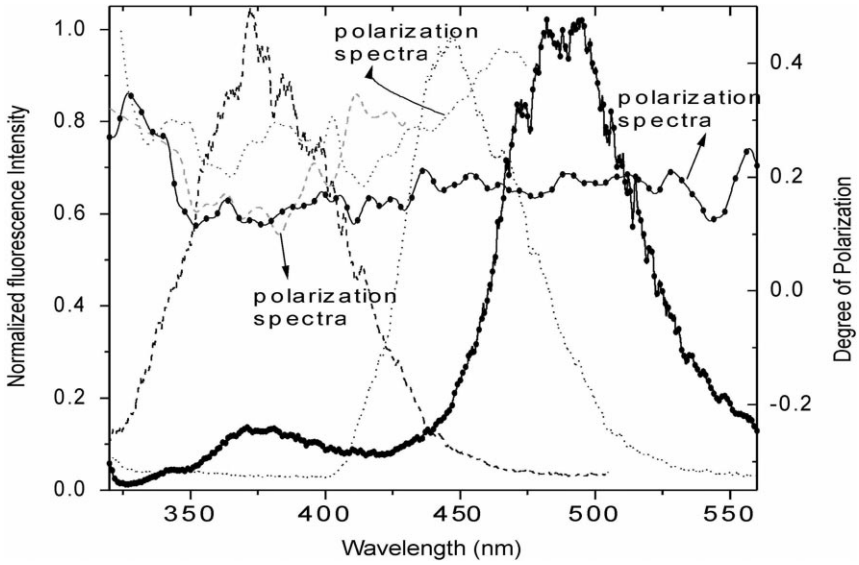


Fig. 8. Fluorescence emission spectra and fluorescence emission polarization spectra of DMACA in ethanol (---), MCH glass matrix (– – –), and in glycerol (—●—●—).

molecular long axis, i.e., both bands have an in-plane molecular long axis polarization.

3.2.5. Fluorescence at 77 K and temperature effect

At 77 K DMACA in dry [47] hydrocarbon (MCH) shows a strong single fluorescence band peaking at the position identical to room temperature fluorescence spectra in MCH and no phosphorescence is observed in glass matrix. The quantum yield of the low temperature fluorescence is five times greater than that of the room temperature fluorescence. At low temperature in glass matrix all probable photoreaction ceases resulting in increase of normal fluorescence. Again in MCH glass, in presence of trace of water molecule in the solvent DMACA shows a strong broad unstructured fluorescence spectra at 415 nm and very weak normal fluorescence negligible compared to the lower energy one. Hence, the appearance of anomalous band in presence of trace of water molecule in MCH glass certainly make us to think that the origin of this band must be due to hydrogen bonding complex of probe molecule with water molecule present in the glass matrix.

In ethanol glass (at 77 K) DMACA shows dual fluorescence spectra very similar to that of DMACA in MCH glass in presence of water molecule. It is also important to note that at 77 K the anomalous fluorescence band is shifted towards blue with respect to that of room temperature with increasing quantum yield. Upon increasing the temperature from 77 K the peak position of the lower energy band shows *bathochromic shift* and the fluorescence band intensity *decreases* whereas, the first band maximum remains *unaltered*. Finally, at ≈143 K the peak position of the anomalous band shows maximum red shift touching the *room temperature band position* with gradual decrease in intensity.

The appearance of dual fluorescence band in ethanol glass is not in conformity with TICT mechanism described elsewhere [8,48]. Moreover, we observed in the previous case [34,49] that the TICT forming molecule shows phosphorescence in the overlapping zone of anomalous fluorescence. In the present case, the observation of dual fluorescence in *ethanol glass* goes against the formation of TICT state. Hence, we can conclude that in protic solvent DMACA does not follow the TICT mechanism to emit dual fluorescence and the appearance of anomalous fluorescence is only due to *hydrogen bonding complex* of DMACA with protic solvent making *zwitterionic form*.

The fluorescence spectra of DMACA shows distinguishably different features depending upon the nature of the solvents. At 77 K the CT emission ceases in aprotic solvents which makes us to think that the hindrance of rotation of dimethylamino group at low temperature might be the reason for disappearance of CT band. This is possibly a proof of our earlier assignment of TICT band. In aprotic solvents, such as in ACN the anomalous emission band of DMACA increases with increase in temperature keeping the first normal band intensity (quantum yield) to be constant (Fig. 9) and the band position remains unaltered. The ratio of quantum yield of two bands increases as a linear function of temperature in the range of observation (283–323 K). Fig. 9 (inset) shows the variation of $\ln(\varphi_A/\varphi_{LE})$ vs. $1/T$, which is well-fitted straight line in the studied temperature range. But in protic solvent group, the variation of fluorescence yield (intensity) of the two bands decreases with increase in temperature. Fig. 10 shows fluorescence spectra of DMACA in butanol as a function of temperature. Both the bands show linear relationship within the temperature range studied.

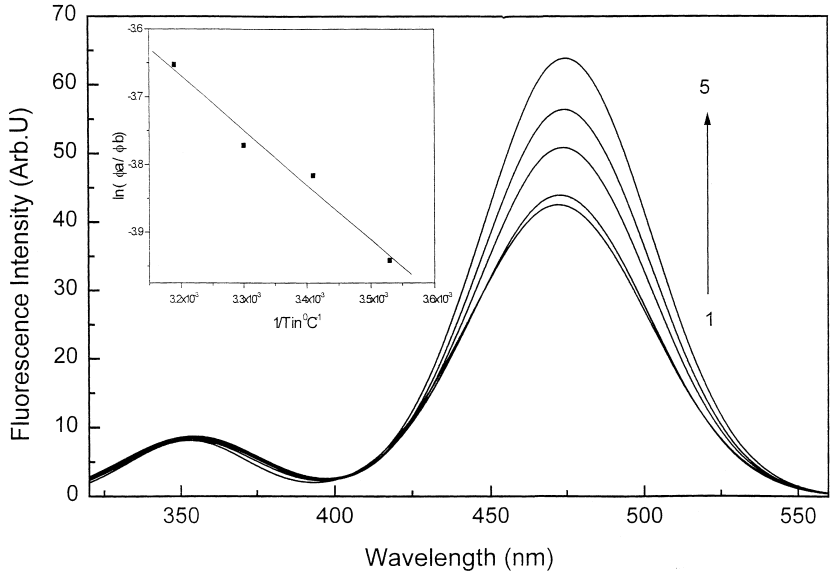


Fig. 9. Temperature dependent fluorescence emission spectra of DMACA in ACN at: (1) 283 K, (2) 293 K, (3) 303 K, (4) 313 K, (5) 323 K. Inset: $1/T$ vs. ln (φ_A/φ_{LE}) plot.

In general, the radiative rate in the molecular electronic transition is independent of temperature, although rare exceptions are there in literature. According to the basic theory the radiative emission rate k_f is proportional to the square of the electronic transition moment M_{ij} and to the factor $\langle n^3\nu^3\rangle$ averaged over the spectral width of the fluorescence, where n is the refractive index and ν is the wave number [50] of the emission. With respect to temperature dependence, the contribution due to n^3 and ν^3 have usually an opposite sign and practically, the term $\langle n^3\nu^3\rangle$ contributes nothing to radiative rate k_f. But in the present case, change in wave number with temperature is nil. So the term $\langle n^3\nu^3\rangle$ should contribute a little on radiative rate k_f. Since the temperature range studied in the experiment is not so wide, we can easily neglect the contribution of refractive index term. Hence, the temperature effects discussed in the present work can be ascribed only to the changes in the transition moment. The fluorescence quantum yield/fluorescence rate constant k_{fa} in ACN (aprotic solvent) for TICT state (A^*) was found to increase with increase in temperature [51]. Due to the zero overlap situation in the perpendicular TICT geometry, the radiative rate k_{fa} normally vanishes (weak emission, difficult to detect) compared to the thermally activated emission from the vibronic level. On increasing the temperature, deviation from $\phi = 90^\circ$ may occur which induces mixing between (transition forbidden) charge transfer and delocalized

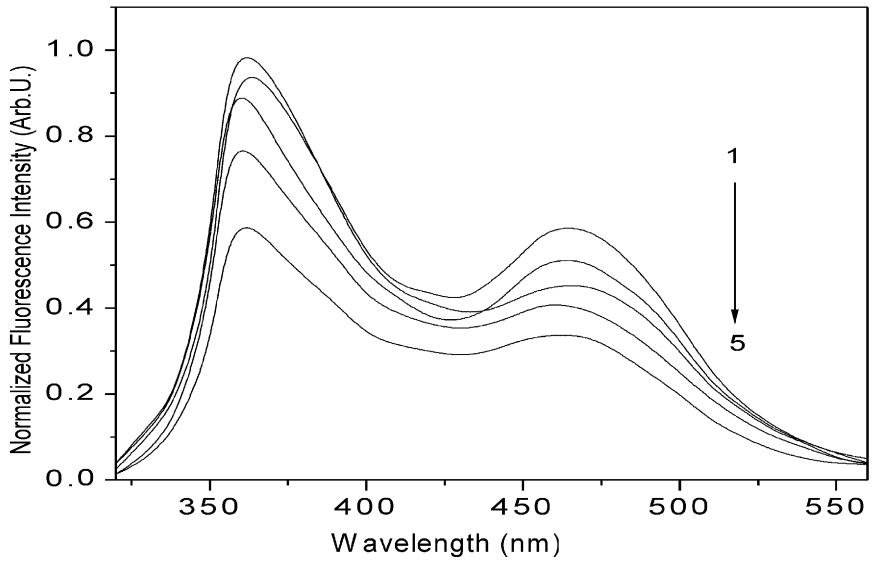


Fig. 10. Temperature dependent fluorescence emission spectra of DMACA in butanol at: (1) 283 K, (2) 293 K, (3) 303 K, (4) 313 K, (5) 323 K.

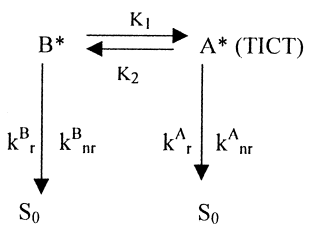
excited state (transition allowed state) and thus leads to the increase in transition moments and φ_A as well as k_{fA} value. So the described results in fluorescence spectra on temperature dependence in ACN solution confirms the TICT state formation of DMACA in aprotic solvents after suitable photoexcitation. On the other hand, lowering of the fluorescence intensity and decreasing of the radiative rate constant for both the bands in protic solvent on increasing the temperature of DMACA could be due to the lowering of viscosity of the solvent.

3.2.6. Decay of emission process

The fluorescence decay measured over the entire emission spectra of DMACA in different solvents are exactly not mono-exponential. In MCH or any hydrocarbon solvents, the fluorescence at 370 nm band is strictly mono-exponential with decay time 1.5 ns, and the same in ACN is 1.01 ns. In ACN solution the fluorescence decay of high energy band is bi-exponential with decay time 0.044 and 1.01 ns. The first one is outside the resolution limit of the instrument used (approximately 500 ps). The fluorescence decay at 470 nm in ACN solution is strictly mono-exponential with decay time 1.40 ns which is very close to the decay time of higher energy fluorescence band B*. As we do not see the rise time of low energy band (A*), it is possible that the lifetime is too fast to be able to detect under present condition. Some intramolecular charge transfer process was found to occur with time constant of 10 ps [52].

Again the fluorescence decay in protic solvents are of different nature. On excitation at 300 nm and monitored at 370 and 480 nm in butanol solution, it shows two distinctly different fluorescence decays with lifetime of 1.2 and 2.32 ns, respectively. The decay constant was observed in MeOH, EtOH and water solution and has also been recorded in Table 1. This lifetime values in protic solvent clearly indicate that two bands are of different origin and nature as well. The mechanism of ICT, CRICT or in typical form TICT should follow Scheme 2.

According to this scheme, a double exponential decay for B* emission and a build up followed by a decay for A* (TICT) form. This is the parallel mechanism of exciplex formation which is well documented elsewhere [53,54]. Unfortunately, the double exponential decay was not well resolved in any measurement reported in aprotic solvent in this paper. But we suspected a double exponential decay of B* which came nearly within the lamp profile of the instrument in aprotic solution. The relaxation of the equilibrium between B* and A* (TICT) should therefore, be faster than the apparatus time resolution of 500 ps. TICT is generally found to be a fast process produced within several pico seconds, e.g., for DMABN the formation time of TICT was recorded to be 20 ps [55]. Moreover, the lifetime of B* emission and ICT/TICT emission are nearly identical to each other which follow the data obtained for a TICT forming molecule 4 (1H-pyrrole 1-yl) benzoic acid [49] and 4-*N*,*N*-dimethylamino cinnamic acid [34]. So the lifetime data in aprotic solvent confirm our earlier conjecture that the long wavelength band of DMACA is of TICT origin.



Scheme 2.

In protic solvents the lifetime of the said two bands are of different order predicting the less interaction or nearly zero interaction between them and the origin of these bands are of different sources. The lifetime of 370 nm band in protic solvents are of the same order with the lifetime of the B* band in aprotic solvent. Hence, we again conclude that the first band of DMACA in protic solvent is due to the delocalized excited state of benzene ring as stated in the case of aprotic solvent. The lifetime of second band is larger than that of the first one which is combined with the fact that the second band is more stable, and this stability comes only from hydrogen bonding interaction with protic solvent making the probe molecule in zwitterionic form with large dipole moment. This again supports our deduction based on earlier results (vide supra).

4. Quantum chemical calculation

Energies of the electronic transitions and dipole moments were calculated by CNDUV99 [56] and MOPAC-CI (6 × 6) version 5 package with AM1 Hamiltonian [57–59] for DMACA in ground and excited states for planar and different non planar conformations. CNDO calculation has been performed using orthogonal molecular Cartesian coordinate obtained from optimized geometry calculated by MOPAC. Fig. 1 shows the calculated spectra in CNDO which exactly fitted with first two bands of experimentally obtained absorption spectra in acidic environment and calculated molar absorption coefficient exactly equal to that obtained experimentally (Table 1).

Chemically speaking, DMACA molecule cannot have a *cis* isomer due to sp^2 hybridization of both C and O atom of C=O group and also due to stearic hindrance of H atoms in *cis* position. Considering the geometry, *cis* and *trans*, we have calculated the ground sate energy and found that *only trans conformer is energetically favorable*.

In ground state $N(CH_3)_2$ group makes very small torsional angle with rigid and planar phenyl ring. One of the CH_3 groups takes a torsional angle of 10.3° with phenyl ring and other CH_3 group has a torsional angle of 169.5° with phenyl ring. The dependence of ground state energy on angle of twist of $N(CH_3)_2$ around C–N bond has negligible

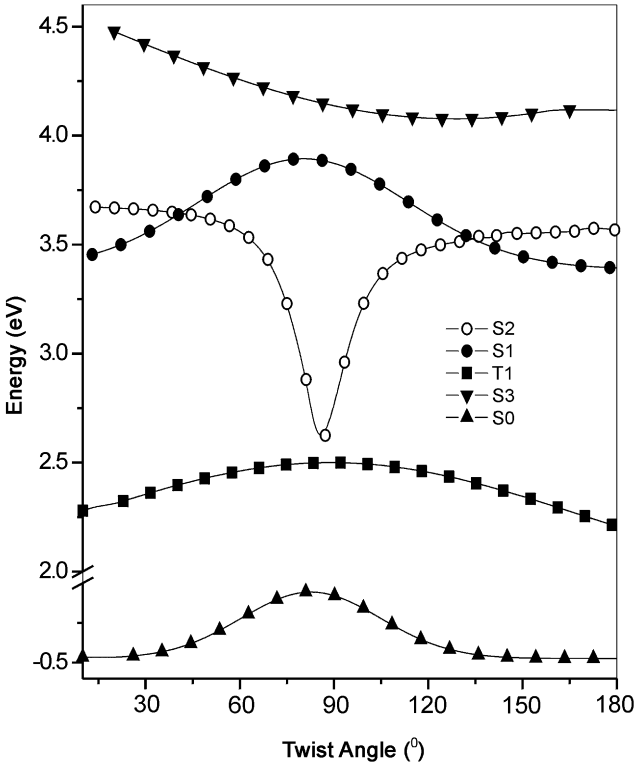


Fig. 11. Variation of singlet and triplet state energy as a function of twist angle of $N(CH_3)_2$ around C–N bond.

effect, showing little rotational barrier (Fig. 11), which confirms that the molecule favors the planar or flat conformation in ground state and also the *trans* isomer is more stable. On the other hand, from the excited state CI calculations, we find the energy difference (ΔE) between ^{1}B and ^{1}A (i.e., S_1 and S_2) is very low and third excited singlet (S_3) is far above S_2 with flat geometry, i.e., planar conformation. The energy dependence of the first three singlet excited states and first triplet state on angle of twist of $N(CH_3)_2$ around C–N bond are shown in Fig. 11. We find that the energy maximum for the first excited singlet state ^{1}B appears around 90° twisted position of $N(CH_3)_2$ group. Now the energy dependence of second excited singlet, i.e., ^{1}A state shows a strong minimum around 90° twisted position of $N(CH_3)_2$ group. So the twist of $N(CH_3)_2$ group around C–N bond is energetically favorable for excited ^{1}A state. In flat geometry, two states are very close and in 40° twisting position of $N(CH_3)_2$ there is a surface crossing between the two states. For perpendicular geometry of $N(CH_3)_2$ group, the charge difference on N atom between ground state and excited state is greater ($\Delta q = 0.7$) than that in planar geometry ($\Delta q = 0.3$). So the second excited state ^{1}A no doubt has a TICT character. The triplet state energy increases with angle of twist of $N(CH_3)_2$ group and at about 85° twist angle it goes very near to S_2 state. So in twisted condition singlet and triplet states are nearly degenerate and the charge transfer in this case is termed as biradical charge transfer [60].

The variation of ground and excited state dipole moments are nearly linear with angle of twist of $N(CH_3)_2$ group. The excited state dipole moment is always greater than that of ground state value. In ground state the dipole moment slightly decreases with increase in twist angle and in excited state the change in dipole moment is rather large and takes its maximum value at around 84° angle of twist of $N(CH_3)_2$ group. The difference in the dipole moment from excited state to ground state is maximum ($\Delta\mu = 6.5$ D) at 85° twist angle of $N(CH_3)_2$ group, which corroborates the experimental value (5.9 D) and confirms that a major redistribution of charge in excited state takes place under twisted conformation of $N(CH_3)_2$ group. These results again speak strongly *about TICT nature of charge transfer state*.

Now, in the light of above quantum chemical calculations the expected mechanism of dual fluorescence of DMACA in aprotic solvent may be through energetically advantageous intramolecular relaxation involving the twisting of $N(CH_3)_2$ around C–N bond. On excitation, the planar molecule achieves a delocalized excited state and then relaxes to twisted geometry taking part in charge transfer reaction. Obviously, the emission from twisted conformer will have a large Stokes shift and also be sensitive to environment effect due to large dipole moment change.

5. Conclusion

We have shown two types of excited states from absorption spectra, a charge transfer state in polar aprotic solvents and zwitterionic state developed from intermolecular hydrogen bonding interaction with hydrogen bond donor molecule in protic environments. Solvent dependent emission spectra help us to identify the origin of two types of anomalous bands, first due to the formation of hydrogen bonding between DMACA and solvent molecule in protic solvents and the other is due to intramolecular charge transfer (ICT). Probable presence of charge transfer state from absorption spectrum and the evidence of the strong dual fluorescence in polar aprotic solution points us to probe the intriguing nature of intramolecular charge transfer (ICT) state. Different experimental evidences (e.g. dipole moment, low temperature emission etc.) and quantum chemical calculations confirm the ICT state to be specifically developed under twisted conformation of $N(CH_3)_2$ group around C–N bond which is called TICT state in aprotic environment. On the other hand, fluorescence emission in glass matrices, polarization spectra of viscous medium and lifetime measurements have confirmed that the anomalous red shifted fluorescence band in protic solvents is the result of hydrogen bond interaction with the carbonyl group of DMACA with hydrogen bond donor part of the solvent molecules which thwarted the formation of TICT state of DMACA in protic solvents. So immediately after photoexcitation of DMACA molecule DE state is formed and thereafter, within a very short time TICT state is formed in aprotic solvents while in protic sol-

vent intermolecular hydrogen bond with solvent molecule is formed which produce anomalous bands in two types of solvents.

Acknowledgements

The authors express their deep sense of gratitude to Professor S. Basak, SINP, Calcutta for kindly allowing them to use the fluorescence lifetime measuring instrument. The authors also thank Professor P.C. Mishra, Physics Department, Banaras Hindu University, India for kindly making available MOPAC and CNDUV99 to them.

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