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# Absorption, Fluorescence Studies and Ab Initio Calculations on Binary Mixture of *p*-Dimethylaminobenzaldehyde

A. Anis Fathima · M. Umadevi · V. Ramakrishnan

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**Abstract** Absorption as well as fluorescence emission studies of *p*-dimethylaminobenzaldehyde (DMABA) in solvents with different polarity have been reported by varying the concentration of the solute. Dual fluorescence corresponding to the non-polar (NP) and twisted intramolecular charge transfer (TICT) states has been observed. The optimized geometry of DMABA was evaluated using ab-initio theory at various levels. The optimized geometries of the hydrogen bonded complexes with the solvent molecules were also calculated with the theory Hartree Fock at the basis set 6-31+G (HF/6-31+G). The results have been used to understand the structure of the molecule and the spectral changes in terms of hydrogen bonding and solute–solvent interaction.

**Keywords** *p*-Dimethylaminobenzaldehyde · Twisted intramolecular charge transfer · Absorption spectra · Emission spectra · Solute–solvent interaction

## Introduction

Investigations of solute–solvent interactions are usually carried on employing single or binary solvents. The solute

solvent interaction becomes particularly important when charges are transferred, as in the case of intramolecular electron or proton transfer processes. The former manifests itself in the phenomenon of dual fluorescence, i.e the occurrence of two distinct fluorescence bands, which is found for a large class of organic donor and acceptor compounds in polar solution [1–4]. Compounds containing dimethylamino group have attracted increasing attention due to their many emerging applications [5–11].

4-(Dimethylamino)benzaldehyde (DMABA; Ehrlich reagent) is a fundamental molecule which attracts much attention in various aspects. One of the unique photo physical characters of DMABA is the dual fluorescence in the polar solvents [12]. This phenomenon introduced by Grabowski et al. [13], is interpreted as a result of simultaneous emission from the locally excited state and the intramolecular charge transferred excited state, the later of which is stabilized in polar environment. In polar solvents, DMABA undergoes a twist in the excited state which forces the plane of heavy atoms of the dimethylamino (–NMe<sub>2</sub>) part to become perpendicular to that of the aldehyde group. This is accompanied by a nearly full electron transfer from the amino group to the aldehyde group. The resulting state, known as the TICT state has a very large dipole moment [14]. The TICT state has been extensively studied in Dimethylaminobenzonitrile (DMABN), a compound closely related to DMABA, which has a cyano group in the para position instead of aldehyde group as in the case of DMABA [15–17].

4-(Dimethylamino)benzaldehyde has been employed as a colorimetric probe since at least 1905 when it was used to identify tryptophan due to the product formed through electrophilic aromatic substitution of a hydrogen on the indole ring [18]. Additional colorimetric applications of DMABA may be found in works by Snell and Snell [19],

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and by Pesez and Bartos [20]. It has been used in hydroxyproline assays [21], optical fiber chemical sensors for hydrazine [22], the determination of absolute conformation in primary amines [23], and as a resonance Raman probe of the active site of alcohol dehydrogenase [24, 25]. In DMABA both the electron donating dimethylamino group and the electron accepting aldehyde group contain a limited  $\pi$  system, and therefore are capable of interacting through the benzenoid ring. It may be inferred from the work of Takemura and Baba [26] that in *p*-substituted benzaldehydes and acetophenones, the  $n, \pi^*$  band is little shifted while the lowest transition undergoes a strong shift under the influence of substituents. DMABA forms a dimer in nonpolar or moderately polar solvents even in dilute solutions.

The aim of this study is to investigate the solvent effects on the electronic spectra of DMABA in single solvents and to probe into the mechanism of solute–solvent interactions.

## Experimental

All the solvents used were of analytical purity. The volume fraction (*V*) of DMABA in the solvents were 0.1, 0.2, 0.3, ...1.0 respectively. The optical absorption spectra were recorded using SPECORD S100 diode array spectrophotometer and the fluorescence spectra were recorded in JASCO FP-6300 spectrofluorimeter. All the experiments were performed at room temperature. HF, DFT and MP2 calculations were performed to obtain the optimized geometry of DMABA in the ground state. GAUSSIAN 03W [27] was used. The 6-31G\* basis set was employed for the HF computation. The DFT calculation was performed with Beck's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP) and also the 6-31G\* basis set.

## Results and discussion

Dielectric constants and refractive indices of the pure solvents were taken from literature and given in the Table 1.

**Table 1** Solvent parameters of the different solvents

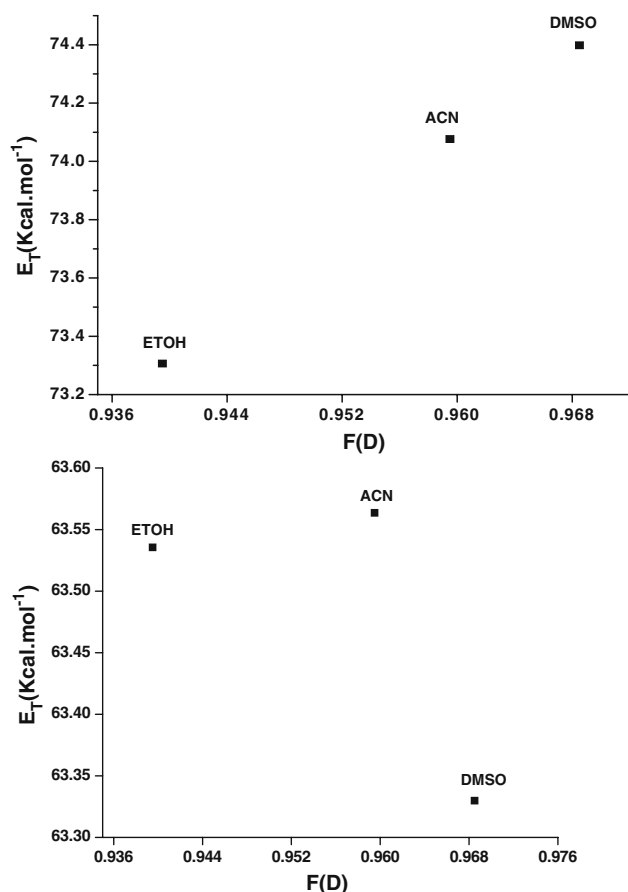
Solvent	<i>n</i>	$\epsilon$	$\mu/D$	$\rho/g\text{ (cm}^{-3}\text{)}$
EtOH	1.36	24.3	1.69	0.789
ACN	1.618	36.6	3.92	0.786
DMSO	1.4785	47.2	3.96	1.092

*n* Refractive index,  $\epsilon$  dielectric constant,  $\mu$  dipolemoment,  $\rho$  density

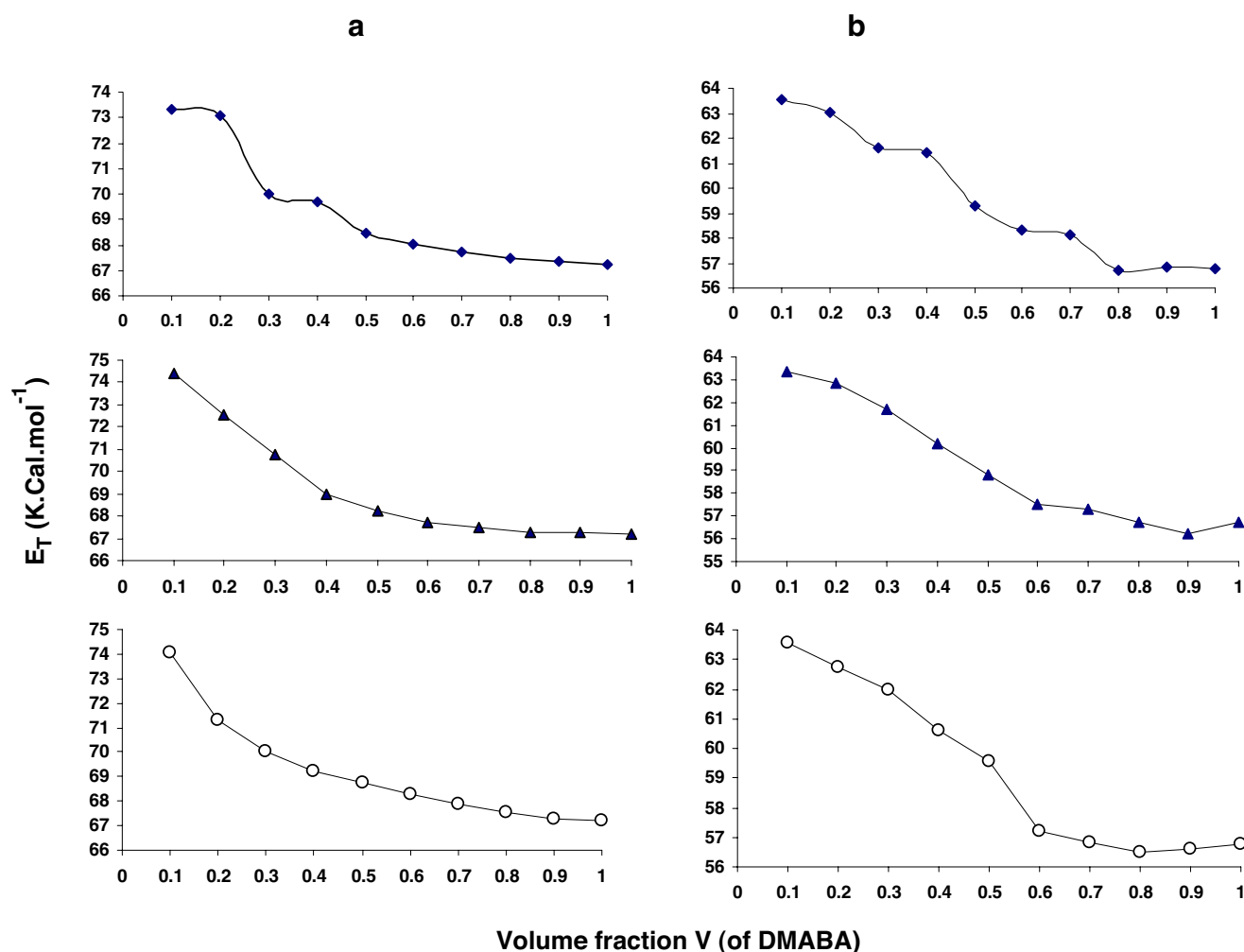
Transition energies  $E_T$  are calculated [28] from the wavelengths of the absorption and emission using the relation given below

$$E_T(\text{kcal.mol}^{-1}) = \frac{28,591}{\lambda_{\text{max}}(\text{nm})}. \quad (1)$$

Figure 1 shows the plot between  $E_T$  and the solvent dielectric polarity  $F(D) = \frac{2(\epsilon-1)}{(2\epsilon+1)}$  in the ground state and the excited state. The position of the pure solvents in the excited state is not same as in the case of the ground state which implies that the strength of the intermolecular hydrogen bond is different from the excited state because of the tortional motion of the groups attached to the benzene ring of DMABA in the excited state. The restriction of charge transfer process from the dimethylamino group due to hydrogen bonding interaction between solvent molecules and the electron lone pair on the donar group [29, 30]. Figure 2 shows that when the concentration of the solvent increases the  $E_T$  value increases in all the three solvents which are polar in nature. The deviation from the linearity in the variation of the  $E_T$  with the volume fraction (*v*) suggests the existence of solute–solvent interactions [31, 32].



**Fig. 1** Plot of ET **a** absorption **b** emission vs  $F(D)$  for DMABA



**Fig. 2** ET For varying volume fraction of DMABA in the ground state (a) and excited state (b) in the three solvents EtOH (square), DMSO (triangle), ACN (circle)

### Estimation of the dipolemoment

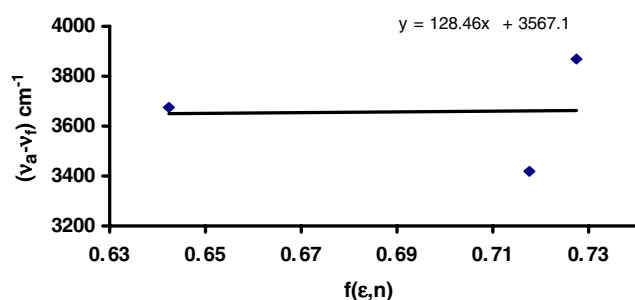
To estimate the ground and excited state dipole moments of the molecule the following equations are used. The equations given below were obtained based on the quantum mechanical perturbation theory of absorption ( $\bar{\nu}_a$ ) and fluorescence ( $\bar{\nu}_f$ ) band shifts (in wave numbers) in different

solvents of varying dielectric constants and refractive index ( $n$ ) as it is used in the previous literatures [33–35].

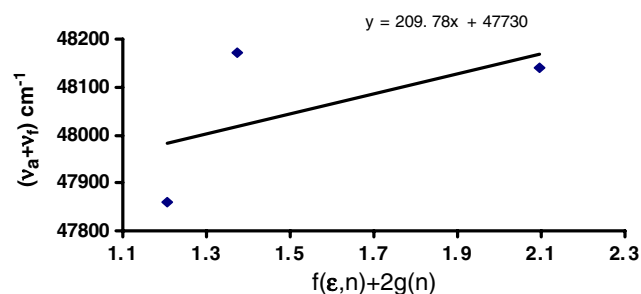
According to Bakshier [36], Chamme and Viallet [37]

$$\bar{\nu}_a - \bar{\nu}_f = m_1 f(\epsilon, n) + \text{const} \quad (2)$$

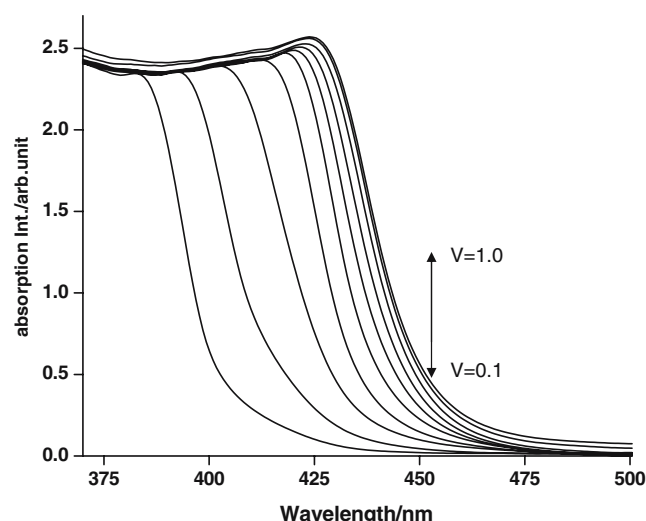
$$\bar{\nu}_a + \bar{\nu}_f = m_2 [(f(\epsilon, n) + 2g(n))] + \text{const} \quad (3)$$



**Fig. 3** Plot of  $(\nu_a - \nu_f)$  versus the solvent polarity function  $f(\epsilon, n)$



**Fig. 4** Plot of  $(\nu_a + \nu_f)$  versus the solvent polarity function  $f(\epsilon, n) + 2g(n)$



**Fig. 5** Absorption Spectra of DMABA in DMSO for varying concentration of DMABA

where

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{n^2 - 1}{n^2 + 2} \frac{2n^2 + 1}{n^2 + 2} \quad (4)$$

$$g(n) = \frac{3}{2} \frac{(n^4 - 1)}{(n^2 + 2)^2} \quad (5)$$

with

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \quad (6)$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \quad (7)$$

where  $\mu_e$  and  $\mu_g$  are excited state and ground state dipole moments of solute molecules respectively. The variable  $h$  is Planck's constant,  $c$  is the velocity of light and  $a$  is the Onsager cavity radius. From Eqs. 6 and 7, the ratio of dipole moments in excited and ground states is given by

$$\frac{\mu_e}{\mu_g} = \left| \frac{m_1 + m_2}{m_2 - m_1} \right| \quad (8)$$

The photophysical parameters have been deduced from the absorption and emission spectra of DMABA in different solvents. Spectral shifts  $\bar{\nu}_a - \bar{\nu}_f$  and  $\bar{\nu}_a + \bar{\nu}_f$  (in  $\text{cm}^{-1}$ ) versus the solvent polarity function  $f(\varepsilon, n)$ ,  $f(\varepsilon, n) + 2g(n)$  are shown in Figs. 3 and 4. The slopes  $m_1$  and  $m_2$  are obtained from the above plots. The ratio of dipole moments of the excited state to the ground state for the present study is found to be 4.15 which means that charge transfer accompanying excitation to the lowest excited singlet state

results in the excited molecule having a greater dipole moment than the ground state [38]. This large change from ground to excited state is caused by the redistribution of atomic charges in excited state which is possible only due to the charge transfer from electron rich donor moiety to acceptor moiety. The value of DMABA reveals an increase in the excited state dipolemoment and confirms the ICT character of the excited state.

#### Absorption and fluorescence spectra

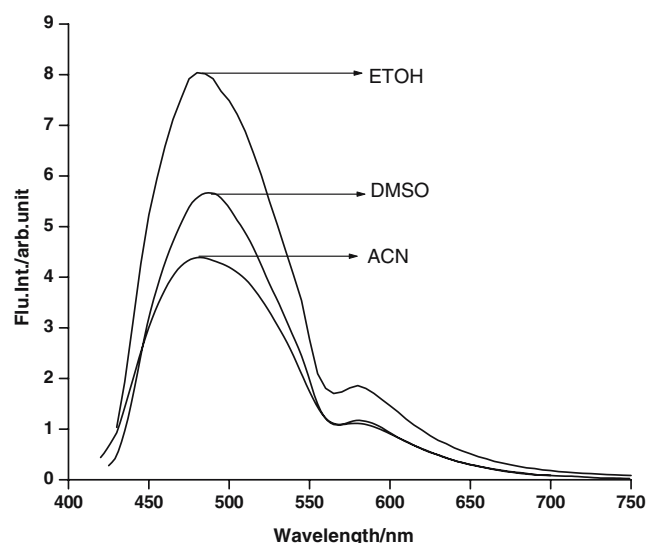
The DMABA gave a broad absorption band in the visible region 380–480 nm. This absorption band should attribute to the charge transfer from the dimethyl amino group to the aldehyde group through phenyl ring in the ground state. The changes in this absorption band are observed in the

**Table 2** Absorption and emission data for DMABA in different solvents

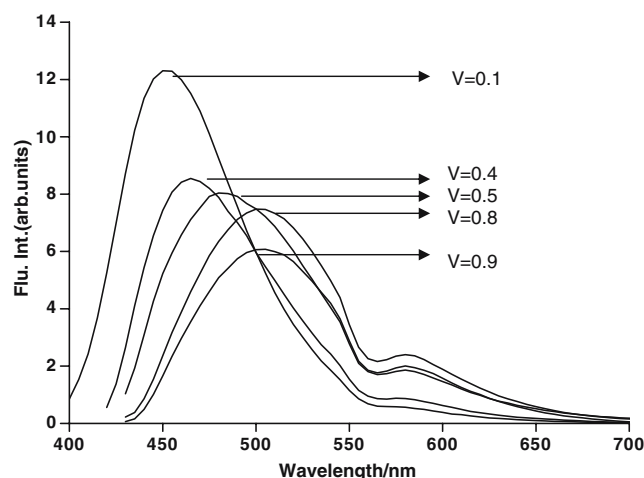
Volume fraction ( $V_{\text{DMABA}}$ )	$\lambda_a$ (nm)	$\nu_a$ ( $\text{cm}^{-1}$ )	$\lambda_f$ (nm)	$\nu_f$ ( $\text{cm}^{-1}$ )	$\Delta\nu$ ( $\text{cm}^{-1}$ )
ETOH					
0.1	390.0	25,639.67	450.0	22,218.76	3,420.90
0.2	391.2	25,563.09	453.6	22,046.34	3,516.74
0.3	408.5	24,480.93	464.0	21,552.65	2,928.28
0.4	410.4	24,369.41	465.5	21,481.35	2,888.05
0.5	417.8	23,937.22	482.3	20,733.55	3,203.67
0.6	420.4	23,789.28	490.1	20,403.99	3,385.28
0.7	422.1	23,690.12	491.8	20,331.81	3,358.31
0.8	423.6	23,604.80	503.9	19,842.45	3,762.35
0.9	424.6	23,552.07	502.8	19,888.22	3,663.84
1.0	425.3	23,511.70	503.7	19,852.69	3,659.01
DMSO					
0.1	385.9	25,909.04	449.80	22,232.03	3,677.01
0.2	401.0	24,934.88	455.86	21,936.25	2,998.63
0.3	408.5	24,482.58	461.42	21,671.95	2,810.63
0.4	413.2	24,202.40	471.78	21,196.32	3,006.08
0.5	415.9	24,041.64	480.12	20,827.85	3,213.78
0.6	418.7	23,882.99	499.96	20,001.44	3,881.55
0.7	421.0	23,751.22	503.24	19,870.87	3,880.34
0.8	423.3	23,625.50	506.06	19,760.31	3,865.19
0.9	424.8	23,539.12	505.12	19,797.02	3,742.09
1.0	425.3	23,511.70	503.71	19,852.69	3,659.01
ACN					
0.1	384.3	26,021.64	451.5	22,150.25	3,871.38
0.2	393.9	25,382.33	455.1	21,972.79	3,409.54
0.3	404.2	24,740.83	463.2	21,589.18	3,151.64
0.4	414.4	24,133.02	475.1	21,049.43	3,083.58
0.5	418.9	23,868.50	486.2	20,568.03	3,300.47
0.6	422.0	23,695.01	496.9	20,125.69	3,569.31
0.7	423.8	23,596.76	499.2	20,032.54	3,564.22
0.8	424.8	23,538.88	504.2	19,831.75	3,707.12
0.9	425.0	23,528.96	508.3	19,673.30	3,855.66
1.0	425.3	23,511.70	503.7	19,852.69	3,659.01

solvents ETOH, DMSO, ACN with varying concentration of these solvents. The absorption spectrum of DMABA in DMSO solvent is shown in Fig. 5 and the corresponding spectroscopic data are presented in Table 2. The absorption spectrum of DMABA in different solvents undergoes a blue shift with increasing concentration of the solvents. Diazo amino benzene derivatives containing intramolecular charge transfer chromophores, therefore, the presence of electron donating and withdrawing moieties will have appreciable effect on their UV–Vis absorption bands.

The transition energy gradually decreases with the increase of the volume fraction of DMABA (Fig. 2) which suggests a possible interaction between the solute and the solvent molecule. As EtOH is a polar protic solvent which can readily give a proton to the carbonyl oxygen of the solute to form O–H...O=C type hydrogen bond. DMSO differs from the other group of solvents used as its dielectric constant and its polarizability are appreciably greater than the other two solvents. The energy of a charge transfer will increase as the strength of such hydrogen bonds increases. CH<sub>3</sub>CN molecules being very small have an exceptionally large dipole moment in the non associated free molecular case. These molecules can form a dimer through self association owing to the strong dipole–dipole interaction between these molecules. These dimers are non polar in nature and hence reduces the polarity of the solvent molecules in the associated CH<sub>3</sub>CN [39]. The observed shifts of the electronic absorption bands of organic compounds induced by solvents are commonly understood as an indication of the extent of charge reorganization of solute molecules upon electronic excitation [40]. The observed shifts in the electronic absorption spectra is an indication of influence of the reorganization of the solvent molecule on the instantaneous charge reorganization of



**Fig. 6** Representative Emission Spectra of DMABA in different solvents at  $V=0.5$



**Fig. 7** Emission Spectra of DMABA in EtOH for varying concentration of DMABA

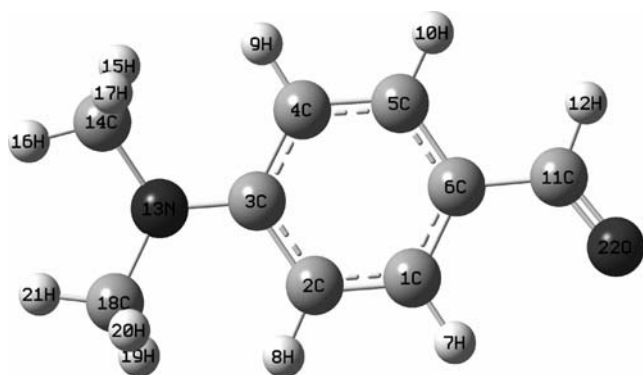
solute molecule upon electronic excitation while varying the concentration of the DMABA.

The emission properties of the solute have changed significantly as the solvent composition is gradually varied. Figure 6 shows the emission spectra of DMABA in all the three solvents which show two peaks. The  $\lambda_{\text{max}}$  observed around 500 nm is ascribed as LE state and the second maximum observed around 580 nm is known as the emission wavelength from the TICT state. As can be seen from the Fig. 7, the peak in the lower wavelength of the fluorescence spectrum suffers a strong hypsochromic shift as the concentration of the solvent is increased in the binary mixture but there is no appreciable shift in the  $\lambda_{\text{max}}$  of the TICT state. The dipole–dipole interactions and the hydrogen bonding with the solute molecules especially in their excited states will encounter for the blue shifts observed in these solvents as in the case of absorption spectra.

#### Theoretical calculations

Quantum chemistry provides a concept to understand the phenomena for achieving and understanding the fundamental bonds in general, and hydrogen bonds in particular [41]. The ground state geometries for DMABA is optimized by the gradient procedure at the second order level of closed shell Moller–Plesset (MP2) perturbation theory employing 6-31+G basis set. Figure 8 represents the optimized geometry of DMABA optimized at the MP2 level. Optimized geometries calculated at the levels HF/6-31+G, MP2/6-31+G and DFT/6-31+G are summarized in Tables 3 and 4. Going from HF through MP2 to DFT generally there is an increase in the bond length. The angles change irregularly. The minimum energies and dipole moment calculated at these levels are also given in the Table 3. From these we can interpret that the minimum energy is observed in the optimized geometry of DMABA at MP2 levels. The





**Fig. 8** Optimized Geometry of DMABA in MP2 level

dipole moment shows an increase when the energy level increases from HF to DFT through MP2.

#### Solute–solvent interaction—theoretical interpretation

Theoretical calculations in the presence of solvent also provide a wealth of information on molecular properties in liquid state. Ab-initio calculations have been used to examine the energies and the vibrational spectra of monomers as well the clusters. The ground state optimized geometries of characteristic intermolecular interactions of DMABA with the solvent molecules are given in the Fig. 9

**Table 3** Bond length for ground state DMABA calculated by HF, MP2 and DFT methods using 6-31G\* basis set

Bond length	HF	MP2	DFT B3LYP
$r(1, 2)$	1.377521	1.403123	1.380045
$r(2, 3)$	1.412944	1.434801	1.419752
$r(3, 4)$	1.408882	1.430712	1.416778
$r(4, 5)$	1.381459	1.406738	1.383341
$r(5, 6)$	1.392283	1.417065	1.402856
$r(1, 7)$	1.072983	1.092103	1.096910
$r(2, 8)$	1.069203	1.089177	1.093974
$r(4, 9)$	1.069163	1.089120	1.093683
$r(5, 10)$	1.075567	1.094536	1.098373
$r(6, 11)$	1.459091	1.477530	1.443836
$r(11, 12)$	1.086912	1.108117	1.120428
$r(3, 13)$	1.373723	1.414467	1.367839
$r(13, 14)$	1.454500	1.479185	1.443393
$r(14, 15)$	1.085299	1.097807	1.108961
$r(14, 16)$	1.078352	1.095258	1.099953
$r(14, 17)$	1.085317	1.105490	1.108961
$r(13, 18)$	1.455138	1.479976	1.443836
$r(18, 19)$	1.085077	1.097641	1.108844
$r(18, 20)$	1.085109	1.105192	1.108843
$r(18, 21)$	1.078379	1.095264	1.100044
$r(11, 22)$	1.222529	1.269032	1.249133
Energy/Kcal.mol <sup>-1</sup>	-476.3356	-477.3782	-476.7938
Dipolemoment/D	6.66	6.77	7.73

The experimentally calculated ground state dipolemoment of DMABA is  $\mu=5.6D$  [1]

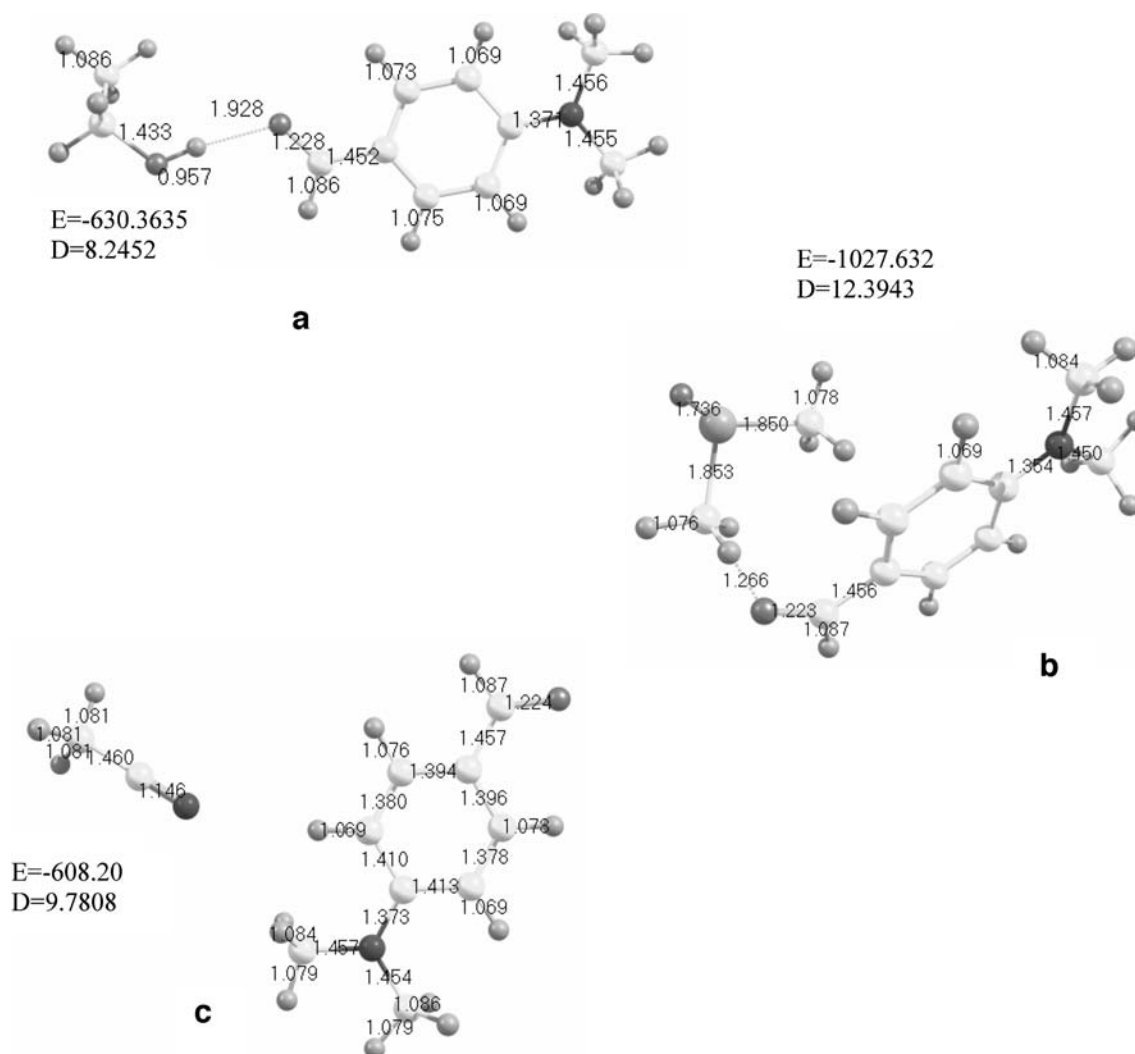
**Table 4** Bondangle for ground state DMABA calculated by HF, MP2 and DFT methods using 6-31G\* basis set

Bond angle	HF	MP2	DFT
$\theta(3-2-1)$	120.888655	121.055182	120.520533
$\theta(4-3-2)$	117.634985	117.642138	118.433689
$\theta(5-4-3)$	120.541864	120.649848	120.188762
$\theta(6-5-4)$	121.605503	121.232611	121.230049
$\theta(7-1-2)$	119.902400	120.005451	121.370584
$\theta(8-2-1)$	118.797972	118.374432	119.570777
$\theta(9-4-3)$	120.542730	120.731118	120.084390
$\theta(10-5-4)$	118.810817	119.102912	119.939144
$\theta(11-6-5)$	120.414518	119.578650	120.245799
$\theta(12-11-6)$	115.842416	115.973099	115.057389
$\theta(13-3-2)$	121.115925	121.033816	120.72499
$\theta(14-13-3)$	120.359916	119.102676	119.906353
$\theta(15-14-13)$	111.584086	110.430108	111.730245
$\theta(16-14-13)$	109.162532	108.269125	109.328994
$\theta(17-14-13)$	111.590827	112.345552	111.730359
$\theta(18-13-3)$	120.463991	119.205999	120.055749
$\theta(19-18-13)$	111.597636	110.535828	111.794508
$\theta(20-18-13)$	111.602635	112.292088	111.793920
$\theta(21-18-13)$	109.112735	108.219422	109.270964
$\theta(22-11-6)$	124.978387	124.902	125.118930

as they were calculated by employing HF theory at 6-31+G basis set. Figure 9a shows the hydrogen bonded complex of the DMABA with ethanol molecule. One hydrogen bond is formed between H atom of the EtOH and the O atom of the DMABA. The hydrogen bond length in this configuration is being 1.928 Å, which is said to be a strong hydrogen bond. The C=O distance in the DMABA has been increased from 1.223 to 1.228 Å. In the case of DMSO solvent also there is a possibility of hydrogen bond between the H atom in the alkyl branch of DMSO and the carbonyl oxygen of the solute molecule and the hydrogen bond length in this case is 1.266 Å (Fig. 9b), which is a very strong hydrogen bond. In the case of ACN there is no formation of hydrogen bonded complex of DMABA Fig. 9c. There is no change in the bond length of solute as well as solvent. From these we can conclude that the DMSO molecule strongly interact with the DMABA than the other two molecules. The weaker hydrogen bond with the ethanol molecule than the DMSO is due to the alkyl group attached to the ethanol molecule and the lower dipole moment than the DMSO.

#### Dipolemoment calculation

The dipole moment of the DMABA computed at HF/6-31G\* level of theory in different environment are given in Table 5. In addition to this the optimization also has been done at HF/6-31G\*. The plot between calculated dipolemoment to the dielectric constant of the various solvent used is

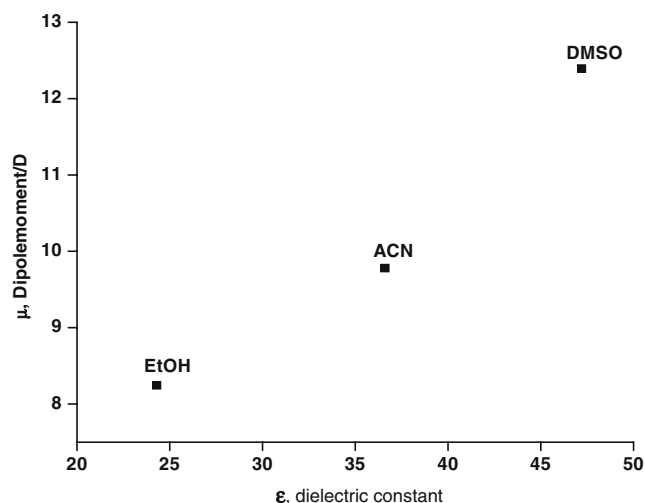


**Fig. 9** Hydrogen bonded complexes of DMABA with solvent molecules. **a** Hydrogen bonded complex of the DMABA with ethanol molecule. **b** In the case of DMSO solvent also there is a possibility of hydrogen bond between the H atom in the alkyl branch of DMSO and the carbonyl oxygen of the solute molecule. **c** In the case of ACN there is no formation of hydrogen bonded complex of DMABA

shown in the Fig. 10. The dipole moment of the system increases as the dielectric constant of the surrounding medium increases. The permanent dipolemoment of the solute induces a dipole moment in the surrounding medium, which in turn will interact with the dipole moment of the solvents.

**Table 5** Calculated dipolemoment and energy value of the DMABA complexes

Solvent	$\mu/D$ (neat)	$\epsilon$	$\mu/D$ (binary)	Energy/K. Cal. $\text{mol}^{-1}$ (binary)	Energy/K. Cal. $\text{mol}^{-1}$ (neat)
EtOH	1.69	24.3	8.2452	-630.36	627.34
ACN	3.92	36.6	9.7808	-608.20	608.19
DMSO	3.96	47.2	12.3943	-1027.63	1,027.73



**Fig. 10** Plot between dielectric constant of the solvent Vs dipolemoment of the DMABA in different solvents



## Conclusion

Absorption and emission spectra of DMABA in different solvents were taken by varying the concentration of the solvents. The  $\lambda_{\text{max}}$  in both the spectra was blue-shifted when the concentration of the solvents is increased in the binary mixture. The feature is given as due to the formation of hydrogen bonding and the dipole–dipole interaction between the solute and the solvent molecule. Optimized geometry of the DMABA were calculated and tabulated for different level. The ratio of the dipole moments between the excited state to the ground state is calculated which shows that  $\mu_e > \mu_g$ . The optimized geometries of the hydrogen bonded complexes of the DMABA are also calculated at HF/6-31+G basis set. Their ground state dipolemoment and energies were evaluated at this level.

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