ORIGINAL PAPER

Excitation Wavelength Dependence of Dual Fluorescence of DMABN in Polar Solvents

Tesfay Atsbeha · Ahmed M. Mohammed · Mesfin Redi-Abshiro

Abstract Steady-state absorption, fluorescence excitation and emission spectra of 4-(*N,N*-dimethylamino)benzonitrile (DMABN) have been measured at room temperature in cyclohexane, 1,4-dioxane, dichloromethane, and acetonitrile solutions. The fluorescence spectra of DMABN are found to exhibit dual emission in 1,4-dioxane, dichloromethane, and acetonitrile solutions and single emission in cyclohexane solution. The effect of solvent polarity and excitation wavelength on the emission spectra has also been studied. The fluorescence excitation spectra of DMABN monitored at the emission bands are different. The presence of two different conformations of the same molecule in the ground state has lead to two close lying excited states; local excited (LE) and charge transfer (CT), and thereby results in the dual fluorescence of the compound. The experimental studies were supported by ab initio density functional theory (DFT) calculations performed at the B3LYP/6-31Gd level of theory. On the basis of the experimental results and our theoretical calculations, we suggest that there are two conformers of DMABN, which are stable in the ground state, equilibrated in solution at room temperature that give rise dual fluorescence upon excitation.

Keywords Dual fluorescence · DMABN · Solvent effects · Excitation wavelength dependency

T. Atsbeha · A. M. Mohammed · M. Redi-Abshiro (✉)
Department of Chemistry, Addis Ababa University,
P .O. Box 1176, Addis Ababa, Ethiopia
e-mail: mesfinr@chem.aau.edu.et

Introduction

The interest in the spectroscopic properties of 4-(*N,N*-dimethylamino)benzonitrile (DMABN) has attracted increasing attention since the first experimental observations by Lippert et al. [1] The main findings of these experiments were an abnormal emission (^1L_a-type according to Platt's notation [2]) in polar solvents, red-shifted from the normal ^1L_b-type fluorescence. The origin of the dual fluorescence observed first in DMABN and later in a large number of other electron donor-acceptor compounds continues to puzzle workers in the field [3], but DMABN still remains one of the most studied cases. The mechanism behind such a phenomenon is highly controversial and has been the subject of many experimental [1, 4–36] and theoretical studies [37–60]. Several models have been proposed to explain the unusual behavior of DMABN and of related compounds initially based on chemical intuition and more recently supported by quantum chemical calculations [37–60]. Two leading models appear to prevail at this time; the twisted intramolecular charge transfer (TICT) and the planar intramolecular charge transfer (PICT).

The TICT model proposed by Grabowski and co-workers [6–12] explains the dual fluorescence as occurring by means of an adiabatic transition leading to two conformations differing in the dihedral angle between the amino group and the phenyl ring. According to the TICT model the initially promoted excited state yields another minimum on the energy surface by twisting the dialkylamino group from a planar (or nearly planar) to a perpendicular position with respect to the benzonitrile ring. The twisting is accompanied by an intramolecular charge transfer (CT) from the donor (the amino group) to the acceptor moiety (the benzonitrile group) in the excited state. The resulting state (also called CT state), character-

ized by a large intramolecular charge separation and an increased dipole, can be stabilized by polar solvents, thus leading to the observed "anomalous" ^1L_a-type fluorescence band. The "standard" ^1L_b-type, on the contrary, is assigned to the less polar locally excited (LE) state, where no twisting has occurred.

An alternative explanation to TICT has been proposed by Zachariasse et al. [16–27, 33, 34] According to the authors, the phenomenon is based on a solvent-induced vibronic coupling between LE and CT states achieved by a sufficiently small energy gap between the two states. In combination with the presence of a promoting mode such as N-inversion of the amino group (usually indicated as wagging motion), this coupling causes a splitting of the quasi-degenerate levels and thereby a considerable energetic stabilization of one state. This represents the charge transfer state leading to the second fluorescence band. In this connection, the term pseudo Jahn -Teller coupling has been introduced even if the authors use the PICT acronym where P stands for planar. Experimental evidence advanced for both models has been largely circumstantial, as direct measurement of the structure of the emitting species turns out to be experimentally difficult.

Nonetheless, equally convincing indirect evidence has been presented for the TICT and PICT models. For instance, by a suitable construction, Dobkowski et al. [61] showed that the CT process is accompanied by syn-anti isomerization around the C_{phenyl}-N bond in the photo-isomerization of 2-(N-methyl-N-isopropylamino)-5-cyano-pyridine, a process that implies the intermediacy of a perpendicular moiety. On the other hand, Yoshihara et al. [35] showed that a planarized molecule that cannot attain a perpendicular geometry exhibits dual emission. The planar rigidized molecule fluorazene (FPP) was shown to undergo fast reversible intramolecular charge transfer (ICT) in the excited state, similar to that of its flexible counterpart N-phenylpyrrole (PP). This result shows that intramolecular charge transfer to a planar ICT state can occur efficiently and thus convincingly demonstrates that large amplitude motions such as those necessary for the formation of a TICT state are not required.

Experimentally, from picosecond infrared [30] and resonance Raman [31] measurements, and calculations of IR frequencies [46], it was concluded that the N-phenyl bond has a single-bond character in the ICT state, which would support the TICT model. Theoretical computations [47] suggest that the ICT state has a strong quinoidal character in the phenyl moiety (which would favor the PICT structure), and a decrease of quinoidality would be expected when the amino group was decoupled from the rest of the molecule in TICT. In their calculations, Zilberg and Haas [47] could only find a planar quinoid ICT state on the S_2 surface of ABN and no quinoidal TICT structure.

However, several calculations [46, 48, 49] have found a quinoidal TICT state on S_1, including the most recent correlated CC2 (coupled-cluster singles and doubles) calculations by Köhn. [49] Thus, the twisted conformation of the amino group and the quinoidality of the phenyl ring may not be as contradictory as first thought.

Theoretical contributions have also given some insight as to the nature of the ICT reaction coordinate. As a general rule, most theoretical studies point toward the amino group twist as the reaction coordinate along which a state switch occurs (either at conical intersection or at an avoided crossing giving rise to a transition state) between the LE and ICT states and leads to a low-lying TICT state [38, 41, 43, 44, 46, 49, 59, 60]. However, recent high level ab initio calculations have suggested that those two states can cross along the pyramidalization of the ring carbon atom to which the dimethylamino group is attached, without the twisting motion [49]. Thus, this pyramidalization coordinate constitutes another possible decay path after initial vertical excitation to the L_a-type state.

More recently, Cogan et al. [62] pointed out that the benzene ring was not acting merely as a spacer between the donor and the acceptor but is essential for understanding the electronic structure of the excited states. This idea that the benzene ring is the principal electron acceptor leads naturally to the four distinct lowest lying electronic excited states in these systems: two are principally of LE nature, whereas the other two are CT-types. It is shown that both planar and twisted forms of the molecule in the CT state may be fluorescent, depending on the structure of the system and on environmental parameters such as the solvent. Further, their model predicts also the existence of a perpendicular quinoid (Q)-form having a large dipole moment. The emitting charge transfer state is due to the transfer of an electron from the donor group to the benzene ring, creating a derivative of the benzene anion radical. Two electronic states are necessarily formed as a consequence of the Jahn-Teller distortion of the benzene anion radical: one has a quinoid structure, the other, an antiquinoid one. The model provides a simple explanation for the direct excitation of the CT states (i.e. not via the LE state) observed in supersonic jets and in argon matrixes.

Despite this effort and numerous papers devoted to this subject published over several decades, the mechanism of the process responsible for the dual fluorescence in polar solvents still is not well understood. All the models gave conflicting interpretations of the dual fluorescence phenomenon in DMABN.

The different methods proposed focus exclusively on the excited state structural rearrangements and give little or no consideration on the ground state possible structural isomers. In this work, the excitation wavelength dependence of dual fluorescence of DMABN in different solvents

is reported. We have investigated dual fluorescence of DMABN in those solvents from the perspective of ground state structural isomeric structures, and DFT calculations are applied to understand qualitatively its photophysical properties.

Experimental details

DMABN was purchased from Aldrich. Samples were prepared in 1 cm quartz cuvettes at concentrations providing optical densities of less than 1 and 0.2 for absorption and fluorescence measurements, respectively.

Absorption measurements were made using a Spectronic Genesys 2PC UV-Vis spectrophotometer with a resolution of 1 nm. Emission and excitation spectra were recorded with a FluoroMax-4 spectrofluorometer. Solvent blanks were subtracted from the emission spectra prior to analysis. Emission spectrum was recorded by keeping the excitation wavelength fixed and varying the emission wavelength. Excitation spectrum was recorded by keeping the emission wavelength fixed and scanning the excitation wavelength.

In the present work it is shown that the DMABN molecules in a polar solvent possess two distinct fluorescence properties. Solutions of DMABN in a non polar solvent, cyclohexane, and polar solvents, acetonitrile, dichloromethane, and dioxane at room temperature and concentrations between of 10^{-5} and 10^{-3} M were investigated.

Computational details

All structural and potential energy surface calculations were performed using the GAUSSIAN 03 W program package [63]. The ground state geometry optimizations were performed at the DFT level with the exchange correlation functional of Becke, and Lee, Yang, and Parr, in its hybrid form, i.e., with inclusion of non-local corrections and some portion of exact Hartree-Fock exchange (B3LYP) [64, 65] as implemented in the program package, coupled with 6–31G(d) basis set. For the ground state calculations, bulk solvation effects were accounted for using the integral equation formalism polarizable continuum model (IEF-PCM) [66].

Calculations on potential energy surfaces (PES) were pursued along the twist coordinate at the donor site. We have used rotational angle θ (shown in Scheme 1) to get the twisting of the donor ($-NMe_2$). The angle was θ varied from 0 to 180° with a step of 30°. It is defined by $(\theta_1 + \theta_2)/2$, where θ_1 represents the dihedral angle 3–4–9–10 and θ_2 corresponds to 5–4–9–11.
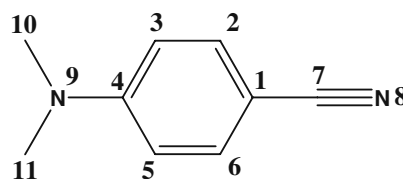
Scheme 1 Chemical structure of *p*-dimethylaminobenzonitrile (DMABN)
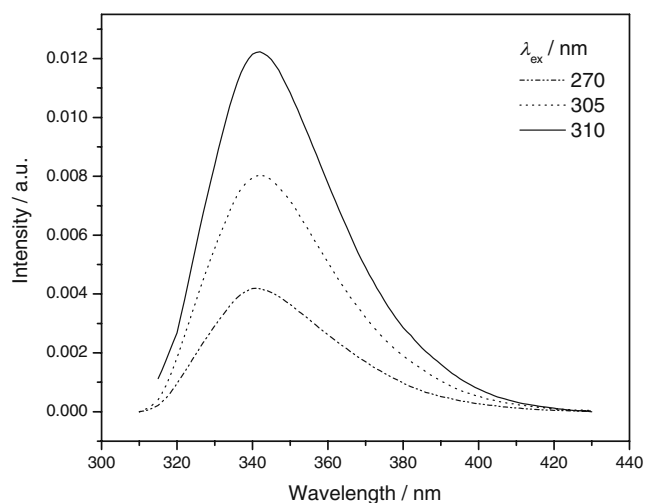
Results and discussion

Emission spectra

A series of fluorescence emission spectra of DMABN were obtained at different excitation wavelengths in solvents of varying polarities, and the effects of polarity and variation of wavelength on the emission behavior were examined. The fluorescence spectra of DMABN in cyclohexane and acetonitrile solvents are shown in Figs. 1 and 2, and peak positions are listed in Table 1. As can be seen from the figures, the emission spectra of the compound are very much influenced by solvent as well as the wavelengths of excitation.

Figure 1 presents the spectra of the emission bands of DMABN in a solution of a nonpolar solvent cyclohexane upon excitation at different wavelengths. Only the band of locally excited state emission at 342 nm is observed, and its spectrum is found to be independent of the excitation quanta upon change in the wavelength from 270 to 310 nm. The contour of the luminescence excitation bands also remains unchanged by the overlapping of the emission spectra.

There is a different situation for DMABN in polar solutions. The fluorescence spectrum from the solution of acetonitrile (Fig. 2), for instance consists of two bands centered at λ_{em}=353 and 469 nm and their intensities seem to depend significantly on the excitation wavelengths. Increasing the excitation wavelength leads to a change in the intensity ratio of the two bands, indicating that the bands represent the emitting levels that originate from two different electronic states. The most interesting property of spontaneous emission by DMABN is the unusually strong dependence of emission bands on the exciting light wavelength in the range 260–310 nm in acetonitrile.

The character of the changes relates to both emission bands and appears as follows. First, the ratio of the intensity maxima of the components I_{LE}/I_{CT} decreases in favor of the charge-transfer (CT) band. At λ_{ex}=260 nm the spectrum is mainly composed of the LE emission. A subsequent increase in λ_{ex} to 280 nm and then to 300 nm causes a further increase in the intensity of the CT band at the expense of the LE band, and at λ_{ex}=310 nm the spectrum is essentially CT emission band with a small shoulder that
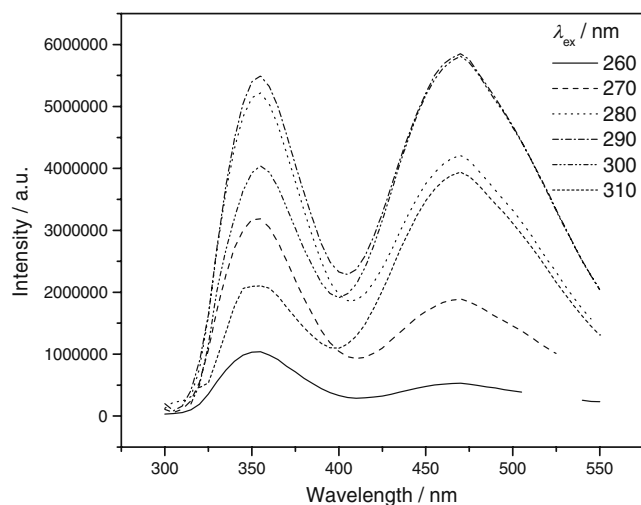
Fig. 1 Emission spectra of DMABN in cyclohexane at different excitation wavelengths

**Table 1** Emission maxima for the LE and CT emissions respectively of DMABN in various solvents

Solvent	λ_{max} (LE)	λ_{max} (CT)
Cyclohexane	342	
1,4-Dioxane	355	426
Chloroform	354	433
Dichloromethane	350	432
Acetonitrile	353	469
Ethanol	354	460

corresponds to LE band. This excitation wavelength dependence of the intensity ratio does not represent an emission from the vibronic levels, in which case the I_{LE}/I_{CT} ration should not vary significantly, rather suggests the existence of more than one structures at the ground state that are responsible for the observed dual emission.

Similar excitation wavelength dependence was observed in spectra recorded in solvents of differing polarities with Stokes shift corresponding to the polarity of the solvents, accompanied by a dramatic decrease in intensity of the LE band and an increase in the CT band. The values are summarized in Table 1. The observed large solvatochromic shift for CT fluorescence is an indication of a high degree of charge-transfer for the emitting state.

In order to estimate the number of possible structures area-normalization of the spectra was carried out and the

result is depicted in Fig. 3. In Fig. 3, a single isosbestic point is observed at about λ_{em}=388 nm, indicating only two emissive species exist in the excited state.
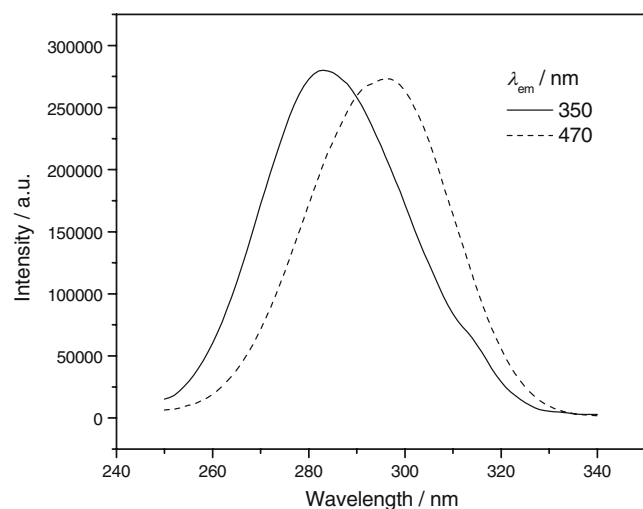
Excitation spectra

Excitation spectra for solution of DMABN in acetonitrile were monitored at different emission wavelengths. At emission wavelengths of λ_{em}=350 nm and 470 nm corresponding to the LE and CT emission bands respectively, the excitation spectra resemble the typical absorption spectrum, except that they are shifted relative to that of absorption, conforming that the emission bands originate from completely different species (Fig. 4).

To further verify this result, 3D emission spectral studies were performed. The 3D spectra recorded for DMABN in cyclohexane and acetonitrile solutions are shown in Fig. 5a. In cyclohexane, only one contour is observed for DMABN. The corresponding excitation spectrum shows only one band at 281 nm, and the emission spectrum shows an emission at 342 nm. In acetonitrile, two contours were observed as shown in Fig. 5b, and the corresponding

Fig. 2 Emission spectra of DMABN in acetonitrile at different excitation wavelengths
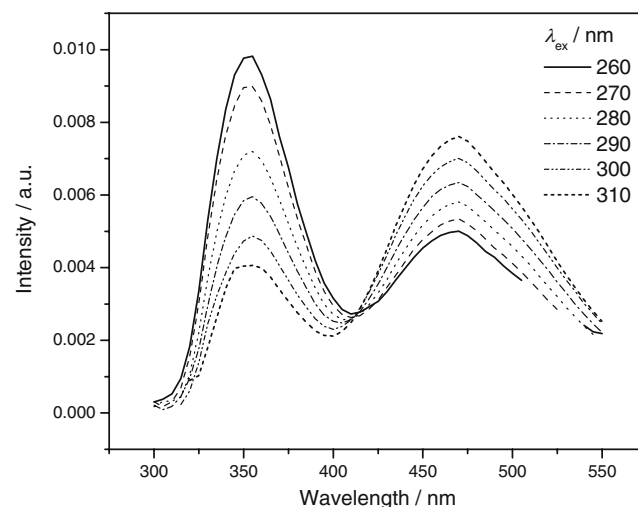
Fig. 3 Area normalized emission spectra of DMABN in acetonitrile

Fig. 4 Excitation spectra of DMABN in acetonitrile and different emission wavelengths

dipole difference between the ground and the excited state the larger will also be the solvent induced red shift. Quantitative determination of the dipole difference may be done using the Eqs. 1 and 2. [69–71]

$$\widetilde{\nu}_{flu} = \widetilde{\nu}_{flu}^0 - \frac{2\mu_e\left(\mu_e - \mu_g\right)}{4\pi\varepsilon_0 a_0^3 \times hc}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \quad (1)$$

where h is Plank's constant, c is the speed of light, $\widetilde{\nu}_{flu}$ and $\widetilde{\nu}_{flu}^0$ are the solvent equilibrated fluorescence maxima and the value extrapolated to gas phase conditions, respectively; the superscript "0" indicates the absence of a solvent (free molecule), μ_g and μ_e are the ground-and excited-state dipole moments, a_o is the radius of the Onsager cavity, ε is the static dielectric constant, and n is the index of refraction of the solvent. The approximation used (rigid point dipole in the center of a spherical Onsager cavity) neglects the

excitation spectrum shows two bands at 285 and 293 nm. The excitation band observed at 285 nm corresponds to LE emission at 353 nm. The excitation band observed at 293 nm corresponds to CT emission at 496 nm (charge transfer between dimethylamino and benzonitrile group).

The excitation and 3D spectra confirm the presence of two species of the same molecule in the ground state. The overlapping of electronic absorption of two species leads to the dual fluorescence at all wavelengths of excitation in the region ~270–330 nm. At the blue edge of excitation, LE-state fluorescence dominates, but at the red edge of excitation, CT-state emission dominates.

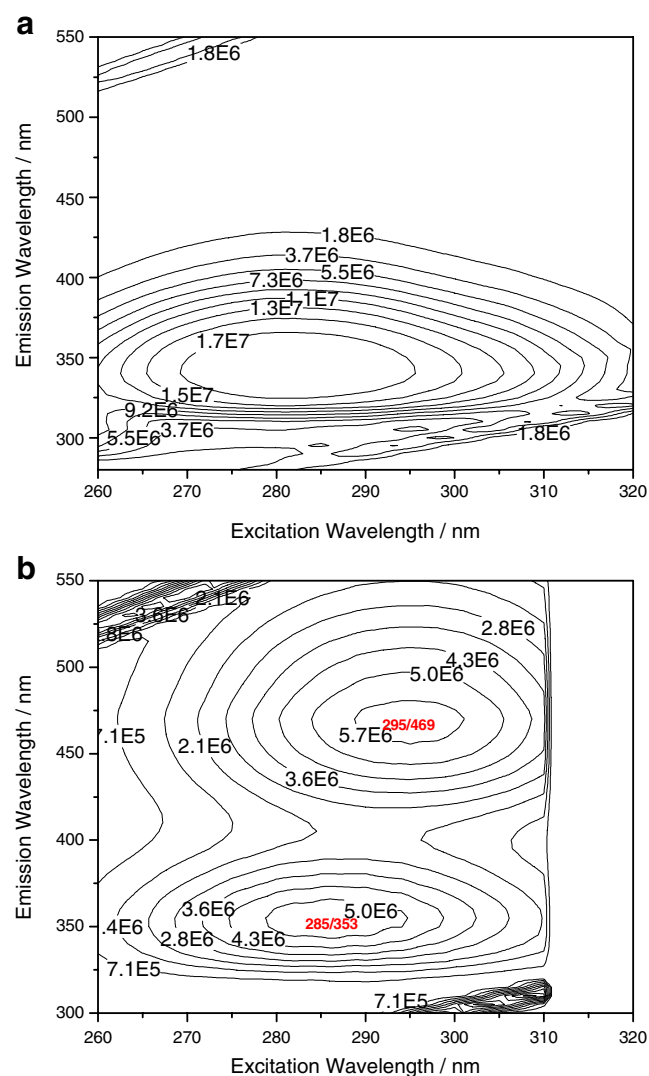Solvatochromic shift and excited-state dipole moments

In order to study the role of polarity in modifying the electronic states of the compound, a series of absorption spectra were recorded in cyclohexane, 1,4-dioxane, dichloromethane, and acetonitrile solutions of different polarity (Fig. 6). The λ_{max} is found to increase with increasing the polarity of the solvents from cyclohexane (280 nm) to dichloromethane (293 nm). Fluorescence spectra were obtained for DMABN in five solvents of varying polarities. The spectra show large solvatochromic shift for the CT fluorescence, indicating a high degree of charge-transfer for the emitting state. The excitation spectra show features corresponding to those in the absorbance spectra, demonstrating that the emissions are not due to impurities.

The red shift observed in the fluorescence spectra with an increase in solvent polarity depends on the difference in permanent dipole moments of the ground and excited state, and this is in accordance with the theory of dielectric polarization [67, 68]. According to this theory the larger the

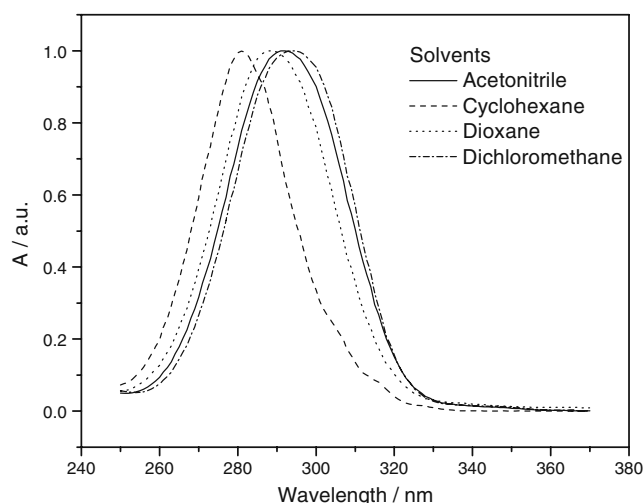**Fig. 5** 3D spectra contour plot of DMABN in cyclohexane (**a**) and Acetonitrile (**b**)

polarizability of the solute. Figure 6 shows a satisfying linear correlation between the energy $hc\tilde{v}_{flu}^{CT}$ and the solvent polarity function $\{f(\varepsilon) - 0.5f(n)\}$, where

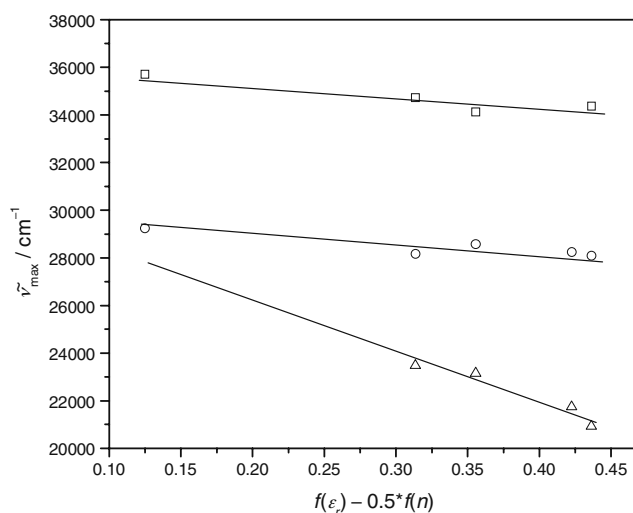$$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1}; f(n) = \frac{n^2 - 1}{2n^2 + 1} \qquad (2)$$

The expressions 1 and 2 relate the measured quantities to the excited-state dipole moments μ_e.

The plot of absorption and fluorescence shift versus Lippert-Mataga solvent polarity parameter for the L_a and L_b states is shown in Fig. 6. The slope obtained for absorption and LE emission was found to be comparable which shows that the dipole moments of the LE and ground states are similar. The slope obtained for the LE and CT states are found to be $-3,361$ cm^{-1} and $-20,090$ cm^{-1}, respectively. The slope is about six times larger for the CT state than the LE state emission. The higher value of the slope is indicative of the fact that the long wavelength band is characterized by a larger charge transfer degree; i.e. the L_b state is more polar than the L_a state. From the slopes of the plot the values of the excited state dipole moments μ_e, estimated with the effective radius of the spherical Onsager cavity $a_0 \approx 0.45$ nm (as calculated by density functional theory employing B3LYP with a 6–31G(6) basis set) are calculated to be $\mu_e = 9.7$ D and $\mu_e = 17.2$ D for the L_a and L_b states, respectively, by adopting the value 6.6 D for the ground state dipole moment (μ) measured for DMABN [19] (Fig. 7).

These results strongly support the hypothesis of the existence of the equilibrium between two species formed in the ground state and which both fluoresce when they are excited. It was found out that the property of the emission spectrum is strongly dependent on the wavelength of the exciting light. This dependency of emission spectrum on

Fig. 7 Dependence of solvatochromic shift of the energy related to absorption (□) and fluorescence maxima of LE (○) and CT (△) bands of DMABN

the wavelength of the exciting light and the presence of the isoemissive as well as isoabsorptive points can only be explained by the presence of two relatively stable systems in equilibrium. Therefore, this fact together with the existence of two excitation bands indicates that DMABN has two stable conformers in the ground state, which are in equilibrium. The calculation confirms also this hypothesis. In the previous models, the observed red shift of the fluorescence spectrum should occur independent of where in the absorption band the molecule is excited. If several ground state conformers of DMABN are populated, the overall spectrum must be a sum of the individual conformer spectra. This might explain the strong excitation-wavelength dependence of the corresponding spectra of DMABN even in a non-polar medium.

Computational results

In this study, the reaction coordinate is defined as the tortional angle between the plane of dimethyl amino group and that of the benzene ring. The energy of the ground electronic state increases along the twisting coordinate and

Fig. 6 Absorption spectra of DMABN in cyclohexane, *p*-dioxane; dichloromethane and acetonitrile solutions

Table 2 The energies of the minima in the solution using cyclohexane and acetonitrile solvents

Medium	Planar (Hartree)	Perpendicular (Hartree)	Energy difference (Hartree)	Energy difference (eV)
Cyclohexane	−458.469	−458.446	0.023	0.626
Acetonitrile	−458.458	−458.441	0.017	0.463

the results predict two minima at the planar and perpendicular structures of DMABN.

The rotational activation energy barrier (defined to be the energy difference in energy between the planar and the orthogonal conformers) to the perpendicular conformation of DMABN from its equilibrium planar structure in the solution state was calculated and listed in Table 2. All stable conformations were calculated, but in what follows only the most stable conformers were discussed. From the table it is clear that the scanned potential energy of the ground state displays similar behavior with two minima at the planar and the perpendicular geometries in all solvents. The energy barrier in cyclohexane and dichloromethane are greater than that of acetonitrile indicating that the perpendicular conformer is more stabilized in polar solvents.

Also, the rotational energy barrier is greater than the thermal energy ($kT \sim 0.026$ eV at room temperature) indicating that the two structures coexist at room temperature. If the rotational barrier is small, they exist as a mixture. However, if the barrier is large with respect to the thermal energy at room temperature, the conformers could be resolved. The rotational potential energy surfaces in all cases are quite similar. However, the barrier for rotation is reduced in the more polar solvent (acetonitrile) as shown in Table 2.

The energy barrier and associated one-dimensional potential of molecule conveys information regarding intramolecular interaction and molecular electronic structure. Knowledge of the energy barriers, which separate conformers, is important for the interpretation of several physical and chemical molecular properties.

A comparison of the present experimental and theoretical studies on DMABN indicates that the dual emission observed may originate from the two different conformations of the same molecule.

Conclusion

In this paper we have examined the excitation wavelength dependency of the emission spectra of DMABN in acetonitrile solution using steady-state fluorescence spectroscopy. Our ultimate goal is to show that the ground state of DMABN consists of two isomers of the molecule.

A closer examination of the excitation spectra of DMABN in polar solvents showed two characteristic independent absorption (excitation) bands. Also examination of its emission spectra showed that the spectrum consists two emission bands with the LE to CT intensity ratio dependent on the wavelength of the exciting light. These observations suggest that the compound, in its ground state, exists in the form of two relatively stable conformers, which are in equilibrium.

As the wavelength of excitation increases, there is a change in band form in the emission spectrum. This shows that one can selectively excite one of the spectral features of the dual fluorescence. After selective excitation, the intensity of the bands is proportional to the excitation wavelength, while the band form remained the same, indicating the presence of two separate absorption bands in the ground state of DMABN. In addition, the ground state structural calculations at DFT levels with respect to the twisting angle in the presence of solvent effects support the experimental results.

On the basis of the experimental results and our theoretical calculations, we suggest that there are two conformers of DMABN, which are stable in the ground state, equilibrated in solution at room temperature that give rise dual fluorescence upon excitation.

References

1. Lippert E, Lüder W, Boos H (1962) In: Mangini A (ed) Advances in molecular spectroscopy. Pergamon, Oxford
2. Platt J (1949) J Chem Phys 17:4840
3. Grabowski ZR, Rotkiewicz K, Rettig W (2003) Chem Rev 103:3899–4031
4. Lippert E, Lüder W, Moll F, Nägele W, Boos H, Prigge H, Seibold-Blankenstein I (1961) Angew Chem 73:695
5. Rettig W, Bliss B, Dirnberger K (1999) Chem Phys Lett 305:8–14
6. Rotkiewicz K, Grellmann KH, Grabowski ZR (1973) Chem Phys Lett 19:315–318
7. Rotkiewicz K, Grellmann KH, Grabowski ZR (1973) Chem Phys Lett 21:212
8. Grabowski ZR, Rotkiewicz K, Siemarczuk A, Cowley DJ, Baumann W (1979) Nouv J Chim 3:443
9. Grabowski ZR, Rotkiewicz K, Siemiarczuk A (1979) J Lumin 18:420
10. Köhler G, Rechthaler K, Rotokiewicz K, Rettig W (1996) Chem Phys 207:85–101
11. Gude CC, Rettig W (1998) J Phys Chem A 102:7754–7761
12. Rettig W, Lutze S (2001) Chem Phys Lett 341:263–271
13. Rettig W (1986) Angew Chem, Int Ed Engl 25:971–988
14. Lippert E, Rettig W, Bonacic-Koutecky V, Heisel F, Miehé JA (1987) Adv Chem Phys 68:1–173, and references therein
15. Rettig W (1994) In: Mattay J (ed) Topics in current chemistry, electron-transfer I, vol. 169. Springer, Berlin, pp 253–299
16. Leinhos U, Kühnle W, Zachariasse KA (1991) J Phys Chem 95:2013–2021
17. Schuddeboom W, Jonker SA, Warman JH, Leinhos U, Kühnle W, Zachariasse KA (1992) J PhysChem 96:10809–10819
18. Zachariasse KA, von der Haar T, Hebecker A, Leinhos U, Kühnle W (1993) Pure Appl Chem 65:1745–1750
19. von der Haar T, Hebecker A, Il'ichev YV, Jiang Y-B, Kühnle W, Zachariasse KA (1995) Recl Trav Chim Pays-Bas 114:430
20. Zachariasse KA, Grobys M, von der Haar T, Hebecker A, Il'ichev YV, Jiang Y-B, Morawski O, Kühnle W (1996) J Photochem Photobiol, A: Chem 102:59–70

21. Il'ichev YV, Kühnle W, Zachariasse KA (1998) J PhysChem A 102:5670–5680
22. Zachariasse KA (2000) Chem Phys Lett 320:8–13
23. Demeter A, Druzhinin S, George M, Haselbach E, Roulin J-L, Zachariasse KA (2000) Chem Phys Lett 323:351–360
24. Zachariasse KA, Grobys M, Von der Haar T, Hebecker A, Il'ichev YV, Morawski O, Rückert I, Kühnle W (1997) J Photochem Photobiol A 105:373–383
25. Chudoba C, Kummrow A, Dreyer J, Stenger J, Nibbering ETJ, Elsaesser T, Zachariasse KA (1999) Chem Phys Lett 309:357–363
26. Daum R, Druzhinin S, Ernst D, Rupp L, Schroeder J, Zachariasse KA (2001) Chem Phys Lett 341:272–278
27. Druzhinin SI, Demeter A, Galievsky VA, Yoshihara T, Zachariasse KA (2003) J Phys Chem A 107:8075–8085
28. Changenet P, Plaza P, Martin MM, Meyer YH (1997) J Phys Chem A 101:8186–8194
29. Su S-G, Simon JD (1988) J Chem Phys 89:908–919
30. Okamoto H, Inishi H, Nakamura Y, Kohtani S, Nakagaki R (2001) J Phys Chem A 105:4182–4188
31. Kwok WM, Ma C, Matousek P, Parker AW, Phillips D, Toner WT, Towrie M, Umapathy S (2001) J Phys Chem A 105:984–990
32. Ma C, Kwok WM, Matousek P, Parker AW, Phillips D, Toner WT, Towrie M (2002) J Phys Chem A 106:3294–3305
33. Techert S, Zachariasse KA (2004) J Am Chem Soc 126:5593–5600
34. Zachariasse KA, Druzhinin SI, Bosch W, Machinek R (2004) J Am Chem Soc 126:1705–1715
35. Yoshihara T, Druzhinin SI, Zachariasse KA (2004) J Am Chem Soc 126:8535–8539
36. Fuss W, Pushpa KK, Rettig W, Schmid WE, Trushin SA (2002) Photochem Photobiol Sci 1:255–262
37. Sudholt W, Sobolewski AL, Domcke W (1999) Chem Phys 250:9–18, and references therein
38. Serrano-Andrés L, Merchán M, Roos BO, Lindh R (1995) J Am Chem Soc 117:3189–3204
39. Sobolewski AL, Domcke W (1996) Chem Phys Lett 259:119–127
40. Sobolewski AL, Domcke W (1996) Chem Phys Lett 250:428–436
41. Sobolewski AL, Sudholt W, Domcke W (1998) J Phys Chem A 102:2716–2722
42. Lommatzsch U, Brutschy B (1998) Chem Phys 234:35–57
43. Parusel ABJ, Köhler G, Grimme S (1998) J Phys Chem A 102:6297–6306
44. Parusel ABJ, Köhler G, Nooijen M (1999) J Phys Chem A 103:4056–4064
45. Parusel ABJ, Rettig W, Sudholt W (2002) J Phys Chem A 106:804–815
46. Dreyer J, Kummrow A (2000) J Am Chem Soc 122:2577–2585
47. Zilberg S, Haas Y (2002) J Phys Chem A 106:1–11
48. Rappoport D, Furche F (2004) J Am Chem Soc 126:1277–1284
49. Köhn A, Hättig C (2004) J Am Chem Soc 126:7399–7410
50. Gedeck P, Schneider S (1997) J Photochem Photobiol, A: Chem 105:165–181, and references therein
51. Moro GJ, Nordio PL, Polimeno A (1989) Mol Phys 68:1131–1141
52. Kato S, Amatatsu Y (1990) J Chem Phys 92:7241–7257
53. Fonseca T, Kim HJ, Hynes JT (1994) J Mol Liq 60:161–200
54. Fonseca T, Kim HJ, Hynes JT (1994) J Photochem Photobiol, A: Chem 82:67–79
55. Broo A, Zerner MC (1995) Theor Chim Acta 90:383–395
56. Gorse A-D, Pesquer M (1995) J Phys Chem 99:4039–4049
57. Soujanya T, Saroja G, Samanta A (1995) Chem Phys Lett 236:503–509
58. Hayashi S, Ando K, Kato S (1995) J Phys Chem 99:955–964
59. Kim HJ, Hynes JT (1997) J Photochem Photobiol, A: Chem 105:337–343
60. Mennucci B, Toniolo A, Tomasi J (2000) J Am Chem Soc 122:10621–10630
61. Dobkowski J, Wojcik J, Kozminski W, Kołs R, Waluk J, Michl J (2002) J Am Chem Soc 124:2406
62. Cogan S, Zilberg S, Haas Y (2006) J Am Chem Soc 128:3335–3345
63. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03, Revision B.01. Gaussian, Inc., Pittsburgh
64. Becke AD (1993) J Chem Phys 98:5648
65. Lee C, Yang W, Parr RG (1998) Phys Rev B 37:785
66. Cammi R, Mennucci B, Tomasi J (2000) J Phys Chem A 104:5631
67. Böttler CJF (1973) In: Van Belle OC, Bordewijk P, Rip A (eds) Theory of electric polarization, vol. 1. Elsevier, Amsterdam
68. Onsager L (1936) J Am Chem Soc 58:1486
69. Lippert E (1955) Z Naturforsch 10a:541
70. Mataga N, Kaifu Y, Koizumi M (1955) Bull Chem Soc Jpn 28:690
71. Liptay W (1974) In: Lim EC (ed) Excited states. Academic, New York, p 129