Dual Fluorescence of 2-(4'-(*N*,*N*-Dimethylamino)phenyl)benzothiazole and Its Benzimidazole Analogue: Effect of Solvent and pH on Electronic Spectra

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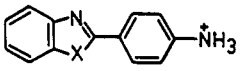
Received: November 22, 1993®

The absorption and fluorescence spectra of 2-(4'-(*N*,*N*-dimethylamino)phenyl)benzothiazole (DMAPBT) and 2-(4'-(*N*,*N*-dimethylamino)phenyl)benzimidazole (DMAPBI) have been recorded in solvents of different polarity and hydrogen-bonding nature. In all the solvents, a dual fluorescence is observed for both the compounds. The normal Stokes-shifted emission (B) originates from a locally excited π^* electronic state, and the large Stokes-shifted band (A) is due to emission from a twisted intramolecular charge-transfer (TICT) state. The dual fluorescence observed, even in nonpolar solvents, indicates that the energy of the TICT state is always lower than that of the locally excited state. Two kinds of monocations, one protonated at the tertiary nitrogen atom and the other protonated at the amino group, are formed simultaneously in the case of DMAPBT. The former is more stable in nonpolar solvents and the latter one in polar solvents. On the other hand, only one kind of monocation is formed in DMAPBI. Fluorimetric titrations have indicated that the radiative lifetimes of the respective conjugate acid–base pairs are shorter than the reciprocal rates of the protonation/deprotonation reactions.

Introduction

During our recent studies on the prototropic reactions of 2-(4'-aminophenyl)benzoxazole (4'-APBO),[1] and its benzothiazole analogue (4'-APBT),[2] it was observed that the absorption spectra of the monocation species of the molecules at pH ~1.5 exhibit two absorption bands, one red-shifted and the other blue-shifted with respect to the long-wavelength band of the respective neutral molecule. Fluorescence spectra obtained by excitation at the wavelengths of the band maxima were different, and as in the absorption spectrum, one of the fluorescence bands is red-shifted and the other is blue-shifted with respect to the fluorescence spectrum of the neutral species. This was attributed to the formation of two different monocation species. The blue-shifted absorption (or fluorescence) band was associated with the monocation (I), formed as a result of protonation at the amino nitrogen, and the red-shifted band with the monocation (II) formed by addition of a proton to the heterocyclic nitrogen. The large



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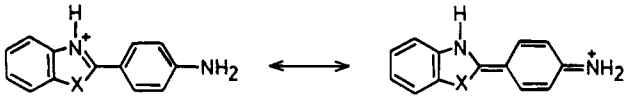

II X = O, S II'

red shift of the spectrum of the monocation (II) was explained by the resonance interaction of the $-NH_2$ group with the heterocyclic ring, leading to structure II', which stabilizes the species.

If the above conclusions are correct, then one should observe similar features in the absorption and fluorescence spectra of the 2-(4'-(*N*,*N*-dimethylamino)phenyl) derivative of the benzazoles with more pronounced effects, because the $-N(CH_3)_2$ group is a stronger electron donor than the unsubstituted $-NH_2$ group. On the other hand, the earlier studies have also indicated that the benzazole ring acts as an electron-accepting group. It has been known that aromatic molecules having the electron-donating $-N(CH_3)_2$ group at the para position of an electron-accepting group (e.g., –CN, –COOH, or –COOEt, etc.) give fluorescence emissions from twisted intramolecular charge-transfer (TICT) states as well as from the locally excited singlet states (LE) in polar and/or nonpolar solvents.[3] Therefore, in the present work, we have chosen 2-(4'-(*N*,*N*-dimethylamino)phenyl)benzothiazole (DMAPBT) and 2-(4'-(*N*,*N*-dimethylamino)phenyl)benzimidazole (DMAPBI) as model compounds to see the effect of the $-N(CH_3)_2$ substituent on the photophysical properties and prototropic reactions of the respective unsubstituted molecule and, hence, to justify the facts described above.

Materials and Methods

DMAPBT was prepared from *o*-aminothiophenol and *p*-(dimethylamino)benzaldehyde by the procedure reported in the literature.[4] The compound was first crystallized from acetic acid and then purified by recrystallization from ethanol several times. DMAPBI was obtained by heating *o*-phenylenediamine with *p*-(dimethylamino)benzoic acid in polyphosphoric acid using the procedure described for 2-substituted benzoxazoles.[5] The product was purified by repeated recrystallization from aqueous ethanol. The purity of the compounds was established by TLC and by verifying that the fluorescence excitation spectrum in methanol was identical when emission was monitored at different wavelengths. Analytical grade cyclohexane (SRL), dioxane (Sarabhai M. Chemicals), ether (Alembic), acetonitrile (E. Merck), methanol (E. Merck) and dichloromethane (BDH), and commercial grade ethanol were purified by the methods described in the literature[6] and fractionally distilled. Spectrograde ethyl acetate and acetone (SD Fine), analytical grade ethanediol and glycerol (SD Fine), and *n*-propanol (BDH) were used directly from the bottle. All the solvents were checked for spurious fluorescence in the region of fluorescence measurements. Triply distilled water was used for pH solutions. Analytical grade sulfuric acid (BDH), potassium hydroxide (Thomas Baker), and orthophosphoric acid (IDPL) were used as received.

Aqueous solutions of pH > 3.0 and pH < 11.0 were prepared by adding appropriate amounts of dilute (~10^{-3} M) solutions of KOH and H_3PO_4. Hammett's acidity scale (H_0)[7] and Yagil's basicity scale (H_-)[8] were followed in preparing solutions of pH < 1.0 and pH > 12, respectively. Because of the poor solubility

* Abstract published in *Advance ACS Abstracts*, February 15, 1994.

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TABLE 1: Absorption Maxima [λ_a (nm)], log ϵ, Fluorescence Maxima [λ_f (nm)], and Fluorescence Quantum Yields (ϕ_f) of DMAPBI and DMAPBT in Different Solvents[a]

	DMAPBI		DMAPBT	
solvent	λ_a (log ϵ)	λ_f (ϕ_f)	λ_a (log ϵ)	λ_f (ϕ_f)
cyclohexane	341 (sh) 327 212	525 500 (65) 385 365 (0.67) 350	347 (4.60) 255 (3.80)	590 560 (60) 535 400 387 (0.89) 370
dioxane	329 (4.36)	520 (74) 375 (~1.00) 365	353 (4.54)	580 (70) 410 (0.93)
ether	325 216	535 510 (92) 370 (0.93) 355	349 (4.58) 225	575 556 (95) 405 (~1.00)
ethyl acetate	328 (4.34)	530 (110) 380 (~1.00)	352 (4.60)	610 (58) 410 (0.95)
dichloromethane	333 (4.35)	535 (55) 385 (~1.00)	357 (4.60)	600 (65) 410 (0.92)
acetone	331 (4.37)	530 (37) 384 (0.36)	356 (4.53)	610 (52) 420 (0.90)
acetonitrile	329 (4.34)	534 (96) 384 (~1.00)	355 (4.56)	600 (72) 418 (0.76)
glycerol	356	570 410	368	620 (65) 430
ethanediol	336 (4.36) 215	545 (80) 390 (~1.00)	366 (4.57)	630 (60) 430 (0.99)
n-propanol	330 (4.34)	535 (75) 380 (~1.00)	358 (4.58)	600 (67) 416 (0.85)
ethanol	331 (4.34)	535 (78) 386 (~1.00)	358 (4.61) 223	600 (58) 420 (0.82)
methanol	332 (4.36)	540 (85) 395 (~1.00)	359 (4.60)	610 (79) 424 (0.84)
water (pH 6.7)	329 (4.32)	565 (40) 396 (0.73)	359 (4.46)	660 625 (45) 440 (0.51)

[a] Underlined wavelengths were used to calculate Stokes shifts ($\bar{\nu}_{SS}$). The numbers mentioned in the parentheses along with the long-wavelength band are in arbitrary units.

of DMAPBT in water, the pH solutions were made in a 20% (v/v) ethanol–water mixture with the acidity scale of Dolman et al.[9] For DMAPBI, the final solutions contained not more than 0.5% (v/v) methanol. All spectral measurements were performed at the solute concentration of $\sim 10^{-5}$ M. Fluorescence quantum yields were determined for solutions having absorbances less than 0.1 at the excitation wavelength and referred to quinine sulfate in 0.1 N H_2SO_4 (ϕ_f = 0.55).[10] For fluorimetric titrations, the solutions were excited at an isosbestic wavelength of the absorption spectra, i.e. 315 and 359 nm for the monocation–neutral and 297 and 360 nm for dication–monocation equilibria of DMAPBT.

Absorption spectra were recorded with a Shimadzu UV-190 spectrophotometer equipped with a 135U chart recorder. Steady-state fluorescence spectra were measured on a scanning spectrofluorimeter fabricated in the laboratory; the details are available elsewhere.[11] Fluorescence spectra reported in this paper were all corrected according to the procedure suggested by Parker.[12] The pH of the solutions was measured in a Toshniwal digital pH meter (Model CL46) fitted with a single probe combined glass electrode (Toshniwal).

Results and Discussion

Absorption Spectra. Table 1 summarizes the spectral properties of DMAPBI and DMAPBT in a series of solvents. The absorption spectrum of DMAPBT in water is blue-shifted relative to that in acetonitrile. The absorption spectrum of DMAPBT in any solvent is red-shifted compared to that of DMAPBI. Also, the spectra of both the molecules are red-shifted relative to the spectra of their respective unsubstituted amino derivative, 4′-APBI (λ_{max} = 310, 330 nm)[13] and 4′-APBT (λ_{max} = 327, 338 nm)[2]. The positions of the absorption maxima of the lowest energy bands of the compounds shift to higher wavelengths in going from nonpolar to polar solvents. The red shift is greater in viscous solvents, e.g. ethanediol and glycerol, whereas λ_{max} remains nearly same.

The similarity of the absorption spectra of the molecules with their respective amino counter parts (4′-APBI and 4′-APBT), the very high extinction coefficients of the absorption bands, and the large fluorescence quantum yields (see Table 1) indicate that the lowest energy transitions in these molecules, like other 2-phenyl-substituted benzothiazoles[14–16] and benzimidazoles,[17,18] are of $\pi \rightarrow \pi^*$ character. The red shift in the longest wavelength band of DMAPBI or DMAPBT as compared to that of 4′-APBI and 4′-APBT, respectively, can be explained by the greater charge-transfer interaction of the $-N(CH_3)_2$ group with the aromatic moiety relative to that of $-NH_2$ group, as discussed below.

Experimental results have indicated that the amino nitrogen atom of aniline is trigonal pyramidal,[19] whereas the amino nitrogen atom in *N,N*-dimethylaniline[20,22] and *p*-nitro-*N,N*-dimethylaniline[23] is trigonal planar. Because of the greater charge-transfer effect of the $-N(CH_3)_2$ group in comparison to the $-NH_2$ group with the aromatic ring and the larger red shift in the absorption spectra in the former case, it is clear that the twist angle (β) between the axis of the lone-pair-electron orbital on the nitrogen atom and the p orbital of the adjacent carbon atom of the aromatic ring is smaller in the former case. The twist angle is also a function of the acceptor strength of the substituent at the para position.[24] For example, the spectroscopic twist angle in *N,N*-dimethylaniline[25,26] is 22° and in *p*-(*N,N*-diethylamino)benzonitrile (DMABN)[27] it is 15°. In the present cases, it seems that the acceptor strength, i.e. electron affinity (EA), of the benzothiazole moiety is more than that of the benzimidazole group. This is indicated by the greater red shift of the absorption spectrum of DMAPBT relative to that of 4′-APBT, in comparison to that of DMAPBI with reference to 4′-APBI. Thus, it can be concluded that the twist angle is greater in DMAPBI than in DMAPBT.

The effect of solvents on the absorption spectral characteristics is similar to that reported in literature, i.e. dispersive interactions shift the band maxima to the red and proton-donating solvents to the blue.

Fluorescence Spectra. The fluorescence spectra of DMAPBT and DMAPBI exhibit dual fluorescence in all the solvents (Table 1). The fluorescence spectra are structured in cyclohexane with vibrational frequency $\sim 1200 \pm 50$ cm^{-1} for the short-wavelength band (B) and $\sim 950 \pm 50$ cm^{-1} for the long-wavelength band (A). The ratio of the intensity of the A band to that of the B band at the respective band maximum is of the order of $\sim 10^{-2}$ (Figure 1). Also, the long-wavelength band is very broad. As the solvent polarity is increased, the emission maxima of both A and B bands shift to red, the shift being greater for the A band. The fluorescence quantum yield (ϕ_f) of the B band in both the compounds is nearly 1.0, but it is quite a bit lower in water as solvent. Since it is not possible to correct the spectrum beyond 580 nm in our instrument, the quantum yield of the A fluorescence could not be measured accurately, but the area under the uncorrected A band in different solvents is reported in Table 1.

Dual fluorescences were reported for DMABN and related compounds.[3] Several mechanisms[28–43] were suggested to explain the origin of the large Stokes-shifted band of DMABN. These include the initial proposal of solvent-assisted level reversal of S_2 and S_1 by Lippert et al.,[28] excimer formation by McGlynn et al.,[29,30,35] protonation in the excited state by Kosower et al.,[33,34] exciplex formation with polar solvent molecules by Viesse[44] and Chandross et al.,[45] and the mechanism proposed here, the twisted intramolecular charge transfer (TICT) put forward by Grabowski et al.[36,38,40] These mechanisms have been tested with the present

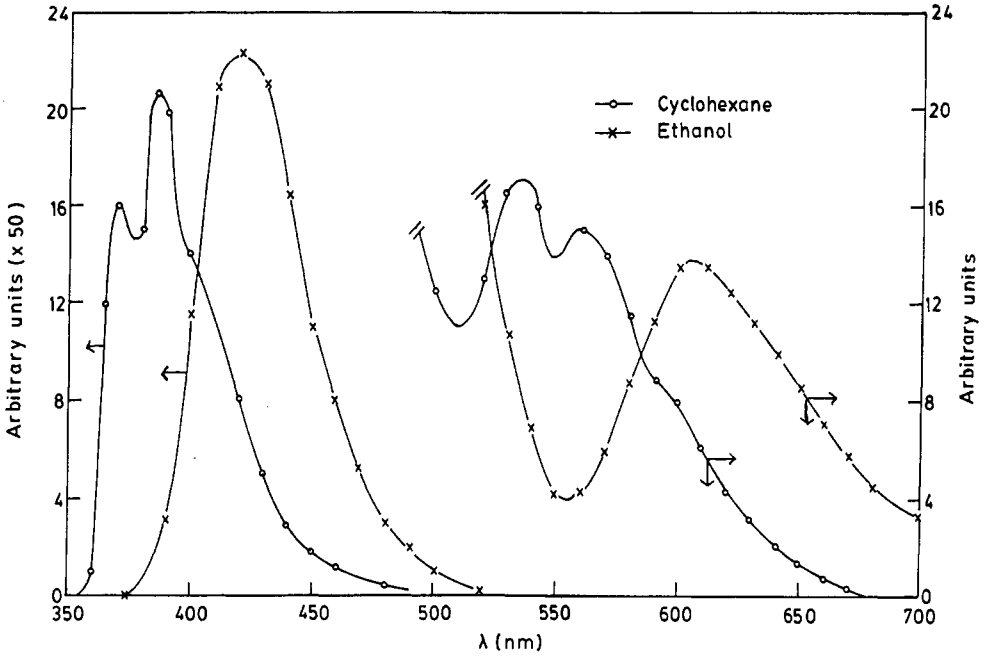


Figure 1. Fluorescence spectra of the A and B bands of DMAPBT in cyclohexane and water at [DMAPBT] = 2×10^{-5} M.

molecules. The possible origin of the A fluorescence is discussed in the following section.

The dual fluorescence resulting from impurities and photochemical products can be rejected on the grounds that (i) the fluorescence excitation spectra of both the molecules recorded at different λ_{max} (flu) resemble the absorption spectra and (ii) no changes were observed during the experiment in the spectral features or in the emission spectra of the compounds measured on freshly prepared samples.

The appearance of the A fluoresence in nonpolar solvents implies that the spectral behavior of the molecules is not due to solute–solvent specific interaction (i.e. complex formation). The two fluoresence bands correspond to the same ground-state forms, because the excitation spectra do not differ. Therefore, they must originate from two different excited states or two different forms of the excited molecule. The possibility of excimer formation can also be rejected on the basis of the following reasons: (i) The ratio of the intensities at the band maxima does not change with an increase of concentration of the fluorophore in the range 5×10^{-6} to 5×10^{-4} M. (ii) The A band of both DMAPBI and DMAPBT is well structured in cyclohexane; aggregated species in general would not exhibit structured fluoresence. (iii) Excimer formation is a diffusion-controlled process in solution, whose pseudo-first-order rate constant is $k_e = k_d[M]$, where k_d is the diffusion-controlled rate constant ($\sim 10^{10}$ M^{-1} s^{-1} at 298 K) and [M] is the monomer concentration. Even at the relatively high concentration (5×10^{-4} M) used for the measurements, k_e would be of the order of 5×10^6, which is much lower than the normal rate of fluorescence ($\sim 10^9$ s^{-1}). (iv) The A band of the molecules is also observed in glycerol (n = 2330 cp) at room temperature.

The appearance of the A band in a hydrocarbon solvent clearly indicates that solvent-assisted excited state reversal, as observed in the case of DMABN,[28] is not the mechanism responsible for dual fluorescence. Thus, it seems that the intramolecular rotational relaxation in the fluorescent states of the molecules is the reason for the multiple fluorescence and the ^1L_a-type state is of lower energy compared to that of the locally excited state arising from the planar configuration of the molecules. Similar behavior has been observed with (*N*,*N*-dimethylamino)benzoic acid and its ester.[46] The rotational relaxation can occur in two ways, (a) rotation of the $-N(CH_3)_2$ group around the C–N bond and (b) rotation of the complete (dimethylamino)phenyl moiety around the C–C′ bond. Earlier studies on 2-(4′-aminophenyl)-benzazoles[1,2,13] have shown that these molecules exhibit only a single normal Stokes-shifted fluorescence band from the locally excited states, and the vibrational frequency of the B band matches that of 2-phenyl-substituted benzazoles. Moreover, had the rotation occurred around the C–C′ bond, a blue shift in the position of the B band relative to that of the respective 2-phenyl derivative (PBT and PBI) should have been observed. Therefore, at this point it would not be unreasonable to assign the double fluorescence of the molecules to the two isomers differing in the orientation of the $-N(CH_3)_2$ group with respect to the plane of the phenyl ring.

In order to further see the effect of rotation of the $-N(CH_3)_2$ group, the fluorescence spectrum of DMAPBT at 298 K was recorded in solutions consisting of different compositions of glycerol–H_2O mixtures. As expected,[47] the fluorescence intensity of band A did not increase with an increase of water content (i.e. decrease of viscosity and of greater free rotation), but a decrease of intensities of both the bands was noticed under the above conditions. The opposite results are consistent with the fact that increases in polarity and hydrogen bonding[48,49] increase the nonradiative intersystem crossing rate and thus decrease the fluorescence intensity of both the bands, in agreement with our results with water as a solvent. The data of Table 1 also indicate that the fluorescence quantum yield of band B nearly remains constant in alcoholic solvents, although these solvents possess a wide range of viscosities. We have also compared the area under the A fluorescence bands in these solvents and found that these are also nearly the same, indicating that the fluorescence intensity of band A in these solvents is independent of viscosity in this range. It has been shown[50] that the fluorescence quantum yield of the A band of DMABN is independent of viscosity up to moderate viscosity, indicating that the rotating group ($-NMe_2$) is quite small and hence the TICT process for this molecule does not involve significant displacement of solvent molecules. Although the rotating group in our case is also the same, it needs further study before we can make such a conclusion.

Effect of Solvents on the Spectral Characteristics. The general observations regarding the effect of the solvents on the spectral characteristics of electron donor–acceptor systems, studied extensively,[28,40,51-57] are as follows: (i) With a rise in polarity the quantum yield and lifetime of B fluorescence decrease with a slight red shift of fluorescence maxima whereas the quantum

TABLE 2: Solvent Polarity Parameters [$f(D,n)$, $E_T(30)$] and Stokes Shifts ($\bar{\nu}_{SS}$) of DMAPBI and DMAPBT in Various Solvents[a]

solvent	$f(D,n)$	$E_T(30)$ (kcal/mol)	$\bar{\nu}_{SS}$ cm^{-1} DMAPBI	DMAPBT
cyclohexane	−0.001	31.2	3184 (10581)	3860 (11003)
dioxane	0.028	36.0	3727 (11164)	4406 (11088)
ether	0.167	34.6	3742 (11161)	3962 (10667)
ethyl acetate	0.201	38.1	4172 (11620)	4019 (12016)
dichloromethane	0.218	41.1	4056 (11338)	3621 (11344)
acetone	0.287	42.2	4169 (11343)	4281 (11697)
acetonitrile	0.305	46.0	4353 (11669)	4131 (11502)
glycerol	0.264	57.0	3700 (10546)	3918 (11045)
ethanediol	0.276	56.3	4121 (11414)	4066 (11449)
n-propanol	0.280	50.7	4125 (11652)	3895 (11266)
ethanol	0.290	51.9	4350 (11565)	4124 (11266)
methanol	0.309	55.5	4804 (11602)	4270 (11462)
water	0.320	63.1	5142 (12696)	5128 (11855)

[a] Quantities within parentheses are for the A fluorescence band.

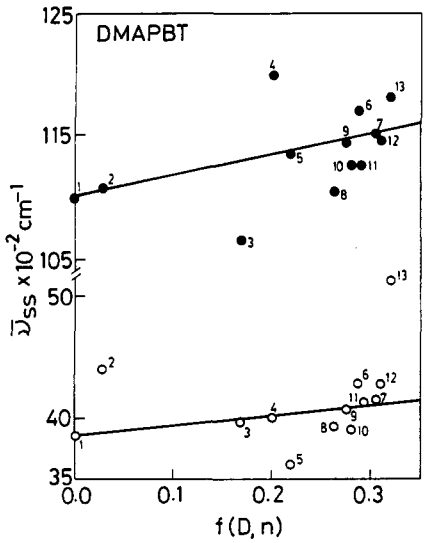


Figure 2. Plot of Stokes shift versus solvent polarity parameter [$f(D,n)$] for DMAPBT: A fluorescence band (—●—); B fluorescence band (—○—).

yield of TICT fluorescence initially increases and after reaching a maximum decreases with a further rise in polarity, while fluorescence maxima shift regularly to the red. The results of Table 1 are quite consistent with the above observations. Although we have not measured the fluorescence quantum yield of band A, as mentioned earlier, the area under the traces of the fluorescence spectra of band A, recorded from the spectrofluorimeter, observed in different solvents follows the same trend as that observed in the case of other compounds.

The Stokes shifts ($\bar{\nu}_{ss}$ cm^{-1}) of the fluorescence spectra of DMAPBT and DMAPBI, in the solvents employed, and the solvent polarity parameters are listed in Table 2. The plots of $\bar{\nu}_{ss}$ versus $f(D,n)$ parameters[58] are shown in Figures 2 and 3. The solvatochromic slopes in Figure 2, which are different for the B and A fluorescences (800 versus 1632 cm^{-1}, in aprotic polar solvents), are indicative of the fact that the dipole moment

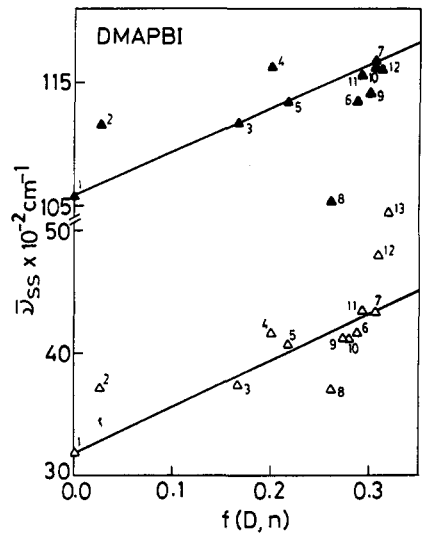


Figure 3. Plot of Stokes shift versus solvent polarity parameter [$f(D,n)$] for DMAPBI: A fluorescence (—▲—); B fluorescence band (—△—).

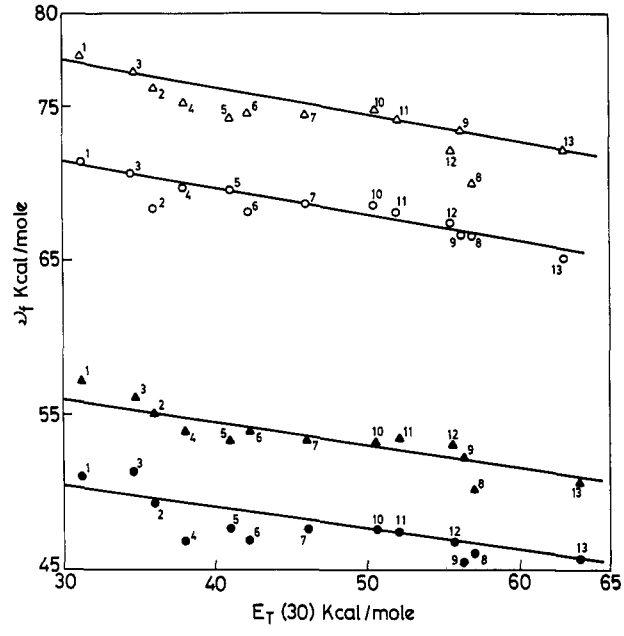


Figure 4. Plot of emission energy versus $E_T(30)$ parameter. Solid circles and triangles represent, respectively, the A fluorescence band of DMAPBT and DMAPBI, and open circles and triangles represent the B fluorescence band of DMAPBT and DMAPBI, respectively.

difference between the excited state and the ground state ($\mu_e - \mu g$) is larger for the TICT state. In DMAPBI, on the other hand, the B band also shows a considerable solvatochromic shift as opposed to the virtual insensitivity of the B band of DMABN to the solvent polarity.[28] The difference between the solvatochromic slopes for the A (3650 cm^{-1}) and B (3100 cm^{-1}) fluorescence of DMAPBI (Figure 3) is not as large as observed for DMAPBT. This is consistent with the earlier conclusion that the equilibrium twist angle (β_e) in the ground state and in the B state of DMAPBI is greater than that in the DMAPBT. The greater the twist angle the larger is the dipole moment and thus the Stokes shift. Similar behavior has also been observed for 2-(4′-aminophenyl)-benzimidazole.[13] Thus, it can be concluded that the B fluorescence of DMAPBI does not correspond to the complete planar configuration of the $-N(CH_3)_2$ group with the aromatic moiety.

The other most effective and practical polarity scale is Reichardt–Dimroth's $E_T(30)$ scale,[59,60] which takes both dispersive and specific (hydrogen bonding) interactions into account. The fluorescence maxima of both the molecules are converted to emission energies (kcal mol^{-1}) and are plotted against the $E_T(30)$

TABLE 3: Absorption Maxima [λ_a (nm)], log ϵ, Fluorescence Maxima [λ_f (nm)], and Fluorescence Quantum Yields (ϕ_f) of Different Prototropic Species of DMAPBI and DMAPBT in Aqueous Solution

	DMAPBI			DMAPBT		
species	λ_a (log ϵ)	λ_f (nm)	ϕ_f	λ_a (log ϵ)	λ_f (nm)	ϕ_f
neutral	329 (4.22)[a]	565		359 (4.46)[b]	660	
		396	0.73		625	
					440	0.51
monoanion	322 (4.26)[c]	535[d]				
	263 (3.72)	385	0.88			
monocation	360 (4.29)[e]	410[e]	0.01	430 (4.22)[f]	475[g]	
				302 (4.18)	390[h]	0.03
dication	298 (4.06)	375	0.97	320 (4.36)	415	0.01
($-H_0$ 2.0)	241 (3.88)			255 (4.10)		

[a] Measured at pH 9.5. [b] 20% ethanol–water mixture. [c] At H_- = 14.0. [d] At H_- = 16. [e] Measured at pH 4.0. [f] Measured at pH 1.34, 20% ethanol–water. [g] At pH = 1.34, λ_{ex} = 430 nm. [h] At pH = 1.34, λ_{ex} = 300 nm.

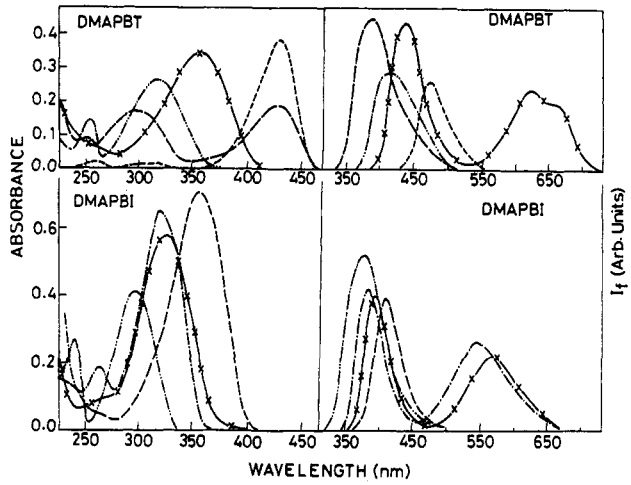


Figure 5. Absorption (left panel) and fluorescence (right panel) spectra of the prototropic species of DMAPBT and DMAPBI: neutral (—×—); monoanion (—·—); monocation I (— —); monocation II in cyclohexane–TFA (---); dication (—··—).

parameters in Figure 4. As expected, good correlation between the emission energies and $E_T(30)$ parameters is obtained for both the A and B fluorescence.

Effect of Acid/Base Concentration

The spectral properties of DMAPBT and DMAPBI in acidic and alkaline solutions are different and therefore will be discussed under different headings. The spectral data of the prototropic species of the molecules are compiled in Table 3, and relevant spectra are displayed in Figure 5.

2-(4′-(*N,N*-Dimethylamino)phenyl)benzothiazole. Unlike 4′-APBT, DMAPBT is present in the neutral form at pH > 4 in both the S_0 and S_1 states because of the absence of a dissociable proton at the amino group. At pH 1.5, the long-wavelength absorption band is replaced by two bands of which one is red-shifted (430 nm) and the other is blue-shifted (302 nm) with respect to that of the neutral molecule (359 nm). The absorption spectra over this pH region exhibit isosbestic points at 315 and 395 nm. The fluorescence spectra obtained by excitation at the wavelengths of the band maxima are respectively blue-shifted (λ_f = 390 nm) and red-shifted (λ_f = 475 nm) with respect to the fluorescence spectrum of the neutral molecule (λ_f = 440 nm). Moreover, the fluorescence excitation spectrum corresponding to the blue-shifted fluorescence band resembles exactly the short-wavelength absorption band, while the fluorescence excitation spectrum for the red-shifted fluorescence band matches that for the long-wavelength absorption band. These facts clearly indicate that the two bands in the absorption spectrum at pH 1.5 are due to two different species which are also present in the S_1 state. The

TABLE 4: pK_a and pK_a* Values for the Prototropic Equilibria of DMAPBI and DMAPBT

		pK_a*	
compound/equilibrium	pK_a	FT[a]	FC[b]
DMAPBI			
dication–monocation	1.4		−10.7
monocation–neutral	5.6		11.0
neutral–monoanion	12.1	14.4	13.5
DMAPBT			
dication–monocation I	−0.3	0.4	3.6
dication–monocation II	−0.3	0.4	−17.1
monocation I–neutral	2.9		−8.0
monocation II–neutral	2.9		12.5

[a] FT = fluorimetric titration; FC = Forster cycle. [b] Calculated by using fluorescence maxima.

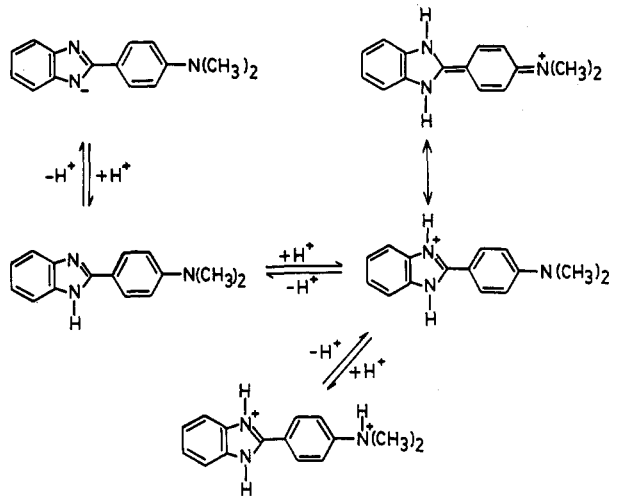
results can be explained as follows. The molecule has two protonation sites, one is the nitrogen atom of the $-N(CH_3)_2$ group and the other is the heterocyclic nitrogen (≥N). Since the lowest energy transition of the molecule is of the $\pi \rightarrow \pi^*$ type, the addition of a proton to the heterocyclic N atom will shift the absorption and fluorescence spectra to the red, whereas the addition of a proton to the $-N(CH_3)_2$ group will shift the spectra to the blue in comparison to that of the neutral species. Thus, it can be concluded that the short-wavelength absorption band and the corresponding blue-shifted fluorescence spectrum (λ_f = 390 nm) are due to the monocation I, and the long-wavelength absorption band and the red-shifted fluorescence spectrum (λ_f = 475 nm) are due to the monocation (II) formed by the protonation of the heterocyclic nitrogen. The large red shift in the spectrum of monocation II could be attributed to the structure II′. In acidic nonaqueous solvents (cyclohexane and trifluoroacetic acid), however, only the red-shifted absorption and fluorescence bands of monocation II have been observed (Figure 5). This can be explained along the same lines as those discussed for 2-(4′-aminophenyl)benzoxazole[1] and 4′-APBT.[2]

The formation of both types of monocations can be explained as follows. It has already been mentioned that the $-N(CH_3)_2$ group is coplanar with the aromatic ring in the S_0 state. Consequently, the lone pair orbital of $-N(CH_3)_2$ overlaps with the π cloud of the aromatic ring. This decreases the charge density at the $-N(CH_3)_2$ group but increases the same on the heterocyclic nitrogen. Thus, the proton can be added to any one of the basic centers with equal ease, leading to the formation of the monocations I and II. This is supported by the fact that the pK_a values for the monocation–neutral equilibria calculated from the spectral changes of the short- and long-wavelength bands are equal (2.9, Table 4). It is also less than the pK_a value for the protonation of the amino nitrogen of 2-(3′-aminophenyl)-benzothiazole (3.4)[2] and greater than the pK_a value for the protonation of the heterocyclic nitrogen of 2-phenylbenzothiazole (O.O)[2]

The molecule is present in the form of the dication in the acidity range of H_0 −2 to −10.4 because the absorption and fluorescence spectra of this species are red-shifted with respect to that of the monocation I and blue-shifted relative to that of the monocation II. This is due to the fact that, in the case of the monocation I, the second proton is added to the tertiary nitrogen atom and, in the monocation II, the proton is added to the $-N(CH_3)_2$ group. The absorption spectra in the region of pH 1.5 H_0 −2.0 exhibit two isosbestic points (297 and 360 nm). The fluorescence spectrum obtained by excitation at 297 nm shifts from 390 to 420 nm and that obtained by excitation at 360 nm shifts from 475 to 420 nm in going from pH 1.5 to H_0 −2.0, indicating the presence of both dication–monocation I and dication–monocation II equilibria in the S_0 and S_1 states.

2-(4′-(*N,N*-Dimethylamino)phenyl)benzimidazole. At the highest base concentration (H_- 16.0), the molecule is present as a monoanion formed by the deprotonation of the imino (>NH)

SCHEME 1



group. The absorption and the fluorescence spectra of the monoanion are blue-shifted relative to those of the neutral molecule. This is contrary to what is normally observed for the deprotonation of the >NH group.[11,61-64] However, this is consistent with similar results obtained in the case of the benzimidazole derivatives, 2-(4′-hydroxylphenyl)benzimidazole[61] and 2-(4′-aminophenyl)benzimidazoles.[13] In the fluorescence spectrum of the monoanion, the A band is more blue-shifted compared to the B band, while the fluorescence intensities of both the bands of the neutral molecule show a gradual decrease with the increase of pH above 11.0. Since this has not been observed with DMAPBT (because there is no dissociable proton in the benzothiazole moiety), it points clearly to the fact that the monoanion is obtained by the deprotonation of the >NH group. This result is different from that of 4′-APBI[13] in the sense that in the latter molecule the monoanion is formed by deprotonation from the >N–H group in the S_0 state while, in the S_1 state, it is formed by the deprotonation from the $-NH_2$ group. Since the DMAPBI molecule has no other dissociable proton except at the >N–H group, the monoanion species in the S_0 and S_1 states are the same. The dissociation of the >NH proton leaves a negative charge on the benzimidazole ring which opposes the charge migration from the $-N(CH_3)_2$ group and thus destabilizes the excited states of the neutral molecule, resulting in blue shifts of the spectral bands.

The increase of H^+ ion concentration below pH 7.0 shifts the absorption and fluorescence spectra to red. But the A band of the fluorescence spectrum completely disappears on going to pH 4. This indicates the formation of the monocation as a result of protonation of the pyridinic nitrogen of the heterocyclic ring, which is consistent with the results discussed above. The disappearance of the A band suggests that the band is due to a TICT transition, because the addition of a proton on the ≥N group will facilitate the conjugation of the $-N(CH_3)_2$ group with the π-system of the molecule. Because of this, the *N*-phenyl bond will have more double-bond character (as shown above), thus decreasing the rotational relaxation of the $-N(CH_3)_2$ group in the S_1 state. The spectra of the monocation undergo blue shifts upon further increase of the H^+ ion concentration, indicating the second protonation at the $-N(CH_3)_2$ group and thus formation of the dication at $H_0 - 1$. The dication spectra remain unaltered in strongly acidic solution ($H_0 < -1$). The various prototropic reactions of DMAPBI are shown in Scheme 1.

Acidity Constants

The dissociation constants of the various prototropic reactions of DMAPBI and DMAPBT in the S_0 state have been calculated using absorption spectroscopy, and the data are compiled in Table 4. The pK_a value for the dication of DMAPBI (1.4) is lower than

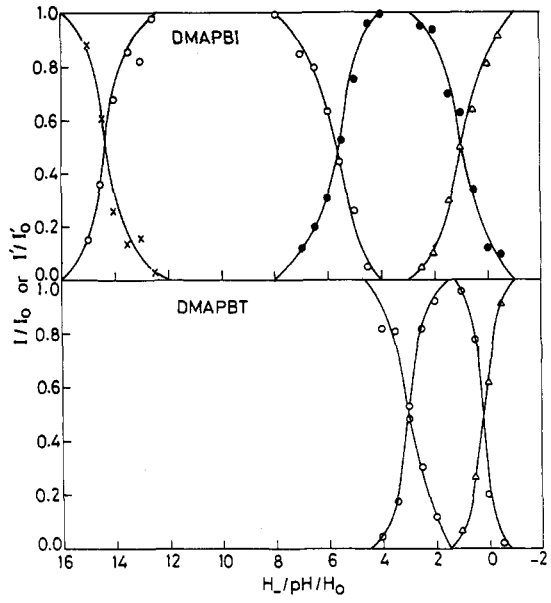


Figure 6. Fluorimetric titration curves for the prototropic species of DMAPBI and DMAPBI.

that for the monocation of DMAPBT (2.9), which is again less than that of *N*,*N*-dimethylaniline[66] (4.22). In all these cases, the protonation occurs at the *N* atom of the $-N(CH_3)_2$ group. This can be easily explained by the degree of conjugation of the $-N(CH_3)_2$ group with the π-systems of the molecules (i.e., the charge density present on the amino nitrogen atom). As mentioned in the previous section, the presence of the heterocyclic ring at the para position of the $-N(CH_3)_2$ group in DMAPBI and DMAPBT increases the conjugation and, hence, decreases the charge density at the amino nitrogen. This conjugation and also the charge migration from the $-N(CH_3)_2$ group to the heterocyclic ring increase further on protonation of the tertiary nitrogen atom of the benzimidazole ring in DMAPBI. As a result, the basicity (pK_a) of the amino nitrogen is lower than that in other molecules. For reasons mentioned earlier, the monocation I and monocation II of DMAPBT have the same pK_a values, and similarly, the pK_a values of the dication–monocation I and dication–monocation II equilibria have the same values. The pK_a's of the monocation–neutral and neutral–monoanion equilibria of DMAPBI are consistent with those of other benzimidazole molecules.

pK_a^* values of all the prototropic reactions of DMAPBI and DMAPBT were determined by fluorimetric titratons and by the Forster cycle method using both absorption and fluorescence maxima. Fluorimetric titrations (Figure 6) have indicated that only ground-state pK_a values are observed in all the cases, even when we used different isosbestic wavelengths of excitation in the case of DMAPBT. This indicates that the lifetimes of the respective prototropic species are shorter than the reciprocal rate constants for the protonation and deprotonation reactions. The values of pK_a^* obtained with the help of the Forster cycle method are consistent with the earlier observations that the tertiary nitrogen atom becomes more basic and the amino nitrogen becomes less basic on excitation to the S_1 state. There is a large discrepency between the pK_a^* values obtained by using absorption and fluorescence maxima. This is because, as mentioned earlier, the solvent relaxations for the respective species are different in the S_0 and S_1 states.

Conclusions

The following conclusions can be arrived at from the above studies. (i) Dual fluorescence is observed in both the molecules. A normal Stokes-shifted band originates from the locally excited $^1(\pi,\pi^*)$ state and a large Stokes-shifted one from the TICT state. (ii) Fluorescence excitation spectra corresponding to both band

maxima are similar and resemble the absorption spectra. This indicates that the ground-state precursor is the same for both the excited-state species. (iii) The observation of a large Stokes-shifted fluorescence band even in nonpolar solvents indicates that the energy of the TICT state is lower than that of the locally excited state. (iv) Two kinds of monocations, one protonated at the tertiary nitrogen atom (II) and the other protonated at the amino group (I), are formed simultaneously in DMAPBT in the S_0 and S_1 states, and pK_a values are equal for both types of monocation–neutral equilibria. The former is more stable in nonpolar solvents and the latter in polar solvents. (v) In the case of DMAPBI, only one kind of monocation produced by protonation of the tertiary nitrogen is formed. (vi) Only one kind of dication is formed in both the molecules. (vii) The monoanion of DMAPBI is formed by deprotonation of the imino group of the benzimidazole moiety, and the two moieties are not in the same plane. (viii) Fluorimetric titrations give only the ground-state pK_a values for various prototropic reactions, indicating that the radiative lifetimes of the conjugate acid–base pairs are shorter than the reciprocal rates of the protonation/deprotonation reactions.

Acknowledgment. The authors are thankful to the Department of Science and Technology, New Delhi, for financial support to project no. DST/CHM/93044.

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