Unusual Spectral Shifts of Bis(4-aminophenyl)ether

Narayanasamy Rajendiran and Meenachisundram Swaminathan*

Department of Chemistry, Annamalai University, Annamalainagar-608002 Tamilnadu, India

(Received March 4, 1996)

Absorption and fluorescence spectra of Bis(4-aminophenyl)ether (DADPE) have been studied in different solvents and at various acid concentrations. The results are compared with the spectral data of 4-Aminodiphenyl ether (ADPE). The fluorescence spectra of DADPE are blue shifted relative to that of ADPE in polar and hydrogen-bonding solvents. A small, but unusual, red shift is observed in the fluorescence spectrum of the monocation relative to that of DADPE in water. These observations reveal that the effect of two amino groups in polar solvents is less than that of one amino group in the excited singlet state. The abnormally red-shifted fluorescence with a peak at around 422 nm at pH 3.5 is due to a dication-solvent exciplex. The formation of the dication-solvent exciplex leads to an excited state equilibria quite different from that in the ground state.

Since Förster[1] and Weller's[2] studies of the effect of the pH on the electronic absorption and fluorescence spectra of 4-aminonaphthalenesulfonic acid, a number of studies have been carried out on the electronic spectra of acids and bases[3—11] which are either monofunctional or bifunctional, with one functional group having electron-withdrawing and the other electron-donating properties. However, very few systematic studies have been carried out for excited-state protonation and fluorescence phenomena of bifunctional molecules in which both of the functional groups are electron-donating.[12—15]. Some bifunctional molecules of these kinds have revealed interesting features.[16—22]

For example, all of the phenylenediamines[16] (*ortho*, *meta*, and *para*) and diaminodiphenyl sulfones[17] give rise to a similar sequence of blue shifts when protonation is carried out stepwise, which is in accordance with the normal behavior of aromatic amines. In 2,7-diaminofluorene (DAF)[18] and 4,4′-diaminobiphenyl (DABP)[19] a small red shift (15 nm) is observed upon the protonation of the first amino group, followed by a large blue shift in the fluorescence spectrum when the second amino group of these compounds is protonated. However, similar reactions when carried out in a nonpolar medium give rise to the normal behavior of aromatic amines.[16,17] On the other hand, in 2,3-diaminonaphthalene (DAN)[23] the fluorescence of the monocation is red shifted in both polar and nonpolar media. The red shifts of DAF and DABP in a polar medium were reported to be due to the large solvent relaxation of the monocation, whereas the red shift in DAN was found to be due to a twisting of the NH_3^+ and NH_2 groups with respect to the naphthalene moiety.[23]

The present investigation was an extension of our work on bifunctional molecules. The aim of this study was to compare the spectral data of DADPE with ADPE,[24] and determine whether its behavior is close to that of the diamino compounds.

Materials and Methods

Bis(4-aminophenyl)ether was obtained from Fluka Chemical Co. and recrystallized from aqueous ethanol. The purity of the compound was checked by noting its melting point, electronic spectrum, and similar fluorescence spectra when excited with different wavelengths. Spectrograde methanol (BDH), analytical-grade sulfuric acid, sodium hydroxide, and trifluoroacetic acid (TFA) were used as obtained. The anala R grade of the other solvents were further purified according to a procedure suggested in the literature.[25] Triply distilled water was used for aqueous solutions. Solutions in the pH range of 1.5 to 12.0 were prepared by adding appropriate amounts of NaOH and H_3PO_4. A modified Hammett's acidity scale[26] ($H_\circ$) for solutions below pH 1.5 (using H_2SO_4–H_2O mixture) and Yagil's basicity scale[27] (H_-) for solutions above pH 12 (using NaOH–H_2O) mixture) were employed. Hammett's acidity function ($H_\circ$) serves especially as a measure of the tendency for the solution in question to transfer a proton to an uncharged or charged base molecule and increasingly negative values corresponding to higher acidity.

The absorption spectra were recorded with a JASCO model-7800 spectrophotometer, while fluorescence measurements were made using a JASCO FP-770 spectrofluorimeter, and pH values in the range of 1.5—12.0 were measured on a ELICO pH meter model (LI-10T). Due to the poor solubility of DADPE in water, a stock solution was prepared in methanol. The concentrations of the solutions were on the order of 10^{-5}—10^{-4} M (1 M = mol dm^{-3}). The solutions for absorptiometric and fluorimetric titrations were prepared just before taking measurements. The isosbestic wavelengths were used as the excitation wavelength for measuring the fluorescence intensities at any analytical wavelength.

Results and Discussion

Effect of Solvents. The absorption and fluorescence spectra of DADPE were observed in solvents of various polarities and hydrogen-bonding abilities. The relevant data for DADPE are compiled in Table 1 along with the spectral data of ADPE in cyclohexane, acetonitrile, methanol, and water.

Table 1. Absorption and Fluorescence Maxima and log ε_{max} of Bis(4-aminophenyl)ether and 4-Aminodiphenyl Ether in Different Solvents and at Various Acid Concentrations

Solvents	DADPE			ADPE[a)]		
	λ_{abs} nm	log ε	λ_{flu} nm	λ_{abs} nm	log ε	λ_{flu} nm
Cyclohexane	298.0	—	346	298.0	3.46	346
	246.8			241.0	4.16	
Diethyl ether	303.4	3.78	355			
	250.8	4.40				
Dioxane	303.0	3.79	354			
	250.4	4.39				
Tetrahydrofuran	302.8	3.80	354			
	250.6	4.42				
Ethyl acetate	303.4	3.77	358			
	254.4	4.34				
Methyl acetate	302.8	3.76	357			
	254.0	4.36				
Dichloromethane	299.2	3.76	350			
	249.0	4.34				
1,2-Dichloroethane	300.0	3.70	351			
	249.4	4.36				
Acetonitrile	302.6	3.75	358	302.0	3.81	360
	250.2	4.39		245.0	4.12	
t-Pentyl alcohol	297.4	3.67	363			
	250.0	4.31				
t-Butyl alcohol	297.6	3.68	354			
	245.4	4.30				
2-Butanol	298.6	3.70	362			
	246.8	4.38				
2-Propanol	298.6	3.72	363			
	246.6	4.34				
1-Butanol	297.2	3.74	361			
	246.6	4.34				
Ethanol	299.0	3.60	357			
	251.2	4.48				
Methanol	299.6	3.74	355	296.0	3.39	366
	251.6	4.46		241.0	4.15	
Ethylene glycol	300.6	3.75				
	250.2	4.45	354			
Water	292.0	—	368	291.0	—	372
(neutral)	241.2	—		236.0	—	
Monocation	290.0	—	371	276.0	—	358s
	238.4		422	269.0		305
				263.4		
				224.0s		
Dication	276.0	—	305	—		—
	269.6					
	264.0					
	222.4s					
Monoanion	323.4	—	—	310.0		
	270.8			259.0	—	—
Dianion	—	—	356	—	—	348

a) From Ref. 24.

Both molecules give two absorption maxima: one at shorter wavelength and the other at longer wavelength. In cyclohexane there is no change in the longer wavelength absorption maxima of DADPE and ADPE, though a small red shift relative to ADPE is observed in other solvents. The shorter wavelength absorption maximum of DADPE is significantly red shifted to ADPE in all of the solvents. In fluorescence there is also no change in the maximum compared to ADPE in cyclohexane. However, an unusual fluorescence shift is observed in other polar solvents. Contrary to the absorption spectra, the fluorescence spectra of DADPE are blue shifted relative to those of ADPE in polar and hydrogen-bonding solvents. This reveals that the net solvent effect of two amino groups in the S_1 state is less than that of one amino group in polar solvents. A similar behavior was observed in DAN,[23] and it was reported to be due to the twisting of two adjacent amino groups with respect to the naphthalene moiety. In the case of the phenylenediamines,[16] an additive effect of two amino groups is noticed. In DADPE the unusual fluorescence blue shift in polar solvents cannot be due to the twisting of two amino groups, which are far away from each other. In this compound the two phenyl rings may attain planarity upon excitation; this increases the delocalization between the rings. Since the amino groups are symmetrically placed along the long axis of the molecule, the solvent interactions of the two similar groups act in opposite directions. Hence, the effect of two amino groups is less than that of one amino group in polar solvents. A similar behavior has also been reported in Bis(4-aminophenyl)sulfone.[28] The opposing solvent interactions in the S_1 state may reduce the dipole moment change upon excitation. The stokes shifts in cyclohexane for both the molecules are same (4655 cm^{-1}), whereas the stokes shift of DADPE in water (7014 cm^{-1}) is less than of ADPE in water (7529 cm^{-1}). This suggests that the dipole-moment change during excitation for DADPE is less than that of ADPE.

An analysis of solvatochromic shifts of DADPE reveals that the absorption maxima are red shifted from cyclohexane to methanol, but blue shifted in water. The fluorescence spectrum is usually red shifted as the polarity and proton donor capacities of the solvent increases. Though the absorption and fluorescence solvatochromic shifts are less than those of ADPE, the shifts are consistent with the characteristic behavior of the amino groups[16–19,23,24] i.e., the absorption spectrum of DADPE should have characteristics similar to that of parent diphenyl ether (DPE) molecule, perturbed by the substituent (amino group); i.e., the lowest electronic transition is of $\pi \rightarrow \pi^*$ character. The vibrational structures of the absorption spectrum are lost because of the charge-transfer interaction of the lone pair of the amino group with the π cloud of the phenyl ring. Further, the amino group can behave in two ways. Protic solvent interacts with the lone-pair electrons on the nitrogen atom of amino group to form a hydrogen bond and hydrogen atom of the amino group also makes a hydrogen bond with solvents. In the former, a blue shift, and in the latter, a red shift, in the absorption spectrum should be observed. Thus, a blue shift in ν_{max} (abs) in methanol and water suggests the formation of a hydrogen bond with the lone pair, thus inhibiting its interaction with the π cloud. The red shift in acetonitrile (which is a poor hydrogen-acceptor solvent) is due to the usual dipole–dipole effect on the $\pi \rightarrow \pi^*$ transition or to the hydrogen-donating

character of the amino group.

As stated in the above paragraph, the solvent dependence of the fluorescence spectra of aromatic amines resemble that of their absorption spectra in hydrogen-donating or hydrogen-accepting solvents, i.e., blue shift in the former and the red shift in the latter solvents compared with those in cyclohexane. The usual red shift in fluorescence can be explained on the ground that charge migration from the amino group towards the benzene ring increases upon excitation, thereby decreasing the charge density on the nitrogen atom and increasing the proton donor capacity of the amino group. Hence, the fluorescence solvatochromic shift is due to polar and hydrogen acceptor interaction of the solvents. In order to confirm this we used theoretically derived solvent polarizability functions, Reicharts solvent parameters $E_T(30)$[29,30] and Bilot–Kawaski parameters BK[31] values, and compared the Stokes shift for DADPE with these values. These parameters as accurate registers of the solvent polarity have been used by several authors to correlate the molecular-spectroscopic properties. The Stokes shift in various solvents along with the BK and $E_T(30)$ values are given in Table 2. The increase in the Stokes shift from cyclohexane to water in DADPE is related to the $E_T(30)$ values, rather than the BK values. The $E_T(30)$ parameter incorporates both hydrogen-bonding and solvent-polarity effects, whereas the BK parameter represents only solvent-polarity effects. Since hydrogen-bonding interactions are predominant in the solvatochromic shifts of DADPE, the Stokes shifts are plotted only against the $E_T(30)$ values (Fig. 1) (correlation coefficient $r=0.8501$). The Stokes shifts are not well correlated with the BK values. This has also been confirmed by the poor correlation coefficient obtained for a plot of the Stokes shift vs. BK ($r=0.6030$) (Table 2).

Table 2. Stokes Shifts (cm^{-1}) Observed for Bis(4-aminophenyl)ether and 4-Aminodiphenyl Ether in Different Solvents with $E_T(30)$ and BK Values

Solvent	Stokes shifts/cm^{-1}		$E_T(30)$[a]	BK[b]
	DADPE	ADPE		
Cyclohexane	4655	4655	30.9	−0.001
Diethyl ether	4791	—	34.6	0.317
Dioxane	4913	—	36.0	0.043
Tetrahydrofuran	4777	—	37.4	0.550
Ethyl acetate	5027	—	38.1	—
Methyl acetate	4970	—	40.0	—
Dichloromethane	4851	—	41.1	0.586
1,2-Dichloroethane	4843	—	41.9	—
Acetonitrile	5114	5488	46.0	0.864
t-Pentyl alcohol	6077	—	41.9	—
t-Butyl alcohol	5274	—	43.9	0.673
2-Butanol	5865	—	47.1	0.734
2-Propanol	5941	—	48.6	0.766
1-Butanol	5947	—	50.2	—
Ethanol	5434	—	53.7	0.812
Methanol	5209	6462	55.5	0.858
Ethylene glycol	4938	—	56.3	—
Water (neutral)	7014	7529	63.1	0.913
Monocation	7492	3974	—	—
	10842	13556		
Dication	3337	—	—	—
Correlation coefficient				
(i) DADPE	—	—	0.8501	0.6030
(ii) ADPE	—	—	0.9301	0.7619

a) From Refs. 29 and 30. b) From Ref. 31.

Effect of the Proton Concentration. The absorption and fluorescence spectra of DADPE have been studied in the H_o/pH/H_- range of −10 to 17.0. The relevant data are compiled in Table 1, and the absorption and fluorescence spectra of various prototropic species of this compound are also shown in Figs. 2 and 3. With a decrease in pH from 8, the absorption spectrum is blue shifted around pH 4.5,; and thus obtained spectrum resembles that of ADPE.[24] This clearly suggests that the species is a monocation obtained by protonating one of the amino groups. With a further increase in the proton concentration a blue-shifted spectrum resembling the spectrum of diphenyl ether (DPE)[24] is obtained. This spectrum is due to the dication formed by protonating the second amino group. The above behavior is similar to that of the aromatic compounds containing the amino group.

After pH 12 the spectrum is red shifted continuously due to the formation of the monoanion having maxima at 324 and 270 nm at H_- 17, the highest basic conditions used. The pK_a value for this proton-transfer reaction could not be calculated because there was no constancy in the isosbestic point.

Although the formation of various prototropic species in the excited state is the same as that obtained in the ground state, the fluorescence spectra of some of the species do not follow the same trend as that observed in the absorption spectra. The neutral species at pH 8 shows a fluorescence maximum of 368 nm. When the pH is decreased a red-shifted maximum appears at 371 nm for pH 5. Since this

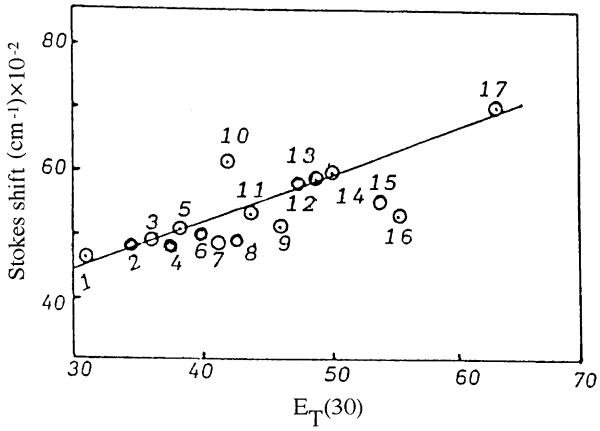


Fig. 1. Correlation of the Stokes shift $\Delta\bar{\nu}_{ss}/cm^{-1}$ of DADPE with the $E_T(30)$ values of different solvents. 1. Cyclohexane, 2. Diethyl ether, 3. Dioxane, 4. Tetrahydrofuran, 5. Ethyl acetate, 6. Methyl acetate, 7. Dichloromethane, 8. 1,2-Dichloroethane, 9. Acetonitrile, 10. *t*-Pentyl alcohol, 11. *t*-Butyl alcohol, 12. 2-Butanol, 13. 2-Propanol, 14. 1-Butanol, 15. Ethanol, 16. Methanol, 17. Water.

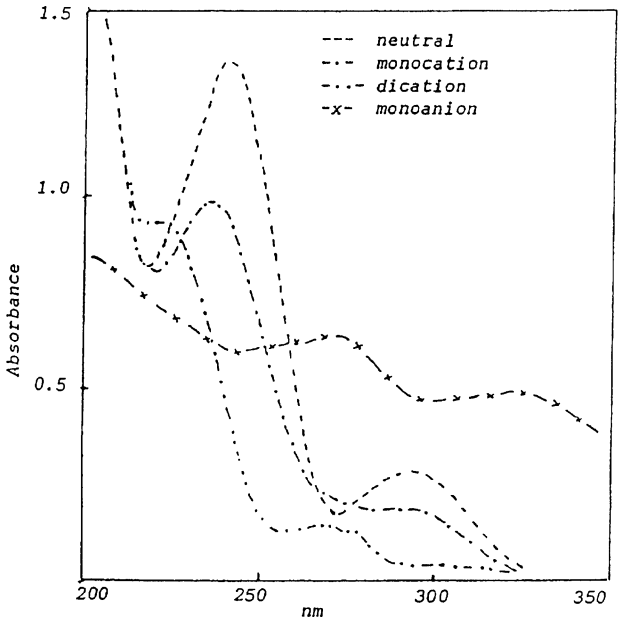


Fig. 2. Absorption spectra of different prototropic species (concentration 4×10^{-5} M) of DADPE at 298 K. --- neutral, –·– monocation, –··– dication,-×- monoanion.

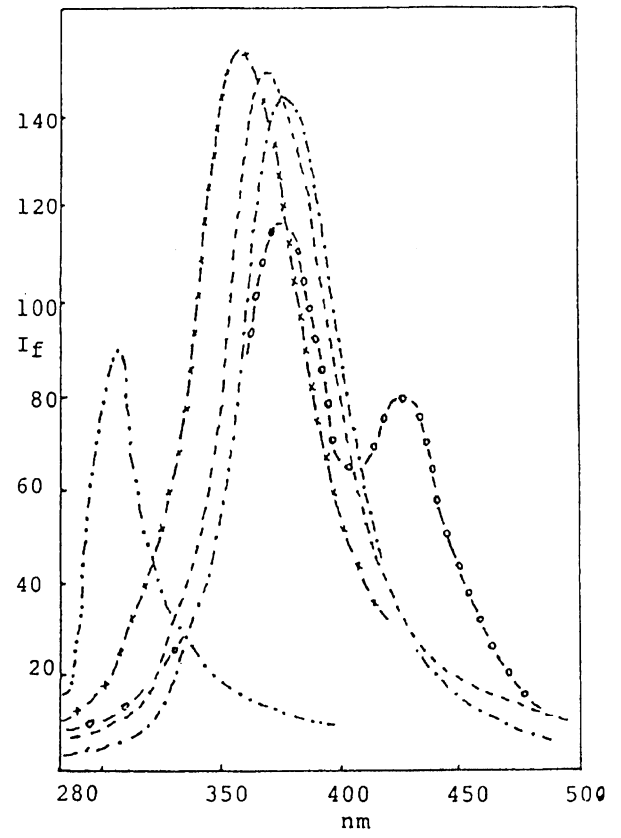


Fig. 3. Fluorescence spectra of different prototropic species (concentration 4×10^{-5} M) of DADPE at 298 K. --- neutral, –·– monocation, –··– dication,-o- dication complex, -×- dianion.

fluorescence maximum is the same as that of ADPE,[24] this spectrum is due to the monocation. Although a decrease in the pH from 5 gives another red-shifted maximum at around 422 nm up to pH 3.5, but after 3.5 both the maxima 371 and 422 nm decrease and a new blue-shifted spectrum with a maximum at around 305 nm appears at pH 1.3. To assign the species for the abnormally red-shifted maximum at 422 nm and the maximum at 305 nm we recorded the fluorescence spectra of DPE in different solvents and in 1 M H_2SO_4 (Fig. 4). The fluorescence spectra of DPE in water gives two maxima: one at shorter wavelength (345 nm) and the other at longer wavelength (410 nm). Although in methanol two closer peaks (300, 325 nm) were also observed, in acetonitrile there was only a small red-shift compared to that in cyclohexane. This reveals that DPE forms a solute–solvent exciplex in hydrogen-donor solvents, such as methanol and water. The well-separated and largely red-shifted solute–water exciplex peak is due to a greater hydrogen-donor capacity of water than that of methanol. Hence, the red-shifted maxima of DADPE at around pH 3.5 is due to the dication–water exciplex. When the pH is decreased, the complex dissociates to form the dication, which has a maximum at 305 nm. This spectrum resembles the spectrum of DPE in 1 M H_2SO_4 (in the same medium). A similar solute–solvent complex for the monocation of ADPE has already been reported.[24] Hence, in this case this red-shifted maximum (422 nm) may be due to the formation of a dication–solvent exciplex. There was no significant change in the spectrum along with a further increase in the acidity up to H_o −10.

Unlike the absorption spectrum, the fluorescence spectrum of the monocation of DADPE shifts to red, which is anomalous. This red shift is due to a large solvent relaxation of $DADPEH^{+1}$ in an aqueous medium. This can be confirmed if one records the spectral changes of these three species in a nonpolar solvent cyclohexane (Fig. 5). Table 3 gives the absorption and fluorescence spectral data of neutral DADPE and the monocation and dication. The latter two species

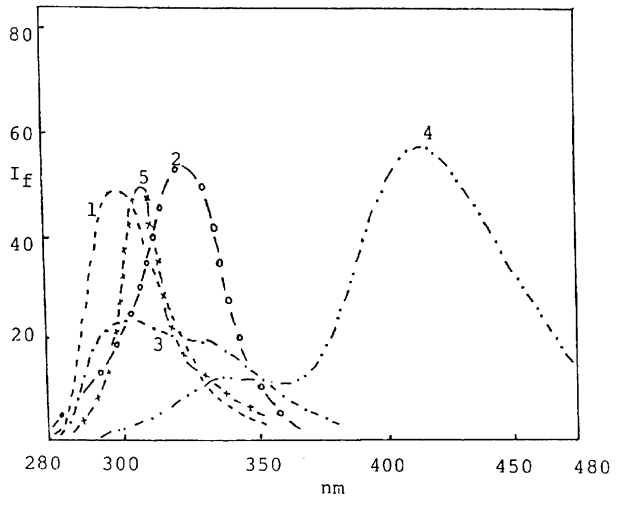


Fig. 4. Fluorescence spectra of DPE in selected solvents at 298 K (concentration 4×10^{-5} M). 1. Cyclohexane, 2. Acetonitrile, 3. Methanol, 4. Water, 5.1 M H_2SO_4 (H_o = −0.26).

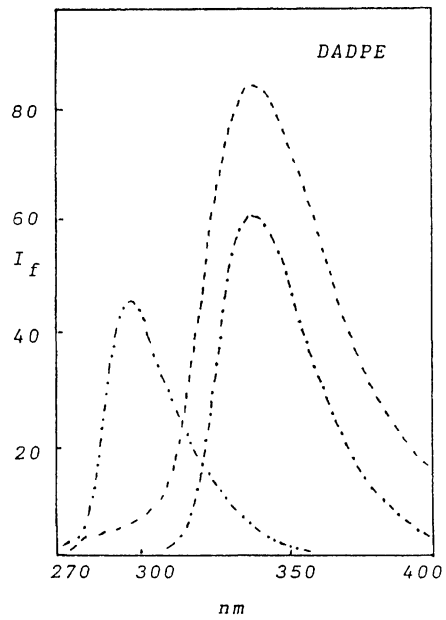


Fig. 5. Fluorescence spectra of different prototropic species (concentration 4×10^{-5} M) of DADPE in nonpolar-TFA medium at 298 K. --- neutral, –·– monocation, –··– dication.

Table 3. Absorption and Fluorescence Maxima and Stokes Shift of DADPE in Cyclohexane–TFA Medium

Solvent	λ_{abs} / nm	λ_{flu} / nm	$\Delta\bar{\nu}_{ss}$ / cm^{-1}
Cyclohexane	298.0 246.8	346.0	4655
Cyclohexane 0.001% TFA	297.6 242.0	345.0	4617
Cyclohexane 0.01% TFA	278.0 272.0 266.0	301.0	2749
Cyclohexane 1% TFA	278.0 271.8 266.0	300.5	2693

were obtained by the addition of different amounts of trifluoroacetic acid (TFA) in cyclohexane. Although the absorption spectra of the ionic species matched those species derived by the addition of sulfuric acid in an aqueous medium, the fluorescence spectra were different under this environment. The

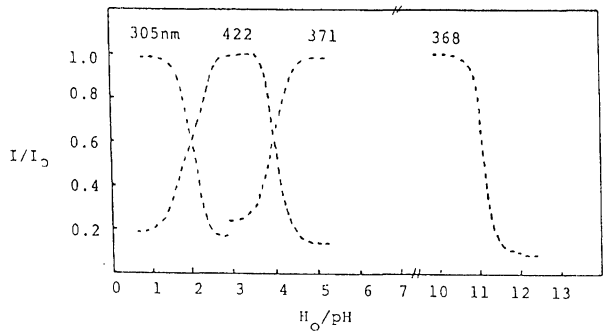
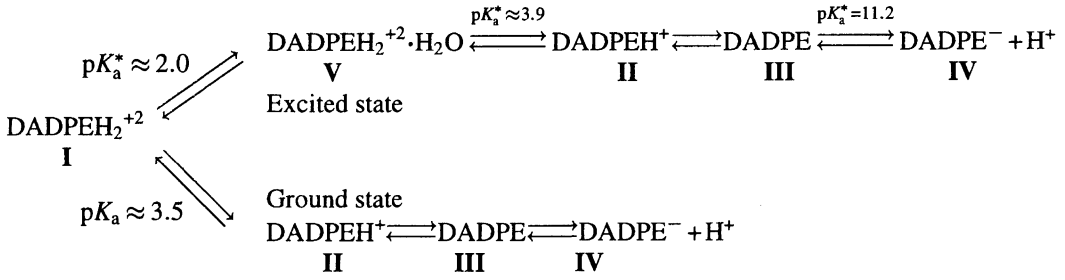


Fig. 6. Plot of I/I_0 vs. pH of the various prototropic species of DADPE.

sequence of fluorescence blue shifts obtained in the cyclohexane–TFA medium was similar to the normal behavior of the aromatic amines. Hence, as explained earlier, in a comparative spectral analysis of DADPE and ADPE in any one polar solvent here the small red shift in the protonation of DADPE in aqueous solution again confirms that the net effect of two amino groups, is less than that of one amino group.

When the pH is increased from 7 the fluorescence at 368 nm is quenched due to the formation of the monoanion. The monoanions of many aromatic amino compounds have been reported to be nonfluorescent.[16—20,35] At a very highly basic solution H_- 16 a blue shifted fluorescence at 356 nm is obtained. Earlier Dogra et al.[36] assigned this band to the dianion species formed by the deprotonation of both protons of the amino group. Doubts have arisen concerning this species due to the results of Chowdhury and Chattopadyay,[37] since the latter workers have observed similar results with *N,N*-dimethyl-2-naphthylamine, where no dissociable protons are present at the amino group. Although, the nature of this species is still doubtful, it can be speculated that it is due to deprotonation of the aromatic ring.[37]

Acidity Constants. As stated earlier, the effect of the proton concentration on the absorption and fluorescence revealed the presence of the following prototropic species in the ground and excited states (Scheme 1): dication (**I**), monocation (**II**), neutral molecule (**III**), monoanion (**IV**), and a dication–water exciplex (**V**). The monoanion is found to be nonfluorescent. The absorption and fluorescence spectra of other species are shown in Figs. 2 and 3. The various proton-transfer reactions in the ground and excited states are given



Scheme 1.

in the following scheme (Scheme 1): The pK_a values for the ground-state equilibria were determined spectrophotometrically, and are listed on the arrows. The formation of a dication–water exciplex leads to excited-state equilibria that are quite different from that of the ground state. The Förster cycle method could not be used to determine the excited-state pK_a (pK_a^*) for the equilibria of the dication–dication exciplex and dication exciplex–monocation, since the species involved in the equilibrium are different in the S_0 and S_1 states. The pK_a^* values have been determined by fluorimetric titrations (Fig. 6), and are given in the Scheme 1. As can be seen in the Fig. 6, the crossing of the fluorimetric titration curves for both equilibria occurs at their middle points of their inflections. This reveals that processes other than the above-mentioned equilibria, such as proton-induced fluorescence quenching, are absent. Furthermore, this also confirms the presence of a species (dication exciplex) between dication and monocation in the excited state. The ground and excited-state pK_a values for the equilibrium between monocation (**II**) and neutral molecule (**III**) could not be determined, since the absorption and fluorescence spectral shifts between the two species are very small (3 nm). In the case of equilibrium between a neutral molecule (**III**) and monoanion (**IV**), there was no constancy in the isosbestic point in the absorption spectra. The pK_a^* value for this equilibrium was determined by fluorimetric titration using a wavelength of constant absorbance as the excitation wavelength. This value shows that the DADPE becomes more acidic in the excited singlet state.

The authors are thankful to Dr. P. L. Sabarathinam, Professor and Head, Department of Technology and Dr. R. Gurumurthy, Professor and Head, Department of Chemistry, Annamalai University for providing lab facilities.

References

1) Th. Förster, *Z. Elektrochem. Angew. Phys. Chem.*, **54**, 42 (1950).
2) A. Weller, *Ber. Bunsenges. Phys. Chem.*, **56**, 662 (1952); **66**, 1144 (1956).
3) A. Weller, *Prog. React. Kinet.*, **1**, 189 (1951).
4) E. Van der Donckt, *Prog. React. Kinet.*, **5**, 273 (1970).
5) E. L. Wehry and L. B. Rogers, "Fluorescence and Phosphorescence Analysis,"ed by D. M. Hercules, Wiley-Interscience, New York (1966), p. 125.
6) S. G. Schulman, "Modern Fluorescence Spectroscopy," ed by E. L. Wehry, Plenum, New York (1976), Vol. 2.
7) S. G. Schulman, "Fluorescence and Phosphorescence Spectroscopy," Pergamon, Oxford (1977).
8) J. F. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.*, **12**, 131 (1976), and a number of references mentioned therein.
9) M. Swaminathan and S. K. Dogra, *J. Am. Chem. Soc.*, **105**, 6233 (1983); *J. Chem. Soc., Perkin Trans. 2*, **1984**, 947; *Can. J. Chem.*, **61**, 1064 (1983).
10) S. Kothainayaki and M. Swaminathan, *J. Photochem. Photobiol. A, Chem.*, **84**, 13 (1994).
11) K. Kalaiyarasan, N. Rajendiran, and M. Swaminathan, *Indian J. Chem., Sect. A*, **33A**, 335 (1994).
12) R. W. Cowgill, *J. Photochem. Photobiol. A, Chem.*, **13**, 183 (1971).
13) J. W. Bridges and R. T. Williams, *Biochem. J.*, **107**, 225 (1968).
14) D. W. Ellis and L. B. Rogers, *Spectrochim. Acta*, **20**, 1720 (1964); **20**, 1709 (1964).
15) R. S. Sarpal and S. K. Dogra, *J. Photochem.*, **38**, 263 (1987).
16) R. Manoharan and S. K. Dogra, *Bull. Chem. Soc. Jpn.*, **60**, 4409 (1987).
17) N. Rajendiran and M. Swaminathan, *J. Photochem. Photobiol. A, Chem.*, **90**, 109 (1995).
18) R. Manoharan and S. K. Dogra, *Can. J. Chem.*, **65**, 2013 (1987).
19) N. Rajendiran and M Swaminathan, *Bull. Chem. Soc. Jpn.*, **68**, 2797 (1995).
20) H. Shizuka, T. Ogiwara, and E. Kimura, *J. Phys. Chem.*, **89**, 4302 (1985).
21) Th. Förster, *Z. Elektrochem.*, **54**, 531 (1950).
22) H. Boaz and G. K. Rollefson, *J. Am. Chem. Soc.*, **72**, 3435 (1950).
23) R. Manoharan and S. K. Dogra, *J. Phys. Chem.*, **92**, 5282 (1988).
24) N. Rajendiran and M. Swaminathan, *J. Photochem. Photobiol. A, Chem.*, **93**, 103 (1996).
25) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry, Organic Solvents," ed by A. Weisberger, Wiley-Interscience, New York (1970), Vol. II, pp. 529, 644, and 695.
26) M. J. Jorgenson and D. A. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).
27) G. Yagil, *J. Phys. Chem.*, **71**, 1054 (1967).
28) N. Rajendiran and M. Swaminathan, *Indian J. Chem., Sect. A*, **35A**, 385 (1996).
29) C. Reichart, *Angew. Chem., Int. Ed. Engl.*, **18**, 98 (1979).
30) C. Reichart and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968).
31) L. Biolet and A. Kawaski, *Z. Naturforsch., A*, **18A**, 621 (1962).
32) R. A. Loutfy and J. H. Sharp, *J. Phys. Chem.*, **83**, 1208 (1979).
33) T. C. Werner and D. B. Lyon, *J. Phys. Chem.*, **86**, 933 (1982).
34) E. M. Kowsar, H. Dodiuk, K. Tanizawa, M. Ottolenghi, and M. Orbach, *J. Am. Chem. Soc.*, **97**, 2167 (1975).
35) A. K. Mishra and S. K. Dogra, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 943.
36) A. K. Mishra, M. Swaminathan, and S. K. Dogra, *J. Photochem.*, **28**, 87 (1985).
37) A. Chowdhury and N. Chattopadyay, *J. Photochem. Photobiol. A, Chem.*, **41**, 337 (1988).