Photoluminescence of 4,4′-Diaminobiphenyl

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(Received January 31, 1995)

Fluorescence solvatochromic shifts of 4,4′-diaminobiphenyl (DABP) were found to be less than those of 4-aminobiphenyl and the difference mainly occured in hydrogen bonding solvents. This shows that the net effect of hydrogen bonding interactions of two amino groups is less than that of one amino group. The unusual fluorescence red-shift observed for the monocation of DABP relative to the neutral form is not because of the amino group becoming more basic, but because of a large solvent relaxation in aqueous media. As the entire molecule becomes planar upon excitation, its behavior is found to be similar to that of 2,7-diaminofluorene in the S_1 state. pK_a values for various prototropic reactions in the S_0 and S_1 states were determined and are discussed.

Solvatochromic and prototropic effects of several bifunctional molecules such as aminoindazoles,[1—3] aminophenols,[4] quinolinecarboxylic acids,[5] and hydroxy aromatic acids[6,7] have been studied. Bifunctional molecules with electron-withdrawing (COOH, pyridinic nitrogen atom) and electron-donating groups (OH, NH_2) behave in a manner similar to that of monofunctional molecules in the ground state. But in some molecules, an increase in the basicity of the electron-withdrawing group or in the acidity of the electron-donating group in the excited state is so large that the site of protonation is different from that in the ground state. For example, at pH 2.5, 5-aminoindazole[1] exists as a monocation, formed by protonating the amino group in the ground state. However, in the lowest excited singlet state, the stable species is also a monocation formed by protonation of the tertiary nitrogen atom. The change in the species formation in the ground and first excited singlet states is termed phototautomerism because it involves proton migration from one functional group to another. This kind of isomerization is called biprotonic phototautomerism because the electron-donating and electron-withdrawing groups are widely separated. In molecules where the electron-donating and electron-withdrawing groups are close to each other, e.g., 2-(2-hydroxyphenyl)benzimidazole,[8] the phototautomerism can occur by intramolecular hydrogen bonding. This is called monoprotonic or intramolecular phototautomerism. Many molecules fall into either of the above categories.

Studies of bifunctional molecules in which both functional groups are electron-donating have revealed some very interesting features.[9—15] For example, all the phenylenediamines[13] (*ortho*, *meta*, and *para*) give rise to a similar sequence of spectral changes when protonation is carried out stepwise, and this agrees with the normal behavior of aromatic amines. However, in the cases of 2,7-diaminofluorene (DAF)[12] and 2,3-diaminonaphthalene (DAN)[14] a red-shift is observed on the protonation of the first amino group (which is anomalous behavior) followed by a large blue-shift in the fluorescence spectrum when the second amino group is protonated. On the other hand, in a nonpolar medium (cyclohexane) DAF exhibits the normal behavior of an aromatic amine, whereas DAN shows the same anomalous behavior. It was reported that the large red-shift of DAF in polar solvents is due to a large solvent relaxation and in DAN the red-shift is due to the steric effects of the adjacent amino groups. Our recent study on bis-(4-aminophenyl) ether[16] also revealed a behavior similar to DAF. The present investigation is an extension of our earlier work on mono and diamino compounds.[17,18] The molecule 4,4′-diaminobiphenyl (DABP) has been selected because a detailed study on 4-aminobiphenyl (ABP)[19] is already available. When the biphenyl[20] moiety of DABP attains planarity upon excitation as in biphenyl, the molecular structure of DABP becomes similar to that of DAF. Hence we would like to find out whether the emission characteristics of this molecule are similar to those of DAF.

Experimental

4,4′-Diaminobiphenyl was obtained from S. D. Fine Chem. 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 at different wavelengths. Spectrograde methanol (BDH), analytical grade sulfuric acid, sodium hy-

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droxide, and trifluoroacetic acid (TFA) were used as such. Anala R grade of other solvents were further purified according to a procedure suggested in the literature.[21] 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,[22] (H_0) for solutions below pH 1.5 (using a H_2SO_4–H_2O mixture) and Yagil's basicity scale,[23] H_- for solutions above pH 12 (using a NaOH–H_2O mixture) were employed. Hammett's acidity function (H_0) serves specifically as a measure of the tendency for the solution in question to transfer a proton to an uncharged or charged base molecule with increasingly negative values corresponding to higher acidity.

Absorption spectra were recorded with a JASCO MODEL 7800 spectrophotometer, while fluorescence measurements were made using a JASCO FP-550 spectrofluorimeter. pH values in the range 1.5 to 12.0 were measured on an ELICO pH meter model LI-10T. Due to the poor solubility of DABP in water, a stock solution was prepared in methanol. The concentrations of the solutions were of the order of 10^{-5}—10^{-4} M (1 M=1 mol dm^{-3}). Solutions for absorptiometric and fluorimetric titrations were prepared just before taking measurements. The isosbestic wavelengths were used for measuring the fluorescence intensities at the analytical wavelengths.

Results and Discussion

Effects of Solvents. The absorption maxima, $\log\epsilon$, and fluorescence maxima of DABP were observed in solvents having various polarities and hydrogen bonding abilities. The relevant data for DABP are compiled in Table 1 along with the spectral data of ABP.[19] In comparison with those of biphenyl[24—26] and ABP, the absorption maxima of DABP are red-shifted in solvents. The absorption peak of DABP in cyclohexane is slightly blue-shifted compared with its peak in other solvents. The spectral shifts observed in the absorption spectrum of DABP in more polar and hydrogen-bonding solvents are consistent with the characteristic behavior of amino groups,[27] i.e., DABP acts as a proton-donor in proton-acceptor solvents but preferably as a proton-acceptor if the solvent has both proton-donor and proton-acceptor properties in the S_0 state.

Table 1. Absorption and Fluorescence Maxima and $\log\epsilon$ of 4,4′-Diaminobiphenyl and 4-Aminobiphenyl in Different Solvents and at Various Acid Concentrations

Solvents	DABP			ABP[a]		
	λ_{abs} / nm	$\log\epsilon$	λ_{flu} / nm	λ_{abs} / nm	$\log\epsilon$	λ_{flu} / nm
Cyclohexane	279.0	—	370	274.8	4.34	345
Dioxane	288.2	4.43	388			
Ethyl acetate	287.4	4.53	387			
Dichloromethane	286.2	4.51	380			
Acetonitrile	288.4	4.48	388	283.8	4.40	359
t-Pentyl alcohol	283.2	4.62	391			
t-Butyl alcohol	283.4	4.59	392			
2-Propanol	283.2	4.52	392			
1-Butanol	283.2	4.60	392			
Methanol	282.4	4.61	392	277.2	4.43	367
Ethylene glycol	287.2	4.50	392			
Water (neutral)	280.2	4.31	393	272.5	4.37	381
Monocation	275.0	—	412	248.5	—	310
Dication	247.0	—	310			
Monoanion	310.0	—	—			
Dianion	—	—	385			

a) Ref. 19.

The fluorescence spectra of DABP in different solvents are displayed in Fig. 1. The fluorescence spectrum is regularly red-shifted as the polarity and proton-donor ability of the solvents increase. The fluorescence spectra results can be explained by charge migration from the amino group to the benzene ring upon excitation. That is, the charge density of the nitrogen atom decreases resulting in an increase in the proton-donor ability of the amino group. Hence the fluorescence solvatochromic shift is due to the polar effects and hydrogen acceptor interactions of the solvents.

Though the fluorescence solvatochromic shifts of DABP are due to the characteristic behavior of amino groups, they are less than those of ABP.[19] The red-shifts seen when changing the solvent from cyclohexane to water are 1582 and 2739 cm^{-1} for DABP and ABP, respectively. This difference is mainly caused by hydrogen-bonding with the solvents. The red-shift from acetonitrile to water for ABP is about 4.5 times greater than that of DABP, i.e., the shift in DABP is 5 nm whereas in ABP it is 22 nm (Table 1). This reveals that the net effect of the hydrogen-bonding of two amino groups with solvents is less than that of one amino group. As reported in biphenyl,[20] in DABP the two phenyl rings become planar upon excitation resulting in an increase in the delocalization between the rings. As the amino groups are symmetrically placed along the long axis of the molecules, the solvent interactions are acting in opposite directions. Since the hydrogen bonding interactions are more predominant in the excited state, the effect of two amino groups is less than that of one amino group in hydrogen-bonding solvents. This is also confirmed by the correlation between the Stokes shift $\{\nu_{abs}(max)-\nu_{flu}(max)\}$ and the solvent parameters. The values of the solvent parameters $E_T(30)$[28,29] and BK[30] as accurate registers of solvent polarity have been used by several authors to correlate molecular spectroscopic properties.[31—33] The Stokes shifts in various solvents along with the $E_T(30)$ and BK values are given in Table 2. The Stokes shifts are related to $E_T(30)$ more than BK. In many monohydroxy[34] and monoamino compounds[17,18,35] a good linear correlation is obtained between the Stokes shift and $E_T(30)$. In this compound, however, a plot of the Stokes shift vs. $E_T(30)$ gave a poor correlation (γ=0.6958) compared to that in the monofunctional derivative ABP (γ=0.7651) (Fig. 2). Similar behavior

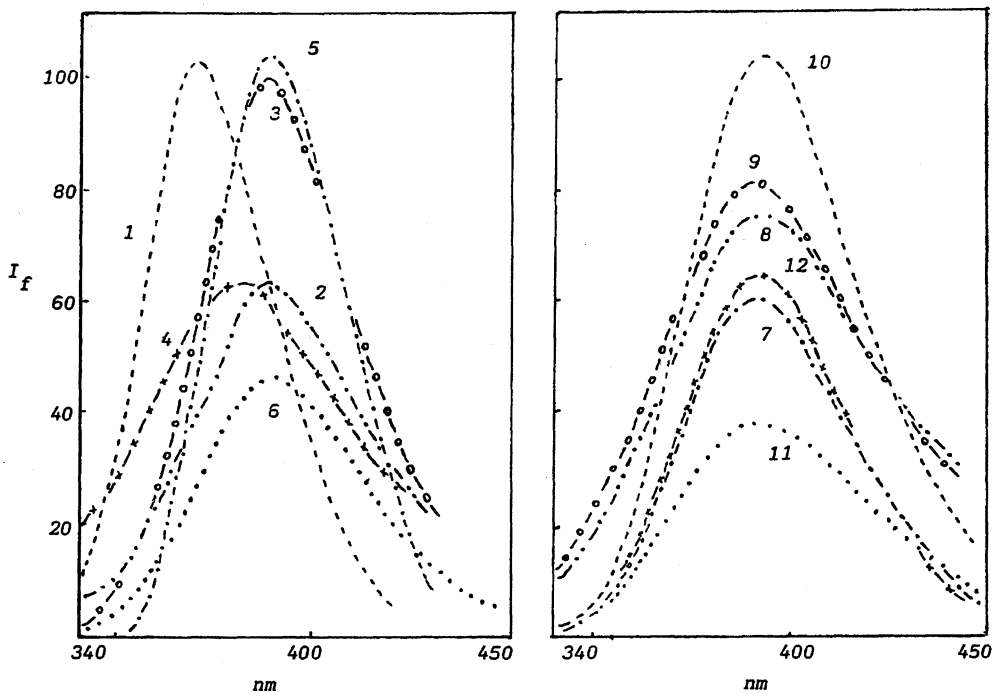

Fig. 1. Fluorescence spectra of DABP in various solvents at 298 K concentration ca. 4×10^{-5} M. 1. Cyclohexane, 2. Dioxane, 3. Ethyl acetate, 4. Dichloromethane, 5. Acetonitrile, 6. *t*-Pentyl alcohol, 7. *t*-Butyl alcohol, 8. 2-Propanol, 9. 1-Butanol, 10. Methanol, 11. Water, 12. Ethylene glycol.

Table 2. Stokes Shifts (cm^{-1}) Observed for DABP and ABP in Different Solvents with $E_T(30)$ and BK Values

Solvents	DABP	ABP[a)]	$E_T(30)$[b)]	BK[c)]
Cyclohexane	8815	7405	31.2	−0.001
Dioxane	8925	—	36.0	0.043
Ethyl acetate	8955	—	38.1	—
Dichloromethane	8625	—	41.1	0.586
Acetonitrile	8901	7381	46.0	0.864
t-Pentyl alcohol	9735	—	41.9	—
t-Butyl alcohol	9513	—	43.9	0.673
2-Propanol	9538	—	48.6	0.766
1-Butanol	9513	—	50.2	0.754
Methanol	9638	8827	55.5	0.858
Ethylene glycol	9046	—	56.3	—
Water (neutral)	10244	10451	63.1	0.913
Monocation	12092	7935	—	—
Dication	8228	—	—	—

a) Ref. 19. b) Refs. 28 and 29. c) Ref. 30.

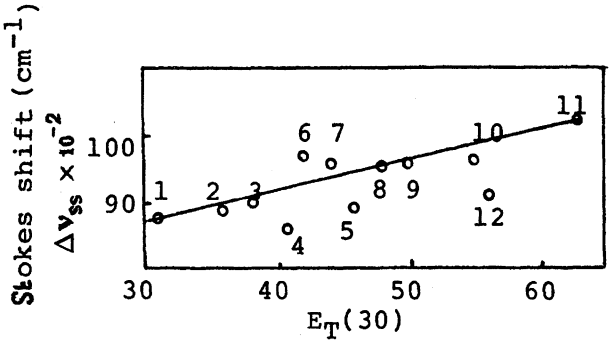

Fig. 2. Correlation of the Stokes shift ν_{ss} cm^{-1} of DABP with the $E_T(30)$ values of different solvents. 1. Cyclohexane, 2. Dioxane, 3. Ethyl acetate, 4. Dichloromethane, 5. Acetonitrile, 6. *t*-Pentyl alcohol, 7. *t*-Butyl alcohol, 8. 2-Propanol, 9. 1-Butanol, 10. Methanol, 11. Water, 12. Ethylene glycol.

was observed in bis(4-hydroxyphenyl) sulfone.[36)] This also reveals that for bifunctional derivatives the change in the dipole moment upon excitation is smaller than that of monofunctional derivatives.

Effects of pH. The absorption and fluorescence spectra of DABP were studied in the H_0/pH/H_- range of −10 to 17.0. The relevant data are compiled in Table 1 and the absorption and fluorescence spectra of the various prototropic species of DABP are also shown in Figs. 3 and 4, respectively. With a decrease in pH from 8 the absorption spectrum is blue-shifted around pH 5 and becomes similar to that of ABP.[19)] This clearly suggests that the species formed is the monocation obtained by protonating one of the amino groups. With a further increase of the proton concentration, another blue-shifted absorption spectrum resembling that of biphenyl[24—26)] is obtained. This spectrum is due to the dication formed by protonation of the second amino group. No further change in the absorption spectrum is noticed even at H_0 −10.

The absorption peak at 280 nm is not much affected until H_- 15 but after that there is a sharp decrease of intensity up to H_- 16 leading to a flat band. At H_- 17 a weak absorption maximum around 310 nm is obtained.

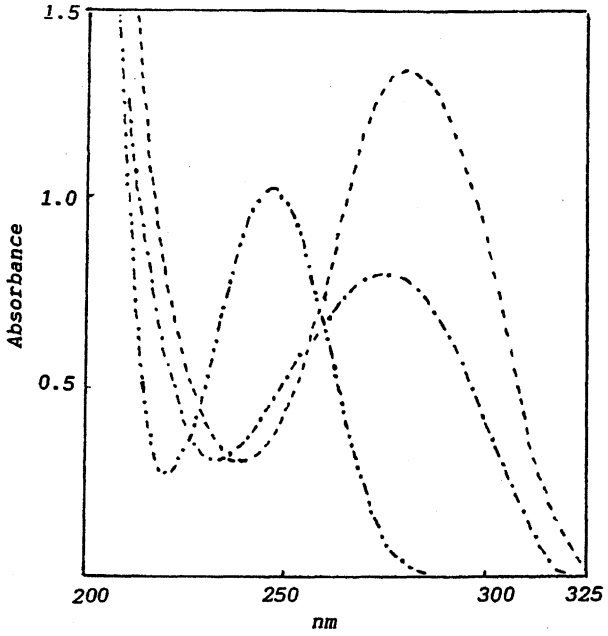

Fig. 3. Absorption spectra of different prototropic species of DABP at 298 K concentration ca. 4×10^{-5} M. --- neutral, –·– monocation, –···– dication.

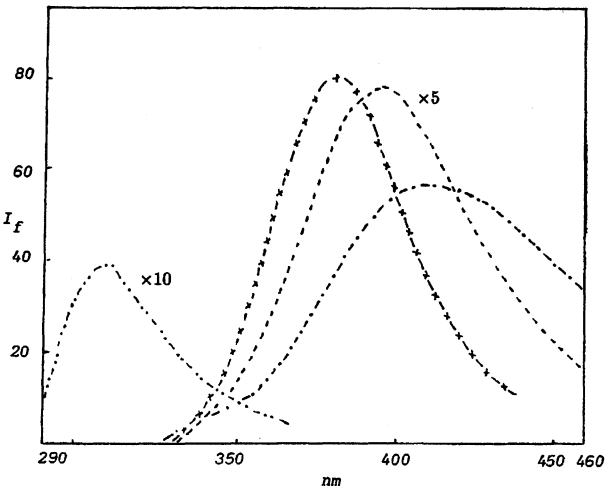

Fig. 4. Fluorescence spectra of different prototropic species of DABP at 298 K concentration ca. 4×10^{-5} M. --- neutral, –·– monocation, –···– dication, –×– dianion.

This may be due to the formation of the monoanion. The pK_a value for this proton transfer reaction could not be calculated because there was no constancy in the isosbestic point.

The fluorescence characteristics of the cationic species of DABP are different from the absorption characteristics. DABP is weakly fluorescent (393 nm) in neutral solution. In the region near pH 5, the weakly fluorescent band is red-shifted and the intensity of the newly-formed fluorescent band (412 nm) increases up to pH 3. When the acidity is increased, the 412 nm fluorescence is quenched from pH 3 to pH 1 and around H_0 −0.5 a large blue-shifted fluorescence spectrum with a maximum at 310 nm appears. Compared with the fluorescence intensity of the neutral species (393 nm), the intensity of the 310 nm fluorescence is very small. This fluorescence spectrum exactly resembles that of the parent biphenyl[24—26] molecule. There is no significant change in the spectrum with a further increase in the acidity up to H_0 −10. The fluorescence with the peak at 310 nm is due to the formation of the dication. The excitation spectrum monitored at 412 nm resembles the absorption spectrum of the monocation. Hence the red-shifted peak at 412 nm is due to the monocation of DABP. Similar behavior was reported for DAF.[12] In DAF, the two phenyl rings are connected by a methylene (CH_2) group making the whole molecule planar.[37] The two phenyl rings in DABP also attain planarity upon excitation and the entire molecule becomes coplanar.[20] Hence its behavior is expected to be similar to that of DAF in the excited singlet state. As reported for DAF, an unusual red-shift observed for the DABP monocation is due to its large solvent relaxation in a polar medium. This is also confirmed by the difference in the fluorescence spectral data of the neutral, monocation, and dication forms of DABP in polar and nonpolar media. Table 3 depicts the absorption and fluorescence maxima of neutral, monocation, and dication DABP in cyclohexane. The latter two species were obtained by the addition of a different amount of trifluoroacetic acid (TFA) in cyclohexane. The absorption spectra of the ionic species matched that of those species derived by the addition of sulfuric acid in aqueous medium, but the fluorescence spectra were different in similar environments. The results obtained in cyclohexane were similar to the normal behavior of the aromatic amines. This indicates that the red-shift in a polar aqueous medium is only due to the large solvent relaxation of the monocation in the excited state. In cyclohexane, the Stokes shift of the neutral, monocationic, and dicationic species are 8815, 6173, and 8392 cm^{-1} respectively, whereas in water they are 10244, 12092, and 8228 cm^{-1} respectively. The large discrepancy between the Stokes shifts for $DABPH^+$ in cyclohexane and water must be due to the large relaxation of the polar solvent (water) molecule. The large Stokes shift of $DABPH^+$ in water also suggests that this species is stabilized in

Table 3. Absorption and Fluorescence Maxima and Stokes Shift of DABP in Cyclohexane in the Presence of TFA

Compound	λ_{abs} / nm	λ_{flu} / nm	Stokes shift / cm^{-1}
Cyclohexane	279	370	8815
Cyclohexane 0.005% TFA	270	324	6173
Cyclohexane 0.1% TFA	246	310	8392

the excited state more than in the ground state.

When the pH is increased from 7, the fluorescence at 393 nm is quenched due to the formation of the monoanion. The monoanions of many aromatic amino compounds are found to be nonfluorescent[38] with a few exceptions.[39] In a very high basic solution (H_- 16), a blue-shifted fluorescence at 385 nm was obtained. The blue-shifted fluorescence is reported to be due to the formation of the dianion. Earlier, Dogra et al.[38b,40] assigned this band to the dianion species formed by the deprotonation of both protons of the amino group. This was questioned by Chowdhury and Chattopadyay,[41] since similar results were obtained in the case of 2-(dimethylamino)naphthalene having no dissociable protons on the amino group. It is speculated that this species is due to the deprotonation of the aromatic ring. However, the nature of the species is still unresolved at present.

Equilibrium Constants in the Ground and Excited States.

$$DABPH_2^{2+} \rightleftharpoons DABPH^+ + H^+ \quad (1)$$

$$DABPH^+ \rightleftharpoons DABP + H^+ \quad (2)$$

$$DABP \rightleftharpoons DABP^- + H^+ \quad (3)$$

The ground state pK_a values of the dication–monocation and monocation–neutral equilibria were calculated spectrophotometrically to be 3.54 and 4.60, respectively. The $pK_a(2)$ value of 4.60 is close to that of aromatic amines (4.5)[42] and the $pK_a(1)$ value is lower than 4.5. This suggests that the molecule becomes less basic when one of the amino groups is protonated. The pK_a^* values for these equilibria in the S_1 state were determined by fluorimetric titrations (FT) (Fig. 5) as well as with the help of the Förster cycle method[43] using absorption, fluorescence, and the average of the absorption and fluorescence maxima. The data are compiled in Table 4. In the case of the neutral–monoanion equilibrium, the pK_a^* value could not be determined by the Förster cycle method since the ground state pK_a value was not known exactly. pK_a^*(FT) obtained by the quenching curve was found to be 13.3.

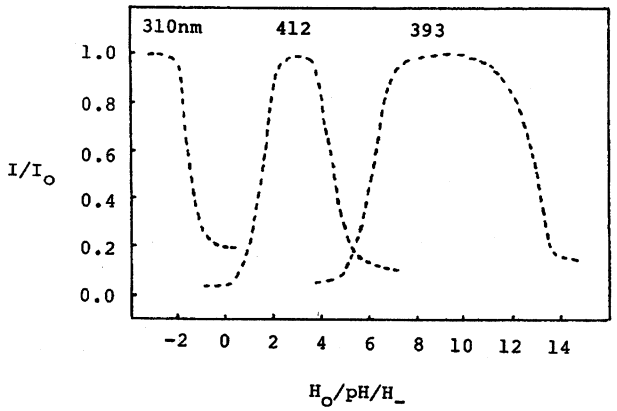

Fig. 5. Plot of I/I_0 vs. $H_0/pH/H_-$ of the various prototropic species of DABP.

Table 4. pK_a Values of the Prototropic Equilibria of DABP in the Lowest Excited Singlet and Ground States[a]

Equilibrium	pK_a (abs)	pK_a^* (FT)	Förster cycle method pK_a^* (abs)	pK_a^* (flu)	pK_a^* (ave)
Dication⇌ monocation	3.54	−1.60	−6.53	−13.23	−9.88
Monocation ⇌ neutral	4.60	4.50	3.46	7.06	5.26
Neutral ⇌ monoanion	>15	13.3	—	—	—

a) (FT)-From fluorimetric titrations, Förster cycle method using (abs)-Absorption data, (flu)-Fluorescence data, (ave)-average of absorption and fluorescence data.

The pK_a^*(FT) value for the monocation–neutral equilibrium is close to that in the ground state. This could be either due to the short lifetimes of the conjugate acid-base pair or that the concentrations of hydrogen ions are so small that the rate of protonation or deprotonation competes with the rate of emission. The agreement with the Förster cycle pK_a^* values is not good. The Förster cycle method using fluorescence data has clearly indicated that the amino group becomes more basic on excitation, which is completely opposite to the normal behavior of aromatic amines. This is because of the unusual fluorescence red-shift observed on protonation of DABP in water. As stated earlier, the unusual red-shift is due to the large solvent relaxation of $DABPH^+$ (12092 cm^{-1}) as compared to that observed for the neutral (10244 cm^{-1}) or dication (8228 cm^{-1}) forms in water. The normal blue-shift observed for $DABPH^+$ in cyclohexane further proves this point. Thus, as suggested by Schulman et al.,[44] the Förster cycle method using the fluorescence maxima and the average of the absorption and fluorescence maxima will not be useful in this equilibria. In the fluorimetric titration between the dication–monocation forms, proton-induced quenching of the monocation is observed. The dication is formed only after complete quenching of the monocation. Similar behavior was reported for the dication–monocation equilibria of DAF. In these cases, the pK_a^* value is calculated from the formation curve of the dication and pK_a^*(FT) for this equilibria is −1.60. The pK_a^* value obtained using fluorescence maxima cannot be compared with other values for the reasons mentioned earlier.

The proton-induced quenching can be described by the simple Stern–Volmer equation

$$I_0/I = 1 + k_q\tau[H^+], \quad (4)$$

where I and I_0 are the fluorescence intensities of the monocation in the presence and absence of $[H^+]$, k_q is

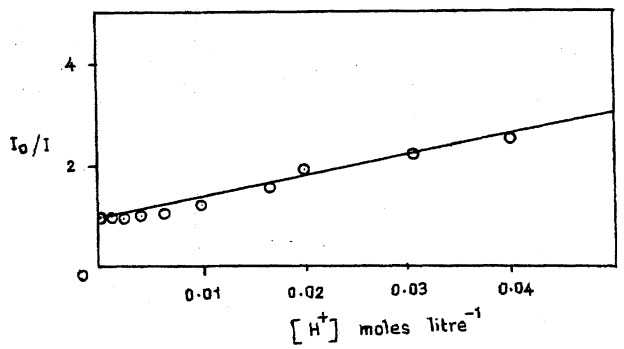

Fig. 6. Plot of I_0/I vs. $[H^+]$.

the proton-induced fluorescence quenching constant and τ is the lifetime of the monocation. $k_q\tau$ is calculated from Fig. 6 and is 26.3 $dm^3\ mol^{-1}$.

The authors are grateful to Dr. P. L. Sabarathinam, Professor and Head, Department of Technology, and Dr. M. Uma, Professor and Head, Department of Chemistry, Annamalai University, for providing lab facilities.

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