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Spectral characteristics of 4-aminodiphenyl ether in different solvents and at various pH values

N. Rajendiran [1], M. Swaminathan *

Department of Technology, Annamalai University, Annamalainagar 608 002, Tamil Nadu, India

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Abstract

The solvatochromic shifts are found to be mainly due to the interaction of solvents with the amino group of 4-aminodiphenyl ether (ADPE). There is an increase in Stokes' shift with the increase in polarity and hydrogen bonding ability of solvents. The abnormal red shift in the fluorescence spectrum on protonation of ADPE is neither due to the amino group becoming more basic nor due to large solvent relaxation in aqueous solution but is due to monocation–solvent exciplex formation. The monocation of ADPE in cyclohexane followed the normal blue shift in the fluorescence spectrum. Contrary to other aromatic amines, ADPE does not undergo proton-induced quenching.

Keywords: Spectral characteristics; 4-Aminodiphenyl ether; Solvatochromic shift; Exciplex; Prototropism

1. Introduction

The spectral characteristics of a number of aromatic amines have been studied in great detail [1–6]. It is well established that protonation of aromatic amines leads to a blue shift in absorption and fluorescence and also the protonation is preceded by the proton-induced fluorescence quenching of neutral molecules. This type of behaviour is not observed in some bifunctional amino compounds. In 2,7-diaminofluorene [7] the absorption spectrum is blue shifted successively on protonations of both amino groups. However, the fluorescence spectrum behaves differently under the above conditions, i.e. a red shift is observed in the fluorescence spectrum of the neutral molecule on protonation, but on the second protonation a blue shift is observed. This abnormal spectral shift in the fluorescence spectrum of the monocation is reported [7] to be due to solvent relaxation in aqueous medium because the normal blue shift is observed when the fluorescence spectrum of the monocation is taken in hydrocarbon as a solvent. The abnormal shift observed in the fluorescence of *o*-phenanthroline on protonation is also explained by the large solvent relaxation in aqueous medium [8]. However, a similar study on bifunctional molecules such as phenylenediamines [9], aminophenols and anisidines [10] shows that their spectral behaviour is the same as that of aromatic amines. The aim of the present study is to see whether 4-aminodiphenyl ether (ADPE) follows the same trend as aromatic amines or whether it behaves in a different fashion. Since ADPE has two electron-donating (ether and amino) groups, we have also studied the effect of solvents on the spectral changes of the molecule.

2. Materials and methods

ADPE (Aldrich) was purified by recrystallization from aqueous methanol. The purity of ADPE was checked by obtaining identical fluorescence when excited at different wavelengths. Triply distilled water was used to prepare the aqueous solutions. BDH spectrograde methanol, AnalaR grade sulphuric acid and sodium hydroxide were used as such. AnalaR grades of other solvents were further purified by the methods described in the literature [11]. A modified Hammet's acidity scale H_0 [12] for solution below pH 1 (using an H_2SO_4–H_2O mixture) and Yagil's basicity scale [13] H_- for solutions above pH 13 (using an NaOH–H_2O mixture) were employed. Absorption spectra were recorded with a JASCO model 7800 spectrophotometer, while fluorescence measurements were made using a JASCO FP-550 recording spectrofluorimeter. pH values in the range 1–13 were measured on a ELICO pH meter model LI-10T.

Because of the poor solubility of ADPE in water, a stock solution was prepared in methanol. Experimental solutions

[1] Present address: S. Chattanatha Karayalar College, Kodikurichi, Tenkasi 627 804, India.

* Corresponding author.

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Table 1
Absorption and fluorescence spectral data of 4-aminodiphenyl ether and diphenyl ether in different solvents and at various acid concentrations

Reference number	Solvent	ADPE			DPE		
		λ_{abs} (nm)	log ϵ	λ_{flu} (nm)	λ_{abs} (nm)	log ϵ	λ_{flu} (nm)
1	Cyclohexane	298 241	3.47 4.16	346.0	278 272 266	3.26 3.31 3.25	295
2	Dioxane	304 246	3.82 4.08	355.0			
3	Ethyl acetate	299	3.30	354.0			
4	Dichloromethane	300 243	3.36 4.11	352.0			
5	Acetonitrile	302 245	3.81 4.13	360.0	278 271 266	3.27 3.33 3.26	298
6	2-methyl-2-butanol	300 242	3.37 4.15	364.0			
7	2-methyl-2-propanol	298 241	3.36 4.17	360.0			
8	2-propanol	298 244	3.41 4.14	364.0			
9	1-butanol	297 243	3.42 4.17	360.0			
10	Methanol	296 241	3.39 4.15	366.0	277 271 265	3.26 3.31 3.24	300 325
11	Water (neutral)	291 236	3.36 4.15	372.0	276 270	3.28 3.25	345 410
12	Monocation (H_0)	276 269		310.0			
13	1 M H_2SO_4	276 269		310.0	276 270		315
14	Monoanion (H_-)	310					
15	Dianion			362.0			

were prepared by adding an aliquot of the stock solution to appropriate $H_0|pH|H_-$ solutions just before taking measurements. The concentration of the resulting solution was about 10^{-5} M. The methanol content of the solution was about 2.5%.

3. Results and discussion

3.1. Effect of solvents

The absorption and fluorescence spectra of ADPE have been observed in solvents of various polarities and hydrogen bonding abilities. The relevant data for ADPE are compiled in Table 1 together with the spectral maxima of diphenyl ether (DPE) [14] in cyclohexane, acetonitrile, methanol and water. As compared with DPE the absorption maximum of ADPE is red shifted in each solvent. The absorption spectrum is red shifted from cyclohexane to acetonitrile but blue shifted in methanol and water. The fluorescence spectrum is regularly red shifted as the polarity and proton donor capacities of the solvent increase. Solvents can interact with both ether and amino group of ADPE. The absorption maximum of ADPE is very close to that of aniline. This shows that the interaction of the amino group is large when compared with the phenoxy group. So the above shifts are mainly due to interaction of the solvents with the amino group of ADPE.

The spectral shifts observed in the absorption spectrum of ADPE in polar and hydrogen bonding solvents are consistent with the characteristic behaviour of the amino group [2,7], i.e. hydrogen acceptor interactions of the solvents produce a red shift while hydrogen donor interactions produce a blue shift. Dioxane, acetonitrile, ethyl acetate are hydrogen acceptor solvents, whereas alcohols and water can behave as both hydrogen acceptor and donor solvents. Hydrogen donor interactions are predominant in methanol and water. It is also

reported that the hydrogen donating capacity of water is more than that of methanol [15]. This is also confirmed by the maximum blue shift observed in water.

The fluorescence of ADPE is found to be more solvent dependent. There is a regular red shift in the fluorescence spectra of ADPE with the increase in the polarity and hydrogen bonding capacity of the solvents (Fig. 1). This regular red shift can be explained on the grounds that charge migration from the amino group towards the benzene ring increases on 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 parameters $E_T(30)$ and Bilot–Kawaski (BK) values and compared the Stokes shift for ADPE with these values. These parameters as accurate registers of solvent polarity have been used by several researchers to correlate the molecular spectroscopic properties [16–18]. The Stokes shifts in various solvents together with BK [19] and $E_T(30)$ [20] values are given in Table 2. The increase in Stokes' shift from cyclohexane to water in ADPE is found to be more in accordance with the $E_T(30)$ than with 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 ADPE the Stokes shifts are plotted only with $E_T(30)$ values (Fig. 2) ($r=0.9301$). The Stokes shifts are not well correlated with BK values. This is also confirmed by the poor correlation coefficient obtained for the plot of Stokes shifts vs. BK values (Table 2) ($r=0.7619$). Because of the poor correlation the plot could not be used for the dipole moment calculation.

Table 2
Stokes' shifts of 4-aminodiphenyl ether and diphenyl ether with $E_T(30)$ and Bilot–Kawaski values

Solvent	Stokes' shift (cm^{-1})		$E_T(30)$ value [a]	BK value [b]
	ADPE	DPE		
Cyclohexane	4655	2073	30.9	−0.001
Dioxane	4726		36.0	0.043
Ethyl acetate	5196		38.1	–
Dichloromethane	4924		41.1	0.586
Acetonitrile	5335	2388	46.0	0.864
2-methyl-2-butanol	5861		41.9	–
2-methyl-2-propanol	5779		43.9	0.673
2-propanol	6085		48.6	0.766
1-butanol	5896		50.2	0.754
Methanol	6467	2768	55.5	0.858
Water	7483	7246	63.1	0.913
Monocation	4917	–	–	–
Correlation coefficient (r)			0.9301	0.7619

[a] From Ref. [19].
[b] From Ref. [18].

3.2. Effect of pH

Absorption spectra of ADPE have been studied for a wide range of basicity–acidity from $H_- = 17$ to $H_0 = -10$. The

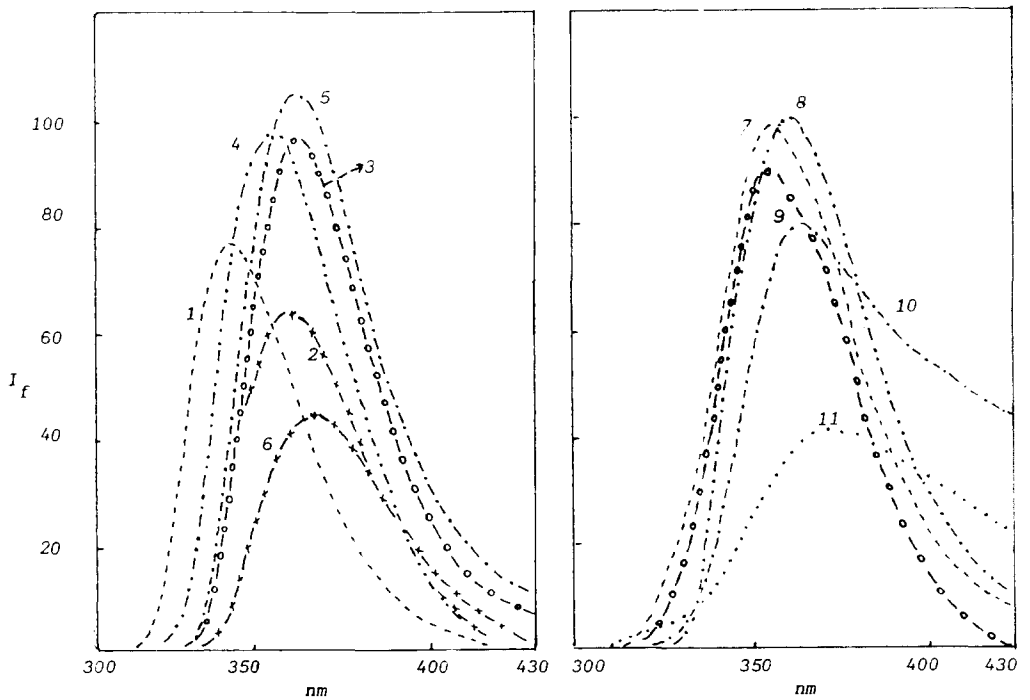


Fig. 1. Fluorescence spectra of ADPE in various solvents at 298 K (concentration, about 4×10^{-5} M): spectrum 1, cyclohexane; spectrum 2, dioxane; spectrum 3, ethyl acetate; spectrum 4, dichloromethane; spectrum 5, acetonitrile; spectrum 6, *t*-pentyl alcohol; spectrum 7, *t*-butyl alcohol; spectrum 8, 2-propanol; spectrum 9, 1-butanol; spectrum 10, methanol; spectrum 11, water.

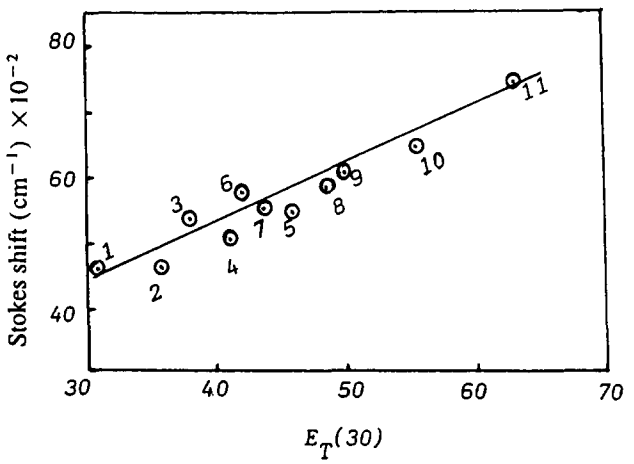


Fig. 2. Correlation of the Stokes shift of ADPE with the $E_T(30)$ values of different solvents: 1, cyclohexane; 2, dioxane; 3, ethyl acetate; 4, dichloromethane; 5, acetonitrile; 6, *t*-pentyl alcohol; 7, *t*-butyl alcohol; 8, 2-propanol; 9, 1-butanol; 10, methanol; 11, water.

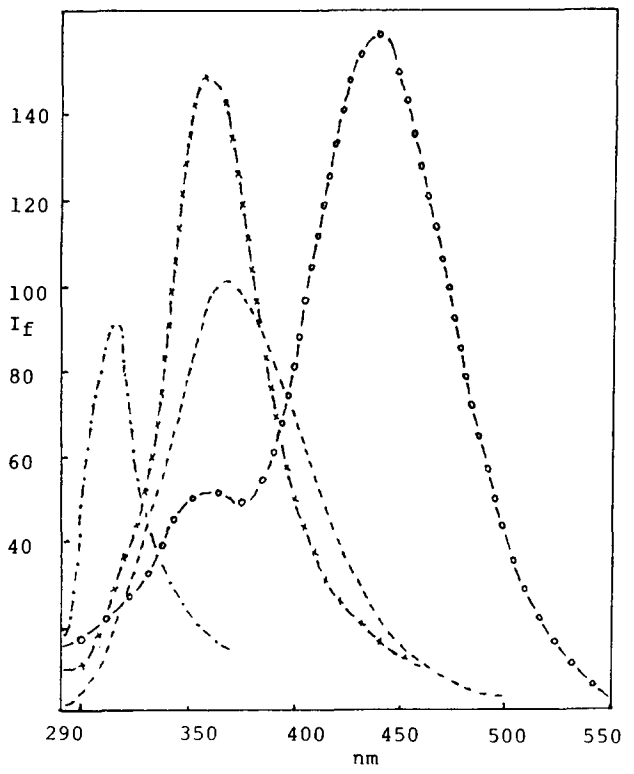


Fig. 3. Fluorescence spectra of different prototropic species of ADPE at 298 K (concentration, about 4×10^{-5} M): – – –, neutral; – · –, monocation; –O–, monocation complex; – × –, dianion.

absorption maxima of the neutral form at pH 7 are at 236 nm and 291 nm. Compared with the structured spectrum of DPE the maxima of ADPE are red shifted with the loss of structure. This is due to the interaction of amino group with the DPE moiety. When pH is decreased a blue-shifted spectrum is obtained around pH 4. This spectrum has a maximum close to that of DPE and hence this maximum corresponds to the monocation. The ground state pK_a value of monocation–neutral equilibrium was calculated spectrophotometrically to be 4.75. With further increase in acid concentration to $H_0 = -5$ the absorption spectrum does not change significantly. At very high acid concentration the solution becomes pink and a different spectrum (242 nm, 500 nm) is obtained. This may be due to the formation of a structurally different compound. On increase in pH from 7 there is no significant change in the absorption spectra up to $H_- = 15.4$. When the basicity is increased further, the absorption maximum is continuously red shifted and a maximum at 310 nm is obtained in most strongly basic solution ($H_- = 17$). This may be due to the formation of a monoanion. The pK_a value for this proton transfer reaction could not be calculated because there is no constancy in the isosbestic point.

The effect of pH on the fluorescence spectrum is found to be very different from that of pH on the absorption spectrum. The fluorescence spectra of ADPE at different $H_0|pH|H_-$ values are shown in Fig. 3. The neutral species at pH 7 exhibits a fluorescence maximum at 372 nm. When the pH is decreased a red-shifted maximum appears, at 435 nm, and it is complete at pH 3. A further decrease in pH gives rise to a blue-shifted maximum at 310 nm with the simultaneous decrease in fluorescence at 435 nm. At $H_0 = -0.26$ (1 M H_2SO_4) only one form exists with the maximum at 310 nm. There is no significant change in the spectrum with the further increase in the acidity. At very high acid concentration, i.e. at 18 M H_2SO_4, as mentioned earlier, a pink-coloured solution results with the fluorescence maxima at 350 and 570 nm.

When the amino group is protonated a blue shift is expected for the monocation. However, in this case we observed an unusual red shift in the fluorescence spectra on protonation. ADPE on protonation becomes equivalent to DPE. Hence to assign the maxima for the monocation we recorded the fluorescence spectra of DPE in different solvents. The fluorescence spectra of DPE in different solvents and in 1 M H_2SO_4 are shown in Fig. 4. Fluorescence spectra of DPE in water

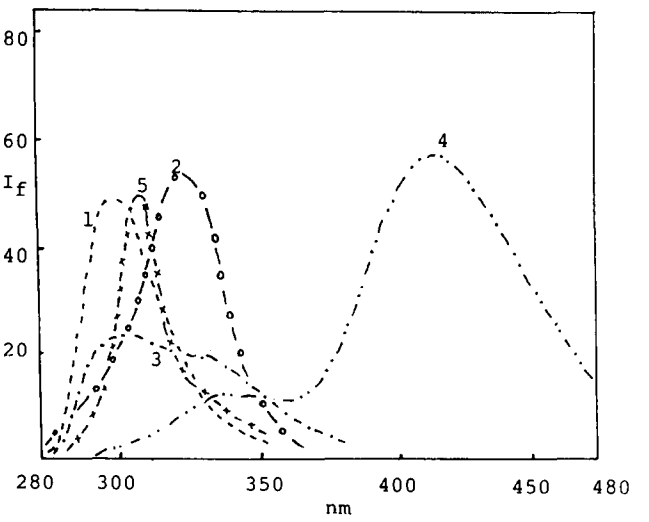


Fig. 4. Fluorescence spectra of DPE in various solvents at 298 K (concentration, about 3×10^{-5} M): spectrum 1, cyclohexane; spectrum 2, acetonitrile; spectrum 3, methanol; spectrum 4, water; spectrum 5, 1 M H_2SO_4 ($H_0 = -0.26$).

Table 3
Absorption, fluorescence maxima and Stokes' shift of 4-aminodiphenyl ether in cyclohexane in the presence of trifluoroacetic acid

Solvent	λ_{abs} (nm)	λ_{flu} (nm)	Stokes' shift (cm^{-1})
Cyclohexane	298.0 241.0	346	4655
Cyclohexane, 0.001% TFA	278.0 272.0 266.0	300	2638
Cyclohexane, 1.0% TFA	278.0 271.8 265.6	300	2638

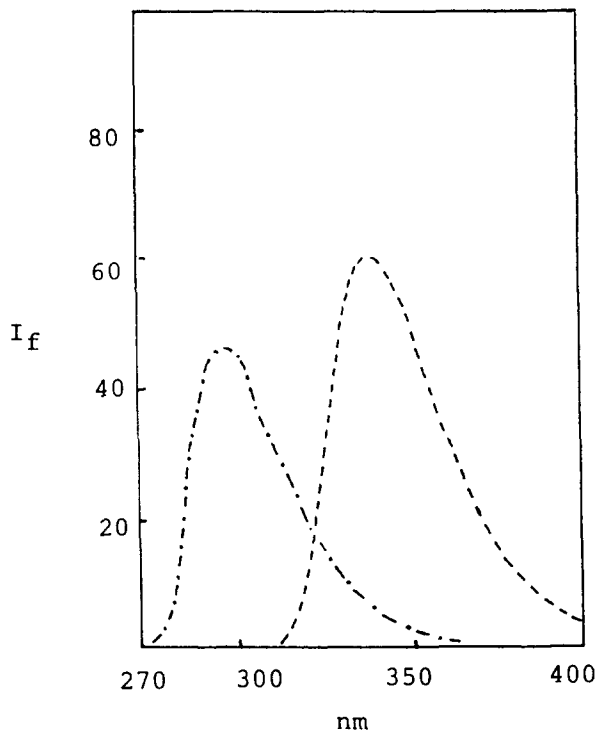


Fig. 5. Fluorescence spectra of different prototropic species of ADPE in non-polar media at 298 K (concentration, about 4×10^{-5} M): – – –, cyclohexane; – · –, TFA in cyclohexane (monocation).

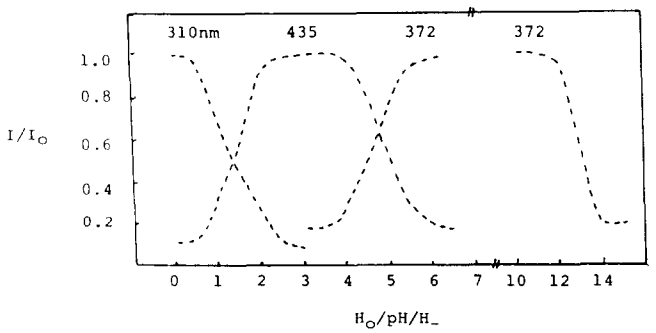
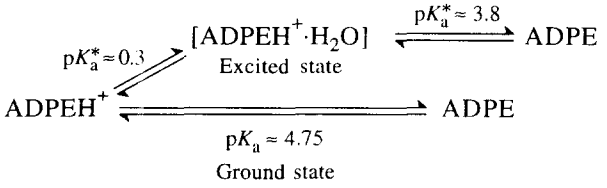


Fig. 6. Plot of I/I_0 vs. H_0|pH|H_- of the various prototropic species of ADPE.

have two maxima, one at shorter wavelength (345 nm) and the other at longer wavelength (410 nm). In methanol also two closer peaks (300, 325 nm) were observed. However in acetonitrile there is only a small red shift when compared with cyclohexane. This reveals that DPE forms a solute–solvent exciplex in hydrogen donor solvents such as methanol and water. The well-separated and substantially red-shifted solute–water exciplex peak is due to the greater hydrogen donor capacity of water than methanol. Hence the red-shifted maximum of ADPE around pH 4 is due to the monocation–water exciplex. When the pH is decreased, the complex dissociates to form the monocation which has a maximum at 310 nm. This spectrum resembles the spectrum of DPE in 1 M H_2SO_4 (in the same medium). To confirm this we have also recorded the fluorescence spectrum of monocation in a non-polar solvent cyclohexane using trifluoroacetic acid (TFA) (Table 3). This gives only a blue-shifted maximum at 300 nm resembling the fluorescence spectrum of DPE in cyclohexane (Fig. 5). This is also confirmed by its close resemblance to the fluorescence spectra of the monocation of 2-aminodiphenyl ether and dication of 4,4′-diaminodiphenyl ether [21]. In the acid range ADPE give two equilibria in the excited state owing to the formation of solute–solvent exciplex, i.e.



Fluorescence titration curves are given in Fig. 6. The equilibrium constants obtained from fluorimetric titrations for the equilibria between monocation–monocation complex and monocation complex–neutral form are 0.3 and 3.8 respectively. For both equilibria the middle point of inflection and intersection of the curve occurs when $I/I_0 \approx 0.5$. This reveals that processes other than these two equilibria such as proton-induced quenching are absent.

When pH is increased the fluorescence at 372 nm is quenched owing to the formation of monoanion. The monoanions of many amino compounds are reported to be non-fluorescent [3,12,23]. In very highly basic solutions ($H_- = 17$) a blue-shifted fluorescence spectrum at 362 nm is obtained (Fig. 3). Earlier Dogra and colleagues [23] assigned this band to the dianion species formed by the deprotonation of both protons of the amino group. Doubts have arisen about this species from the results of Chowdhury and Chattopadyay [24] as the latter workers have observed similar results with 2-(dimethylamino)naphthalene where no dissociable protons are present at the amino group. Thus the nature of this species is still doubtful, but it can be speculated that it is due to the deprotonation of the aromatic ring proton [24].

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