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Solvatochromism and prototropism of diaminodiphenyl sulphones and 2-aminodiphenyl sulphone: a comparative study by electronic spectra

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Abstract

A comparative study of absorption and fluorescence maxima of 4,4'-diaminodiphenyl sulphone (4DADPS), 3,3'-diaminodiphenyl sulphone (3DADPS) and 2-aminodiphenyl sulphone (2ADPS) in different solvents reveals that (i) solvatochromic shifts are found to be mainly due to interaction of solvents with amino group, (ii) in any one solvent the net solvatochromic shifts of two amino groups are less than that of one amino group, (iii) fluorescence shift from cyclohexane to water is a maximum for 4DADPS and a minimum for 2ADPS and (iv) 4DADPS and 3DADPS possess more twisted intramolecular charge transfer character than 2ADPS. The excited-state acidity constants, determined by fluorimetric titration and Förster cycle methods, have been reported and discussed.

Keywords: Solvatochromism; Prototropism; Diaminodiphenyl sulphones; 2-Aminodiphenyl sulphone; Twisted intramolecular charge transfer; Excited state acidity constants

1. Introduction

The derivatives of diphenyl sulphones are found to be pharmaceutically and industrially important. Some of them are employed as antimalarial and antileprotic drugs [1] and some are used in the preparation of industrially important products such as thermal recording materials, dyes, binding and vulcanizing agents [2]. In the diphenyl sulphone molecule the ground-state structure has two rings perpendicular to the plane defined by C–S–C bonds [3]. X-ray analysis of aminodiphenyl sulphone [3] also confirms the geometry of two phenyl rings. The possibility of d-orbital participation in an all-planar arrangement has been established by electron spin resonance data [4]. For a number of diphenyl sulphone derivatives it has long been known that high absorption leads to excited states with different electron density distributions depending on the nature and position of the substituents [5]. A dual luminescence in polar solvents due to twisted intramolecular charge transfer (TICT) states has been reported for 4DADPS and its dimethylamino derivative [6,7]. The temperature dependence of 2ADPS has been carried out to find out the activation energy of charge delocalization or separation processes [8]. However, no attempt has been

made to study the acid–base properties of the aminodiphenyl sulphones. Recently we have been studying the solvatochromic and prototropic effects of diphenyl [9], diphenyl ether [10] and diphenyl sulphone [11] with one or two electron-donating groups such as OH or NH₂. In most cases the solvatochromic effects of two similar functional groups (either OH or NH₂) is less than that of one group. The present study has been carried out to compare the effect of solvents and pH on the electronic spectral behaviours of 4,4'-diaminodiphenyl sulphone, 3,3'-diaminodiphenyl sulphone and 2-aminodiphenyl sulphone.

2. Experimental details

4,4'-Diaminodiphenyl sulphone, 3,3'-diaminodiphenyl sulphone and 2-aminodiphenyl sulphone were obtained from Aldrich Chemical Co. and recrystallized from an ethanol–water mixture. The purity of the compound was checked by similar fluorescence spectra when excited with different wavelengths. Cyclohexane, methanol and other solvents (AR grade) were further purified according to the procedure suggested in the literature [12]. Triply distilled water was used for aqueous solutions. Solutions in the pH range 1.5–13.0 were prepared by adding appropriate amounts of NaOH and H₃PO₄. A modified Hammett acidity scale (*H*₀) [13] for the H₂SO₄–H₂O mixtures and the Yagil [14] basicity scale

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(H_-) for NaOH–H₂O mixtures were used below pH 1 and above pH 13 respectively. The Hammett 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, increasingly negative values corresponding to higher acidity.

Absorption spectra were recorded using a JASCO model-7800 spectrophotometer and fluorescence measurements were made using a JASCO FP-550 spectrofluorimeter. The pH values of solutions in the range 1.5–13 were measured with an ELICO pH meter model LI-10T. Owing to poor solubility of sulphones in water, a stock solution was prepared in methanol and experimental solutions were prepared just before taking spectral measurements. The concentration of the solutions were of the order of 10^{-5} – 10^{-4} mol dm⁻³.

3. Results and discussion

3.1. Effect of solvents

The absorption and fluorescence spectra data of 2ADPS, 3DADPS, 4DADPS and diphenyl sulphone (DPS) [15] in various solvents are compiled in Table 1 and their fluorescence spectra are displayed in Figs. 1–3. Because of the very low solubilities of 4DADPS and 3DADPS in cyclohexane, their maxima were obtained using 1% dioxane solution of cyclohexane. These maxima will be very near to the maxima if obtained from pure cyclohexane as the polarity of dioxane is close to cyclohexane. Furthermore the trend observed in the maxima of three aminodiphenyl sulphones in cyclohexane is similar to the trend in other solvents. The data indicate that the long-wavelength absorption bands are intense, broad and largely red shifted compared with those of DPS owing to the interaction of amino group. However, in any one solvent the red shift decreases from 2ADPS to 4DADPS. The absorption maxima of 4DADPS and 3DADPS are red shifted from cyclohexane to methanol, a more polar and hydrogen bonding solvent, but blue shifted in water compared with methanol. A similar trend is observed in 2ADPS but the blue shift observed in water for this compound is more significant (10 nm).

In sulphones, it is reported [3–8,16] that both phenyl rings are perpendicular to C–S–C plane and the π clouds of phenyl rings participate with the sulphur d orbital in the ground state. Solvents can interact with either the SO₂ or the NH₂ group. The interaction of solvents with the lone pair of the SO₂ and NH₂ groups will lead to a blue shift and the solvent interaction with the hydrogen atom of the NH₂ group will lead to a red shift in both absorption and fluorescence. The absorption solvatochromic shifts in more polar and hydrogen bonding solvents are consistent with the characteristic behaviour of the amino group [17]. The amino group acts as a proton donor to all the solvents except water. In water it behaves as a proton acceptor since the proton-donating capacity of water is found to be more than that of methanol and other alcohols.

Hence a blue shift is observed in water compared with methanol. This interaction of the solvent with the amino group is also confirmed by the insignificant solvatochromic shift observed for DPS [15]. When we compare the absorption maxima of the sulphones in any one solvent, 4DADPS should have the longest-wavelength maximum owing to the presence of 2-amino groups at the *para* position, but it has a maximum at a shorter wavelength than 2ADPS. This is because the 4DADPS molecule is twisted and both phenyl rings are perpendicular to the C–S–C plane or N–S–N plane in the ground state. However, in 2ADPS the phenyl rings are not twisted much owing to hydrogen bonding between NH₂ and SO₂ groups. This hydrogen bonding also enhances the delocalization, giving rise to a red shift.

The fluorescence of three aminodiphenyl sulphones is found to be strongly solvent dependent. In a non-polar solvent cyclohexane the fluorescence spectrum is blue shifted in 4DADPS when compared with 2ADPS as in the absorption spectrum. On the contrary in alcoholic solvents and water the fluorescence maxima of all the three sulphones are closer. The fluorescence maxima of three sulphones are red shifted from cyclohexane to water but the red shift decreases from 4DADPS to 2ADPS. Furthermore, in polar solvents, 4DADPS gives a broad fluorescence band. When we compare the fluorescence maxima of the sulphones individually in all solvents, all the three sulphones undergo a red shift from cyclohexane to water but the red shift is a maximum for 4DADPS (7576 cm⁻¹) and a minimum for 2ADPS (4447 cm⁻¹). The red shifts observed in hydrogen-bonding solvents are due to the interaction of solvents with hydrogen atom of the NH₂ group, but the maximum red shift observed for 4DADPS can be explained as follows. Aminodiphenyl sulphones are reported to undergo TICT in the excited state [4,6,8] and it has been found that these molecules yield two emitting states only in polar solvents. During the excitation the formation of TICT is more favoured in 4DADPS and 3DADPS than in 2ADPS because the presence of intramolecular hydrogen bonding in 2ADPS restricts the rotation of the anilino group. This TICT character present in 4DADPS increases the solvent relaxation, leading to a maximum red shift in alcoholic solvents. The red shift from cyclohexane to water for 3DADPS is less than for 4DADPS. This is because of the smaller interaction of the amino group in the *meta* position. A similar trend is observed in the fluorescence shift from cyclohexane to methanol also. Although the TICT character is less in 2ADPS, the fluorescence maximum is close to other aminodiphenyl sulphones because of the increased delocalization by hydrogen bond formation. The fluorescence solvatochromic shift reveals that solvent interaction of polar and hydrogen bonding solvents are predominant. In order to confirm this we used theoretically derived solvent parameters $E_T(30)$ [18,19] and BK [20] values and compared the Stokes shift for three sulphones with these values. These values of solvent polarity have been used by several workers as accurate registers to correlate molecular spectroscopic properties [21]. The Stokes shift in various solvents together

Table 1
Absorption and fluorescence spectral data of various aminodiphenyl sulphones in different solvents and at various pH

Solvents	2ADPS		3DADPS		4DADPS		DPS, λ_{abs} (log ϵ)
	λ_{abs} (log ϵ)	λ_{flu}	λ_{abs} (log ϵ)	λ_{flu}	λ_{abs} (log ϵ)	λ_{flu}	
Cyclohexane with 1% dioxane	316.2 (4.01) 273.0 (3.13) 226.0 (4.27)	368	301.6 (3.82) 222.2 (4.20)	345	279.4 (4.60) 252.2 (4.44)	330	
Dioxane	322.6 (3.71) 274.0 (3.15) 241.0 (4.17)	400	315.0 (3.83) 261.8 (3.84)	395	288.0 (4.62) 257.0 (4.47)	338	
Ethylacetate	323.4 (3.88) 274.0 (3.18)	400	313.4 (3.76)	385	287.0 (4.60) 256.0 (4.45)	336	
Dichloromethane	319.2 (3.82) 274.0 (3.19) 231.4 (4.44)	390	309.0 (3.81) 233.0 (4.51)	374	285.0 (4.50) 255.0 (4.36)	331	
Acetonitrile	323.0 (3.86) 273.0 (3.14) 231.4 (4.51)	410	313.4 (3.78) 229.6 (4.57)	396	291.0 (4.42) 258.0 (4.26)	345–388	
<i>tert</i> -Pentyl alcohol	326.6 (3.71) 273.5 (3.17)	405	312.6 (3.85) 247.0 (4.29)	410	293.0 (4.36) 257.0 (4.19)	378–388	
<i>tert</i> -Butyl alcohol	325.8 (3.72) 274.0 (3.19) 227.6 (4.44)	408	312.4 (3.73) 230.0 (4.54)	422	293.0 (4.57) 259.0 (4.38)	390–400	
2-Propanol	326.4 (3.68) 274.0 (3.20) 227.4 (4.37)	408	313.8 (3.77) 228.2 (4.56)	420	295.0 (4.45) 260.0 (4.29)	385–395	
1-Butanol	324.8 (3.67) 273.5 (3.21) 228.6 (4.46)	406	313.6 (3.74) 238.6 (4.50)	420	294.6 (4.51) 260.0 (4.57)	390–395	
Methanol	324.2 (3.82) 273.5 (3.18) 228.2 (4.47)	410	314.2 (3.73) 232.6 (4.53)	408	294.0 (4.53) 260.0 (4.59)	400–415	274 (3.13) 266 (3.31) 260 (3.23) 235 (4.19)
Water	313.8 (3.79) 273.0 (3.20) 225.6 (4.50)	440	304.2 (3.74) 228.2 (4.55)	410	290.0 (4.54) 257.6 (4.59)	435–445	274 (3.15) 266 (3.36) 235 (4.29)
Monocation	274.0 (3.25) 267.5 (3.40) 236.8 (4.19)	302	308.0 (3.40) 230.0 (4.42)	354	289.0 (4.28) 233 s (2.24)	380	274 (3.23) 268 (3.42) 258 (3.38) 238 (4.16)
Dication	–	–	274.0 (3.26) 266.5 (3.43) 234.4 (4.21)	302	273.0 (3.28) 266.8 (3.38) 234.2 (4.17)	302	–
Monoanion	343.2	–	324.4	–	327.4	–	–
Dianion	–	410	–	425	–	385	–

with the $E_T(30)$ and BK values are given in Table 2. Of these two parameters, $E_T(30)$ incorporates both hydrogen bonding and solvent polarity effects and so the increase in the Stokes shift from cyclohexane to water is more in accordance with $E_T(30)$ than with BK. A good linear correlation is obtained for 2ADPS with $E_T(30)$. The correlation of 4DADPS and 3DADPS are poor when compared to 2ADPS (Fig. 4). This is again due to more TICT character in these compounds, leading to two emitting states.

3.2. Effect of pH

The absorption and fluorescence spectra of all aminodiphenyl sulphones have been studied in the $H_0/pH/H_-$ range from -10 to 17.0 . The relevant data are compiled in Table 1. The absorption spectra of various prototropic species are given in Fig. 5. With a decrease in pH from 7 (depending on the particular amine) the absorption maximum of the long-wavelength band is slightly blue shifted in 4DADPS whereas

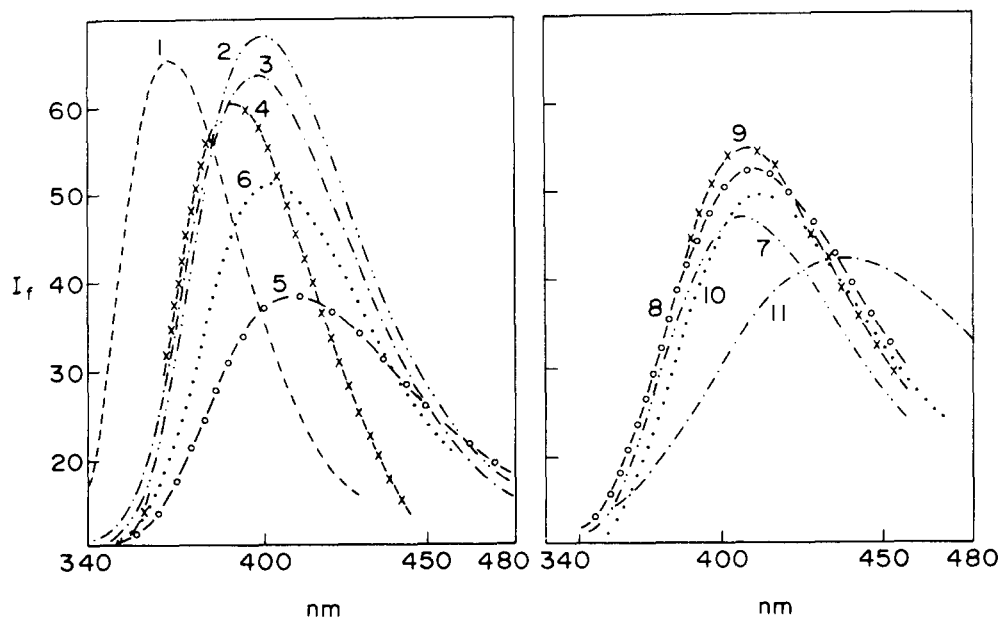


Fig. 1. Fluorescence spectra of 2ADPS in various solvents at 298 K (concentration, 3×10^{-5} M) (for numbers refer to Table 2).

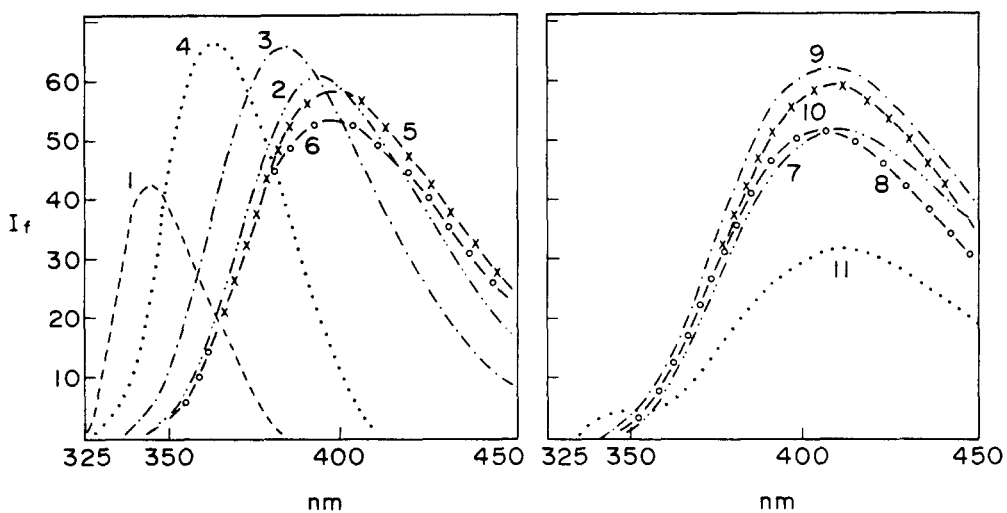


Fig. 2. Fluorescence spectra of 3DADPS in various solvents at 298 K (concentration, 3×10^{-5} M) (for numbers refer to Table 2).

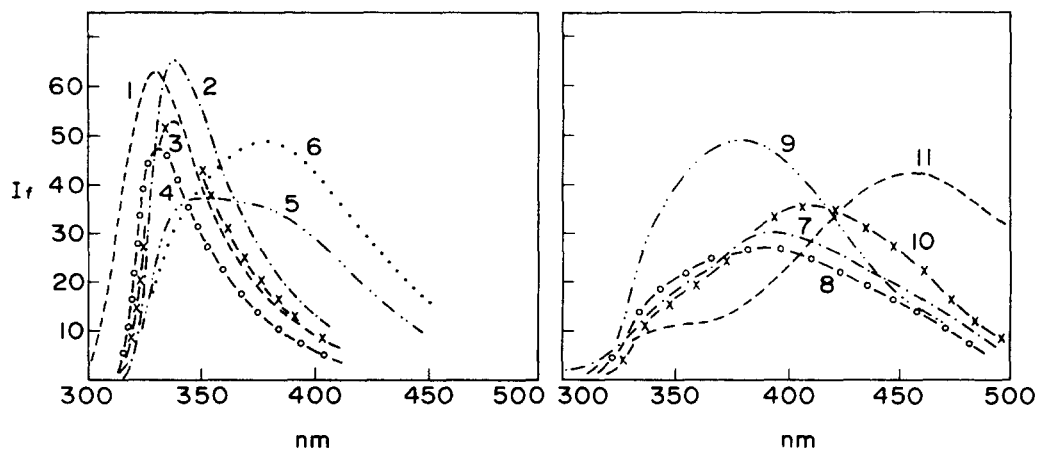


Fig. 3. Fluorescence spectra of 4DADPS in various solvents at 298 K (concentration, 3×10^{-5} M) (for numbers refer to Table 2).

it is red shifted in 3DADPS and the absorption spectra so obtained resemble that of 4-aminodiphenyl sulphone [22] and 3-aminodiphenyl sulphone [22] respectively. This clearly suggests the formation of a monocation obtained by the protonation of one of the amino groups. With further increase in proton concentration the absorption spectra are blue shifted in both cases. The blue-shifted spectrum is due to the formation of a dication obtained by the protonation of the second amino group. The absorption spectra of the dications of 4DADPS and 3DADPS are similar to the spectra of DPS. In the case of 2ADPS, when the pH is decreased from 7, a blue-shifted absorption spectrum similar to that of DPS [15] is obtained at pH 1.0 owing to the protonation of aminogroup. No further change in absorption spectrum is noticed even at $H_0 - 10$ in all the three sulphones.

The absorption spectra of aminodiphenyl sulphones do not change when the basicity is increased, until $H_0 - 15$ but then a regular red shift is noticed and it is continued even up to $H_0 - 17$, the highest basic condition used. The red-shifted spectra may be due to the formation of a monoanion but the isosbestic points were not constant in all the cases. This behaviour is generally observed in aromatic amino compounds [23–25].

The fluorescence spectra of various prototropic species of the three aminodiphenyl sulphones are shown in Fig. 6. The behaviour of fluorescence in these acid regions is the same as observed in the ground state for 4DADPS and 2ADPS but it is different for 3DADPS. When the pH is decreased from 7, the fluorescence spectrum of 4DADPS and 3DADPS are blue shifted and give maxima of 380 nm and 355 nm respectively. Around $H_0 - 2$, both give a new fluorescence spectra further blue shifted in each case with a band maxima of 302 nm and these resemble closely the fluorescence spectra of DPS. The above results clearly suggests that in each case the former species is a monocation formed by the protonation of one amino group and the second species is a dication obtained

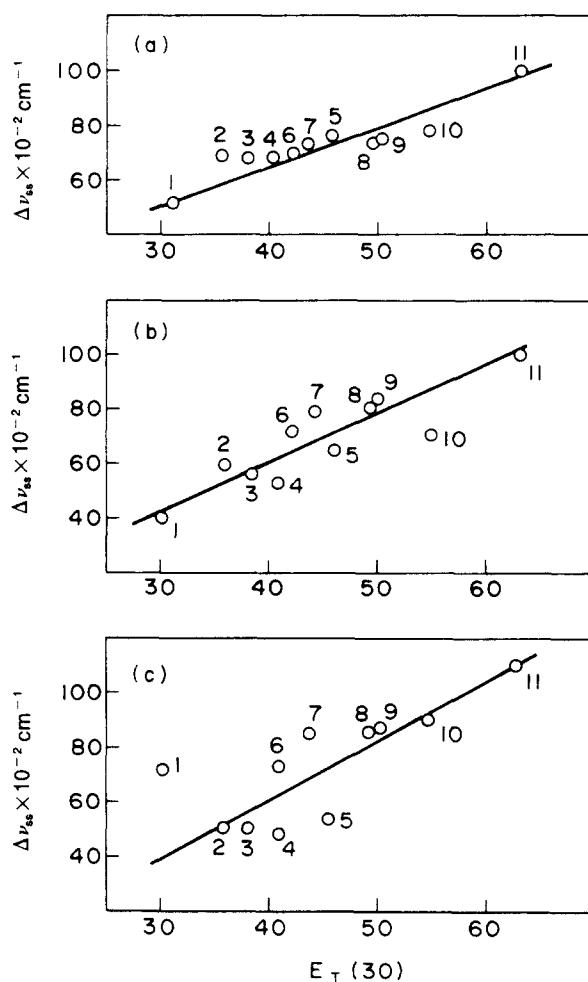


Fig. 4. Correlation of the Stokes shift ν_{ss} cm^{-1} of three aminodiphenyl sulphones with the $E_T(30)$ values of different solvents: (a) 2ADPS; (b) 3DADPS; (c) 4DADPS. (For numbers, refer to Table 2.)

by the protonation of the second amino group. In the case of 2ADPS, when the pH is decreased from 2, the fluorescence

Table 2
Stokes shifts observed for various aminodiphenyl sulphones in different solvents with $E_T(30)$ and BK values

Number Solvent	Stokes shift (cm^{-1})			$E_T(30)$	BK
	2ADPS	3DADPS	4DADPS		
1 Cyclohexane	4452	4431	7061	31.2	-0.001
2 Dioxane	5998	6430	5136	36.0	0.043
3 Ethylacetate	5921	5934	5081	38.1	-
4 Dichloromethane	5687	5624	4876	41.1	0.586
5 Acetonitrile	6570	6656	5379	46.0	0.864
6 <i>tert</i> -Pentyl alcohol	5927	7600	7814	41.9	-
7 <i>tert</i> -Butyl alcohol	6184	8314	8489	43.9	0.673
8 2-Propanol	6127	8058	8257	48.6	0.766
9 1-Butanol	6158	8078	8303	50.2	0.754
10 Methanol	6455	7317	9014	55.5	0.858
11 Water	9140	10146	11755	63.1	0.913
12 Monocation	3384	4219	8286	-	-
13 Dication	-	3384	3517	-	-
Correlation coefficient	0.8618	0.7619	0.7853	-	-

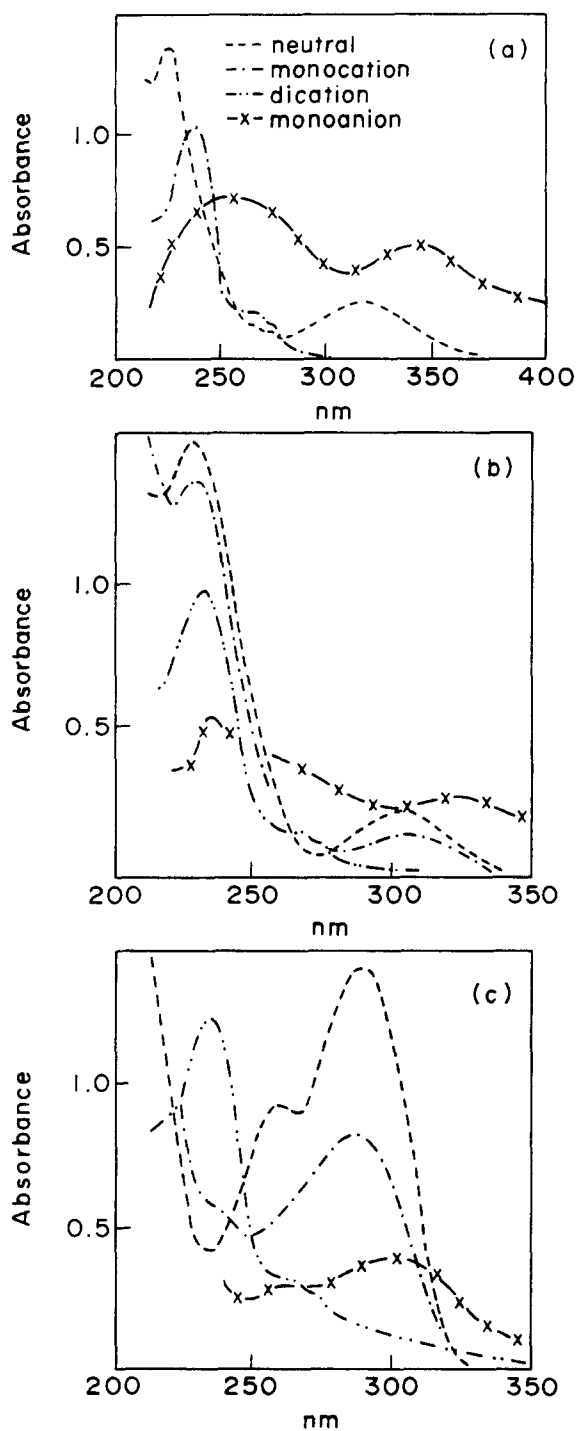


Fig. 5. Absorption spectra of different prototropic species of (a) 2ADPS, (b) 3DADPS and (c) 4DADPS at 298 K: ---, neutral; - · - ·, monocation; · · · ·, dication; - x -, monoanion.

is quenched up to $H_0 = -0.4$. A new fluorescence band at 302 nm starts to appear from $H_0 = -1$ and this also resembles the fluorescence spectrum of DPS. There is no correspondence between the fluorescence quenching of the neutral form and the fluorescence of the monocation. This suggests proton-induced fluorescence quenching in 2ADPS. The assignment of the dication fluorescence of 4DADPS and 3DADPS is also

confirmed by the fact that their fluorescence is similar to the monocation fluorescence of 2ADPS.

When the pH is increased from 7, the quenching of fluorescence starts from pH 12 in all the sulphones owing to the formation of monoanion. This is consistent with the earlier results that monoanions formed by deprotonation of aromatic amines, in general, are non-fluorescent [23–25]. At very high basicity (H_{-16}), blue-shifted fluorescence spectra are obtained for both 4DADPS and 2ADPS. This behaviour is also exhibited by many aromatic amino compounds [26] and the blue-shifted fluorescence is reported to be due to the formation of dianions. For 3DADPS at a very high basic condition a red-shifted fluorescence is obtained. For this compound the blue shift is not observed as in the other two cases.

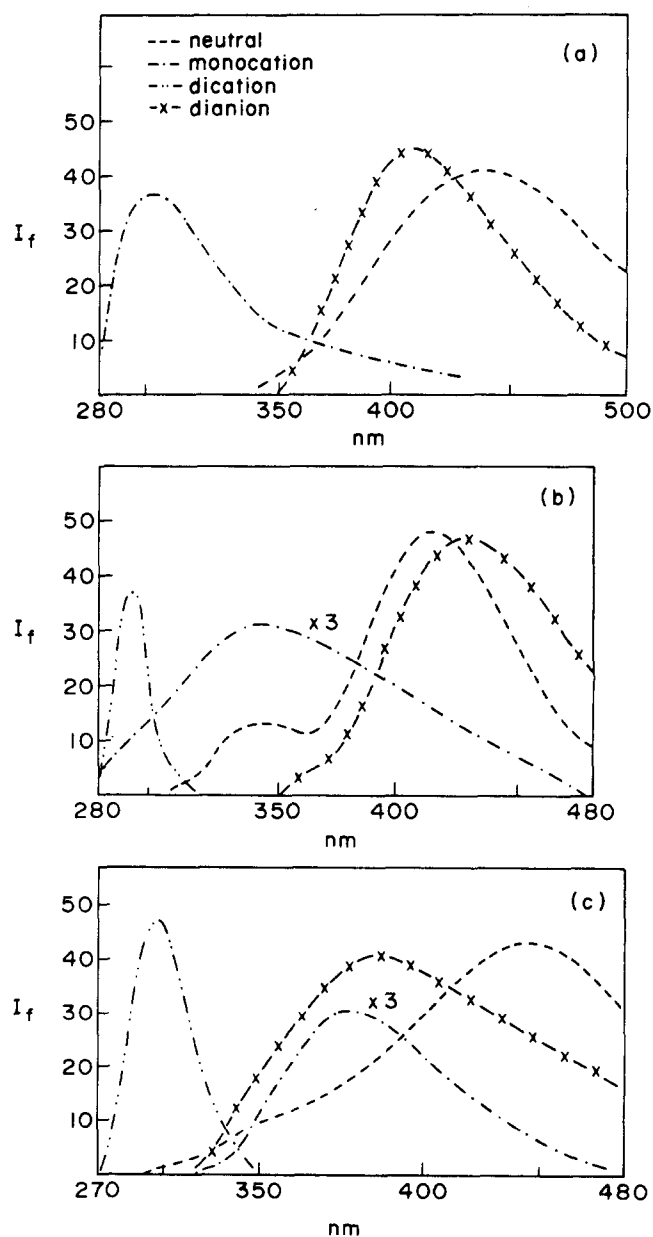


Fig. 6. Fluorescence spectra of different prototropic species of (a) 2ADPS, (b) 3DADPS and (c) 4DADPS at 298 K: ---, neutral; - · - ·, monocation; · · · ·, dication; - x -, dianion.

Table 3
 pK_a values of different prototropic equilibria of various aminodiphenyl sulphones in the S_0 and S_1 states

Equilibrium	pK_a	pK_a^* (FT)	Förster cycle		
			pK_a^* (abs)	pK_a^* (flu)	pK_a^* (ave)
2ADPS					
Monocation \rightleftharpoons neutral	-0.16	-3.80	-9.88	-21.97	-15.93
Neutral \rightleftharpoons monoanion	> 15.00	12.80	-	-	-
3DADPS					
Dication \rightleftharpoons monocation	2.10	-1.00	-6.14	-8.11	-7.13
Monocation \rightleftharpoons neutral	3.18	1.40	3.81	-4.92	-0.56
Neutral \rightleftharpoons monoanion	> 15.00	14.40	-	-	-
4DADPS					
Dication \rightleftharpoons monocation	0.52	-1.50	-3.74	-14.22	-8.98
Monocation \rightleftharpoons neutral	1.97	1.50	1.72	-6.10	-2.19
Neutral \rightleftharpoons monoanion	> 16.00	14.50	-	-	-

The Förster cycle method uses absorption (abs) data, fluorescence (flu) data, and the average (ave) of absorption and fluorescence maxima; pK_a^* (FT) values obtained from fluorimetric titrations.

This may be due to the NH_2 group present in the *meta* position in 3DADPS.

3.3. Prototropic equilibria

The ground-state pK_a values for various prototropic reactions were calculated spectrophotometrically and are listed in Table 3. The pK_a for the neutral-monoanion equilibria for all the three sulphones could not be determined because the absorption maxima in each case was continuously red shifted even at the highest basic conditions used. The difference between the pK_a values of monocation-neutral equilibrium for 4DADPS and 3DADPS is small but the difference between the pK_a values for 3DADPS and 2ADPS is quite large. The effect of SO_2 group is felt more in 4DADPS and 2ADPS where the amino group is in the *ortho* or *para* position. The large difference in the pK_a value of 2ADPS is due to intramolecular hydrogen bonding and steric effect.

The excited-state pK_a values (pK_a^*) for the different proton transfer reactions of sulphones were calculated with the help of fluorimetric titration (FT) and the Förster [27] cycle method (Table 3). The excited-state pK_a values obtained by fluorimetric titrations between monocation and neutral form of all the three sulphones show that they become less basic in the excited singlet state. The pK_a^* (FT) values are closer to their ground-state pK_a values in 4DADPS and 3DADPS. The pK_a^* (FT) values for dication-monocation equilibrium in 4DADPS and 3DADPS show that the formation of dication requires a very high acidity as the monocation becomes much less basic on excitation. In both the equilibria the agreement between Förster cycle pK_a values is not good. The difference between the values obtained using the absorption and fluorescence data is due to (i) the difference between solvent relaxations of the species in the ground and excited states and (ii) the fact that the band maximum is used instead of the 0–0 transition. Furthermore the sulphones undergo a geom-

etry change, giving rise to two emitting states: that is they possess TICT character.

In the case of neutral-monoanion equilibrium the pK_a^* values for all the three sulphones could not be determined accurately as the isosbestic points were not constant. Since the monoanion is non-fluorescent, the Förster cycle method is also not applicable. However, the pK_a^* values from the quenching curves, obtained by the formation of non-fluorescent monoanions show that the amino group in sulphones becomes more acidic in the S_1 state.

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