Indian Journal of Chemistry
Vol. 35A, October 1996, pp. 818-824

Dual fluorescence of 2-phenoxyaniline

Narayanasamy Rajendiran & Meenakshisundaram Swaminathan*
Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

Received 20 November 1995; revised 6 March 1996

2-Phenoxyaniline (2POA) shows a dual fluorescence in hydrogen bonding solvents. The increase in Stokes shift with increase in polarity is much more for longer wavelength abnormal fluorescence band (FA) than for shorter wavelength fluorescence band (FN). It is found that FA band arises only due to bulk properties of solvent and not due to complex formation. A mechanism involving twisted intramolecular charge transfer (TICT) state is proposed for the dual fluorescence of 2POA. *p*H studies indicate that the stretched sigmoid curve obtained for the neutral-monocation equilibrium is due to overlap of proton induced fluorescence quenching and monocation formation curves.

A dual fluorescence was first reported by Lippert *et al.*[1] for *p*-(dimethylamino)benzonitrile (DMABN) and in this the long wavelength fluorescence band was ascribed to the emission from a *twisted intramolecular charge transfer* (TICT) state[2-4] with a full electron transfer and mutually perpendicular conformation of donor and acceptor planes. Several mono- and bi-chromophoric systems of general structure M-X-M where two identical aromatic moieties (M) are joined to each other by a single bridging group (X = CH_2, , NH, SO_2, etc) have been reported to have photoinduced charge transfer leading to a TICT state[5]. The dual fluorescence of 3, 3′- and 4, 4′-diaminodiphenyl sulphones and 2-aminodiphenyl sulphone are found to be due to the formation of TICT state[6-8]. A dual fluorescence was also observed in polar solvents for some diaryl system without a bridging group. In 2-hydroxybiphenyl[9] the dual fluorescence is reported to be due to solute-solvent complex formation. Hence several models like TICT, formation of excimers, presence of two species such as keto-enol forms and solute- solvent exciplex have been proposed to explain dual fluorescence[6-11]. During our study on amino and hydroxyphenoxy benzenes[12-14] we observed dual emission for 2-phenoxyaniline (2POA, **I**) in polar solvents. The present investigation was carried out to analyse the dual fluorescence of 2POA. We have also studied the effect of *p*H on absorption and fluorescence spectra of 2POA.

Materials and Methods

2-Phenoxyaniline was obtained from Aldrich and recrystallized from ligroin. The purity of the compound was checked by its melting point, and similar fluorescence spectra when excited with different wavelengths. Spectrograde methanol(BDH), analytical grade sulphuric acid and sodium hydroxide were used as such. Other solvents (AnalaR) were further purified by literature methods[15]. Triply distilled water was used for aqueous solutions. Solutions in the *p*H 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[16] (H_0) for solutions below *p*H 1.5 (using H_2SO_4-H_2O mixture) and Yagil's basicity scale[17] (H_-) for solutions above *p*H 13 (using NaOH-H_2O mixture) were employed. Hammett's acidity function (H_0) serves specifically as a measure of the tendency of 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 with a JASCO model-7800 spectrophotometer, while fluorescence measurements were made using a JASCO FP-770 spectrofluorimeter, *p*H values in the range 1.5-12 were measured on a ELICO *p*H meter model LI-10T. Due to poor solubility of 2POA in water a stock solution was prepared in methanol. The concentrations of the solutions were of the order of 10^{-5}-10^{-4} mol dm^{-3}. The solutions for absorptiometric and fluorimetric titrations were prepared just before taking measurements. The isosbestic wavelengths were used for measuring the fluorescence intensities at any analytical wavelength.

Results and Discussion

Effect of solvents

The absorption and fluorescence spectra of 2POA have been observed in solvents of various polarities and hydrogen bonding abilities. The relevant data for 2POA are compiled in Table 1 along with the spectral data of 4-phenoxyaniline (4POA) and phenoxybenzene(POB)[12]. When compared to POB the absorption maxima of all 2POA bands are red-shifted in any one solvent. Absorption solvatochromic shifts of 4POA in all solvents are found to be more than those of 2POA indicating that in the ground state the charge transfer interaction of amino group in *para* position is larger than in *ortho* position. The less charge transfer interaction of the amino group in *ortho* position is also confirmed by the structured absorption spectrum of 2POA. The absorption spectrum of 2POA should have the characteristics similar to that of parent POB molecule. Compared to cyclohexane, the absorption maxima of 2POA are red-shifted in aprotic solvents and blue-shifted in protic solvents. The spectral shifts observed in the absorption spectrum of 2POA in polar or hydrogen bonding solvents are consistent with the characteristic behaviour of amino group[18,19], i.e. the amino group can behave in two ways. It can interact with hydrogen donating solvents through the lone pair on the nitrogen atom of amino group or it can donate a hydrogen atom of the amino group to the hydrogen accepting 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 $\bar{\nu}_{max}$ (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

Table 1—Absorption maxima, log ε_{max} and fluorescence maxima of 2-phenoxyaniline, 4-phenoxyaniline and phenoxybenzene in different solvents and various acid concentrations

Solvents	2POA			4POA			POB		
	λ_{abs} nm	log ε	λ_{flu} nm	λ_{abs} nm	log ε	λ_{flu} nm	λ_{abs} nm	log ε	λ_{flu} nm
Cyclohexane	288.4	3.63	325	298.0	3.46	346	278.0	3.26	295
	276.6	3.65		241.0	4.16		272.0	3.31	
	270.4	3.61					266.0	3.25	
Diethylether	292.0	3.60	348						
	276.6	3.62							
	270.4	3.58							
Dioxane	292.0	3.62	348						
	276.8	3.63							
	270.6	3.60							
Tetrahydrofuran	292.4	3.63	332						
	276.8	3.64							
	270.6	3.60							
Ethyl acetate	290.2	3.62	330						
	276.6	3.63							
	270.8	3.60							
Methyl acetate	290.4	3.60	331						
	276.6	3.64							
	270.4	3.62							
Dichloromethane	288.8	3.62	334						
	276.6	3.64							
	271.2	3.61							
1, 2-dichloroethane	289.0	3.61	333						
	276.4	3.64							
	271.4	3.61							

Contd.

Table 1—Absorption maxima, log ε_{max} and fluorescence maxima of 2-phenoxyaniline, 4-phenoxyaniline and phenoxybenzene in different solvents and various acid concentrations—*Contd*

Solvents	2POA			4POA			POB		
	λ_{abs} nm	log ε	λ_{flu} nm	λ_{abs} nm	log ε	λ_{flu} nm	λ_{abs} nm	log ε	λ_{flu} nm
Acetonitrile	289.8	3.67	334	302.0	3.81	360	276.2	3.27	298
	276.2	3.68		245.0	4.12		272.4	3.33	
	270.2	3.65					266.2	3.26	
tert-Pentyl alcohol	288.2	3.58	340s						
	276.6	3.60	374						
	270.6	3.56							
	235s								
tert-Butyl alcohol	286.8	3.52	340s						
	276.4	3.58	392						
	270.6	3.52							
	235s								
2-propanol	287.2	3.51	340s						
	276.4	3.56	393						
	270.6	3.50							
	235s								
2-Butanol	287.2	3.52	340s						
	276.6	3.58	392						
	270.2	3.50							
1-Butanol	287.0	3.51	340s						
	276.6	3.56	392						
	270.4	3.51							
Ethanol	287.0	3.44	340s						
	276.0	3.56	394						
	270.4	3.42							
	235s								
Methanol	287.0	3.46	340s	296.0	3.39	366	277.0	3.26	300s
	276.4	3.56	395	241.0	4.15		271.0	3.31	325
	270.2	3.45					265.0	3.24	
	235s								
Ethylene glycol	286.0	3.30	330s						
	276.2	3.34	394						
	271.0	3.29							
	235s								
Water	281s	3.47	344s	291.0		372	276.0	3.28	345s
(neutral)	274.8	3.51	412	236.0			272.0	3.25	410
	235s						263.4	3.25	
Monocation	274s		295	276.0		305	276.0*	3.15	310*
	268.0			269.0			272.0	3.25	
	262.0			263.4			263.4	3.25	
	235s			224s					
Monoanion	303.0			310.0					
	279.0			259.0					
	259.0								
Dianion	—		348			362			

s—shoulder; *—1 *M* H_2SO_4

solvent) is due to the usual dipole-dipole effect of the $\pi \rightarrow \pi^*$ transition or to the hydrogen-donating character of the amino group.

The fluorescence spectra of 2POA in different solvents are displayed in Fig. 1. There is much difference between the solvent effects on fluorescence spectra of 2POA and 4POA. In all solvents 4POA gives only one broad structureless fluorescence band, whereas 2POA gives one emission maximum in nonpolar solvent, and a dual fluorescence in polar solvents. Among the two bands one occurs in shorter wavelength region around 340 nm (fluorescence normal, FN) and the other in longer wavelength region around 410 nm (fluorescence abnormal, FA). The regular red-shift in the fluorescence spectra of 2POA shows that it is acting as proton donor in the excited singlet state. This is because the charge migration from the amino group to the phenyl ring is increased on excitation. The dual fluorescence of 2POA could be attributed to a variety of causes; *viz*, formation of solute-solvent exciplex, excimer, TICT, etc. To test the formation of exciplex we recorded two fluorescence spectra of 2POA in cyclohexane with 1% methanol and with 1% water (v/v) and compared these with spectrum of cyclohexane. There is no significant difference between the fluorescence spectra. So it is clear that FA band arises only due to the bulk properties of solvent and not due to complex formation. In otherwords, polar solvents strongly enhance the FA band. The red shifts of the FA band are well correlated with solvent polarity (Fig. 2). Moreover, the increase in Stokes shift with increase in polarity is much larger for FA band than for FN band (Table 2). The red shifted FA band of 2POA indicates the formation of TICT state which is more stabilized by polar solvents. It is also reported that some of the bichromophoric diaryl systems of general structure M-X-M, where two identical aromatic moieties (M) are joined to each other by a single bridging group (X = CH_2, O, NH, SO_2. etc.), undergo photoinduced charge transfer[5]. This TICT state is observed only for 2POA and not for 4POA. In 2POA as indicated by its absorption spectra the interaction of the amino group is found to be less in the ground state. It is reported that in diphenyl and related compounds the phenyl rings attain planarity during excitation[20]. Amino groups also attain planarity leading to increased charge transfer interaction with the ring in excited state. In 2POA attainment of coplanarity of amino group and phenyl rings is not possible due to the interaction of ether group with amino group in the *ortho* position. Hence amino group is twisted in the excited state leading to the charge separated TICT state.

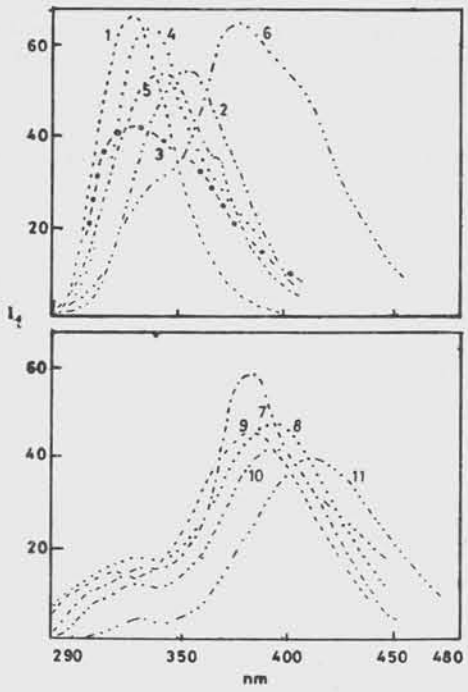

Fig. 1—Fluorescence spectra of 2POA in various solvents at 298K concentration $\approx 4 \times 10^{-5}$ mol dm $^{-3}$ 1, Cyclohexane; 2, dioxane, 3,ethyl acetate; 4,dichloromethane; 5, acetonitrile; 6, *tert*-pentyl alcohol; 7, *tert*-butyl alcohol; 8, 2-propanol; 9, 1-butanol; 10, methanol; 11, water

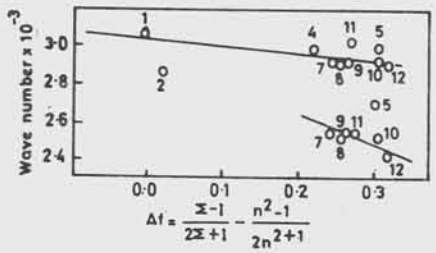

Fig. 2—Correlation of the $\Delta f = \frac{\Sigma-1}{2\Sigma+1} - \frac{n^2-1}{2n^2+1}$ with the wave number of 2POA.
1, Cyclohexane; 2, dioxane; 3, ethyl acetate; 4, dichloromethane; 5, acetonitrile; 6, *tert*-pentyl alcohol; 7, *tert*-butyl alcohol; 8, 2-propanol; 9, 1-butanol; 10, methanol; 11, water; 12, ethylene glycol

Effect of proton concentration

The absorption and fluorescence spectra of 2POA have been studied in the $H_0/pH/H_-$ range of -10 to 17. The relevant data are compiled in Table 1 and the absorption and fluorescence spectra of various prototropic species of this

Table 2—Stokes shift ($\Delta\nu_{ss}$ cm^{-1}) of 2-phenoxyaniline, 4-phenoxyanilin and phenoxybenzene in solvents of different Δf values and at various *p*H

Solvents	$\Delta\nu_{ss}$ (cm^{-1})				
	2POA		4POA	POB	Δf
	FN	FA			
Cyclohexane	3905		4655	2073	−0.0004
Diethylether	5511				
Dioxane	5511				0.02115
Tetrahydrofuran	4079				—
Ethylacetate	4156				
Methylacetate	4224				
Dichloromethane	4686				0.2182
1, 2-Dichloroethane	4573				
Acetonitrile	4566		5335	2388	0.3064
tert-Pentyl alcohol	5286	7960			
tert-Butyl alcohol	5455	9355			0.2453
2-propanol	5407	9438			0.2739
2-Butanol	5431	9374			—
1-Butanol	5431	9333			0.2625
Ethanol	5431	9462			
Methanol	5431	9527	6467	2768	0.3092
Ethylene glycol	4662	9584			0.2745
Water (neutral)	6517	11315	7529	7246	0.3201
Monocation	2592	—	3444		
Correlation coefficient	0.7447	0.8659			

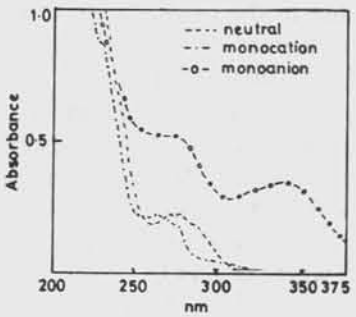

Fig. 3—Absorption spectra of different prototropic species of 2POA at 298K concentration ≈ 4×10^{-5} mol dm^{-3}. (– – neutral, – – – monocation, –x– monoanion)

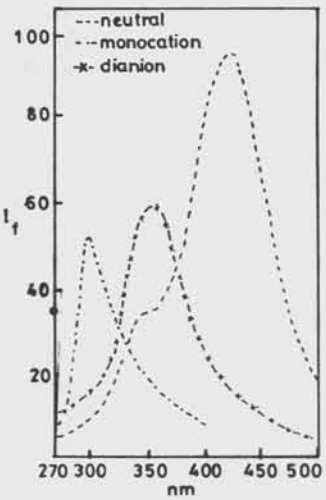

Fig. 4—Fluorescence spectra of different prototropic species of 2POA at 298K concentration ≈ 4×10^{-5} mol dm^{-3}, (– – neutral, – – – monocation, -x-dianion).

amine is also shown in Figs 3 and 4 respectively. When the *p*H is decreased from 7 to around 3, a blue-shifted absorption spectrum resembling that of POB[12] is obtained. This spectrum is due to the formation of monocation. No further change in absorption spectrum is observed with increase in acidity upto $H_0 = -10$. When the *p*H is increased from 7 no significant change in the absorption spectrum is noticed upto $H_- = 15.0$. But the absorption maximum is continuously red-shifted with further increase in basicity and a new absorption spectra with the maxima of 334 nm and 270 nm is obtained in most strongly basic solution. Aromatic amino compounds on deprotonation give a red-shifted spectrum and this spectrum may be due to the monoanion. The ground state pK_a value for neutral-monoanion equilibrium could not be determined because there was no constancy in the isosbestic point.

The effect of *p*H on the fluorescence spectrum is the same as observed in the ground state. The neutral species at *p*H 7 shows a fluorescence maximum of 412 nm. When the *p*H is decreased fluorescence is quenched from *p*H 5 to 3 and at *p*H 3 a blue-shifted fluorescence spectrum starts appearing. At *p*H 1 a spectrum with the maximum at 295 nm resembling POB[12] molecule is obtained due to the formation of monocation. The fluorescence intensity decrease from *p*H 5 to 3, without the formation of monocation, is due to proton induced quenching. Since monocation starts forming at *p*H 3 the quenching is not complete. There is no significant change in the spectrum with further increase in the acidity from 0.83 to −5.0.

When the *p*H is increased from 7 the fluorescence at 412 nm is quenched due to the formation of monoanion. The monoanion of many aromatic amino compounds are found to be nonfluorescent[21,22] with few exceptions[23,24]. At very high basic solution, $H_- = 16$ a blue-shifted fluorescence spectra at 348 nm is obtained. Earlier Dogra *et al.*[25] assigned this band to the dianion species, formed by the deprotonation of both protons of the amino group. Doubts have arisen about this species by the results of Chowdhury and Chattopadyay[26] as the latter workers have observed si-

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