Electronic Spectra of 9,10-Phenanthrenediamine: Effects of Solvents and Acid Concentrations

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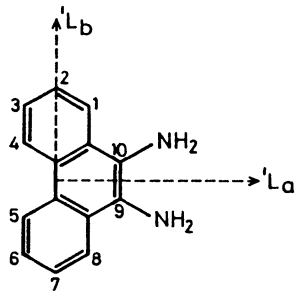
Dual fluorescence is observed from 9,10-phenanthrenediamine (PDA) in defferent solvents. Normal Stokes shifted fluorescence band is a structured one with vibrational frequency of ca. 750 cm^{-1} and is polarized along the longer axis (^1L_b state). Large Stokes shifted fluorescence is a broad band and is polarized along the shorter axis of phenanthrene (^1L_b state). Fluorescence intensities of both the bands decrease with the increase of polarity and hydrogen-bond formation tendency of the solvents, but the preferential decrease in the fluorescence intensity of latter band system is more than that of the former band system under the above environments. Equilibrium for the prototropic reaction of monocation-free base is not established in the S_1 state within the lifetimes of the conjugate acid-base pair. Proton-induced fluorescence quenching constant for monocation is found to be 2×10^7 $dm^3\,mol^{-1}\,s^{-1}$ and this low value, as compared to that for neutral aromatic amines, is because of the presence of positive charge on the monocation.

In the cata-condensed aromatic hydrocarbons, generally three electronic absorption bands are very prominent.[1,2] The long wavelength band (also known as α or ^1L_b band) is a long axis polarized weak band. Next band of high energy [polar(p) or ^1L_a band] is short axis polarized and is stronger than the α band. The third one is either a mixture of short axis and long axis polarized transitions (^1B_a or ^1B_b) or a single band i.e. β (^1B_b) and it is the most intense band. p-band is more easily susceptible to any change in the geometry of the molecule or to the presence of basic substituent along the short axis. For example α- and p-bands are well separated in benzene but are mixed in case of anthracene. In 1-naphthoic acid,[3] the long wavelength absorption band is of ^1L_a character whereas in naphthalene it is ^1L_b, which is of the lowest singlet energy.

As said earlier, the p-band is more polar and easily succeptible to the changes in the molecule or environments than the α-band. The presence of basic substituent at position-1 of linearly condensed systems will affect the p-band very much because roughly speaking the transition moment vector coincides with dipole moment vector. On the other hand the presence of basic substituent at 2-position affects both the α- and p-bands because dipole moment vector is lying in between the long axis and the short axis. Due to this, the dipole moment vector will have finite value along the short and the long axes of the molecule. However, the long axis polarized band will be affected more than the short axis polarized.

Because of the presence of benzo group along the angular direction, phenanthrene molecule belongs to C_{2v} symmetry point group. Due to this, unlike anthracene, α- and p-bands are well-separated and α-band possesses a nice vibrational structure, with vibrational frequency of 705 cm^{-1}. As can be seen from the structure of the phenanthrene molecule, the presence of basic groups at positions 9 and 10 will affect the p-band more than the α-band. The present study on



Scheme 1.

9,10-phenanthrenediamine (PDA) is in continuation of our earlier studies on the molecules containing similar two functional groups[4-6] to find out (i) how the amino groups affect the various band systems of phenanthrene and (ii) how the various prototropic species formed by the protonation or deprotonation of the amino groups will affect the α- and the p-bands. The conclusions are based on the absorption and fluorescence spectra recorded in different solvents and at various proton concentrations. The pK_a values for the different prototropic reactions have been determined in s_0 and s_1 states and are discussed. Lastly, this study was undertaken because the molecule, 9-phenanthrenamine is studied thoroughly.[7-9]

Experimental

9,10-Phenanthrenediamine (PDA) was obtained from Aldrich Chemical Company and was recrystallized from benzene. Finally, PDA was purified by vacuum sublimation and was stored under nitrogen atmosphere. The purity was checked by noting its sharp melting point, absorption spectrum and getting the similar fluorescence band maxima when excited at different wavelengths. Being very sensitive to air and light, the compound and the stock solutions were kept in amber-colored bottles and in oxygen free nitrogen atmosphere. Spectrograde methanol (BDH), trifluoroacetic acid (TFA, Fluka), analytical grade sulfuric acid, sodium hydroxide, and orthophosphoric acid were used without

further purifiction. Whereas cyclohexane, ether, and acetonitrile were further purified according to the procedure suggested in the literature.[10] Triply distilled water was used for aqueous solutions. pH of the solutions in the range of 3—10 was adjusted by adding appropriate quantities of sodium hydroxide and orthophosphoric acid, since the small quantities or phosphate buffers do not quench the fluorescence of the species and do not alter the pK_a of the prototropic reactions.[11] Hammett's acidity scale[12] for the solutions with pH<1 (prepared by the mixture of H_2SO_4 and water) and Yagil's basicity scale[13] for the solutions with pH>13 (prepared by the mixture of NaOH and water) were used.

The abosrption spectra were recorded on Shimadzu 190UV spectrophotometer, equipped with 135U recorder. The fluorescence measurements were carried out on a recording spectrofluorimeter fabricated in our laboratory of which details are available elsewhere.[14] Both the monochromators were calibrated from time to time with low-pressure mercury lamp. The band width used for excitation purposes is 8 nm. The concentration of the solution was kept at 5×10^{-5} M (1 M=1 mol dm^{-3}), containing not more than 5% (v/v) methanol. For titration purposes, the solutions were prepared just before taking the measurements and the solutions were excited using the isosbestic wavelengths. The excitation wavelength used in determining the equilibrium constants for dication-monocation, monocation-free base and free base-monoanion equilibria in S_1 state were 300, 370, and 350 nm. The fluorescence quantum yields were determined from the solutions whose absorbances were less than 0.1. The fluorescence spectra were corrected[15] and quantum yields were calculated using quinine sulfate in 0.05 M H_2SO_4 as a standard.[16] The wavelength used for excitation was 385 nm. The pH of the solutions in the range of 1—13 were measured with Toshniwal's pH meter model CL 44A.

Results

The absorption spectra of PDA in different solvents and at different proton concentrations are depicted in Figs. 1 and 2 respectively. The relevant data are compiled in Table 1. Data of Table 1 clearly indicate that the absorption spectra of PDA can be divided into three band systems above 250 nm. One around 400 nm, the second around 330 nm and the third around 270 nm. The 400 nm band is broad and less structured as compared to the long wavelength band of phenanthrene,[1] whereas the structure is observed in the 274 nm band system and unlike other band systems, the structure of this band is retained in polar as well as hydrogen-bonding solvents. The vibrational frequency observed in the long wavelength band in cyclohexene is nearly equal to 730±30 cm^{-1}. A small red shift is noticed in the long wavelength absorption band in going from cyclohexane to acetonitrile, whereas a blue shift is observed in 400 and 330 nm bands in methanol and water.

With the decrease of pH (ca. 2), the 400 nm band system develops into a very nice vibrational structured absorption band which is red-shifted as compared to neutral one, whereas the other band systems follow a small blue shft. The absorption band systems at 303

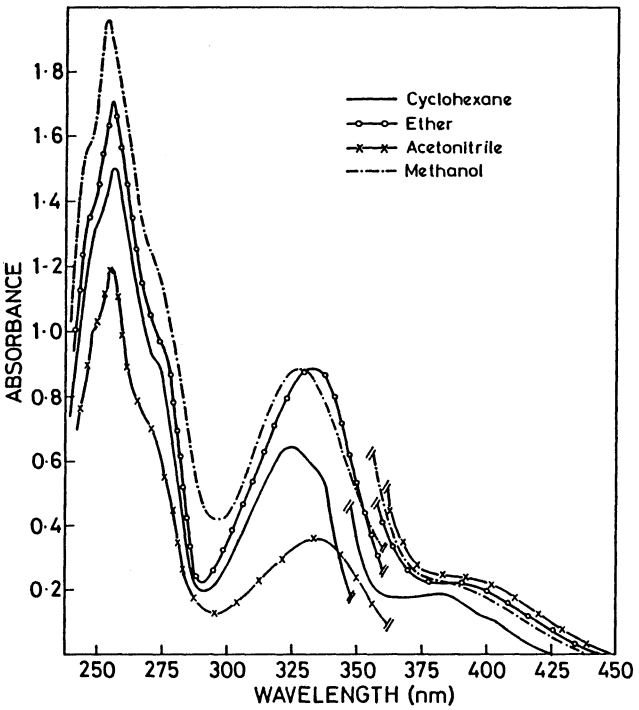


Fig. 1. Absorption spectra of PDA in different solvents at 298 K, concn=7×10^{-5}M.

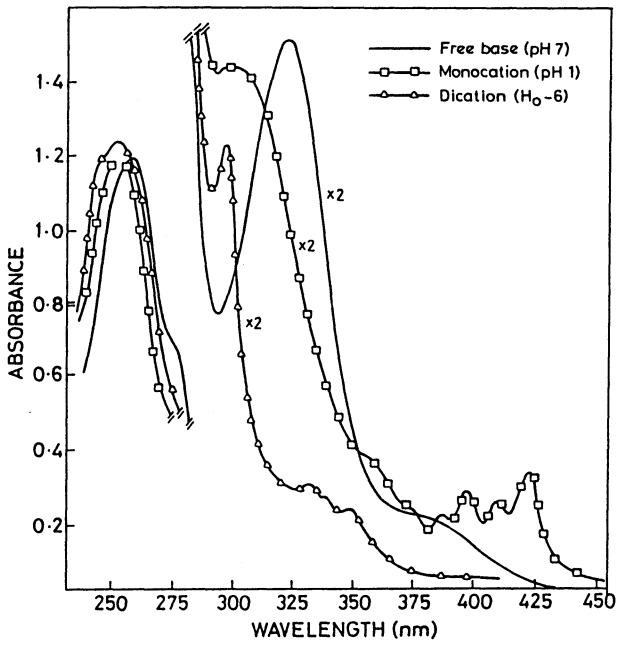


Fig. 2. Absorption spectra of the various prototropic species of PDA at 298 K.

and 252 nm resemble with that of 9-phenanthrenamine.[7] The vibrational frequency observed in the long wavelength band is 740±20 cm^{-1}. This spectrum is assigned to the monocation of PDA formed by the protonation of one of the amino groups. With further increase of proton concentration, all the band systems are blue-shifted and exactly agree with the band systems of phenanthrene,[1] both in the band maxima

Table 1. Absorption and Fluorescence Maxima (nm), log ε_{max} and ϕ_f of 9,10-Phenanthrenediamine in Different Solvents and at Various Proton Concentrations

Solvent/ species	λ_{max}(abs) (log ε_{max})			λ_{max}(flu) (ϕ_f)	
Cyclohexane	408	333	274	422, 438	—
	384	324	260	(0.07)	
			253		
Ether	395	333	277(4.23)	431	
	(3.15)	(4.05)	270(4.20)	418	492(0.04)
			259(4.32)	405	485[a]
Acetonitrile	400	332	274(4.27)	434	
	(3.10)	(4.05)	270(4.36)	420	511(0.02)
			258(4.53)	408	490[a]
Methanol	388	328	275(4.16)	430	
	(2.9)	(3.91)	270(4.22)	416	522(0.01)
			256(4.30)	406	475[a]
Water pH 7	383	323	275(4.21)		—
(Free base)	(3.13)	(3.96)	260(4.45)	—	448[a]
Monocation	421	303	252		430(0.02)
pH 1	408	(3.35)	(4.36)	—	400, 425[a]
	396				410[b]
	385				405[c]
	374				
	360				
Dication	348	299	252	—	390
H_0-6	(3.15)	(3.56)	(4.25)		368(0.31)
	337	288	246		354
	(3.22)	(3.53)	(4.19)		343, 359, 380, 390[a]
	332	278			
	(3.26)	(3.67)			
		265			
		(3.91)			
Monoanion	395	330	248	—	410
(H_16)		304	227		

a) 77 K. b) Cyclohexane+0.5% (v/v) trifluoroacetic acid. c) 0.75 M H_2SO_4 in methanol.

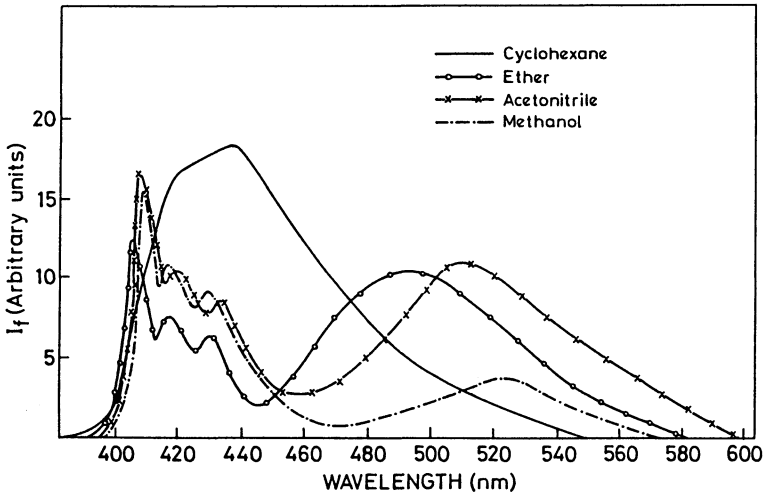


Fig. 3. Fluorescence spectra of PDA in different solvents at 298 K, concn=3×10^{-5}M.

and the vibrational frequencies observed in α- and p-bands. This species is thus assigned to dication formed by the protonation of both the amino groups. In the basic region above pH 14, a red shift is observed in the absorption spectrum, indicating the formation of monoanion. This equilibium is not complete, even at H– 16, the highest basic solution used.

The fluorescence spectra of PDA in different solvents and at various proton concentrations are depicted in Figs. 3 and 4 respectively. The relevant

data are compiled in Table 1. In cyclohexane, only one normal stokes shifted fluorescence band (422 nm) is observed, whereas in other solvents, both the normal Stokes shifted and large Stokes shifted fluorescence (495 nm) bands are noticed. The normal Stokes shifted fluorescence band is nicely structured in all the solvents, with the vibrational frequency of ca. 720±20 cm^{-1}, whereas a large stokes shifted fluorescence emission is a broad band. With the increase in solvent polarity and proton donor capacity of the solvets, the fluorescence band maximum of large Stokes shifted band gets red-shifted, whereas that of normal Stokes shifted band remains unaffected. The fluorescence intensities of both the bands decrease under the above environments, but the relative decrease in the fluorescence intensity of the large Stokes shifted band is more than that of the normal Stokes shifted one. In water as solvent, PDA is nonfluorescent.

The prototropic species formed in the excited singlet state are the same as formed in the ground state. That is a blue-shifted fluorescence band (430 nm) is ovserved at pH 1 and this resembles with that of 9-phenanthrenamine in water as a solvent[9] and thus can be assigned to the monocation. At H_0-6 a large blue shifted structured fluorescence band is observed, agreeing nicely with that of phenanthrene.[17] The species formed thus a dication, obtained by protonating both the amino groups. No other fluorescence bands are observed even on increasing the proton concentration to H_0-10. Free base is nonfluorescent in the pH range of 6—14. Only at H_- 15, a fluorescence band (ca. 410 nm) appears and it reaches maximum intensity at H_- 16.5. This band system agrees with the fluorescence band maximum observed in case of 9-phenanthrenamine[9] at H_- 15. This can be assigned to monoanion.

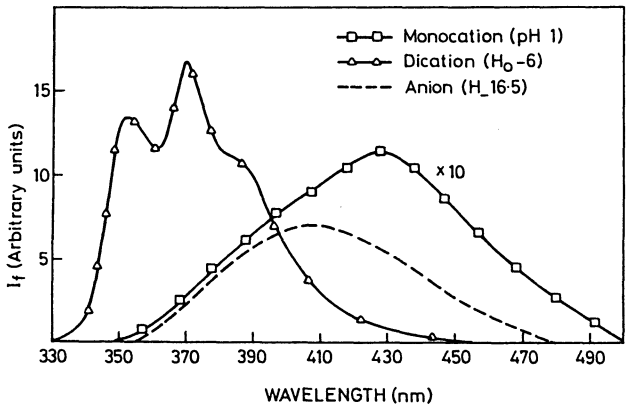


Fig. 4. Fluorescence spectra of the different prototropic species of PDA at 298 K.

The pK_a values of the various prototropic reactions are determined spectrophotometrically and are listed in Table 2. The pK_a for the monocation-free base equilibrium is much lower than that observed for similar reactions of other aromatic amines,[18] but agrees with the pK_a value obtained in case of 2,3-naphthaleneamine.[6] Similar is the case for dication-monocation equilibrium. The smaller pK_a value is because of the steric hindrance offerred by the two adjacent amino groups. The ground state pK_a value for the free base-monoanion equilibrium cannot be determined because the formtion of monoanion is not complete even at H_- 16.5, the highly basic solution used. The excited singlet state pK_a values are determined with the fluorimetric titrations (Fig. 5) and the values so obtained are listed in Table 2. Förster cycle method[19] cannot be used for the monocation-free base equilibrium as free base molecule is nonfluorescent in water at 298 K and the absorption spectrum of cation gets some complex structure (see later). Fluo-

Table 2. pK_a Values of Various Prototropic Reactions in S_0 and S_1 States

Equilibrium	pK_a	pK_a^{*} a)		
		abs	flu	Ft
Dication ⇄ Monocation	0.25	−10.2	−4.7	−4.2
Monocation ⇄ Free base	3.5	8.4		3.3
Monoanion ⇄ Dianion	>16	—	—	14.5

a) pK_a^{*} values using Förster cycle method and absorption and fluorescence data. Ft=Fluorimetric titration.

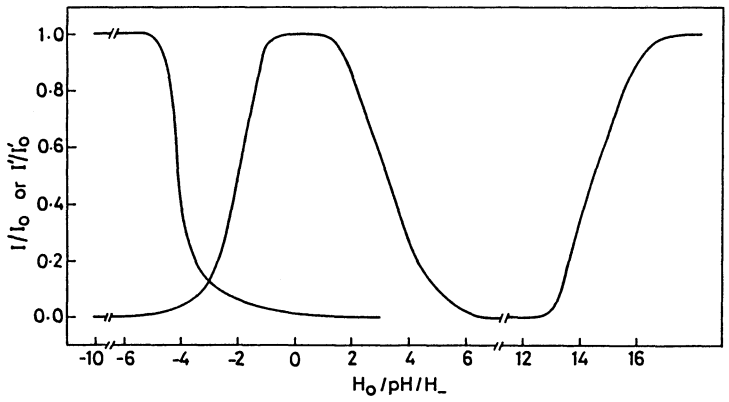


Fig. 5. Plot of relative fluorescence intensities of various prototropic species versus H_0/pH/H_-.

rescence data at 77 K and Förster cycle method do indicate that the ammonium ion becomes stronger acid in S_1 state. On the other hand, fluorimetric titrations have yielded the ground state pK_a for the monocation-free base equilibrium. This indicates that the prototropic equilibrium is not attained in the S_1 state during the short lifetimes of the conjugate acid-base species. Similar results have been observed in some other systems,[4-6,20] although it is anomalous. Similar to the normal behavior of aromatic amines, no correspondence is observed between the decrease in fluorescence intensity of monocation and the increase in the fluorescence intensity of the dication. The pK_a^* values for this reaction has been determined using fluorimetric titrations but from the formation curve of the dication only (Fig. 5) and is listed in Table 2.

As described earlier no correspondence is observed between the decrease and increase in the fluorescence intensity of the monocation and dication of PDA respectively. This has been attributed to the proton-induced fluorescence quenching of monocation.[21-29] This is because there was no quenching effect due to the counterion SO_4^{2-} under the experimental conditions. Applying the similar model as suggested by Shizuka et al.[27] and under conditions that proton concentration is small and thus rate for the backward protonation reaction is small as compared to its lifetime, the final equation reduces to a simple Stern-Volmer equation i.e.

$$I_0/I = 1 + k_q\tau[H^+]$$

where I and I_0 are fluorescence intensities in the presence and absence of quencher, k_q is the proton-induced fluorescence quenching rate constant and τ is the lifetime of the monocation. I_0/I vs. $[H^+]$ has been plotted in Fig. 6 and the slope obtained is 0.02 $dm^3 mol^{-1}$. The natural lifetime τ_{FM} is calculated using Strickler and Berg[30] equation and τ by using $\tau=\tau_{FM}\phi_f$ equation. The value of τ obtained is 1.1 ns and that of k_q is 2×10^7 $dm^3 mol^{-1} s^{-1}$. This value is quite small as compared to that observed for the similar reactions of other aromatic amines.

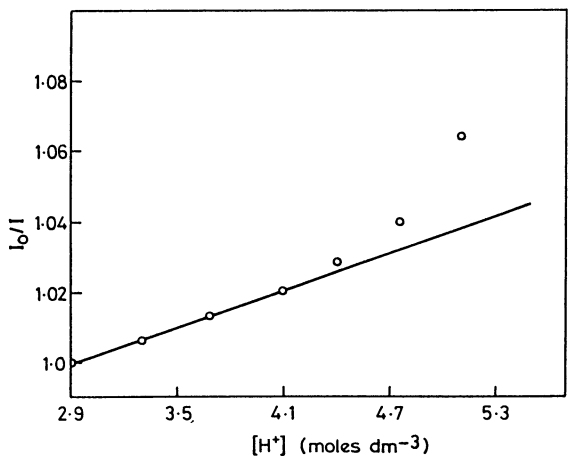


Fig. 6. Stern-Volmer plot for proton-induced fluorescence quenching of the monocation of PDA.

Discussion

Phenanthrene molecule has three band systems, one near 340 nm, highly structured with vibrational frequency 705 cm^{-1} (α-band), the other at 290, moderately structured with vibrational frequency 1320 cm^{-1} (p-band) and the third around 250 nm (β-band). Tsutsumi et al.[31] have clearly indicated with the help of semi-empirical SCF-MO-CI method that the charge migration from the amino group to the phenanthrene ring in the ^1L_a (p-band) occurs much more than in the other states in case of 9-phenanthrenamine. Thus based on these results the two amino groups in phenanthrene will perturb the above transitions but the effect will be more on the p-band than on the α- and β-bands. This is clear from the Scheme 1 shown earlier. Though the perturbation due to the presence of amino groups is more on the p-band, it is believed that the long wavelength band in PAD and its prototropic species is still the α-band. This is based on the following results:

(i) Molecular extinction coefficient of the long wavelength band (1.26×10^3 $dm^3 mol^{-1} cm^{-1}$) is less than that of second band (1.1×10^4 $dm^3 mol^{-1} cm^{-1}$). The former is more close to that of phenanthrene (0.4×10^3 dm^3 $mol^{-1} cm^{-1}$). The increase in the ε_{max} of this band of PDA is due to the interaction of amino groups with the phenanthrene moiety.

(ii) The difference between the two band maxima in phenanthrene is ca. 56 nm. Though the two band systems may get mixed up in PDA but it is highly improbable that the p-band will be of lower energy than that of α-band. It is also clear from the absorption spectrum (Fig. 1) that ca. 400 nm band appears as shoulder to the 333 nm band system.

(iii) Lastly the vibrational frequency observed in the long wavelength band (730 ± 30 cm^{-1}) resembles with that noticed in the absorption spectrum of phenanthrene (705 cm^{-1}).

The loss in the vibrational structure of α- and p-bands is because of the interation of lone pairs of the amino groups with the aromatic ring, which is commonly observed. Further, the loss of vibrational structure with the increase in the polarity and hydrogen-bond-forming tendency of the solvents is due to the interaction of the solvents with PDA. The data of Table 1 indicate that the molecule is acting as a proton acceptor in the ground state.

The blue shift observed in the p- and β-bands of the absorption spectra of PDA with the increase of proton concentration is consistent with the protonation of one of the amino groups, leading to the formation of monocation and protonation of both the amino groups, to the formation of dication. The band maximum in the former resembles with that of 9-

phenanthrenamine[9] and that of latter resembles with phenanthrene molecule.[1] But the behavior of α-band system is different from that of the other two. The absorption band maximum is slightly red-shifted and the band system has very nice structure, with vibrational frequency of 720±20 cm^{-1}. This structure is similar to the α-band system of phenanthrene molecule. The similar behavior is also observed in the α-band of PDA in cyclohexane when different amounts of TFA is added. Though the formation of monocation of PDA is confirmed but it is difficult to explain the appearance of a red-shifted structured absorption spectrum.

From the data of Table 1, we assign the normal Stokes shifted fluorescence band to the transition from ^1L_b. This is because the vibrational frequency observed in the short wavelength emission (ca. 750 cm^{-1}) spectrum agrees with that noticed in the absorption spectrum, indicating that the mirror image symmetry is observed between the long wavelength band of absorption and the short wavelength of fluorescence spectrum. This proves that the excited electronic state involved in the long wavelength absorption band and the short wavelength fluorescence band is the same i.e. ^1L_b. More evidences will be given later on. We assign the long wavelength fluorescence band to ^1L_a transition. This assignment is further based on the following evidences:

(i) The excitation spectra were recorded in two different solvents (ether and acetonitrile) at both the fluorescence band maxima and are shown in Fig. 7. The excitation spectrum recorded at long wavelength band does possess a small peak at 400 nm but the vibrational structure present in the absorption band is absent and the most intense band is around 350 nm, agreeing with the ^1L_a transition of absorption spectrum. On the other hand the excitation spectrum recorded at short wavelength fluorescence band possesses the vibrational structure, with the similar vibrational frequency as noticed in the long wavelength absorption spectrum. This spectrum does not contain the band around 350 nm, arising out of ^1L_a transition. The mixing of the small absorbance due to 400 nm band in the excitation spectra recorded at 500 nm is due to the mixing of these two bands in the absorption spectrum of PDA. (ii) ^1L_a electronic excited state is generally more polar than the ^1L_b electronic state. The presence of electron donating groups in the proper direction makes it further more polar. It has been shown by Tsutsumi et al.[31] that the charge migration from amino group to phenanthrene ring, in case of 9-phenanthrenamine, is much larger in the ^1L_a state than others. Due to this ^1L_a state is stabilized much more as compared to that of ^1L_b in more polar solvents and thus it appears at lower energy than the ^1L_b state. This is further manifested from the effect of solvents on the fluorescence spectrum of PDA, recorded in different solvents. The fluorescence band maximum at 400 nm is hardly affected by the polarity or proton-donor capacity of the solvents, whereas a large red shift is noticed in 500 nm band under the similar environments. (iii) Although the fluorescence intensities of both the fluorescence bands decrease in going from ether to water (molecule is nonfluorescent in water), the ratio of I_{500}/I_{400} decreases very rapidly in the above environments. This could be due to the fact that ^1L_a state is more polar and will have more interactions with the polar and proton donor or aceptor solvents. This will increase the rates of radiationless processes of the polar state. (iv) The more polar nature of ^1L_a state is further confirmed from the results of the fluorescence spectra of PDA recorded in cyclohexane containing TFA. The cyclohexane solution containing TFA upto 2×10^{-2} % (v/v) does produce a blue shift in the ^1L_a band system of absorption spectrum but ^1L_b band system becomes more structured, similar to the results observed in the absorption spectrum of PDA in aqueous solution containing H_2SO_4. But the fluorescence spectrum contains both the band systems and the red shift in the large Stokes shifted fluorescence band

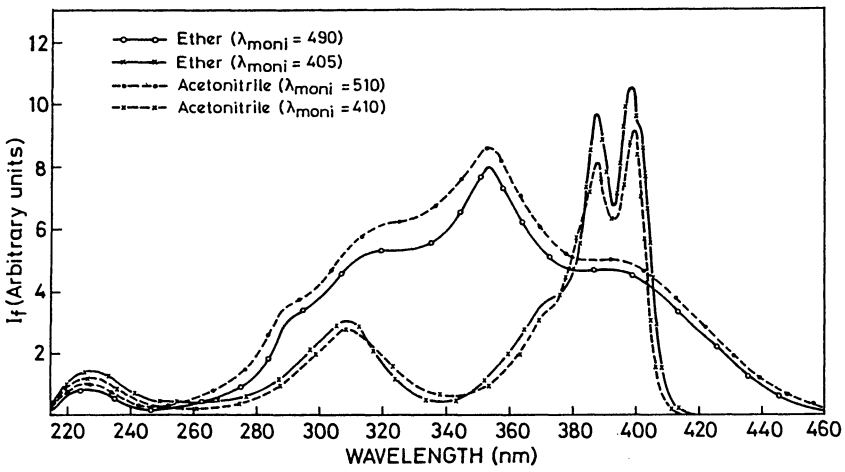


Fig. 7. Excitation spectra (uncorrected) of PDA recorded at 510 and 400 nm.

Table 3. Absorption and Fluorescence Band Maxima of PAD in Cyclohexane + Different Amount of Trifluoroacetic Acid (TFA)

% TFA (v/v)	λ_{max}(ab) nm			λ_{max}(fluo) nm	
Cyclohexane+0.00	408	333	274	438	—
	384	324	268	422	
			253		
0.001	408		287	442	
	396	309	277	430	494
	385			416	
	375			410	
	365				
	348				
0.002	408		288	442	
	396	312	277	430	502
	385			416	
	375			410	
	—				
	341				
0.02	408		286	430	502
	396	320		416	
	385	300		400	
	375				
	350				
	341				
0.2	357			Nonfluorescent	
	340	325			
		312			
1.0				410	

increases with the increase in the TFA concentration upto 2×10^{-2} % (Table 3). This is because TFA makes the cyclohexane polar and stabilizes the ^1L_a electronic state more than the ^1L_b one. This is further manifested from the fact that fluorescence intensities of both the emission bands decrease with increase of TFA in cyclohexane and PDA is nonfluorescent in cyclohexane containing 0.2% (v/v) TFA. (v) Last possibility that the long wavelength fluorescence belongs to the excimer is ruled out on the ground that the ratio of I_{500}/I_{400} does not change with the increase in the concentration of PDA by thousand fold.

The fluorescence spectra of the various prototropic species of PDA are consistent with the behavior of aromatic amines. The 430 nm fluorescence band of monocation, formed by protonating one of the amino group is originating from the ^1L_a electronic state, because this band maximum, similar to large Stokes shifted fluorescence band of PDA, is solvent dependent i.e. band maximum is red-shifted with the increase in the polarity of the solvent. Further monocation of PDA is similar to 9-phenanthrenamine, where it has been shown that ^1L_a is the lowest excited singlet state.[8] Finally, the structured fluorescence spectrum at H_0-6 is assigned to dication, formed by protonating both the amino groups, as this spectrum resembles with that of phenanthrene. In general, the fluorescence intensity of neutral aromatic amine is quenched by pH 14, without observing fluorescence from the monoanion, formed by the deprotonation of amino group, with few exceptions.[32] In our case, the additional problem is that the free base is also nonfluorescent in pH range 6—14, so it cannot be said with certainity that monoanion is formed in the excited state, but from the results of literature, the formation of this species can be speculated in the excited state. Based on our earlier results on 9-phenanthrenamine,[9] the 410 nm band can be assigned to a dianion formed by the deprotonation of either $-NH^-$ or $-NH_2$ group. This was further based on the similar results observed for 1- and 2-naphthylamine.[33] The results of Choudhury and Chatopadhyay,[34] on 2-naphthylamine and *N,N*-dimethyl-2-naphthylamine have clearly shown that the fluorescence band ovserved at H_- 15 is due to the species formed by the deprotonation of ring hydrogen rather than from $-NH^-$, as *N,N*-dimethyl-2-naphthylamine has no dissociable proton. Based on these results and the similarity of the fluorescence band observed in PDA, with that of 9-phenanthrenamine it is possible that this species is similar to that formed in case of 2-naphthylamine. Fluorimetric titration curve has indicated that pK_a^* value for the equilibrium between the monoanion and the latter species (may also be monoanion) is 14.5, which actually agrees with the results of 9-phenanthrenamine.[9]

Results of fluorimetric titrations indicate that the prototropic equilibrium between monocation and free base pair is not established in the excited state during the lifetimes of the conjugate acid-base pair. This result is anomalous but similar behavior has been shown by the aromatic systems containing two amino groups,[4-6] 6-indazolamine,[35] and 4-(9-anthryl)-*N,N*-dimethylaniline.[20] This can be attributed to the short lifetimes of the two species. The pK_a^* value for the dication-monocation equilibrium has indicated that the ammonium ion becomes stronger acid on excitation.

Lastly, the small value of k_q observed for the proton-induced fluorescence quenching as compared to that for normal aromatic amines, is due to the presence of positive charge on the monocation.

Conclusion

Following conclusions can be drawn from the above study. (i) Dual fluorescence is observed in all the solvents. Abnormal Stokes shifted fluorescence arises from more polar and short axis polarized state, whereas the normal Stokes shifted, structured fluorescence is assigned to the less polar, long axis polarized state. (ii) The equilibrium between the monocation-free base species is not attained in the S_1 state and is due to the short lifetimes of the conjugate acid-base pair. (iii) Proton-induced fluorescence quenching for the monocation is observed and k_q value is found to be 2×10^7 $dm^3\,mol^{-1}\,s^{-1}$. The small value is due to the presence of positive charge on the monocation.

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