  Bull. Chem. Soc. Jpn., 60, 4409—4415 (1987)

Spectral Characteristics of Phenylenediamines and Their Various Protonated Species

R. MANOHARAN and Sneh Kumar DOGRA*
Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India
(Received November 25, 1986)

Increase in the Stokes shift [$\bar{\nu}_{abs}(max)-\bar{\nu}_{flu}$ (max)] with an increase in the polarity and hydrogen-bonding capacity of the solvents is the maximum for *p*-phenylenediamine and the minimum for *m*-phenylenediamine. These studies have indicated that the two amino groups in *o*- and *p*-phenylenediamines are not in the same plane of the benzene ring. Spectral characteristics of monocations and dications resemble to those of aniline and benzene respectively. pK_a values for the dication-monocation and monocation-neutral equilibria have been determined, both in S_0 and S_1 states, and discussed.

If $\pi\rightarrow\pi^*$ is the lowest energy transition, the protonation at the tertiary nitrogen atom leads to the red shift in the absorption and fluorescence spectra of the molecule.[1] Schulman et al.[2] in their study of prototropic reactions of 1,10-phenanthroline have revealed that the spectral changes, observed in the absorption spectrum on protonation, followed the normal trend, but the emitting state of the monocation, formed by protonating one of the tertiary nitrogen atom is of lower energy than that of the dication, formed by protonating the second tertiary nitrogen atom i.e., red shift is followed by the blue shift in the above prototropic reactions. This anomalous behavior has been attributed to the very large solvent relaxation in the S_1 state of monocation and this has been further confirmed when the similar study was carried out in nonpolar medium, where the solvent relaxation is negligible. The similar behavior has been observed in our earlier study on 2,7-fluorenediamine,[3] where the two amino groups are symmetrical, like the two tertiary nitrogen atoms of 1,10-phenanthroline.

The aim of the present study is to see whether 1,2-, 1,3-, 1,4-phenylenediamines follow the similar trend or these molecules behave in a different fashion. Secondly, most of the prototropic studies carried out on the disubstituted benzenes are on the donor-acceptor substituents.[4-7] This kind of study, carried on the donor-donor substituents is very rare.[8-11] Since amino groups are electron donating, we have undertaken this study to see the effect of solvents and pH on the spectral changes of these three isomers of phenylenediamines.

Method and Material

o-Phenylenediamine (*o*PA) and *p*-phenylenediamine (*p*PA) were obtained from Aldrich Chemical Co. and *m*-phenylenediamine (*m*PA) was prepared by the reduction of *m*-nitroaniline as suggested in literature.[12] *o*PA was recrystallized from water, *m*PA from benzene, and *p*PA from diethyl ether repeatedly.[13] The purity of these compounds was checked by their sharp mp, absorption data and getting the similar fluorescence spectra when excited with different wavelengths. Spectrograde BDH methanol, analytical grade sulfuric acid, orthophosphoric acid, and sodium hydroxide (BDH) were used without further purification. Cyclohexane (IDPL), ether (BDH), and acetonitrile (E. Merck) were further purified by the procedures, as suggested in literature.[14] Triply distilled water was used for the aqueous study. Modified Hammett's acidity scale[15] for aqueous H_2SO_4 and Yagil's basicity scale[16] for aqueous NaOH were used for solutions below pH 1 and above pH 13 respectively. pH of the solutions in the range of 3 to 11 was adjusted by the addition of appropriate amount of NaOH and H_3PO_4.

Absorption spectra were recorded on a Shimadzu spectrophotometer, model UV 190, equipped with a chart recorder, model U 135. Fluorescence measurements were carried out on a scanning spectrofluorimeter, fabricated in our laboratory, the details of which were available elsewhere.[17] Both monochromators were calibrated from time to time with low-pressure mercury lamp and the band width of the excitation monochromator was 8 nm. pH of the solutions in the range of 1—13 was measured on a Toshniwal's pH meter, model CL-44A. Fluorescence quantum yields were measured on the solutions, having absorbance less than 0.1, fluorescence spectra were corrected and quinine sulfate in 0.05M H_2SO_4 (1M=1 mol dm^{-3}) was used as a standard.[18] The excitation wavelengths (λ_{exc}) used for *o*PA, *m*PA, and *p*PA were 275, 285, and 288 nm respectively. For absorptiometric and fluorimetric titrations, the solutions were prepared just before taking measurements and the concentrations of the solutions were of the order of 1×10^{-4} M (1M=1 mol dm^{-3}). To measure the fluorescence intensity at any analytical wavelength, isosbestic wavelengths were used for excitation. For dication-monocation equilibria of all diamines, a mercury-xenon lamp was used instead of a xenon lamp, normally used in the spectrofluorimeter. This is because of the low intensity of the xenon arc lamp below 270 nm.

Results and Discussion

Effect of Solvents. Table 1 depicts the absorption maxima, log ε_{max}, fluorescence maxima, and quantum yields of *o*PA, *m*PA, and *p*PA in the solvents of different polarity and hydrogen bond forming tendency, as well as at different proton concentrations. Figures 1—3 show the fluorescence spectra of these three diamines under the above environments. Data in Table 1 clearly indicate that the absorption spectra of all isomers are largely red shifted and the vibrational structure of the long wavelength band is completely lost in any one of the solvents compared to those of benzene. The intensity of each band of benzene is increased. The above results are quite consistent with

Table 1. Absorption and Fluorescence Spectral Data of Phenylenediamines in Different Solvents and at Various pH

Solvent (pH)	*o*-Phenylenediamine		*m*-Phenylenediamine		*p*-Phenylenediamine	
	λ_{abs} (log ε)	λ_{flu} (ϕ_f)	λ_{abs} (log ε)	λ_{flu} (ϕ_f)	λ_{abs} (log ε)	λ_{flu} (ϕ_f)
Cyclohexane	290.0(3.59) 234.0(3.85) 209.5(4.45)	330(0.020)	(sh)301.5(3.33) 293.3(3.42) 241.0(3.86) 214.0(4.46)	318(0.096)	316.5(3.23) 246.3(3.81) 207.5(3.69)	365(0.13)
Ether	294.0(3.55) 239.0(3.79) 212.0(4.35)	350(0.056)	296.3(3.5) 242.0(3.92) 218.5(4.47)	322(0.087)	320 (3.37) 247.5(3.96) 207.5(3.79)	381(0.17)
Acetonitrile	295.0(3.66) 240.0(3.90) 208.0(4.55)	352(0.02)	297.5(3.46) 243.0(3.89) 217.0(4.49)	326(0.015)	321.0(3.25) 247.5(3.84) 200.0(4.20)	388(0.065)
Methanol	293.5(3.52) 238.7(3.79) 210.0(4.48)	355(0.019)	292.5(3.36) 242.5(3.85) 213.5(4.48)	332(0.011)	307.5(3.27) 242.5(3.96) 204.0(4.05)	395(0.073)
Water	288 (3.53) 232.0(3.88) 205.0(4.57)	— —	289.0(3.30) 238.0(3.86) 210.0(4.51)	— —	302.5(3.28) 239.0(3.90) 197.5(4.33)	— —
Monocation (pH=3.5)	280 (3.24) 222.5(3.83) 194.0(4.16)	335(0.048)	282.5(3.24) 232.0(3.85) 205.0(4.08)	340(0.027)	283.5(3.08) 233.5(3.87) 201.3(4.01)	345(0.019)
Dication (H_0=−8)	261.0(2.16) 256.5(2.32) 251.5(2.36) 246.5(2.31) 237.0(2.10) 206.5(2.98)	275 —	262.0(2.0) 257.5(2.19) 252.5(2.22) 247.5(2.15) 237.5(1.92) 207.5(2.99)	275 —	262.5(2.27) 257.5(2.4) 252.5(2.39) 244.0(2.26) 236.0(2.13) 206.0(3.0)	275 —

ε values are in $dm^3 mol^{-1} cm^{-1}$.

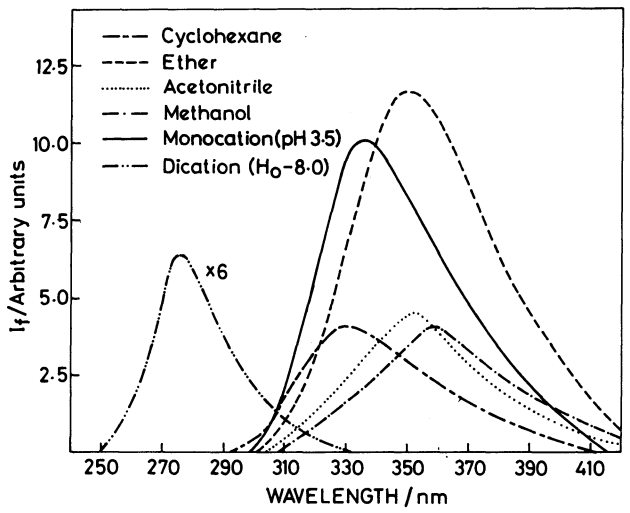


Fig. 1. Fluorescence spectra of *o*PA in different solvents and pH at 298 K. Concd=5.0×10^{-4} M.

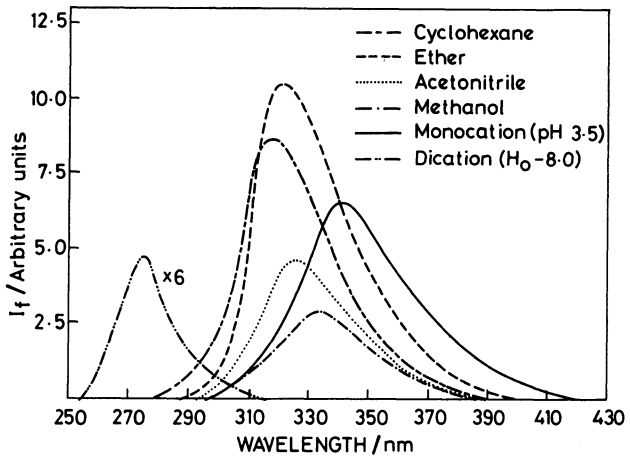


Fig. 2. Fluorescence spectra of *m*PA in different solvents and pH at 298 K. Concd=5.0×10^{-4} M.

the presence of amino groups in the ring, because it completely destroys the hexagonal symmetry of the benzene ring. Therefore the symmetry forbidden selection rule is reduced resulting in an increase in the value of the transition dipole moment. The large red shift in λ_{max} and loss in the vibrational structure of the absorption spectrum are due to the strong interactions of the amino group with the π cloud of the benzene ring.

The absorption maxima of all bands of diamines are red-shifted with an increase in the polarity of aprotic solvents but are blue-shifted with an increase in the

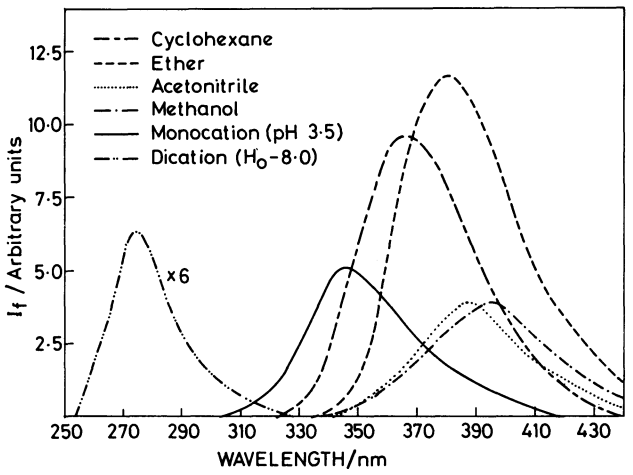


Fig. 3. Fluorescence spectra of *p*PA in different solvents and pH at 298 K. Concd=5.0×10^{-4} M.

proton-donor capacity of solvents. On the other hand, the fluorescence maxima of all diamines are regularly red-shifted under the above environments. The fluorescence quantum yield is quite small and further decreases in going from cyclohexane to water, where it is completely nonfluorescent at room temperature. The effect of solvents on the absorption and fluorescent maxima is agreeing with results observed earlier in the case of amino groups[19] i.e., the dispersive interactions and proton-donor nature of the solute lead to red shift and the proton-acceptor of solute leads to the blue shift in the absorption and fluorescence spectra of molecule if $\pi\rightarrow\pi^*$ is the lowest energy transition. Our data clearly indicate that in S_0 state, all diamines are acting as a proton donor in ether and acetonitrile, whereas a proton acceptor in methanol and water. The results of fluorescence spectra can be explained on the ground 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. The decrease in the fluorescence quantum yield of all diamines, under the above environments is due to their strong interactions with the solvents and thus increasing the rates of radiationless processes. This is further manifested from the Stokes shift, which increases with the increase in the polarity of the solvents.

The Stokes shift [$\bar{\nu}_{abs}$(max)$-\bar{\nu}_{flu}$(max)] observed for three amines is minimum for *m*PA (2630 cm^{-1}) and nearly same for *o*PA and *p*PA (4180, 4200 cm^{-1}) in cyclohexane. But an increase in the Stokes shift with an increase in the solvent polarity is the maximum for *p*PA and the minimum for *m*PA (See Table 2). Although no data is available for the polarity or dipole moment of these molecules in the excited states but it is quite clear from the data that the polarity and dipole moment of these molecules increase upon excitation. Our data further suggest that two amino groups present at the para position are not in the plane

Table 2. Stokes Shifts (cm^{-1}) Observed for Phenylenediamines in Different Solvents

Solvent	*o*PA	*m*PA	*p*PA
Cyclohexane	4180	2625	4200
Ether	5440	2730	5000
Acetonitrile	5480	2940	5380
Methanol	5902	4070	7200
Water (pH=8)	—	—	—
Monocation (pH=3.5)	5860	5990	6290
Dication (H_0=−8)	1950	1800	1800

of benzene ring. Had these groups been planar to the benzene ring, the dipole moment of *p*PA would have been zero, and thus the molecule would have been nonpolar in both S_0 and S_1 states. The dipole moment data of these molecules, available in the ground state,[20] do indicate that $-NH_2$ groups in the cases of *o*PA and *p*PA are not in the same plane of the benzene ring whereas in the case of *m*PA these groups are in the same plane of benzene. These conclusions are based on the fact that the calculated dipole moments of diamines (based on the vector addition of amino groups) do not agree with the observed ones. We, also, conclude from our data that the similar geometries of these molecules are present in the first excited singlet state.

Effect of Proton Concentration. The absorption and fluorescence spectra of all diamines have been studied in the H_0/pH/H_- range of −10 to 17. The relavent data are compiled in Table 1 and the fluorescence spectra of the various prototropic species of these amines are also shown in Fig. 1—3 respectively. The results observed are on the right track. With the decrease of pH (from≈8, depending on the particular diamine) the absorption spectra of all diamines are blue shifted and the absorption spectra so obtained resemble to that of aniline.[21] This clearly suggests that the species so formed is a monocation, obtained by protonating one of the amino groups. With the further increase of proton concentration, the absorption spectra are further blue-shifted and the long wavelength broad band is replaced by a structured spectrum, in each case. This spectrum resembles to that of benzene molecule.[22] This is further manifested from the similar vibrational frequencies as observed in the case of benzene coupled with the electronic transition, as well as from a decrease in the molecular extinction coefficient of the absorption bands of this species, resembling more closely to that of ^1L_b transition in benzene. The above results clearly indicate that the latter species is a dication, formed by protonating the second amino group. The above behavior clearly resembles to that of the aromatic compounds containing the amino group.[19,23-25]

The absorption spectra of ortho- and metadiamines do not change till pH 14 but after and at H_- 15, a small but a regular red shift is noticed and it continued even upto H_- 17, the highest basic conditions used and the

band maxima is observed at the same wavelength (295 nm). On the other hand, the absorption spectrum of *p*PA starts getting red shifted at pH $\geqslant$13 and is continuously red-shifted even at H_- 17, with a band peak at 313 nm. The above results are consistent with the results that deprotonation of the amino group leads to a red shift in the spectra.

The behavior of fluorescence spectra of the various species formed in these acid region is the same as observed in the ground state, i.e., around pH 4, the fluorescence spectrum of each amine is blue-shifted and resembles to the fluorescence spectrum of aniline ($\approx$340 nm in ethanol).[21] Around H_0 −8, the fluorescence spectrum is further largely blue-shifted in each case, with the band maximum at 275 nm and this resembles more closely to the fluorescence spectrum of benzene, without the band structure.[21] The above results clearly suggest that the former species is a monocation formed by the protonation of the amino group and the second species is a dication, formed by the protonation of the second amino group. The loss in the structure of the second species in the fluorescence spectrum, as compared to that in the ground state, is due to the stronger interactions in such a highly ionic medium. The assignment of the species is further confirmed by getting the fluorescence band maximum of the monocation nearly at the same wavelength and that of dication exactly at the same point in cases of the diamines studied. This is because, during these prototropic reactions, the species formed in the first case is close to aniline and in the second case, it is close to benzene, as the lone pairs are mopped by protons.

No fluorescence emission is observed from the neutral species as well as from the monoanions of these amines at room temperature and even upto H_- 17, the highest basic conditions used. This is consistent with the earlier results that monoanions formed by the deprotonation of aromatic amines, in general, are non-fluorescent, with few exceptions.[27,28]

Equilibrium Constants in the Ground and Excited States. pK_a values of dication-monocation and monocation-neutral equilibria have been calculated spectrophotometrically and are compiled in Table 3. The values of pK_a's obtained agree with literature values within experimental errors.[29] The pK_a for the neutral-monoanion cannot be determined because the absorption maxima in each case was constantly red-shifted even at the highest basic conditions used but one thing is certain that the pK_a value of neutral-monoanion equilibrium of *p*PA is smaller than that of *o*PA and *m*PA. The difference in the pK_a values of monocation-neutral equilibria between *o*PA and *m*PA is quite small but it is quite large in the case of *p*PA. Further the pK_a values for *o*PA (4.50) and *m*PA (4.80) are not very different from that of aniline (4.66).[30] Since the amino group is an electron donating group and it is ortho- and para-directing, it will not change the charge densities at the nitrogen atom of the other $-NH_2$ group in case of *m*PA. Thus the pK_a value for *m*PA will be close to that of aniline, as observed. For *o*PA, it was expected that its value should be greater than that of aniline. However the small decrease in the pK_a value of *o*PA was observed. This may be due to the steric hindrance of the two amino groups adjacent to each other. The high pK_a value for monocation-neutral equilibrium of *p*PA can be explained as follows: Because of the symmetry of the amino groups, the average charge densities at both nitrogen atoms will be same. But at any particular instant, if one of the nitrogen atom becomes more acidic, the other will

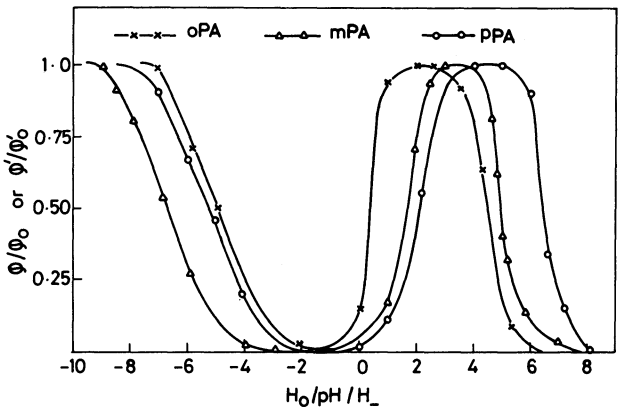


Fig. 4. Plot of relative intensities (ϕ/ϕ_0) vs. H_0/pH/H_- for different phenylenediamines.

Table 3. pK_a Values of Different Equilibria of Phenylenediamines in the S_0 and S_1 States

Equilibrium	pK_a[a]	pK_a[b]	p$K_a(S_1)$[c]	p$K_a(S_1)$[d]	p$K_a(S_1)$[e]
***o*PA**					
Dication-monocation	1.86	1.20	−5.2	−11.5	−5.2
Monocation-neutral	4.65	4.50	2.42	—	4.35[f]
***m*PA**					
Dication-monocation	1.89	2.0	−3.8	−12.6	−6.9
Monocation-neutral	4.86	4.8	3.1	—	4.9[f]
***p*PA**					
Dication-monocation	2.54	2.4	−5.9	−13.1	−5.1
Monocation-neutral	6.11	6.10	1.3	—	6.2[f]

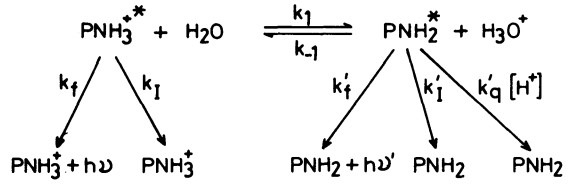
a) Literature value. b) Present work. c, d) Calculated using the Förster cycle method with absorption and fluorescence data respectively. e) Fluorimetric method. f) Apparent pK_a* value.

become more basic and since the steric hindrance is minimum for *p*PA, the pK_a value for the monocation-neutral equilibrium would be the highest, whereas it would be the lowest for neutral-monoanion equilibrium among the diamines.

pK_a^* values for all equilibria have been calculated fluorimetrically (Fig. 4) as well as using the Förster cycle method[27] wherever it is applicable, except for the neutral-monoanion case where both species are nonfluorescent. All values have been compiled in Table 3. For the monocation-neutral equilibrium, the formation curves of the monocations are plotted only because the neutral species are nonfluorescent in aqueous medium. It is clear from Fig. 4 that the fluorimetric titration curves have given only the ground state pK_a values for the monocation-neutral equilibria. Whereas the Förster cycle method, using absorption data only, have shown that the amino group becomes stronger acid on excitation to the first excited singlet state. It is thus concluded that the radiative lifetimes of the neutral and singly protonated species must be too short for proton exchange to occur appreciably within these lifetimes at pH 4—6. Due to this reason the prototropic equilibrium is not established within the lifetimes of the lowest excited singlet states of these molecules. Thus the fluorescence intensities measured at pH ≈4—6 reflect the ground-state concentrations of neutral and monocation species. Consequently, the ground-state pK_a is determined by fluoremetric titrations in this case. Secondly, though the neutral molecules are nonfluorescent, the fluorimetric curves by giving the ground state pK_a values have clearly shown that the proton-induced fluorescence quenching is not observed for the neutral species, before forming the monocations. Otherwise one would have observed a different pK_a value from the formation curve of monocation, if the proton-induced fluorescence quenching of the neutral species had been observed. This behavior is very similar to that observed for 4-(9-anthryl)-*N*,*N*-dimethylaniline by Shizuka et al.[31] Shizuka et al. have clearly shown from their time dependence fluorescence study that the lifetimes of the conjugate acid-base pair is very short, even though the intramolecular charge-transfer state $^1A^*_{CT}$ is very rapidly produced via $^1A^*$. Similar explanation can be offered in the cases of all diamine derivatives of benzene.

In the dication-monocation equilibrium the fluorescence of monocation is quenched in the pH region where the dication is present in the ground state but not fluorescent in the S_1 state. The dications start emitting only below H_0 −4. This behavior is similar to the prototropic reactions of aromatic monoamines and decreases in the fluorescence intensity of monocations is attributed to the proton-induced fluorescence quenching. Thus the pK_a^* values have been calculated from the formation curves of the dications and the values are listed in Table 3. The data of Table 3 clearly indicate that the $-NH_3^+$ group is a stronger acid in the S_1 state than in the S_0 state, consistent with the earlier results.[19,23-26] The pK_a^* values calculated with the help of the Förster cycle method and using absorption and fluorescence data do not agree with each other. This is because: (i) The long wavelength absorption band of monocation is broad whereas that of dication is structured. On the other hand the fluorescence spectrum of both species are broad and structureless, (ii) the solvent relaxation for monocation in the S_1 state is very large in comparison to that observed for dication. This can be seen from the Stokes shift observed for the monocation (≈5960 cm^{-1}) and for the dication (≈1900 cm^{-1}). Thus it can be concluded that pK_a^* values determined by fluorimetric titrations will be more close to the actual values. The pK_a^* values for neutral-monoanion equilibrium cannot be calculated because neither neutral species nor monoanion is emitting.

Proton-Induced Fluorescence Quenching. As said earlier no correspondence is observed between the decrease in the fluorescence intensities of the monocations and the increase in the fluorescence intensities of the dications. This has been attributed to proton-induced fluorescence quenching in the pH range of 1 to 4. This is because the SO_4^{2-} ion concentration (produced by adding K_2SO_4) equivalent to that obtained by the addition of H_2SO_4, do not quench the fluorescence of monocations. The model suggested by Shizuka et al.[32-34] can be transformed to simple Stern-Volmer plot under the conditions that the lifetimes of the



P=Monocations of phenylenediamines

Scheme 1.

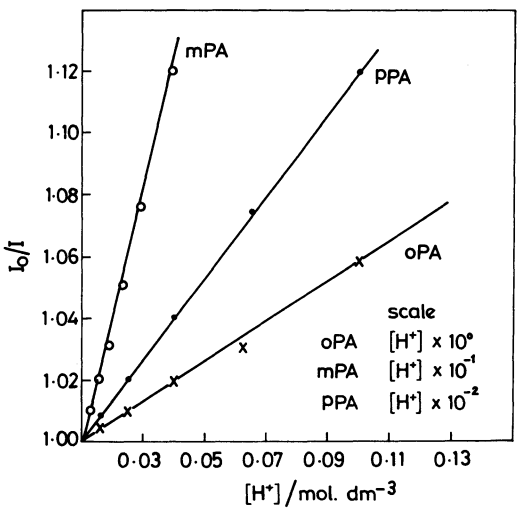


Fig. 5. Stern-Volmer plot for the monocations of different phenylenediamines.

Table 4. Proton Transfer Kinetic Data for Monocations of Different Phenylenediamines

Compd.	$\kappa_q\tau$	τ_{FM}	ϕ_f	τ	κ_q
	$dm^3\,mol^{-1}$	ns		ns	$dm^3\,mol^{-1}\,sec^{-1}$
oPA	0.63	35	0.048	1.68	3.8×10^8
mPA	45	39	0.027	1.1	4.1×10^{10}
pPA	128	45	0.019	0.86	1.5×10^{11}

monocations are short in comparison to those of dications and concentration of H^+ are small to have any backward reaction, dipicted in Scheme I. i.e.

$$\frac{I_0}{I} = 1 + k_q\tau[H^+]$$

where I and I_0 are the fluorescence intensities with and without the quencher respectively, k_q is the proton-induced fluorescence quenching constant and τ is the lifetime of the basic species. I_0/I vs. $[H^+]$ is plotted in Fig. 5 and the $k_q\tau$ values obtained for all three monocations are listed in Table 4. The natural radiative lifetimes of monocation of three diamines are estimated from the corrected fluorescence spectra, using Strickler and Berg's relations.[37] The actual lifetimes are determined from the relation $\tau=\tau_{FM}\,\phi$ where ϕ is the quantum yield of the respective monocation. These values for three species are listed in Table 4. To the first approximation, assuming that the monocations of the three diamines will behave like aniline, the results obtained about the τ_{FM} of monocations of *o*-, *m*-, and *p*- diamines [35, 39, 45 ns respectively] are not very far off from the experimentally determined τ_{FM} of aniline in ethanol (34 ns). The difference in τ is due to the difference in the quantum yields of these species. The smallest lifetime of the para species is due to the larger interactions with solvent molecules which is further manifested by the greater Stoke's shift observed for this species. From our study it is difficult to offer any exact explanation for the large increase in the $k_q\tau$ value in going from the monocation of *o*PA to *p*PA. It may be speculated that steric factor may be playing the major role in the proton-induced fluorescence quenching, although the Stokes shift observed for the monocation of *p*PA is the maximum but do not differ so much from those of other amines if energy of the state has to do anything for this quenching.

Conclusion

Large spectral changes, both in the absorption and fluorescence spectra of *o*PA and *p*PA have clearly indicated that the two amino groups in *p*PA are not in the same plane of the benzene ring. Larger pK_a value for the monocation-neutral equilibrium of *p*PA as compared to *o*PA and *m*PA, indicates that the charge density at the nitrogen atom of amino group is larger than that at the respective atom of other two compounds. In case of *o*PA, the steric hindrance plays the role in having the minimum pK_a value for this equilibrium. Fluorimetric titration curves have indicated that the lifetimes of the monocation-neutral conjugate acid-base pair are quite short to allow the acid-base equilibria in the excited singlet state.

The authors are thankful to the Department of Science and Technology, for the financial support to the project entitled "Proton Transfer reactions in the excited states."

References

1) J. F. Ireland and P. A. H. Wyatt, *Adv. Phys. Org. Chem.*, **12**, 132 (1976).
2) S. G. Schulman, P. T. Tidwell, J. J. Cetorelli, and J. D. Winefordner, *J. Am. Chem. Soc.*, **93**, 3179 (1971).
3) R. Manoharan and S. K. Dogra, *Can. J. Chem.*, in press.
4) W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962).
5) E. L. Wehry and L. B. Rogers, *J. Am. Chem. Soc.*, **87**, 4234, 4237 (1965).
6) J. D. Winefordner, S. G. Schulman, and L. B. Sanders, *Photochem. Photobiol.*, **13**, 381 (1971).
7) E. L. Wehry, *J. Am. Chem. Soc.*, **89**, 41 (1967).
8) R. W. Cowgill, *Photochem. Photobiol.*, **13**, 183 (1971).
9) J. W. Bridges and R. T. Williams, *Biochem. J.*, **107**, 225 (1968).
10) D. V. S Jain, F. S. Nandel, and Prem Lata, *Indian J. Chem*, **21A**, 559 (1982).
11) R. S. Sarpal and S. K. Dogra, *J. Photochem.*, **38**, 263 (1987).
12) B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, and A. R. Tatchett, "Vogel's Text Book of Practical Organic Chemistry," ELBS, London (1980), p. 660.
13) J. G. F. Druce, *J. Chem Soc.*, **113**, 715 (1918).
14) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley Interscience, New York (1970), pp. 592—594, 798—805.
15) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).
16) G. Yagil, *J. Phys. Chem.*, **71**, 1034 (1967)
17) M. Swaminathan and S. K. Dogra, *Indian J. Chem.*, **22A**, 853 (1983).
18) S. R. Meech and D. Phillips, *J. Photochem.*, **23**, 193 (1983).
19) A. K. Mishra and S. K. Dogra, *J. Photochem.*, **23**, 163 (1983); *J. Chem. Soc., Perkin Trans. 2* **1984**, 943.
20) C. P. Smyth, "Dielectric Behaviour and Structure," McGraw Hill, New York (1955), pp. 326—333.
21) I. B. Berlman, "Hand book of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York (1965), pp. 59, 60.
22) F. A. Matsen, R. S. Becker, and D. R. Scott, "Techniques of Organic Chemistry," ed by W. West, Wiley Inter-

science, New York (1968), Vol. IX, p. 261.
23) A. K. Mishra and S. K. Dogra, *Indian J. Chem.*, **24A**, 285 (1985); **24A**, 364 (1985); *Bull. Chem. Soc. Jpn.*, **58**, 3587 (1985); *J. Photochem.*, **31**, 333 (1985).
24) M. Swaminathan and S. K. Dogra, *J. Am. Chem. Soc.*, **105**, 6223 (1983); *Can. J. Chem.*, **61**, 1064 (1983).
25) P. Phaniraj, A. K. Mishra, and S. K. Dogra, *Indian J. Chem.*, **24A**, 913 (1985).
26) R. V. Subba Rao, M. Krishnamurthy, and S. K. Dogra, *J. Photochem.*, **24**, 55 (1986); *Indian J. Chem.*, **25A**, 917 (1986).
27) Th. Förster, *Z. Elektrochem.*, **54**, 42 (1950).
28) U. K. Pandey, N. B. Joshi, and D. D. Pant, *Chem. Phys. Lett.*, **72**, 209 (1980).
29) "Dictionary of Organic Compounds," ed by J. Bukingham, 5th ed, Chapman and Hall (1982), pp. 1529, 1530.
30) D. D. Perrin, "Dissociation Constants of Organic bases in Aqueous Solutions," Butter Worths, London (1965), p. 58.
31) H. Shizuka, T. Ogiwara, and E. Kimura, *J. Phys. Chem.*, **89**, 4302 (1985).
32) K. Tsutsumi and H. Shizuka, *Chem. Phys. Lett.*, **52**, 485 (1977); *Z. Phys. Chem., N.F.*, **111**, 129 (1978); *J. Photochem.*, **9**, 334 (1978); *Z. Phys. Chem., N.F.*, **122**, 129 (1980).
33) H. Shizuka, K. Tsutsumi, H. Takeuchi, and I. Tanako, *Chem. Phys. Lett.*, **62**, 408 (1979).
34) K. Tsutsumi, S. Sekiguchi, and H. Shizuka, *J. Chem. Soc., Faraday Trans. 1*, **78**, 1087 (1982).
35) H. Shizuka and S. Tobika, *J. Am. Chem. Soc.*, **104**, 6919 (1982).
36) H. Shizuka, *Acc. Chem. Res.*, **18**, 141 (1985).
37) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).