Prototropic Equilibria in Few β-Hydroxy-Substituted 1-Naphthylamines in the Ground and Excited Singlet States

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The longest wavelength transition in the absorption spectra of β-hydroxy-substituted 1-naphthylamines is long axis polarised, whereas the fluorescence occurs from the more polar, short axis polarized state. This is based on the spectral characteristics in different solvents. Five different prototropic species are formed in the ground state and six species are obtained in the S_1 state. The ground state precursor for the formation of zwitterion is the monocation. pK_a values for the different prototropic reactions have been calculated in the ground and excited singlet states.

It is now well-established that the amino and hydroxyl groups[1–5] become stronger acids in their first excited singlet states. The monoanion formed by the deprotonation of amino group is generally nonfluorescent,[6–10] with few exceptions.[11,12] Further the proton-induced fluorescence quenching of the free aromatic amine is generally observed before it is protonated to form the monocation.[13–15] Recently, a few exceptions have been observed, where the lifetimes of the aromatic amines are very short and no fluorescence quenching is noticed by the proton,[16,17] even though the charge-transfer state is of lowest energy, a prime condition for the proton-induced fluorescence quenching. The latter is a common feature during the first protonation of the aromatic diamines[18–20] and in these cases the fluorimetric titrations give rise to the ground state pK_a values for the first prototropic equilibrium. On the other hand, most of the phenoxide ions are nonfluorescent,[21–24] whereas the naphtholate ions are fluorescent.[25–28] Further, the fluorimetric titrations in the former cases yield the ground state pK_a values and this may be due to the shorter lifetime of the conjugate acid-base pairs. In case of naphthols, stretched sigmoid curves are observed, giving rise to both the ground state and excited state pK_a values.

Molecules containing electron-donating and electron-withdrawing groups have been studied extensively.[5] On the other hand, molecules containing electron-donating groups only, have not been investigated in detail and very few such examples are available in literature.[23,24,29–31]

The present study is on the molecules containing electron-donating groups only (i.e. -NH_2 and -OH) and the molecules are 2-hydroxy- (1,2 NA), 6-hydroxy- (1,6 NA), and 7-hydroxy-1-naphthylamines (1,7 NA), i.e. hydroxyl group is at the β-position and the amino group is at the α-position. Literature survey has indicated that the above molecules along with 1,3 NA and similar other molecules have been studied by Ellis and Rogers.[32] These workers have predicted the presence of zwitterion for some aminonaphthols in the excited singlet state in the pH range of ca. 4 to 10. The argument given is that the excited singlet state deprotonation constant of 2-naphthol (2 NOH) is 2.8[28] and it is enough to protonate the amino group (pK_a≈4) to form the zwitterion. But on the other hand, the excited state protonation constant of 1-naphthylamine (1 AN) is (−1.0)[33] and thus it may not be possible to form the phototautomer in the pH range of ca. 4 to 10 in the S_1 state, especially when the phototautomerism is biprotonic in the case of 1,6 NA and 1,7 NA, as the proton migration depends on the environment. The purpose of this study is to resolve this controversy and to find out why the zwitterion has not been observed for 1,7 NA and 1,2 NA. To supplement the above study, 7-methoxy-1-naphthylamine (1,7 MNA) has been prepared. Solvent effects have been studied and pK_a values of the various prototropic reactions have been determined and discussed.

Materials and Method

1-Amino-2-naphthol hydrochloride and 1,7 NA were procured from Aldrich Chemical Company. 1,6 NA was obtained from ICN Pharmaceuticals. 1,6 NA and 1,7 NA were purified from ethanol by repeated crystallization. Neutral 1,2 NA was prepared by titrating its salt with sodium hydrogencarbonate maintaining the pH≈5. 7-Methoxy-1-naphthylamine (1,7 MNA) was prepared from 1,7 NA by the method suggested by Ellis and Rogers.[32]

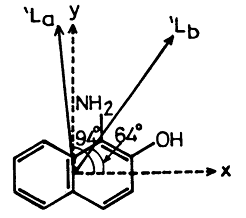
The purity of these compounds, purification of the solvents, instruments used, and the procedure used for calculating the various parameters are the same as described in our recent papers.[18–20] Pariser-Parr-Pople (PPP)[34,35] method was employed to calculate the transition energies, ground and excited state charge densities at the various centers of the molecules and their monoanions. The program was obtained from QCPE Indiana University, Bloomington, U.S.A. Different parameters required for calculations were taken from the literature.[36] The one center two electron repulsion integrals were calculated by Pariser approximation.[37] Two center electron repulsion integrals were calculated by the Nishimoto-Mataga method.[38] All the configurations obtained by single-electron excitation from occupied molecular orbitals to unoccupied molecular orbitals were considered in calculating all the configurational interaction. The species were assumed to be planar and the rings are taken as regular hexagon. The data regarding the

Table 1. Band Maxima, Oscillator Strength, Direction of Polarization (α), Ground and Excited States Charge Densities at the Nitrogen and Oxygen Centers of Amino and Hydroxyl Groups of Aminonaphthols

Compound	λ_{max} expt. /nm	log ε_{max}	λ_{max} PPP /nm	Osc.St.	α	Charge density			
						Free molecule		Monoanion	
						N	O	N	O
1 AN	324	3.62	312	0.010	359	1.9345	—	—	—
	314	3.70				(1.915)			
	305	3.70	297	0.258	85				
2 NOH	326	3.23	311	0.009	108	—	1.9661	—	—
	312	3.17					(1.953)		
	281	3.56	289	0.213	94				
1,2 NA	335		315	0.024	62	1.9376	1.9686	1.9471	1.7461
						(1.916)	(1.955)	(1.927)	(1.305)
			300	0.228	94				
1,3 NA			314	0.016	298	1.9344	1.9661	1.9347	1.7321
			298	0.237	80	(1.918)	(1.954)	(1.942)	(1.338)
1,6 NA	336	3.55	314	0.014	233	1.9346	1.9693	1.9355	1.733
	299	3.63	298	0.243	90	(1.918)	(1.960)	(1.94)	(1.321)
1,7 NA	334	3.45	315	0.017	125	1.9351	1.9666	1.9377	1.7357
	300	3.62	298	0.24	81	(1.917)	(1.954)	(1.935)	(1.318)
1,7 MNA	330	—	322	0.048	130	1.9358	1.9133	—	—
	316	—	298	0.205	75	(1.920)	(1.820)		
	286								

α is the angle measured counter clock-wise with respect to x-axis.

charge densities on nitrogen and oxygen atoms of $-NH_2$ and $-OH/OMe$ groups of aminonaphthols have been listed in Table 1. The relevant data for 1 AN and 2 NOH are also listed in Table 1 for comparison. The directions of the axes are shown below.



Results and Discussion

Effect of Solvents. Figure 1 depicts the fluorescence spectra of these compounds in different solvents and relevant spectral data are compiled in Tables 2 and 3. Data of Table 2 indicate that the molecular extinction coefficient of each band system decreases with the increase in the wavelength. With the increase in the polarity of solvents, a red shift is noticed in each band system, but in methanol and water, the absorption spectra are blue shifted. On the other hand, a continuous red shift is observed in the fluorescence spectra of these molecules under the similar environments. The fluorescence band maxima of 1,6 NA, 1,7 NA, and 1,7 MNA are nearly at the same wavelength, whereas that of 1,2 NA is slightly red shifted. The above data show that molecules behave as proton donor in polar solvents and proton acceptor in methanol and water in the ground state, whereas proton donor in all the solvents in the first singlet state.

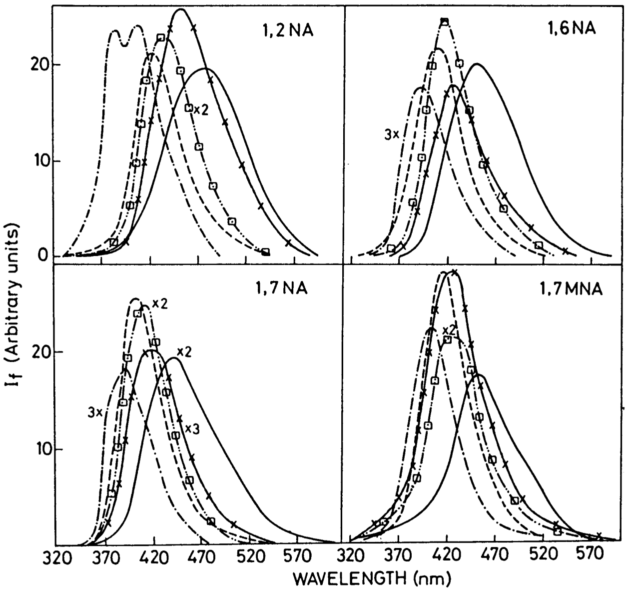


Fig. 1. Fluorescence spectra of 1,2 NA, 1,6 NA, 1,7 NA, 1,7 MNA in different solvents.
λ_{exci}, 1,2 NA and 1,6 NA (337 nm); 1,7 NA (355); 1,7 MNA (330); (—●—) cyclohexane, (------) dioxane, (—□—) acetonitrile, (—×—) methanol, (———) water.

In naphthalene molecule,[39] 312 nm band is weak and long axis polarized ($^1A \rightarrow {}^1L_b$); 286 nm band is moderately strong and short axis polarized ($^1A \rightarrow {}^1L_a$). The longest wavelength band of 1-naphthylamine (1 AN) is broad and a mixture of $^1A \rightarrow {}^1L_a$ and $^1A \rightarrow {}^1L_b$ transitions (322 nm in ethanol),[39] whereas that of 2-

Table 2. Absorption Maxima (nm) and log $\varepsilon_{\mathrm{max}}$ of Some Aminonaphthols in Different Solvents and Proton Concentration at 298 K

Solvent/Species	1,6 NA		1,7 NA		1,7 MNA	1.2 NA
	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	λ_{max}
Cyclohexane	253		248		244	248
	300		304		284	278
	315		—		—	290
	337		336		333	339
Dioxane	258	(4.44)	253	(4.49)	246	248
	—	—	—	—	282	—
	316	(3.74)	312	(3.76)	—	315
	343	(3.78)	341	(3.69)	334	350
Acetonitrile			251		245	247
			—		282	—
			310		—	312
			339		334	347
Methanol	254	(4.35)	248	(4.39)	243	241
	298	(3.69)	—		282	298
	302	(3.68)	308	(3.68)	—	—
	341	(3.65)	337	(3.60)	331	339
Free aminonaphthol	249	(4.29)	244	(4.34)	240	228
pH 6.5	299	(3.63)	300	(3.62)	286	288
	—		—		316	—
	336	(3.55)	334	(3.45)	330	335
Monoanion	260	(4.38)	248	(4.43)		
pH 12	294	(3.74)	295	(3.76)	—	—
	—		301	(3.74)		
	350	(3.54)	351	(3.52)		
Monocation	267	(3.61)	264	(3.58)	261	268
pH 0	276	(3.69)	274	(3.66)	273	274
	287	(3.59)	285	(3.54)	283	286
	318	(3.27)	320	(3.28)	315	314
	328	(3.33)	331	(3.35)	329	327
Dianion	265		254		268[a)]	
H_{-} 17	296		298			
	—		308		307	
	356		359		344	
Dication	252		250			
H_0 −1	262		261			
	275		275		278	284
	290		285			312
	304		308		314	330
	329		325		334	400

a) Monoanion of MNA.

naphthol (2NOH) is $^{1}\mathrm{A}\rightarrow{}^{1}\mathrm{L}_{b}$ (335 nm, ethanol).36) Further, the resonating effect of the amino group on the spectral transitions is more than that of hydroxyl group. The molecules studied in our work contain the amino group along the shorter axis which will perturb $^{1}\mathrm{L}_{a}$ state and the hydroxyl group along the longer axis will primarily affect the $^{1}\mathrm{L}_{b}$ state. From the data of Table 2, 340 nm band can be assigned to $^{1}\mathrm{A}\rightarrow{}^{1}\mathrm{L}_{b}$, whereas 315 nm and 300 nm band to $^{1}\mathrm{A}\rightarrow{}^{1}\mathrm{L}_{a}$ transitions. This is because: (i) the effect of solvents on ca. 340 nm band is less than that observed on ca. 300 nm band, (ii) the molecular extinction coefficient of 340 nm band is less than that of 300 nm, even though the difference is not so large as observed in naphthalene molecule.39) The increase in the molecular extinction coefficient of 340 nm band could be partly because of the presence of -OH group and partly due to the mixing of the two transitions, (iii) two peaks around 300 nm band are the vibrational bands of $^{1}\mathrm{A}\rightarrow{}^{1}\mathrm{L}_{a}$ transition. The vibrational frequency of ca. 1580 cm^{-1} further substantiates our point, as the vibrational frequency associated with $^{1}\mathrm{A}\rightarrow{}^{1}\mathrm{L}_{b}$ transition39) is ca. 1000 cm^{-1}, (iv) the above results are further manifested from PPP calculations (Table 1). The agreement between the band maxima, predicted by PPP method and experimental results is not bad. The oscillator strength clearly indicate that the long wavelength band is more forbidden than the short wavelength one. The polarization direction of the second transition is always along the shorter axis (y-axis), indicating that it is $^{1}\mathrm{L}_{a}$ one. Whereas the polarization direction of the long wavelength band depends upon the position of the -OH group. Though the direction of this transition does not cor-

Table 3. Fluorescence Maxima (nm) and Fluorescence Quantum Yields of Some Aminonaphthols in Different Solvents and Proton Concentration at 298 K

Solvent/Species	1,6 NA		1,7 NA		1,7 MNA		1,2 NA	
	λ_{max}	(ϕ_f)	λ_{max}	(ϕ_f)	λ_{max}	(ϕ_f)	λ_{max}	(ϕ_f)
Cyclohexane	388	(0.26)	388	(0.14)	400	(0.25)	380, 406	
Dioxane	405	(0.45)	406	(0.55)	410	(0.33)	418	(0.24)
Acetonitrile	413	(0.53)	411	(0.32)	421	(0.21)	432	(0.26)
Methanol	420	(0.33)	416	(0.35)	422	(0.16)	448	—
Free aminonaphthol pH 6.5	443	(0.55)	443	(0.44)	448	(0.104)	470[b)]	—
Monoanion pH 12	416	(0.33)	414	(0.47)			—	
Dianion H_-16	518	(—)	418		418[a)]		—	
Zwitterion pH 1	424	(—)	426	(—)	—		428	—
Monocation H_0-1	364	(0.07)	366	(0.09)	366	(0.05)	356[c)]	(0.07)
Dication H_0-10	346,363,370		336,353,364		378	(—)	356	

a) Monoanion of MNA. b) pH 4. c) H_0-4.

respond exactly along the longer axis (x-axis), it lies between the x- and y-axes. This indicates that the long wavelength band is influenced by the short wavelength one. This is also reflected by the molecular extinction coefficient, observed for the long wavelength band.

The fluorescence band maxima of each compound is close to that of 1 AN (445 nm, water)[40,41] than to that of 2 NOH (353 nm).[26] Based on the data of Table 3, we speculate that the reversal of ^1L_a and ^1L_b states takes place and ^1L_a becomes the lowest energy singlet state. This can be explained as follows: (i) ^1L_a state is more polar than ^1L_b and its polarity is further increased by the presence of amino group along the shorter axis. (ii) The energy gap between ^1L_a and ^1L_b states is not very large. (iii) Solvatochromic effect observed in case of these compounds resembles more with that of 1 AN[41] than with 2 NOH.[26] (iv) Though the PPP calculations show that the lowest energy state is ^1L_b, these calculations do not take account of solvent interactions and thus the agreement between the results calculated by PPP method and those obtained by fluorescence spectroscopy will not be good. The near consistency of the fluorescence band maxima in all the compounds indicates that the effect of -OH group on the spectral characteristics is same, so long as it is at the β-position of naphthalene moiety. The larger red shift observed in case of 1,2 NA could be either due to the presence of both the groups on the same ring or due to the presence of intramolecular hydrogen bonding.

Effect of Acid Concentration. 1,2 NA decomposes at pH > 5, so its spectral characteristics are studied in the H_0/pH range of −10 to 5, whereas those of 1,6 NA, 1,7 NA, and 1,7 MNA have been investigated in the H_0/pH/H_- range of −10 to 17. The absorption and fluorescence spectra of the various prototropic species are shown in Figs. 2 and 3 respectively. The relevant data have been compiled in Tables 2 and 3. The absorption band maxima of monocation, neutral and monoanion (wherever these exist) of 1,2 NA and 1,7 NA agree with the literature values.[32]

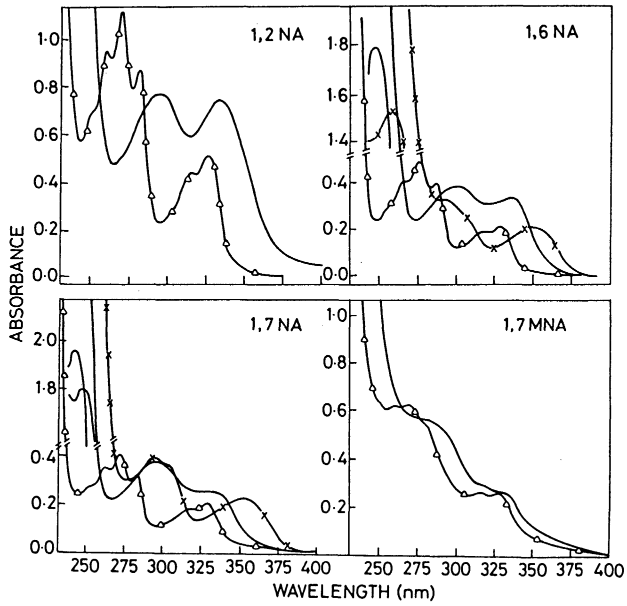


Fig. 2. Absorption spectra of various prototropic species of 1,2 NA, 1,6 NA, 1,7 NA, 1,7 MNA. (———) neutral, (—×—) monoanion, (—△—) monocation.

Spectral characteristics accompanying the prototropic dissociation are related to the electron donor properties of the hydroxyl or amino group i.e. dissociation of hydroxyl or amino group will lead to red shift, whereas the protonation reaction will lead to the

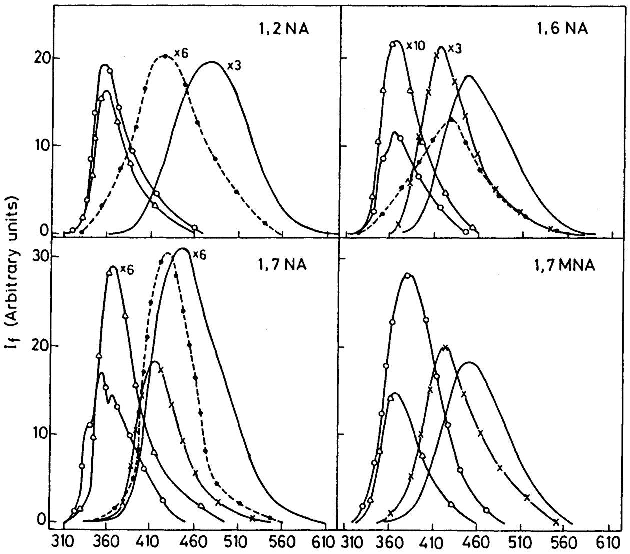


Fig. 3. Fluorescence spectra of various prototropic species of 1,2 NA, 1,6 NA, 1,7 NA, 1,7 MNA. (———) neutral, (—X—) monoanion, (—△—) monocation, (—●—) zwitterion, (—O—) dication.

blue shift in the absorption and fluorescence spectra if $\pi \rightarrow \pi^*$ is the lowest energy transition.

7-Methoxy-1-naphthylamine. Based on above arguments, the molecule exists as a neutral species in the pH/H_- range of 5 to 15. At $H_- > 15$, the species is a monoanion, formed either by the deprotonation of -NH$_2$ group or by one of the C-H bond. Chattopadhyaya and Chowdhury[42] have shown that the absorption spectra of 1 AN and *N,N*-dimethyl-1-naphthylamine are exactly same at $H_- > 15$. The latter compound does not possess the dissociable proton at the amino group. Thus the deprotonation of one of the C-H bond is preferred over the deprotonation of amino group. At pH$<$4, the species is a monocation. Resemblance of absorption spectrum of this species with that of 2-methoxynaphthalene[15] further confirms this assignment. At $H_0 < -4$, the species is a dication formed by protonating the ring carbon atom of monocation, because protonation of -OH/OMe leads to blue shift.[43–45] Besides this at H_0 -7, the monocation starts decomposing to give a large red shifted absorption spectrum and yellow-colored solution. This is an irreversible reaction and the results obtained are not very accurate in this range of acid concentration.

Prototropic reactions occurring in the S_1 state are exactly same as observed in the S_0 state i.e. dication, $H_0 < -4$; monocation, H_0 -3 to pH 3; neutral, pH 4 to 13 and monoanion, pH$>$13. The shifts observed in the fluorescence maxima are similar to those observed in the absorption spectra.

The ground state dissociation constant of monocation-free amine was calculated using absorption spectral data and is found to be 3.5. This value agrees with that observed in case of 1 AN. Data of Table 1 also show that the charge density at the nitrogen center of amino group at position 1 is not affected by the presence of methoxyl group at position 7. The equilibrium constants for dication-monocation and free amine-monoanion could not be determined as the formation of dication and monoanion were not complete even at the extreme acid/base conditions.

The pK_a's in the excited singlet state were determined with the help of fluorimetric titrations (Fig. 4). The fluorescence intensities of monoanion and dication were not plotted in Fig. 4 as the intensities for the respective species were quite small. The pK_a^* value for the free amine-monoanion equilibrium is thus determined from the decrease in the fluorescence intensity of neutral species, whereas that for dication-monocation is speculated. The spectral data indicate that the C-H bond and amino group become stronger base and acid respectively in the excited singlet state, whereas the fluorimetric titrations have yielded the ground state pK_a values for dication-monocation and monocation-free amine equilibria. The former is consistent with earlier results that the equilibrium for the ring protonation is not established in the S_1 state. The latter result is anomalous in the sense that proton-induced fluorescence quenching is not observed before the amino group is protonated, which is a common feature of this reaction. Recently few exceptions are observed[16,17] and thus it can be concluded that the lifetimes of the conjugate acid-base pair are very short and the prototropic equilibrium is not established in S_1 state. The proton-induced fluorescence quenching of monocation of 1,7 MNA is consistent with earlier results of 2-methoxynaphthalene,[1] with the difference that it is observed at higher acid concentration. This is due to the presence of positive charge on the monocation of 1,7 MNA.

7-Hydroxy-1-naphthylamine. The ground state prototropic species of 1,7 NA, formed in the H_0/pH range -10 to 8 are exactly same as observed for 1,7 MNA, i.e. dication, -10 to -4; monocation, -4 to pH 3; neutral, pH 3 to 8. At pH$>$8, the species is a

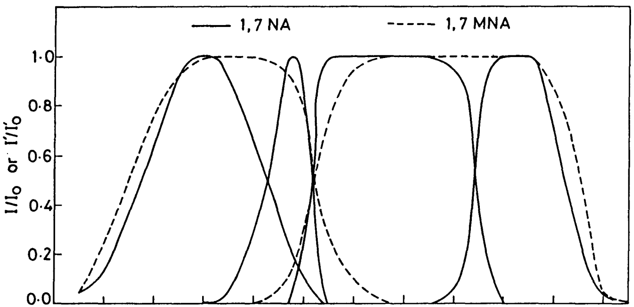


Fig. 4. Fluorimetric titration curves of the various prototropic species of 1,7 NA and 1,7 MNA.

monoanion, formed by deprotonating -OH group. At $H_- < 15$, the species is a dianion, obtained by further deprotonating the C-H bond, rather than $-NH_2$ group. This can be explained on the same lines as has been done for the monoanion of 1,7 MNA. The pK_a values for the monocation-free amine and free-amine-monoanion equilibria, determined by using absorption spectral data, are 3.35 and 9.8 respectively. These values are not very different from the protonation constant of 1 AN (3.92) and deprotonation constant of 2 NOH (9.5).[26] As explained for 1,7 MNA, these pK_a's are not affected much by the presence of hydroxyl group or amino group respectively. This is further manifested from the data of Table 1, i.e. formal charge densities at the oxygen atom of -OH group of 1,7 NA and that of 2 NOH are nearly equal. Same is true for the nitrogen atom of amino groups of 1,7 NA and 1 AN.

The prototropic reactions of 1,7 NA occurring in the H_0/pH range of −10 to 0 are the same as observed for 1,7 MNA in S_1 state i.e. dication, −10 to −4; monocation, −4 to pH 0 and proton-induced fluorescence quenching of monocation of 1,7 NA is also observed prior to the formation of dication. This behavior is similar to that of 2 NOH, except that this process is taking place at higher acid concentration and this is due to the presence of positive charge on the 1,7 NA monocation.

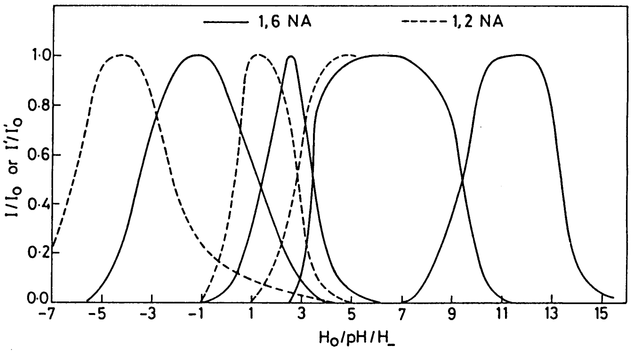
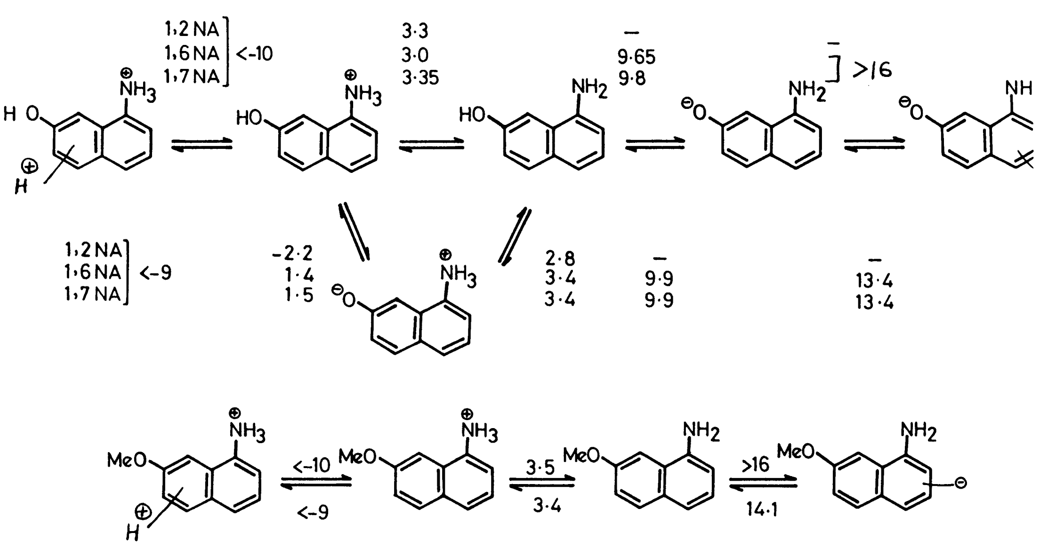


Fig. 5. Fluorimetric titration curves of the various prototropic species of 1,2 NA and 1,6 NA.

In the H_0/pH range −1 to 4 two fluorescence bands were observed. One at 426 nm and the other at 443 nm. The latter one is assigned to a neutral species because this band maximum nearly resembles that of 1,7 MNA, where there is no dissociable -OH group. The former is assigned to a zwitterion, formed by the deprotonation of the -OH group of monocation in the S_1 state. The monocation is the ground state precursor of zwitterion and the above assignment is based on the following results. (i) The fluorescence excitation spectrum of the zwitterion resembles the absorption spectrum of monocation, rather than the neutral molecule. (ii) Had the neutral molecule been the ground state precursor for the zwitterion, the similar results should have been observed at the earlier pH range and the fluorescence spectrum of this species in the pH range of 4 to 0 would have resembled the neutral molecule in nonpolar solvents and that of 1,7 MNA. (iii) The fluorescence spectrum of zwitterion resembles closely the β-naphtholate ion (418).[27] The fluorimetric titration curves in the pH range 4—0 cannot be drawn accurately, as three species are present simultaneously. Assuming that only two species are present in the given range (this assumption is not bad as the fluorescence intensity of monocation is never more than 10% of the fluorescence intensity of zwitterion, where the zwitterion-free-amine species are present) fluorimetric titration curves are drawn (Fig. 4) and the approximate pK_a value is listed on the arrows of Scheme 1. The value cannot be off by more than 10%.

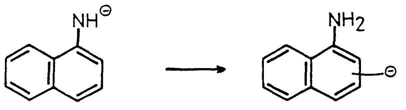
At pH > 9, the 414 nm band is assigned to monoanion formed by the deprotonation of -OH group. The



Scheme 1. Scheme representing the various prototropic reactions in the S_0 and S_1 states.

fluorimetric titration curves have given the ground state pK_a value, indicating that free naphthol-monoanion equilibrium is not established in S_1 state. This result is anomalous from that of 2 NOH,[27] in the sense, that extended sigmoid curve is not observed in case of 1,7 NA. It could be due to the shorter lifetimes of the conjugate acid-base pair.

At the extreme basic conditions H_- 16, 418 nm band is assigned to the dianion, formed either by deprotonating the -OH and $-NH_2$ groups or -OH group and the C-H bond. The latter process is preferred because of the following reasons: (i) The monoanion of 1 AN[12] is nonfluorescent and its pK_a* is 12.2, whereas that of 2 AN[12] is fluorescent [λ_{max}(flu)520] with pK_a* 12.3. At H_- 15, 412 nm fluorescence band of 1 AN is assigned to a kind of monoanion (**2** as shown below) by Choudhury and Chattopadhyay,[42] based on their study of 1 AN and 1-(dimethylamino)naphthalene. In general the deprotonation reaction of $-NH_2$ group in S_1 state starts at pH≈11 and is completed by pH≈14, whereas in case of 1,7 NA, this process occurs at pH > 14 and the correspondence is observed between the decrease of the fluorescence intensity of monoanion and the increase in that of dianion. (ii) The pK_a* value, determined from Fig. 4, falls in the same region as observed for the ring deprotonation of 1 AN.[12] (iii) Data of Table 1 clearly indicate that the charge density at the nitrogen atom of amino group of monoanion of 1,7 NA is equal to that on the amino group of 1 AN in S_0 state but in S_1 state, the charge density in case of former species is more than that of the latter species. This indicates that the pK_a* for this deprotonation reaction of $-NH_2$ group will increase on excitation as compared to that of 1 AN. (iv) The fluorescence band maximum of dianion of 1,7 NA falls in the same region where the species (**2**) of 1 AN fluorescence.[12] The intensity of 418 nm fluorescence band is weak and pK_a in S_1 state for monoanion-dianion equilibrium is determined from the decrease in the fluorescence intensity of monoanion (Fig. 4).



1 **2**

6-Hydroxy- and 2-Hydroxy-1-naphthylamines. The spectral characteristics of 1,6 NA in H_0/pH/H_- −10 to 16 are exactly similar and the results can be explained in the similar manner, whereas 1,2 NA decomposes at pH > 5.

The Scheme 1 represents the various prototropic reactions occurring in S_0 and S_1 states pK_a* values are depicted on the arrows.

Conclusion

Following conclusions can be drawn from the above study. (i) In absorption spectrum, the long wavelength band is long axis polarized, whereas the fluorescence is observed from ^1L_a state. (ii) The ground state precursor for the formation of zwitterion in the S_1 state is monocation. (iii) At high basic strength, the dianions are formed by the deprotonation of -OH group and one of the C-H bond.

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