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Excited-State and Ground-State Proton-Transfer Reactions in 5-Aminoindole

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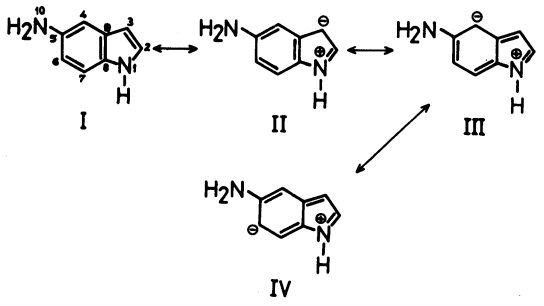
Dual fluorescence emissions are observed when the electron-donating group ($-NH_2$) is present at the position 5 of indole moiety. From the study of solvent effect and the large blue shift observed in the fluorescence spectra at 77 K, it is concluded that the long wavelength fluorescence band (480 nm) is assigned to the more polar state and the short wavelength band (350 nm) to the less polar state of 5-aminoindole (AI). Monocation is formed by protonating the amino group and no proton-induced fluorescence quenching of the neutral species is observed prior to its being protonated. This is mainly due to the shorter life of the conjugated acid-base pair. CNDO/S calculations indicate that dication is formed by protonating the C-3 position of the monocation of AI in the S_0 state but position 4 of monocation of AI in the S_1 state. Monoanion is formed by the deprotonation of >NH group in the S_0 state, but from the deprotonation of $-NH_2$ group in the S_1 state.

It is now well-established that the monocation of 5-hydroxy derivatives of indole fluoresces at ≈520 nm[1-5] and this band is used as an analytical tool for the diagonosis as well as for the estimation purposes. Unlike the other prototropic reactions of indole and indole derivatives,[6] the proton is added either at position 6 or at position 4[3-5] (the latter is preferred) of the 5-hydroxy derivatives, rather than at position 3 in the former compounds. The fluorescence band of the monocations of 5-hydroxy derivatives is very large red shifted (520 nm) as compared to that of the neutral molecules (≈360 nm) and no explanation is available in literature.

Recently, we have reinvestigated the spectral characteristics of some of the indole derivatives (mostly the carboxylic acids)[7-9] in different solvents and at various pH. It has been found that a new weak fluorescence band (≈460 nm) has been observed only in the compounds where 5-OH or 5-OCH_3 group is present in the indole moiety.[5] For example, in the fluorescence spectrum of 5-hydroxy-3-indoleacetic acid the ≈460 nm band is observed in the neutral species as well as in the case of monoanion formed by the deprotonation of -COOH group, but this band is absent if the deprotonation takes place from the -OH group. It has been further shown[4,5] that the charge densities in S_0 and S_1 states are maximum at position 6 or 4 in the case when -OH or -OMe group is present at position 5 of indole, and this leads to cannonical structure III or IV rather than II (Scheme 1) which is generally present in the other indole derivatives. If this phenomenon is due to the presence of electron-donating groups at position 5, the fluorescence band at ≈480 nm should also be observed in the case of amino group. The present study has been undertaken to see whether the observation of two fluorescence bands is due to the characteristic feature of the presence of electron-donating groups at position 5. The effects of solvents and pH on the spectral characteristics have also been studied. The ground state and excited-state pK_a values have been determined and discussed.



Scheme 1. Various cannonical forms of 5-aminoindole.

Method and Material

5-Aminoindole (AI) was obtained from Aldrich and was recrystallized from ethanol. The purity of the compound was checked by noting the sharp mp, absorption spectrum, and getting the similar fluorescence spectra when excited at different wavelengths. Spectrograde methanol, analytical grade sulfuric acid, sodium hydroxide, and phosphoric acid (BDH) were used. Analytical grade acetonitrile (E. Merck), cyclohexane (IDPL), ether, and ethanol were further purified by the procedures, as described in literature.[10] Triply distilled water was used for aqueous solutions. pH of the solutions in the range of 3—12 were adjusted by adding appropriate amount of sodium hydroxide and phosphoric acid, as phosphate buffers do not quench the fluorescence. A modified Hammett's acidity scale[11] for H_2SO_4-H_2O mixtures and Yagil's basicity scale[12] for NaOH-H_2O mixtures were used for aqueous solutions of pH less than 1 and pH greater than 13 respectively.

The absorption spectra were recorded on a Shimadzu spectrophotometer model UV 190, equipped with a chart recorder model U 135. The fluorescence measurements were carried out on the laboratory made scanning spectrofluorimeter, details were available elsewhere.[13] Both monochromators were calibrated with a low-pressure mercury lamp from time to time and the band width used for excitation was 8 nm. Fluorescence quantum yields were determined with the solutions having absorbance less than 0.1 and from the corrected fluorescence spectra, using quinine sulfate in 0.05 M (1 M=1 mol dm^{-3}) H_2SO_4 as a reference.[14] For absorptiometric and fluorimetric titrations, the solutions were prepared just before taking measurements. Isosbestic wavelengths were used as exciting wavelengths to measure the

Table 1. Absorption Maxima (λ^{ab}_{max}) and Molar Extinction Coefficients (ε) of 5-Aminoindole in Various Solvents and Its Prototropic Forms in Aqueous Solutions

Specie	Solvent	λ^{ab}_{max}/nm (log ε)[a]		
Neutral	Cyclohexane		270 sh	229 sh
		314	263	214
Neutral	Ether	316(3.32)	268(3.60)	214(4.26)
Neutral	Acetonitrile	315(3.26)	269(3.70)	219(4.42)
Neutral	Methanol	308(3.43)	270(3.76)	213(4.41)
Neutral	Ethanol	306(3.44)	270(3.76)	214(4.42)
Neutral	Water (pH=8)	305(3.43)	269(3.69)	199(4.51)
Anion	KOH (H_-=17)	312(3.69)	230(4.44)	
Cation	Water (pH=3)	286(3.70)	218(4.47)	200(4.17)
		280(3.75)		
Dication	H_2SO_4 (H_0=−7)	280(3.73)	236(3.62)	204(3.98)
			228(3.62)	191(4.05)

a) ε values are in $dm^3\,mol^{-1}\,cm^{-1}$.

fluorescence intensity. The concentrations of the solutions were of the order of 10^{-4}—10^{-5} mol dm^{-3}.

Both Pariser-Parr-Pople (PPP)[15,16] and CNDO/S[17] methods were employed to calculate the transitions energies, ground and excited state charge densities at various centres of the molecule and its prototropic species. All configurations obtained by single electron excitation from occupied molecular orbital to unoccupied molecular orbital were considered in all configuration interaction calculations. The species were assumed to be planar and the rings were taken as regular pentagon and hexagon. All ring C-C, C-N, and C-NH_2 bond lengths were taken as 1.40 Å.

Results and Discussion

Effect of Solvents. Table 1 lists the absorption maxima, log ε_{max} and Table 2 the fluorescence band maxima and quantum yields of AI in different solvents. The data in Table 1 clearly indicate that the absorption band maxima of AI are large red-shifted as compared to indole[6] or even 5-hydroxyindole (HI).[5] All band maxima are red-shifted as the polarity or the proton accepting nature of the solvents increases while a blue shift is noticed if the proton donor capacity of the solvents increases. Similar to 5-hydroxy derivatives, AI also exhibits dual fluorescence band systems, one at ≈350 nm and the other at ≈480 nm. The fluorescence intensity of the latter band system is much less than that of the former. The ratio of the band intensities remains the same value in different solvents as well as with the 100 fold change in the concentration of AI. The fluorescence maxima of both bands are red-shifted with change of solvents from cyclohexane to water, where the red shift observed in the shorter wavelength band is less than that in the longer wavelength band. In the measurements of fluorescence spectra at 77 K, the blue shift observed in the long wavelength fluorescence band (≈80 nm) is very large compared to that in the shorter wavelength band (≈30 nm). These data are compiled in Table 2 and the spectra are depicted in Fig. 2. The fluorescence quantum yield decreases under the above environments, such that we are unable to detect the long wavelength emission in water.

Table 2. Fluorescence Maxima (λ^{fl}_{max}) and Quantum Yield (ϕ_f) of 5-Aminoindole in Various Solvents and Its Prototropic Forms in Aqueous Solutions at 298 K

Specie	Solvent	λ^{fl}_{max}/nm (ϕ_f)		
Neutral	Cyclohexane	482	352	(0.27)
Neutral	Ether	495	362	(0.30)
Neutral	Acetonitrile	503	368	(0.39)
Neutral	Methanol	512	370	(0.30)
Neutral	Ethanol	519	372	(0.19)
Neutral	Water (pH=8)	—	374	(0.03)
		432	345	—
Anion	KOH (H_-=17)	460	365	
Cation	Water (pH=3)		357	(0.32)
			328	—
Dication	H_2SO_4 (H_0=−8)			
			—	—

a) Values underlined are at 77 K.

It is now well-established that the long wavelength absorption band of indole is a mixture of ^1L_b and ^1L_a bands[15-18] i.e., the absorption band near 285 nm is due to the transition from the ground state to the ^1L_b state, around 272 nm to the ^1L_a state, whereas the band maximum near 220 nm is due to the ^1B state. The larger red shift observed in the 285 nm band system of AI as compared to that in 272 nm band system, is consistent with the earlier results that the former transition is polarised along the longer axis and the latter along the shorter axis. The -NH_2 group situated along the longer axis may perturb the ^1L_b state more than the ^1L_a state. The larger red shift observed in the absorption maximum is because of the fact that the lone-pair electrons on the amino group perturb the π cloud of the aromatic moiety much better than those on the hydroxyl group.

The fluorescence spectrum of indole and its derivatives in polar solvents has been proposed as the combination of two emission bands[18-22] i.e., due to the emission from the two closed lying ^1L_a and ^1L_b states. The assignment of the fluorescence spectrum as a combination of two bands is based on the results of polarized fluorescence excitation, fluorescencspectra,

and the fluorescence decay times of indoles. The present study also suggests the presence of two closed lying excited electronic states, because the absorption spectrum and the excitation spectra recorded at both fluorescence maxima resemble each other. The large difference in the fluorescence band maxima is due to the increased polarity in one of the electronic states, that is, one of them is much more stablished. This phenomenon has been further confirmed from the study of fluorescence spectra recorded at 77 K. The blue shift observed in the case of long wavelength band is much larger (≈80 nm) than that in the shorter wavelength band (≈30 nm). Further, stability of the states depends upon the nature, orientation and position of the substituent in the parent molecule. Similar to 5-hydroxyindole,[4] spectral data and charge densities at various atomic centres have been carried out on AI by the semiemperical-SCF MO-CI method (PPP) and by CNDO/S methods. The data are listed in Table 3 and 4 respectively. The data in Table 3 indicate that values of λ_{max} predicted by the CNDO/s method agree nicely with those observed for various species and the result proves the validity of the method. The data in Table 4 have clearly indicated that, similar to those of 5-hydroxyindole, the charge densities increase at the positions 4 and 6 (preferably at latter center) in comparison to position 3, normally observed in the case of indole. This suggests that charge migration takes place from heterocyclic to homocyclic ring leading to polarize the indole molecule. Cannonical structures arising from this intramolecular charge transfer are given in Scheme 1. Thus 480 nm band represents the fluorescence band may be due to more polarized cannonical structure II or IV of AI. This band cannot be assigned to the excimer or exciplex emission as the I_{480}/I_{350} ratio remains the same even when the concentration of AI is varied by 100 fold or the solvent is changed. The long wavelength emission is due to the presence of electron-donating group because on protonation of $-NH_2$ group to produce $-NH_3^+$ (see later) the 480 nm band disappears. Lastly this 480 nm band also cannot be assigned to the phosphorescence spectra on the basis of no effect of dissolved oxygen on the emission intensity. Oxygen from the solutions was removed by bubbling nitrogen and no phosphorescence was observed at 298 K, using an Amino-Bowman

Table 3. Theoretical Values of Absorption Maxima (in nm) and Oscillator Strength(f) of Different Prototropic Forms of 5-Aminoindole

Method	PPP	(f)	CNDO/s	(f)	Experimental
Neutral	296.7	0.04	314.5	0.03	314
	263.0	0.19	266.9	0.10	263, 270
	221.0	0.12	233.6	0.19	
	208.2	0.34	229.8	0.39	229
			214.9	0.25	214
Monocation ($-NH_3^+$)			312.7	0.01	
			283.9	0.10	286, 280
			236.1	0.23	
			221.8	0.44	218
			210.7	0.08	200
Monoanion ($>N^-$)			317.3	0.04	312
			244.0	0.68	
			237.1	0.08	230
					218
					200

Table 4. Ground and Excited State Charge Densities at Various Centers of the Different Prototropic Forms of 5-Aminoindole

		N_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	N_{10}
Neutral	PPP	1.689	1.070	1.087	1.040	0.996	1.037	1.034	1.070	1.034	1.941
		(1.645)	(1.122)	(0.991)	(1.037)	(0.994)	(1.048)	(1.039)	(1.058)	(1.052)	(1.935)
Neutral	CNDO	5.126	4.05	3.982	3.996	3.970	4.000	4.05	3.96	4.06	5.220
		(5.112)	(4.138)	(3.988)	(4.057)	(3.925)	(4.001)	(4.144)	(3.852)	(4.066)	(5.137)
Cation	CNDO	5.114	3.833	4.150	4.090	3.935	4.055	4.001	3.920	3.960	4.846
		(5.054)	(3.758)	(4.003)	(4.154)	(3.792)	(4.086)	(4.036)	(3.946)	(3.985)	(4.844)
Anion	CNDO	5.442	3.953	4.226	4.147	3.918	4.122	4.051	3.975	3.994	5.254
		(5.170)	(4.097)	(3.968)	(4.245)	(3.896)	(4.172)	(4.233)	(3.996)	(4.038)	(5.237)

The values in the parentheses are the excited state charge densities. The numbering of the atomic centers are shown in Scheme 1.

phosphorescope. The similar kind of behavior has been observed in the case of monocations of benzimidazole and methyl-substituted benzimidazoles.[23-25]

The dependence of the shifts of absorption and fluorescence band maxima of AI upon solvent polarity or hydrogen-bond-formation capacity of solvents is consistent with the earlier findings on the similar groups that proton-donating nature of solute leads to red shift and that proton-accepting nature of solute to blue shift. Thus ether and acetonitrile are acting as proton-accepting solvents, whereas methanol and water as proton-donating ones in the S_0 state. Since the intramolecular charge transfer from $-NH_2$ group to the ring is more effective in the S_1 state than in S_0, this group acts as a better proton donor in S_1 state. The decrease in the fluorescence quantum yield with increase in the solvent polarity or hydrogen-bonding power of solvents is due to interactions between the S_1 state and solvent molecules resulting in an increase of the rates of radiationless processes. This is further manifested by an increase in the Stokes shift under similar conditions.

Effect of pH. The absorption and fluorescence spectra of AI have been investigated in the H_0/pH/H_- range of −10 to 17. The relevant data are compiled in Tables 1 and 2 respectively. The absorption and fluorescence spectra of the various prototropic species are shown in Figs. 1 and 2. The spectral changes observed in the absorption spectrum of AI are consistent with the earlier results of the compounds containing amino groups. The neutral AI exists over the range of pH 14 to 3. With a decrease in pH, the absorption spectrum of AI is blue-shifted and the blue shift observed in the long wavelength band is so large that it is merged with the ^1L_a band system, resembling with that of indole molecule.[6] This clearly indicates that the monocation is formed by protonating the

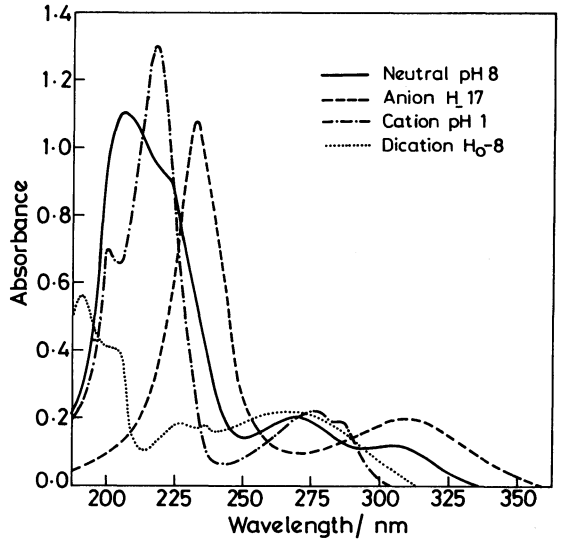


Fig. 1. Absorption spectra of various prototropic forms of AI at 298 K.

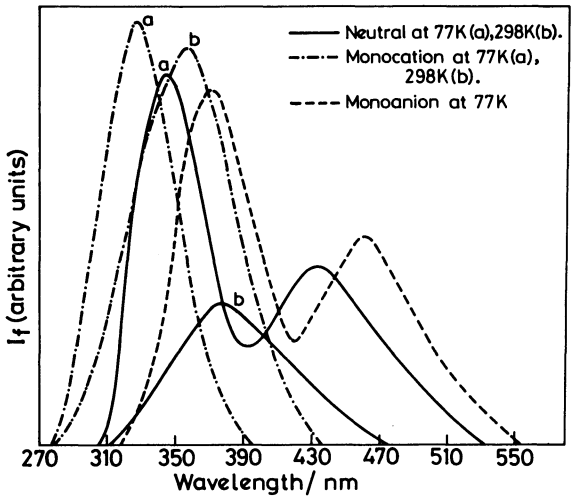


Fig. 2. Fluorescence spectra of AI in different solvents and at different pH at 298 K.

amino group in the S_0 state. Further increase in the acid strength, does not involve much change in the long wavelength band, except the vibrational structures, however, the intensity of 218 nm band system decreases and it is replaced by the two band systems, one at 236 and the other at 204 nm. This is a characteristic feature of the ring carbon atom of indole moiety.[6] Since there is already a presence of positive charge on the carbocyclic ring due to the presence of $-NH_3^+$ group, it is proposed that the protonation will take place at C-3 position normally observed for the indole molecule. This is further confirmed from calculated data of Table 4 that the charge density at position 3 is the maximum in the ground state of AI monocation (AI^+). With an increase in the basic strength, the absorption spectrum of AI is red-shifted and indicates the formation of monoanion. The monoanion can be formed by the deprotonation of either >NH group or $-NH_2$ group leading to the red shift. Further the pK_a values of both deprotonation reactions fall in the same range of basic strength.[12,26] The charge-density calculations, as shown in Table 4, have clearly indicated that the formal charge at the nitrogen atom of >NH group of indole molecule does not change due to the presence of amino group at position 5. Further the charge density at the nitrogen atom of >NH group is less than that at the nitrogen atom of $-NH_2$ group. This indicates that monoanion (AI^-) is formed by the deprotonation of imino group rather than amino group.

Thefluorescence spectrum of AI also follows the similar changes as observed in the absorption spectrum, within the same acidic and basic range i.e., the neutral species exists in the pH range of 7 to 14, monocation starts appearing below pH 6. Only one fluorescence band, similar to indole, has been observed for AI^+, indicating that the presence of electron-donating group is necessary at the position 5 for the emission of long wavelength fluorescence band. Dication of AI is nonfluorescent and this behaviour is similar to the

monocation of indole or other indole derivatives. Although the charge density is maximum at position 3 of AI^+ in the ground state, the charge density is maximum at position 4 of AI^+ in the first excited singlet state, similar to the neutral AI molecule and actually it decreases at position 3 in the S_1 state in comparison to S_0 (Table 4). The driving force behind this intramolecular charge migration from the heterocyclic to the carbocyclic ring is due to the presence of positive charge on the latter ring. On the basis of charge densities at the various atomic centers, it is concluded that the dication in the S_1 state is formed by protonating the carbon center at position 4 rather than at position 3. Similar to dication, the monoanion of AI is also nonfluorescent. Literature data show that monoanion formed by the deprotonation of >NH group of indole and some of its derivatives as well as the monoanions formed by the deprotonation of similar group in indazoles and benzimidazoles[2,13,27-29] are fluorescent, whereas that formed by the deprotonation of $-NH_2$ group is nonfluorescent,[30-32] with few exceptions.[33] Our data suggest that, though the ground state prototropic reaction is from the >NH group, but in the excited state, it is from the $-NH_2$ group.

Further charge density data at the two nitrogen centres do not point out clearly but the decrease in the formal charges at the nitrogen atom of $-NH_2$ (0.09) is larger than that at the nitrogen atom of >NH group (0.01). So the deprotonation in the excited singlet state, most probably is from the $-NH_2$ group. This is confirmed from the fluorescence spectral study at 77 K. Since at such a low temperature and in the frozen state, the species is present in the ground state environments, even when excited. The observation of two fluorescence bands at H_ 16 and at 77 K, clearly indicate that the electron-donating group at position 5 is not disturbed in the highly basic conditions and confirming that the deprotonation in the S_0 state takes place from the >NH group. Similar behavior has been observed in the case of 2-aminobenzimidazoles[34] and aminoindazoles.[35-37]

pK_a Values. The pK_a values for the different prototropic reactions have been determined absorptiometrically and are listed in Table 5. The values of pK_a's obtained for neutral-monoanion[12] and monocation-neutral[26] equilibria are in the range of pK_a's for similar reactions. The pK_a for the protonation of indole-ring carbon atom is less than that of indole (3.5)[6] and it is due to the presence of positive charge on the carbocyclic ring.

The pK_a^* values have been determined with the help of fluorimetric titration method (Fig. 3) and Förster cycle method,[37] using absorption and fluorescence data, wherever applicable. For example, pK_a^* for the neutral-monoanion equilibrium can not be calculated by the latter method as the equilibrium involved in S_0 and S_1 states are different. Similarly pK_a^* for dication-monocation equilibrium, because the protonation involves change in the structure of indole moiety as well as the dication is non-fluorescent. The

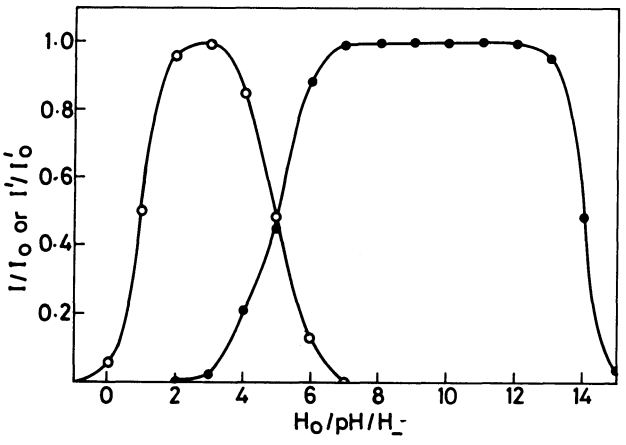
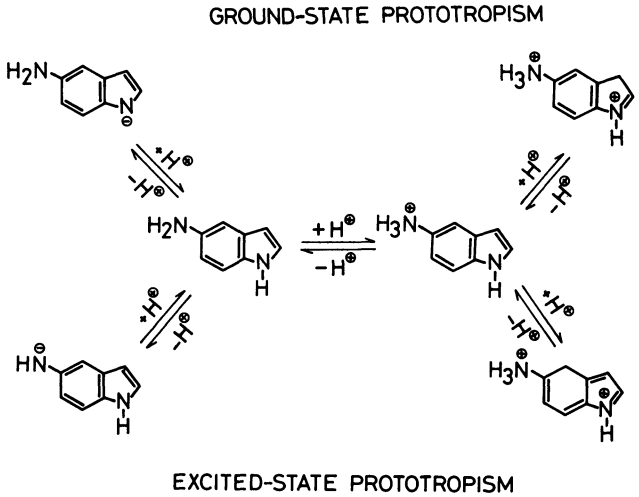


Fig. 3. Plot of I/I_0 vs. H_0/pH/H_ at 298 K.



Scheme 2. Different prototropic reactions of 5-aminoindole.

Table 5. The pK_a Values of the Prototropic Equilibria of 5-Aminoindole in Aqueous Solutions

Equilibrium	p$K_a(S_0)$	p$K_a(S_1)$[a]	p$K_a(S_1)$[b]	p$K_a(S_1)$[c]
Neutral ⇌ Anion	16.1	14.0	14.5	12.8[d]
Cation ⇌ Neutral	5.0	5.0	0.4	0.3
Dication ⇌ Cation	−4.7	1.0	—	—

a) By fluorimetric titration. b, c) By Förster's method using absorption (b) and fluorescence (c) maxima. d) Using fluorescence maxima at 77 K.

results of fluorimetric titrations have indicated that the $-NH_2$ group becomes strong acid and carbon centre of indole more basic on excitation. These results are consistent with the earlier findings. Only ground state pK_a is obtained from the fluorimetric titrations for monocation-neutral equilibrium, which is little unusual for this kind of prototropic reaction, because in general, proton-induced fluorescence quenching[30,31,38] is observed before $-NH_2$ group gets protonated. Since the Förster cycle method has clearly indicated that $-NH_3^+$ group becomes stronger acid on excitation, it is 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 of conjugated species at pH≈5. Therefore, a prototropic equilibrium is not established within the lifetimes of the lowest excited singlet states of these molecules and thus fluorescence intensities measured at pH≈5 reflect the relative ground state concentrations of AI and AI^+. Hence, the ground-state pK_a is determined by fluorimetric titration in this case. Similar behavior has been observed in the prototropic reaction of 4-(9-anthryl)-*N*,*N*-dimethylaniline.[39] The difference between the pK_a^* values obtained by the Förster cycle method and absorption and fluorescence data is due to the different solvent relaxation for the conjugated species in S_0 and S_1 states. All the prototropic reactions are mentioned in Scheme 2.

Conclusion

The presence of electron-donor group at the position 5 of indole molecule, leads to the dual fluorescence, one nearly at≈360 nm and the other at≈480 nm. The latter one is because of more polar electronic state than that of the former. Monocation is formed by protonating the $-NH_2$ group and the dication further protonating the C-3 position in S_0 state but the position 4 of indole moiety in the S_1 state. The deprotonation of >NH group takes place in the S_0 state but of $-NH_2$ group in the S_1 state to form the monoanion. No proton-induced fluorescence quenching is observed before protonating amino group, and fluorimetric titrations have given the ground state pK_a value, indicating that the lifetimes of the conjugate species are very small to achieve the prototropic equilibrium in S_1 state.

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