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Ground and excited states acid–base properties of acridine-1,8-dione dyes

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Abstract

The acid–base properties of an interesting and important bifunctional group of compounds, acridinedione dyes, were studied in a 95:5 water–methanol mixture. The dyes exist in neutral, deprotonated and protonated forms in equilibrium at appropriate acid–base conditions. The neutral form of the dyes absorbs around 380–400 nm and emits around 440–460 nm in the water–methanol mixture. The deprotonated form of the dyes absorbs around 450–470 nm and emits around 500–520 nm. The protonated form of the dyes absorbs around 410–430 nm and emits around 470–500 nm. The pK_a* values are calculated using Förster's and fluorimetric titration methods. The variation of the enhancement in the fluorescence intensity and lifetime of the protonated and deprotonated form of the dyes with substituent are discussed. The influence of substituent on the pK_a and pK_a* values are discussed. The dyes are more acidic in the excited state when compared to the ground state. The fluorescence lifetime of the neutral form is around 6.0–9.0 ns and that of the protonated and deprotonated forms of the dye is 3.0–6.0 ns.

Keywords: Acridinedione; Acid–base; Excited state; Ground state

1. Introduction

The interaction between an acid and a base is one of the most fundamental processes in chemistry [1–4]. Proton transfer reactions are among the simplest type of acid–base reactions, but they provide a large amount of information on equilibria, kinetics, isotope effects, free energy relationship, etc., as compared to many other class of reactions. Bifunctional molecules possessing proton acceptor and proton donor groups undergo various interesting photoinduced processes [5]. One particular group of proton transfer processes that has received much attention of late, consists of photoinduced proton transfer reactions in molecules whose excitation alters their acid–base properties [6,7].

In recent years, the excited state proton transfer reactions have generated a lot of interest because of their wide spread implications in the action of many lasing dyes [8] and photostablizers for polymers [9]. An excited aqueous species with functional groups which has large a pK difference between ground and excited states may undergo protonation or deprotonation in the excited state [10].

In the excited state, the molecules containing N, O or S hetero atoms will have an increase or decrease in the density of the lone electron pair on the hetero atoms which alters the acid–base properties of organic molecules. Weber [11] observed the change in the fluorescence spectrum of 1-napthylamine-4-sulphonate as the acidity of the solution was altered, although the absorption spectrum remains unchanged. Förster [12–14] attributed the above phenomenon to the change in the acid–base properties of the molecules in the excited state. Later the problem of the acid–base properties of 1-napthylamine-4-sulphonate was investigated in detail by Weller [15–17].

Acridinedione dyes deserve special attention due to their lasing efficiency [18] comparable to coumarin 102. Acridinedione dyes have a structural similarity to 1,4-dihydropyridines. 1,4 dihydropyridines are analogous to NADH, which are coenzymes in biological systems and recently the intermediates in the oxidation of dihydropyridines, a derivative of AZT related to AIDS dementia, was studied by nanosecond laser flash photolysis [19]. Acridinedione dyes are used as photosensitizers [20] and initiators in photopolymerisation [21]. In this paper we have discussed the acid–base properties of some of these dyes in the ground and excited states using absorption, steady-state fluorescence and lifetime measurements.

The dyes used for the studies are given below.

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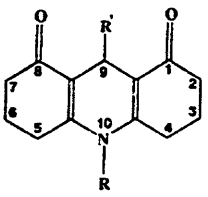


Dye No	R	R'
1	H	H
2	H	CH_3
3	H	C_3H_7
4	H	C_6H_5
5	H	$C_6H_4OCH_3$
6	H	C_6H_4Cl
7	$C_6H_4CH_3$	H
8	$C_6H_4CH_3$	CH_3

2. Experimental

The dyes used in this work were synthesized following the procedure reported in the literature [18,22]. The absorption and emission measurements were carried out with 1×10^{-5} M dye solutions. All the solvents used were of HPLC grade purchased from Qualigens, India Ltd. Sodium hydroxide and sulphuric acid were of Excelar and Analytical grade from Qualigens India. Yagil's [23] basicity scale was followed for preparing alkaline solutions of pH greater than 10. Dolman and Stewart's [24] acidity scale was followed for preparing the acidic solution of pH less than 1. Due to the low solubility of the dyes in neat water the solutions were prepared in a water:methanol mixture (95%:5% v/v). Distilled water used in these experiments was triply distilled over alkaline permanganate in an all-glass apparatus. Absorption spectra were recorded using a Hewlett–Packard 8452A Diode array spectrophotometer. Fluorescence spectra were recorded using a Perkin–Elmer LS5B Luminescence spectrometer. The fluorescence lifetimes were measured on a IBH-5000, UK, single photon counting spectrofluorimeter. A gated hydrogen filled lamp with a pulse width of 1.4 ns was used for excitation and a Hamamatsu photomultiplier (3235) tube was used for the detection of the fluorescence. The fluorescence decay curves were analysed by an iterative fitting program provided by IBH.

3. Results and discussions

3.1. Reactions with base

The dyes absorb around 380–400 nm in a 95:5 water–methanol mixture. A red-shifted new absorption is observed for the dyes **1–6** on adding sodium hydroxide. As the pH of the solution is increased, the absorbance around 380–400 nm for the dyes **1–6** decreases with a simultaneous appearance of a new peak around 450–470 nm with an isosbestic point around 410–420 nm as shown in the Fig. 1. The absorption around 380–400 nm is unaffected and no new peak is seen in the absorption spectrum for the dyes **7** and **8** in the presence of sodium hydroxide.

The absorption around 380–400 nm for the dyes is due to the neutral form. The appearance of a new peak for the dyes **1–6**, which has hydrogen on the nitrogen center, around 450–470 nm and no new peak for dyes **7** and **8**, which do not have hydrogen on the nitrogen center, in the presence of NaOH reveal that the new peak around 450–470 nm is due to the deprotonated form of the dye. As the pH of the solution is increased the equilibrium is shifted towards the deprotonated form. The presence of an isosbestic point shows the existence of an equilibrium between the neutral and the deprotonated forms of the dye.

The dyes emit around 440–460 nm in the water–methanol mixture. The emission peak around 440–460 nm for the dyes **1–6** is red-shifted by 70 nm on adding sodium hydroxide. As the concentration of NaOH is increased, the intensity of the new emission peak around 500–520 nm enhances with simultaneous decrease in the intensity of the 440–460 nm peak on exciting at the isosbestic point as shown in Fig. 2. No new peak is seen in the emission spectrum for dyes **7** and **8** in the presence of NaOH. The enhancement in the intensity of the new emission around 500–520 nm for dyes **1–6** depends on the substituent in the ninth position.

The emission around 440–460 nm for the dyes is due to the neutral form. The appearance of new emission peak for the dyes **1–6** and no new emission peak for the dyes **7** and **8** reveal that the new emission around 500–520 nm is due to the deprotonated form of the dye. At pH = 14, the emission due to the neutral form completely disappears and peak around 500–520 nm alone is seen. The absorption and emission experiments in the presence of sodium hydroxide prove beyond doubt that the new peak observed for the dyes **1–6** under basic conditions is due to the deprotonation at the nitrogen center.

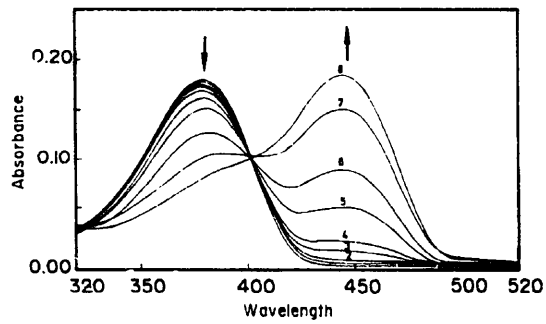


Fig. 1. Absorption spectrum of dye **1** in a 95:5 water–methanol mixture: (1) pH 11.4, (2) pH 11.78, (3) pH 12.0, (4) pH 12.3, (5) pH 12.47, (6) pH 12.6, (7) pH 13.0, (8) pH 13.3. pH adjusted with NaOH.

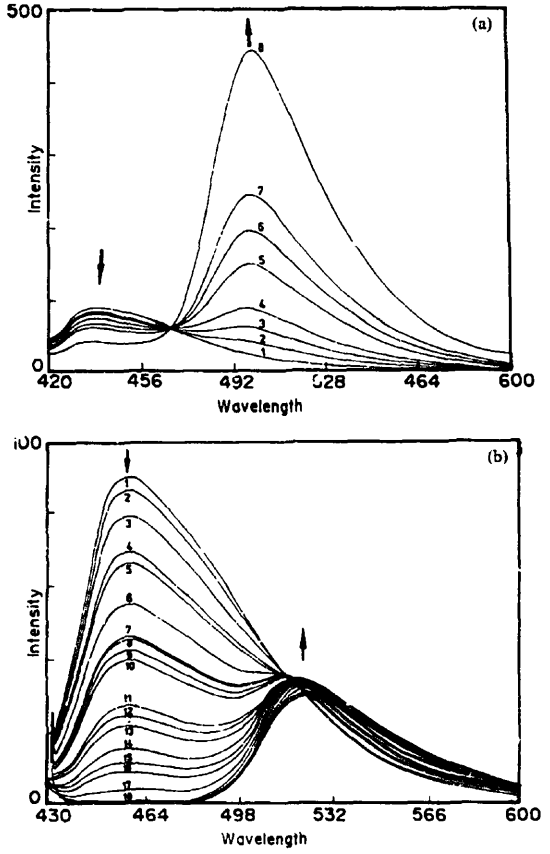


Fig. 2. (a) Emission spectrum of dye **5** in a 95:5 water–methanol mixture: (1) dye alone, (2) pH 11.4, (3) pH 11.78, (4) pH 12.0, (5) pH 12.3, (6) pH 12.47, (7) pH 12.6, (8) pH 13.0, pH adjusted with NaOH. (b) Emission spectrum of dye **1** in a 95:5 water–methanol mixture: (1) dye alone, (2) pH 11.0, (3) pH 11.4, (4) pH 11.7, (5) pH 11.8, (6) pH 11.9, (7) pH 12.0, (8) pH 12.1, (9) pH 12.2, (10) pH 12.3, (11) pH 12.4, (12) pH 12.5, (13) pH 12.6, (14) pH 12.8, (15) pH 12.9, (16) pH 13.0, (17) pH 13.3, (18) pH 13.7, pH adjusted with NaOH.

The enhancement in the intensity of deprotonated emission depends on the substituent in the ninth position and the order of enhancement of new emission is

$$C_6H_4OCH_3 > C_6H_4Cl > C_6H_5 > C_3H_7 > CH_3 > H$$

Dye **5** shows a much enhanced intensity of new emission compared to other dyes and this is due to the presence of an anisyl group in the ninth position which decreases the charge density on the nitrogen center when compared to other substituents and which favours deprotonation from nitrogen.

3.2. Reaction with acids

The absorption spectrum of the dyes remains unchanged in the pH range of 5 to 1. As the concentration of the acid is increased further, the peak around 380–400 nm keeps on shifting with an increase in the absorbance as shown in the

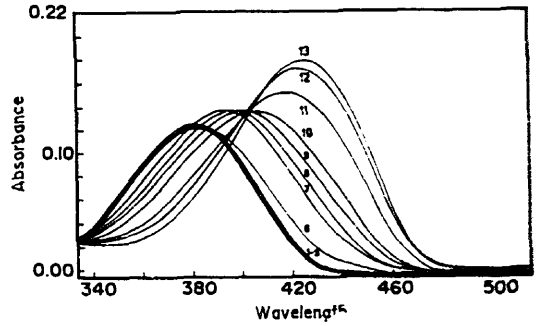


Fig. 3. Absorption spectrum of dye **2** in a 9[illegible] water–methanol mixture: (1–5) dye, pH 5, 4, 2, 1, (6) $H_0 = 0$, (7) $H_0 = -1$, (8) $H_0 = -2$, (9) $H_0 = -3$, (10) $H_0 = -4$, (11) $H_0 = -5$, (12) $H_0 = -6$, (13) $H_0 = -7$, pH adjusted with H_2SO_4.

Fig. 3. The absorption around 380–400 nm for all the dyes is red-shifted by 20–30 nm on addition of the acid in the range of $H_0 = 0$ to -7. The nitrogen containing molecules are known to be protonated on the nitrogen atom in their ground state [25–27]. The new peak around 410–430 nm in the absorption spectra for all the dyes for $H_0 < 1$ is assigned as due to the protonation at the nitrogen center.

In the emission spectra the peak around 460 nm, which is due to the neutral form, is quenched between the pH 5 and 1. At the acid concentration of $H_0 = 0$ the emission around 440–460 nm is completely quenched and a new emission peak appears around 470–500 nm on exciting at 390 nm. As the concentration of the acid is further increased the intensity of the new emission peak around 490 nm increases as shown in Fig. 4. The new emission peak around 470–500 nm is due to the protonation of the nitrogen center. The appearance of new emission for all the dyes shows that the protonation does not depend on the substitution on the nitrogen center. Since there is no change in the absorption spectrum in the pH range 5 to 1, the quenching of the emission peak around 440–460 nm in this pH range is due to the excited state reaction of the dye with protons. A reverse trend in the emission intensity enhancement is observed for the protonation of the nitrogen center when compared to deprotonation on varying the substituents in the ninth position. The presence of a methyl group in the ninth position in dye **2** increases the charge density greatly on the nitrogen compared to dye **5**, in which the presence of an anisyl group decreases the charge density on the nitrogen. So the protonation of dye **2** is more favoured compared to dye **5**, hence we observe a strong protonated emission for dye **2** and weak protonated emission for dye **5**. The absorption and emission spectra of the neutral, deprotonated and protonated forms of dye **1** are given in Fig. 5 and the data for the other dyes are also collated in Table 1.

3.3. Proton induced fluorescence quenching

The fluorescence quenching of all the dyes by protons occurred significantly without any change in the absorption

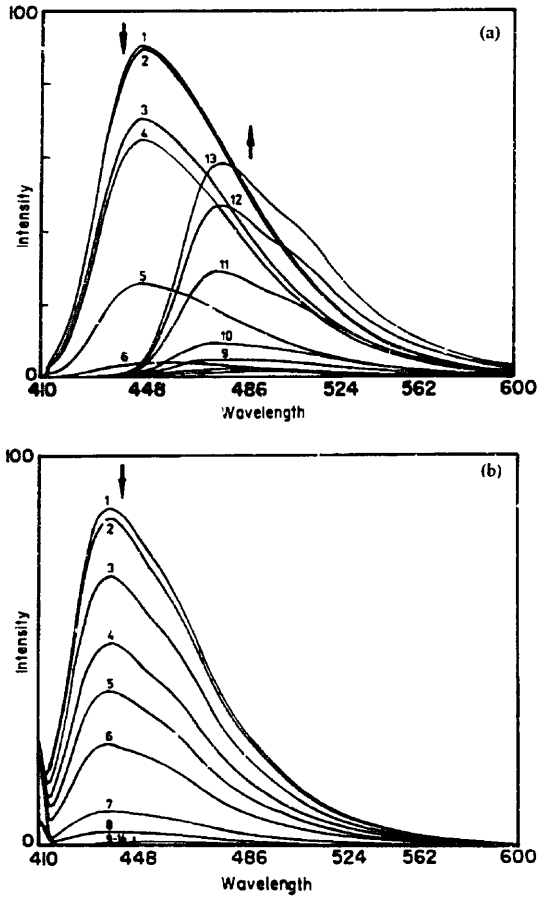


Fig. 4. (a) Emission spectrum of dye **2** in a 95:5 water–methanol mixture: (1) dye alone, (2) pH 5, (3) pH 3.5, (4) pH 3.1, (5) pH 2.5, (6) pH 2, (7) pH 1.5, (8) pH 1, (9) $H_0 = -3$, (10) $H_0 = -4$, (11) $H_0 = -5$, (12) $H_0 = -6$, (13) $H_0 = -7$. pH adjusted with H_2SO_4. (b) Emission spectrum of dye **5** in a 95:5 water–methanol mixture: (1) dye alone, (2) pH 3, (3) pH 2, (4) pH 1.6, (5) pH 1.3, (6) pH 1, (7) pH 0.8, (8) pH 0.5, (9–14) $H_0 = 0$ to -5. pH adjusted with H_2SO_4.

spectrum between pH 5 to 1. Since the acid used was H_2SO_4, the presence of any quenching due to the SO_4^{2-} anion have been examined by using external SO_4^{2-} salts and found to be absent. This rules out the quenching due to a counter ion in the acid. Excited aromatic molecules having intramolecular charge transfer in the fluorescent state were quenched effectively by protons [28–31]. Proton induced fluorescence quenching of naphthol [28], naphthylamines [29,30], 1-methoxynaphthalene [31] and several other compounds have been carried out in polar solvents at low acid concentration ($[H_2SO_4] = 0.3$ M).

The Stern–Volmer plot of I_0/I or τ_0/τ vs. concentration of H_2SO_4 gave a linear relation, where I_0 and I denotes relative fluorescence intensity and τ_0 and τ are fluorescence lifetime without and with protons, respectively. Acridinediones have an ICT (intramolecular charge transfer) state in which partial

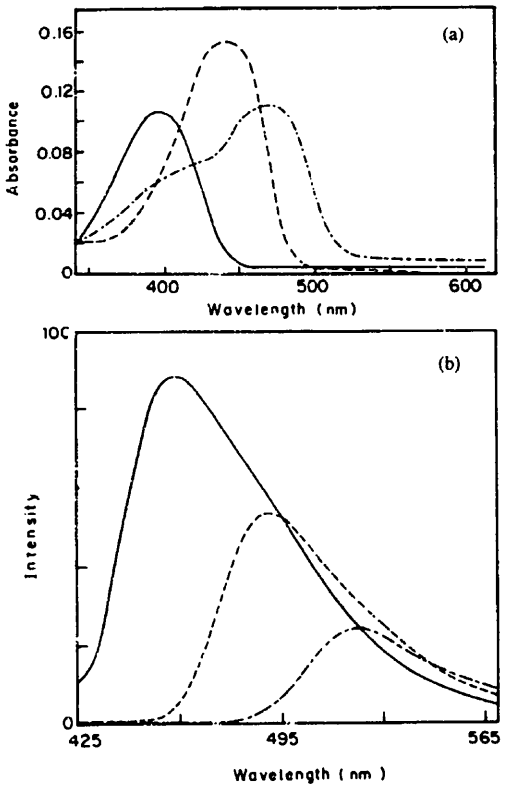


Fig. 5. (a) Absorption spectra of the neutral (———), deprotonated (- - -) at pH 14, protonated (— - —) at $H_0 = -7$ forms of dye **1** in 95:5 water–methanol. (b) Emission spectra of the neutral (———), deprotonated (- - -) at pH 14, protonated (— - —) at $H_0 = -7$ forms of dye **1** in 95:5 water–methanol.

electron transfer occurs from the nitrogen to one of the oxygen centers in the excited state. It is reasonable to consider that the CT structure plays an important role in the proton induced fluorescence quenching. The proton induced fluorescence quenching is due to the protonation of the oxygen center in the excited state.

3.4. Fluorescence lifetimes

The neutral form of the dyes have a lifetime around 7.0–9.0 ns in the 95:5 water–methanol mixture at 440–460 nm on excitation at their absorption maxima and a representative lifetime data analysis is given in Fig. 6. The lifetime of the neutral form decreases on adding acid or base. In strongly basic medium (pH = 14) the deprotonated forms of dyes **1–6** have a lifetime of 3.0–6.0 ns around 500–520 nm on excitation at the new absorption maximum. The fluorescence lifetime of the neutral, protonated and deprotonated forms of the dyes are given in Table 2. The data in Table 2 indicate that the protonated and deprotonated forms of the dyes have a lifetime almost half of that of the neutral form, except for dye **5**. Dye **5** has slightly higher lifetime for the deprotonated

Table 1
Absorption and emission data of the neutral, deprotonated (pH 14) and protonated ($H_o = -7$) forms of dyes **1–8** in a 95:5 water–methanol mixture

Dye No.	Absorption λ_{max}, nm			Isosbestic point in NaOH	Emission λ_{em}, nm		
	Neutral	Deprot. (pH 14)	Prot. ($H_o = -7$)		Neutral	Deprot. (pH 14)	Prot. ($H_o = -7$)
1	396	472	410–430	420	458	522	491
2	382	448	390–425	404	450	512	482
3	380	450	390–420	406	454	515	494
4	378	446	380–420	406	440	500	470
5	378	444	380–420	404	440	488	466
6	384	450	390–420	408	439	500	466
7	400	-	410–430	-	466	-	510
8	382	-	390–430	-	454	-	498

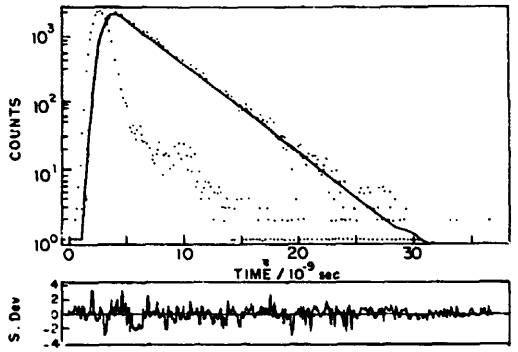


Fig. 6. Lifetime profile of dye **1** in a 95:5 water–methanol mixture

Table 2
Fluorescence lifetime of the neutral, deprotonated (pH 14), protonated ($H_o = -7$) forms of dyes **1–6** in a 95:5 water–methanol mixture

Dye No.	Lifetime (ns)		
	Neutral	Deprotonated (pH 14)	Protonated ($H_o = -7$)
1	6.8	3.0	3.4
2	8.4	4.3	6.1
3	8.7	4.9	4.2
4	8.7	5.7	3.0
5	5.0	5.7	3.6
6	9.0	6.8	3.6

form in the presence of sodium hydroxide than that of the neutral form.

The lifetime of the neutral form of the dyes decreases between pH 5 and 1, and at pH 1 the lifetime is less than 1 ns which is measured around 440–460 nm on exciting at their absorption maxima. In strongly acidic conditions ($H_o = -7$), the protonated form of all the dyes have a lifetime of 3.0–6.0 ns around 470–500 nm, on excitation at 390–430 nm.

3.5. Determination of pK_a values

The ground state pK_a values were determined spectrophotometrically and the excited state pK_a values were determined using fluorimetric titration and Förster's method. The excited state pK_a values calculated using the shift in the absorption, fluorescence, the $E_{0,0}$ value and fluorimetric titration are given in Table 3. The excited state pK_a values were calculated using Förster's equation.

$$pK_a - pK_a^* = \frac{Nhc(\nu_A - \nu_B)}{2.303\ RT}$$

A reliable value of pK_a^* can be calculated using the absorption or fluorescence shifts, which depend on the thermal relaxation differences in the ground and excited states. In the case of molecules which are more polar in the excited state, thermal relaxation will usually be more in the excited state and thus the calculation of pK_a^* from the fluorescence provides the best estimate of pK_a^*. Whereas for the molecules which are more polar in the ground state, the absorption shift will be the best method to calculate the pK_a^* values. The pK_a^* values can be calculated using the fluorescence shifts, absorption shifts and the average of both, or the $E_{0,0}$ value if all the three forms, the neutral, the deprotonated and the protonated have different absorption and emission maxima. Since in our case all three forms have strong absorption and emission, we have calculated the pK_a^* values using the shift in absorption, fluorescence and $E_{0,0}$ value. Since the average method does not give the exact $E_{0,0}$ value we have calculated the $E_{0,0}$ values from the intersection of absorption and emission spectra.

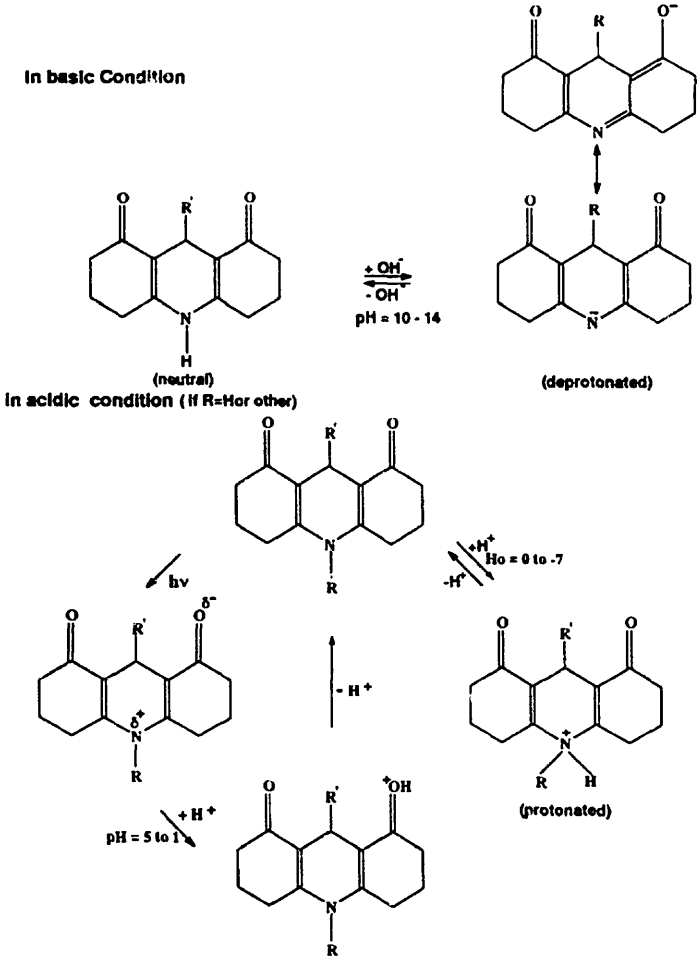
Table 3
pK_a and pK_a^* values calculated using different methods for dyes **1–6**

Dye no.	pK_a value	pK_a^* values			
		Fluorimetric titration	Absorption	Emission	$E_{0,0}$
1	13.7	-	5.18	8.29	7.18
2	13.7	12.05	5.63	8.07	7.31
3	13.75	12.05	5.17	8.28	7.53
4	13.4	12.2	4.95	7.68	6.78
5	13.55	12.8	5.31	8.0	6.67
6	13.45	12.0	5.34	7.63	6.80

The data in Table 3 indicate that the pK_a^* values obtained from the fluorimetric titration are close to the ground state pK_a values, which exemplifies the fact that the prototropic equilibrium is not established in the singlet state due to the shorter singlet lifetime of the deprotonated form. Similar behaviour has been observed for most of the heterocyclic [32–37] systems whose pK_a values were in the medium pH range (3–11).

The pK_a^* values can be calculated using the proton induced quenching technique which has been followed in recent years [30,31] for the systems which undergo protonation, whereas this may not be useful for our case since we are interested in the pK_a^* values for the deprotonation equilibrium. Under this condition the best method to calculate the pK_a^* value will be Förster's method. In systems like 6-aminochrysene [38], an agreement has been observed between pK_a^* (FT) and pK_a^* (av), which is argued as the solvent relaxation in the ground and excited states cancelling in the average method. The pK_a^* values calculated for our dyes from the absorption and fluorescence maxima using Förster's method show discrepancies which may be due to the difference in solvent relaxation in the ground and excited states. So, we report pK_a^* calculated by Förster's method using $E_{0,0}$ values as the excited state pK_a value of the dyes under investigation in the basic condition. In our recent findings [39], in the reaction of the title dyes with amines with pK_a values 11.2 to 7.5, such as diethylamine, triethylamine, DABCO, *N,N*-dimethyl benzylamine, morpholine and triethanolamine, we are able to deprotonate dyes **1–6** in the excited state, whereas no change is observed in the ground state. The amines with pK_a values less than 7, such as *N,N*-diethylaniline, *N,N*-dimethylaniline and aniline, are not able to deprotonate dyes **1–6** in the excited state, which shows that the excited state pK_a values are around 7 for the dyes. This evidence supports the fact that the pK_a^* values calculated with the $E_{0,0}$ value using Förster's method is more appropriate for the neutral and deprotonated species equilibrium.

In acidic conditions no equilibrium exists in the ground state in the pH range 5 to 1, while there is an excited state



Scheme 1.

reaction in this pH range. The absorption spectrum of the neutral form changes when the pH of the solution is decreased below 1. The absorption maximum keeps shifting in the H_0 range 0 to −7 and the ground state pK_a value could not be estimated. The emission of the neutral form is quenched completely at pH = 1 and the protonated emission appears from $H_0 = 0$ onwards. Since the appearance of the protonated emission is passing through the excited state reaction and no clear isosbestic point is seen for excitation, the excited state pK_a values could not be evaluated for the acidic condition.

The equilibrium species present in the presence of acid and base are as shown in Scheme 1.

It is inferred from the pK_a and pK_a^* values that the dyes are less basic in the excited state when compared to the ground state. In the case of acridine, the basicity of the molecule increases on excitation [40,41]. Since the nitrogen center does not have any acidic proton in acridine and no charge transfer between oxygen and nitrogen in the excited singlet state as in the case of our molecules, the excited state pK_a values are higher than the ground state pK_a in the case of acridine. The observation of a low pK_a^* value for dye **5** is in conformity with the observation of the much enhanced intensity of deprotonated emission of dye **5**.

4. Conclusion

The protonated and deprotonated forms of the dye have strong red-shifted absorption and emission in the presence of H_2SO_4 and NaOH, respectively. The proton induced fluorescence quenching in the pH range of 5 to 1 is attributed to the protonation of the oxygen center in the excited state of the dyes. The protonated and deprotonated forms of the dye have a lower lifetime than the neutral form. The presence of an anisyl group in the ninth position of dye **5** decreases the charge density on the nitrogen center and favours deprotonation compared to other dyes, hence much enhanced deprotonated emission and lower pK_a^* value. The presence of a CH_3 group in the ninth position of dye **2** increases the charge density and hence has a stronger protonated emission than other dyes. The ground state pK_a value for the dyes does not vary much on changing the substituents. Dye **5** has a lower pK_a^* value compared to other dyes which is very obvious from the much enhanced deprotonated emission intensity. The pK_a and pK_a^* values reveal that the dyes are more acidic in the excited state compared to the ground state.

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