EXCITED STATE PROTOTROPISM OF 6-AMINOCHRYSENE

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Summary

Absorption and fluorescence spectra obtained in various solvents indicate that the amino group acts as a hydrogen acceptor in the S_0 state and a hydrogen donor in the S_1 state. The lack of correspondence between the disappearance of 6-aminochrysene (CNH_2) and the appearance of CNH_3^+ in the fluorometric titration is due to proton-induced quenching of the 6-aminochrysene. The value of the quenching constant is about 10^9 dm^3 mol^{-1} s^{-1}.

1. Introduction

It is well known that arylammonium ions ($ArNH_3^+$) are stronger acids in the S_1 electronic state than in the ground state [1]. Fluorometric titrations have revealed that the fluorescence intensity of these aromatic amines is first quenched by protons at moderate hydrogen ion concentrations without the appearance of $ArNH_3^+$ ions, whereas the $ArNH_3^+$ species is observed at low H_0 values and its fluorescence intensity increases with a further decrease in H_0. This unusual behaviour of the fluorometric titration curves of the aromatic amines has been explained by Schulman and Liedke [2] as being due to the formation of a non-fluorescent solute–solvent complex in the excited state at moderate $[H^+]$ values. It has recently been shown in nanosecond time-resolved spectroscopy and fluorometry studies [3 - 9] that the above behaviour is due to the proton-induced fluorescence quenching of the amines.

In the work reported here the Förster cycle and fluorometric titration were used to determine $pK_a^*(S_1)$ for the following equilibria of 6-aminochrysene (CNH_2):

$$CNH_3^+ \rightleftharpoons CNH_2 + H^+ \quad (1)$$

$$CNH_2 \rightleftharpoons CNH^- + H^+ \quad (2)$$

where CNH_3^+ and CNH^- are the cation and the anion respectively of 6-aminochrysene. We also investigated the solvent dependence of the absorption and fluorescence spectra.

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2. Experimental details

6-aminochrysene obtained from the Aldrich Chemical Co. was purified further. Analytical grade H_2SO_4 and NaOH were used to prepare acidic and basic solutions. A modified Hammett acidity scale [10] for aqueous H_2SO_4 and Yagil's basicity scale [11] for aqueous NaOH were used for solutions below pH 1 and above pH 13 respectively. Methanol, acetonitrile and cyclohexane were of BDH analytical grade and were purified further by methods described in the literature [12]. Triply distilled water was used to prepare the solutions. pHs from 1 to 13 were measured using a Toshniwal model Cl-44A pH meter. Absorption spectra were recorded using a Cary 17D spectrophotometer. The fluorescence spectra were recorded using a scanning spectrofluorometer fabricated in our laboratory, the details of which are described elsewhere [13]. Concentrations of the order 2×10^{-5} M (except for water where a saturated solution was used) were used to obtain the fluorescence spectra. A 30%CH_3OH–H_2O mixture was used for the fluorometric titration, and the isosbestic point was used to determine the choice of excitation wavelength (320 ± 5 nm). The quantum yields in various solvents were calculated using quinine sulphate in 1.0 M H_2SO_4 as a standard.

3. Results and discussion

The absorption and fluorescence spectra of 6-aminochrysene were determined in various solvents, and the latter are shown in Fig. 1. The values of λ_{max}(abs) and $\log \epsilon_{max}$ are given in Table 1, and the values of λ_{max}(fl)

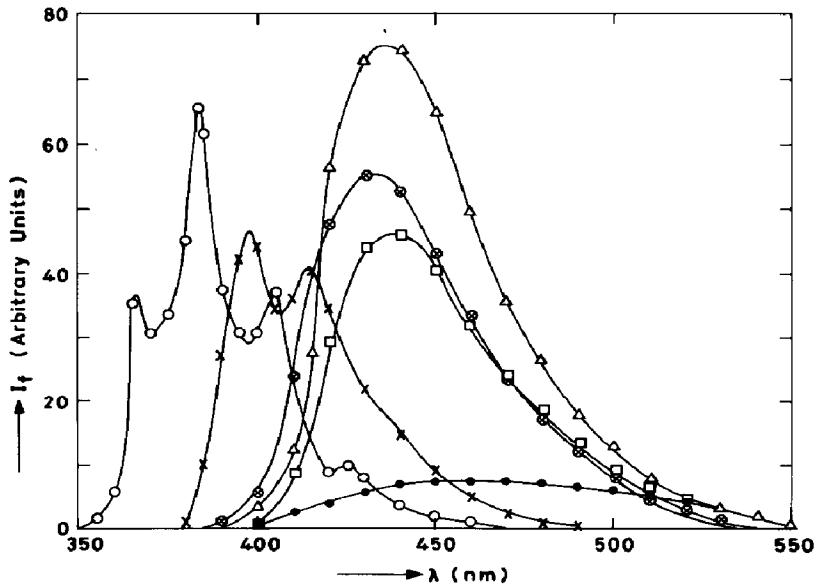

Fig. 1. Fluorescence spectra of 6-aminochrysene and CNH_3^+ in various solvents: ×, cyclohexane; ⊗, acetonitrile; □, methanol; △, ethanol; ●, water; ○, H_2SO_4 (H_0 −5).

TABLE 1

Absorption maxima λ_{max} and log ϵ for 6-aminochrysene in various solvents

Cyclohexane		*Acetonitrile*		*Methanol*		*Ethanol*		*Water*
λ_{max} (nm)	log ϵ	λ_{max} (nm)	log ϵ	λ_{max} (nm)	log ϵ	λ_{max} (nm)	log ϵ	λ_{max} (nm)
338	4.34	341	4.29	339	4.29	339	4.28	340
276	5.28	276	4.96	273	4.96	273.5	4.96	273
242	4.39	242.5	4.59	242	4.59	242	4.58	233
228	4.77	228	4.71	227	4.72	227	4.71	—

ϵ is in cubic decimetres per mole per centimetre.

TABLE 2

Fluorescence maxima and ϕ_f values of 6-aminochrysene in various solvents

Solvent	λ_{max}(fl) (nm)	ϕ_f	$\tau^{(20)}$ (ns)
Cyclohexane	398, 414, 440	0.28	
Acetonitrile	430	0.20	
Methanol	440	0.18	
Ethanol	436	0.25	
Water	470	0.16	6.0
H_2SO_4 (H_0 −5)	365, 383, 406, 429	0.17	50.0

and ϕ_f in each solvent are given in Table 2. Owing to the low solubility of 6-aminochrysene in water, the absorption spectra were determined in a saturated solution. The long wavelength absorption band is very broad compared with the structured spectrum of chrysene in all the solvents (particularly water), and it is difficult to assign λ_{max}. The fluorescence spectrum in hexane is structured, but the structure is lost as the polarity and hydrogen-bonding capacity of the solvents increases. This loss of structure is due to the perturbation of the lone pair of the nitrogen atom by the π cloud of the ring. This is confirmed by the absorption and fluorescence spectra of protonated 6-aminochrysene (where the lone pair of the amino group is hindered) which are structured, blue shifted compared with the spectra of 6-aminochrysene and resemble those of the parent chrysene molecule [14].

As stated earlier, owing to the width of the 338 nm band there is no observable effect on λ_{max}(abs), but the 276 and 242 nm bands are slightly blue shifted with increasing polarity and hydrogen bonding capacity of the solvents. However, a continuous red shift in the fluorescence maxima and a decrease in the quantum yield was observed under the above conditions. The fluorescence spectrum of 6-aminochrysene in water is much broader and more red shifted than that in the other solvents.

The amino group attached to the chrysene ring possesses two functional characteristics. It can accept a proton from hydrogen-donating solvents to form a hydrogen bond with the lone pair and to produce a blue shift compared with cyclohexane, and it can also donate a proton to the hydrogen acceptor solvents which results in a red shift compared with cyclohexane. Although it is very difficult to draw any conclusions regarding the solvent interaction with the solute molecule from the effect of solvents on the 338 nm absorption band, the effects on the 276 and 242 nm bands as well as on the absorption spectra of the protonated species, which is an extreme case of hydrogen bond formation, clearly show that only the hydrogen donor interaction of the solvent with the lone pair takes place. However, the red shift observed in the fluorescence spectra on changing the solvent from cyclohexane to water shows that in the excited state the availability of the lone pair is markedly reduced by a greater charge transfer interaction of the lone pair of the amino group with the ring. The decrease in the quantum yield of fluorescence under the above conditions can be explained by a similar mechanism.

4. Prototropic phenomena in the ground and excited states

Because of the poor solubility of 6-aminochrysene in water, the prototropic equilibria (1) and (2) were studied in 30%CH_3OH–H_2O solutions. The absorption spectra of 6-aminochrysene were investigated in the basicity–acidity range from H_- 16 to H_0 −8. As stated earlier the absorption spectrum of the cation is blue shifted, structured and resembles that of chrysene. The pK_a for equilibrium (1) was calculated spectrophotometrically to be 3.15 which is in good agreement with the published value [15]. The pK_a of equilibrium (2) could not be calculated as there was no significant change in the absorption spectrum of 6-aminochrysene even at H_- 16.

The fluorescence spectra of 6-aminochrysene were studied in the range H_- 16 to H_0 −6 in 30%CH_3OH–H_2O solutions. Only two species, the neutral molecule and the cation, were observed. As has been found for 9-phenanthrylamine [16], the aminoquinolines [17] and 5-aminoindazole [18] the imino anion does not emit in basic media, and, unlike 9-phenanthrylamine [16] and the α- and β-naphthylamines [18], no dianion emission is observed at 298 K under highly basic conditions.

The pK_a* of equilibrium (1) at 298 K was calculated using the Förster cycle method [19] from which the following equation is obtained:

$$pK_a - pK_a^* = 2.1 \times 10^{-3}(\bar{\nu}_{HA} - \bar{\nu}_A) \quad (3)$$

where $\bar{\nu}_{HA}$ and $\bar{\nu}_A$ are the band maxima (0–0 transitions are difficult to locate in 6-aminochrysene) of the acid and its conjugate base respectively. The values calculated using relation (3) and the absorption, fluorescence and mean absorption and fluorescence maxima are listed in Table 3. These values do not agree with those reported by Tichy *et al.* [15]. The errors obtained in

TABLE 3

Values of pK_a and pK_a^* for equilibria (1) and (2)

Equilibrium	pK_a	*Förster cycle method*			pK_a^*(FT)[a]
		pK_a^*(abs)	pK_a^*(fl)	pK_a^*(av)	
(1)	3.15	−2.35	−4.17	−3.26	−3.4
(2)	>14	—	—	—	12.6

[a] pK_a^* values determined from the fluorometric titration curves.

the calculation using the Förster relation and the absorption data could arise from the assignment of $\bar{\nu}_{HA}$ and $\bar{\nu}_A$ because the absorption spectrum of 6-aminochrysene (as reported by Tichy *et al.* [15]) is very broad and that of CNH_3^+ is structured with three bands of almost equal intensity. The fluorescence spectra of the two species are better behaved than the absorption spectra.

The fluorometric titration curves are shown in Fig. 2 and the pK_a^* values determined from these curves for the two equilibria are given in Table 3. It can be seen from Fig. 2 that the fluorescence intensity of 6-aminochrysene is quenched with decreasing pH and H_0. The midpoint of the quenching is at pH 1.1, which cannot be the pK_a^* of equilibrium (1) as the fluorescence spectrum of CNH_3^+ is only observed below pH 0, and its intensity increases with increasing hydrogen ion concentration. The midpoint of this increase is at H_0 −3.4 which is the pK_a^* of equilibrium (1). The sharp fluorometric titration curves show that the formation of CNH_3^+ is completed within the lifetime of the neutral species. The difference of 0.77 units between the value of pK_a^* determined using the Förster relation and the value obtained from the fluorescence spectrum may be due to the difference in the solvent relaxation of the excited conjugate acid–base pair in highly concentrated acid solutions. The agreement between the pK_a^*(FT) and pK_a^*(av) for equilibrium (1) may be due to cancellation of the solvent relaxation in the ground and excited states. The lack of correspondence between the onset of the fluorescence quenching of 6-aminochrysene and the appearance of CNH_3^+ fluorescence clearly indicates that the fluorometric titration curves do not describe a simple conjugate acid–base pair equilibrium in the S_1 electronic state [9]. Rather, they indicate proton-induced quenching of 6-aminochrysene fluorescence at moderate hydrogen ion concentrations, and it has been shown that this process competes with the proton transfer reaction. Similar behaviour has been observed in many aromatic amino compounds [3 - 9]. Although under these circumstances an accurate value for the pK_a of equilibrium (1) can only be determined using time-dependent fluorometry, the midpoint of the increase in the CNH_3^+ fluorescence curve will be near the true value.

A kinetic model to explain the above behaviour has been suggested by Tsutsumi *et al.* [9] who showed that the complete equation reduces to the

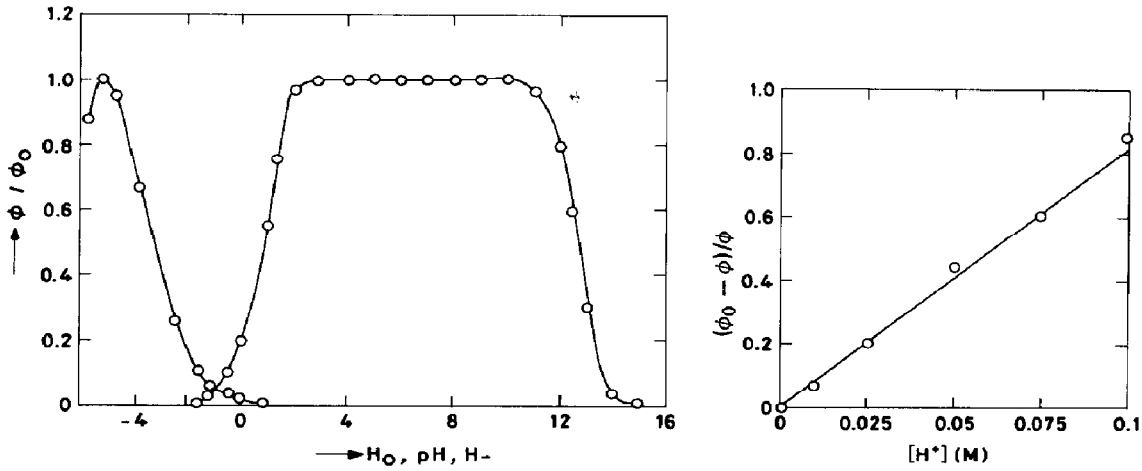

Fig. 2. Plot of the relative fluorescence intensities of 6-aminochrysene *vs.* the acidity (H_0 and pH) and basicity (pH and H_-) of the solution.

Fig. 3. Plot of $(\phi_0 - \phi)/\phi$ *vs.* $[H^+]$.

following simple Stern–Volmer relation if the hydrogen ion concentration is small enough for the rate of formation of CNH_3^+ to be negligible in comparison with its rate of decomposition and the lifetime of CNH_3^+ is longer than that of 6-aminochrysene:

$$\frac{\phi_0}{\phi} = 1 + k_q \tau [H^+] \tag{4}$$

where ϕ_0 and ϕ are the fluorescence intensities of the molecule in the absence and the presence of the quencher (*i.e.* H^+) respectively, k_q is the proton-induced quenching rate constant and τ is the lifetime of the neutral molecule. Values of $(\phi_0 - \phi)/\phi$ for 6-aminochrysene are plotted *versus* $[H^+]$ (10^{-2} - 10^{-1} M) in Fig. 3, and the value of $k_q\tau$ obtained from the slope is 8.1 $dm^3\ mol^{-1}$. The lifetime of 6-aminochrysene was calculated using the equation given by Strickler and Berg [20] and was found to be 5.6 ns. The value of k_q thus obtained is $1.5 \times 10^9\ mol^{-1}\ dm^3\ s^{-1}$ which is the same order of magnitude as that observed for other amino compounds (10^8 - $10^9\ dm^3\ mol^{-1}\ s^{-1}$) [3 - 9].

The fluorescence of the neutral molecule is again quenched when the pH is increased above 10, and quenching is complete at pH 14. This may be due to the formation of the CNH^- species as the imino anions of aminoquinolines [17], 9-phenanthrylamine [16] and 5-aminoindazole [18] are known to be non-fluorescent. The midpoint of this quenching occurs at pH 12.6, which is the pK_a for equilibrium (2) between the neutral molecule and CNH^-. This indicates that 6-aminochrysene is more acidic in the S_1 state than in the S_0 state as has been found for other aromatic amines. Unlike 9-phenanthrylamine [16] and the α- and β-naphthylamines [18], the dianion of 6-aminochrysene is not formed even at H_- 16, or if it is formed under such conditions it does not emit.

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