

Photoluminescence of 3-Aminofluoranthene

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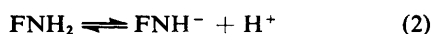
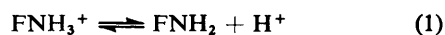
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The effect of pH on the fluorescence intensity of 3-aminofluoranthene shows that the rate of proton-induced quenching is much smaller than the rate of protonation in the S_1 state. This behaviour is quite different from that observed for other arylamines.

Fluorimetric titration has been found to be a good technique in calculating pK_a^* values, as it is free from the assumptions involved in the Förster cycle method and other approximations involved in theoretical calculations, except that the prototropic equilibrium is attained in the excited singlet state. But recently it has been shown that even the values of pK_a^* obtained from these titrations should be treated cautiously. For example, it has been noted that there is no correspondence in the decrease of fluorescence intensity of neutral aromatic amines¹⁻⁶ and the increase in the fluorescence intensity of the protonated form as $[H^+]$ is increased. This unusual behaviour, at moderate hydrogen ion concentrations, has recently been explained as resulting from the proton-induced quenching of the amino-group (from a study of nanosecond spectrometry and fluorimetry) rather than the formation of a non-fluorescent solute-solvent complex in the S_1 state.⁷

The fluoranthene molecule belongs to the non-alternant class of hydrocarbons with the 1-, 2-, 3-, 7-, and 8-position being non-equivalent. But it can be visualised as two alternant hydrocarbon systems, joined by two essentially single bonds, with the electronic transitions arising from the naphthalene and benzene moieties. The introduction of an NH_3^+ group to any of the non-equivalent positions does not shift the absorption peaks of the parent molecule appreciably,⁸ which is contrary to expectations for a non-alternant system. But the pK_a values of different amino-substituted fluoranthenes differ widely, thereby clearly indicating the non-alternant nature of fluoranthene.⁹

The present study on 3-aminofluoranthene (FNH_2) has been carried out to examine the effect of hydrogen ion concentration on the fluorescence spectrum and to calculate the pK_a^* values for equilibria (1) and (2). In addition, the effect of solvents of different polarity on the fluorescence and absorption spectra has also been investigated.



Experimental

3-Aminofluoranthene was obtained from Aldrich Chemical Company and was recrystallised from methanol. Analytical grade H_2SO_4 and NaOH were used to prepare acidic and basic solutions. A modified Hammett's acidity scale¹⁰ for H_2SO_4 - H_2O and Yagil's basicity scale¹¹ for NaOH- H_2O were used for the solutions below pH 1 and above 13, respectively. Spectroscopic grade methanol (B.D.H.) was used as such, whereas analytical grade acetonitrile (E. Merck) and hexane (B.D.H.) were further purified as described in the literature.¹² The pH values in the range 1-13 were measured on a Toshniwal pH meter model CL-44A. Absorption spectra were recorded with a Cary 17D spectrophotometer and fluorescence spectra were recorded with a scanning spectrofluorimeter made in our laboratory, the details of which are available elsewhere.¹³

Table 1. Absorption maxima (nm) and $\log \epsilon_{max}$ (in parentheses) of 3-aminofluoranthene

Cyclohexane	Acetonitrile	Ether	Methanol	Ethanol	Water
398.5 (3.93)	414 (3.78)	420 (3.78)	414 (3.81)	410 (3.88)	406
368 (3.87)	368 (3.44)	368 (3.40)	368 (3.50)	368 (3.55)	366
327.5 (3.97)	326 (3.79)	327 (3.85)	325 (3.84)	325 (3.91)	325
292.5 (4.29)	293 (4.09)	293 (4.09)			
245 (4.72)	245.5 (4.52)	246 (4.52)	245 (4.50)	245 (4.59)	244
225 (4.74)	225 (4.56)	227 (4.53)	225 (4.54)	225 (4.60)	220
305 (4.58)	305 (4.30)	307 (4.32)	306 (4.25)	306.5 (4.34)	300

Triply distilled water was used to prepare the solutions. Owing to the poor solubility of the compound, 30% methanol-water was used for fluorimetric titration and the concentrations used were in the range 10^{-5} - $10^{-4}M$. The quantum yield was measured using quinine sulphate in 2M- H_2SO_4 as a standard and 313 nm as the excitation wavelength with an 8 nm band width. For fluorimetric titrations, the isosbestic point (364 ± 5 nm) was chosen as the excitation wavelength.

Results and Discussion

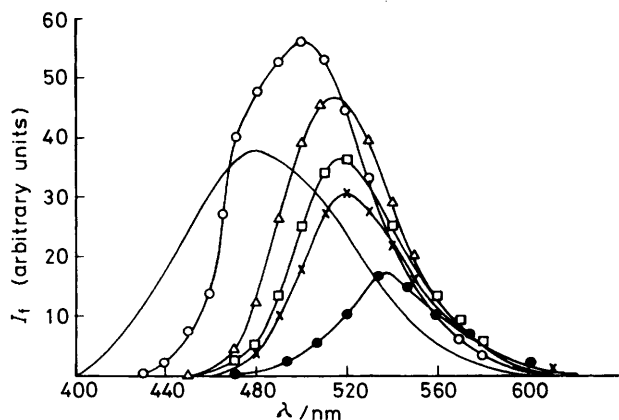
The absorption and fluorescence spectra of FNH_2 at 298 K have been recorded in different solvents.† The λ_{max} (abs) values along with ϵ_{max} in each solvent are listed in Table 1. The ϵ_{max} value in water could not be calculated as the absorption spectrum was observed in saturated solution. The agreement with previous results in the respective solvents (*i.e.* cyclohexane and ethanol¹⁴) is good, within the accuracy of experimental measurement. The data indicate that except for the first transition, the other transitions are hardly affected by a change in the polarity or in the hydrogen-bond-formation interaction of the solvents. The first transition is red-shifted in all solvents compared with cyclohexane. But this red shift is a maximum in ether, *i.e.* the hydrogen-accepting solvent, and decreases as the hydrogen-donating character of the solvent increases.

Table 2 gives the λ_{max} (flu) values of FNH_2 in different solvents, along with the fluorescence quantum yield (ϕ_f). Unlike the absorption spectra, there is a regular bathochromic shift in λ_{max} (flu) and a decrease in ϕ_f as the polarity and the hydrogen-bond-formation tendency of the solvent increases. On protonation, the fluorescence maximum is blue-shifted.

† The fluorescence spectra are shown in Figure 1.

Table 2. Fluorescence maxima (nm) and ϕ_f of 3-aminofluoranthene in different solvents

Solvent	$\lambda_{\text{max.}}$ (nm)	ϕ_f	τ_0 (ns)
Cyclohexane	500	0.222	
Ether	515	0.218	
Acetonitrile	518	0.170	
Ethanol	520	0.155	
Methanol	520	0.145	
Water	535	0.15	3.53
Cation	475	0.224	~35

**Figure 1.** Fluorescence spectra of 3-aminofluoranthene in different solvents and of the cation. O-O-O, cyclohexane; Δ - Δ - Δ , ether; \square - \square - \square , acetonitrile; \times - \times - \times , ethanol; \bullet - \bullet - \bullet , water; —, cation.

The solvent molecule can interact with the solute molecule in three different ways, (i) through dispersive, (ii) hydrogen acceptor-solvent, and (iii) hydrogen donor-solvent interactions. In the case of a solute molecule with an electron-donating substituent and $\pi^* \leftarrow \pi$ as the lowest energy transition, the first two effects lead to a red shift whereas the last effect leads to a blue shift in $\lambda_{\text{max.}}$ (abs). The complications or irregularities arise if more than one effect, acting in opposite directions, is present. The amino-group can act as a hydrogen acceptor as well as a hydrogen donor, thereby resulting in a blue shift in the former case and a red shift in the latter. Moreover, it has been shown by Thulstrup *et al.*¹⁵ that the first transition in FNH_2 is long-axis polarised whereas the second and third are short-axis polarised. For FNH_2 , the amino-group is substituted along the longer axis of fluoranthene, and it is expected that the longer-axis polarised transition will be affected much more than the shorter-axis polarised one. The results show this behaviour. Acetonitrile and ether are hydrogen-accepting solvents only whereas methanol, ethanol, and water can behave in both ways. Thus, on the above arguments, an increase in red shift of the absorption spectra for ether is quite natural as the first two effects will be predominant in polar and hydrogen-accepting solvents. In methanol, ethanol, and water, the third effect, which behaves in the opposite direction to the first two, is also operative and thus the combined effect of these kinds of solvents on spectral shifts is diminished. From the results in Table 1, it is clear that water acts as a better hydrogen donating than hydrogen-accepting solvent. On the other hand, the regular red shift in the fluorescence band maxima clearly shows that the amino-group behaves like a hydrogen donor species and this is in agreement with known results that due to

Table 3. Equilibrium constants of reactions (1) and (2) in the S_0 and S_1 states

Equilibria	pK_a	pK_a^*		
		FC	FT	DA
(1)	3.15	-1.8	-2.2	-1.5
(2)	>14		13.8	

* FC = Förster cycle (approximate value), FT = fluorimetric titration, DA = dynamic analysis.

the greater charge migration from the amino-group to the aromatic ring in the S_1 state, the amino-group behaves as a stronger acid in the S_1 than in the S_0 state. The decrease in the ϕ_f could also be explained along the same lines.

pH Effects.—Owing to the poor solubility of FNH_2 in water, the prototropic equilibria (1) and (2) have been studied in 30% methanol- H_2O . The absorption spectra of FNH_2 in this media have been recorded in the basicity-acidity range of $H_- 16$ to $H_0 -6$. The absorption spectra of FNH_3^+ cation is blue shifted, structured, and resembles that of fluoranthene, as expected. $pK_a(1)$ is calculated spectrophotometrically and the value obtained is 3.15. Agreement with the literature value of 2.85 (50% methanol-water) is quite good. The $pK_a(2)$ could not be calculated as there was no significant change in the absorption spectra even up to $H_- 16$, indicating that $pK_a(2)$, as for other amino-compounds, is >16 .¹⁶

The fluorescence spectra of FNH_2 have been studied over the range $H_- 16$ to $H_0 -6$ in 30% methanol-water. Only the neutral and cation species were observed to fluoresce. The fluorescence of FNH_2 was quenched after $H_- 14$ and unlike α - and β -naphthylamine¹⁷ and 9-phenanthrylamine,¹⁸ emission from no other species was detected even up to $H_- 16$. The absorption spectrum of FNH_3^+ resembles that of fluoranthene very closely and it has also been noted that band reversal takes place between the two longest wavelength absorption bands of fluoranthene when the amino-group is substituted at the 3-position,¹⁷ so that FNH_3^+ emits from a different electronic state than FNH_2 . Thus, the Förster cycle method, employing absorption or fluorescence data, cannot be used with accuracy. Moreover, even when using high concentrations (*ca.* 10^{-3}M), we were unable to identify properly the much less intense longest wavelength absorption bands of FNH_3^+ , which is buried under the relatively more intense second band.

The fluorimetric titration curve is shown in Figure 2. The appearance of the fluorescence intensity of the cation and the disappearance of the fluorescence intensity of the neutral species do not exactly correspond to each other, *i.e.* the two curves do not intersect exactly at the middle (50%), indicating that a very slight proton-induced quenching of the neutral species may be taking place. The $pK_a^*(1)$ values was obtained from the curve indicating the formation of FNH_3^+ and the value calculated is -2.2. This behaviour of FNH_2 is quite different from that of other aromatic amines, where there is no correspondence to the disappearance of neutral amines and the appearance of the respective ammonium ion. Thus, appreciable proton-induced quenching of the neutral species at moderate hydrogen ion concentrations is observed in the latter cases.¹⁻⁶ It has been shown for the quenching mechanism induced by protons that (i) the intramolecular charge-transfer structure in the excited state is responsible for the proton-induced quenching and (ii) the proton-induced quenching is caused by electrophilic protonation at one of the carbon atoms of the aromatic ring.¹⁹ In the present case, it has been

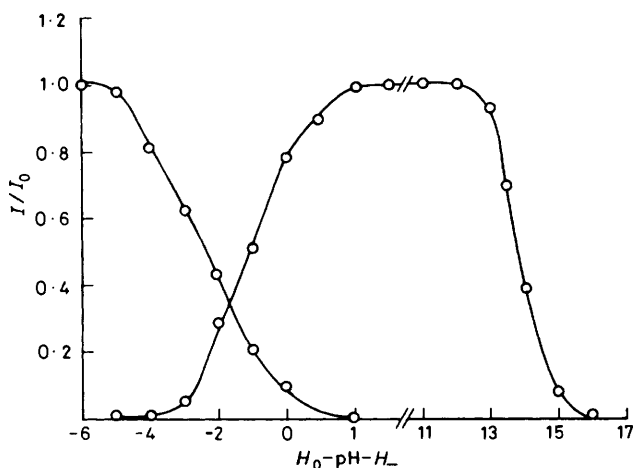
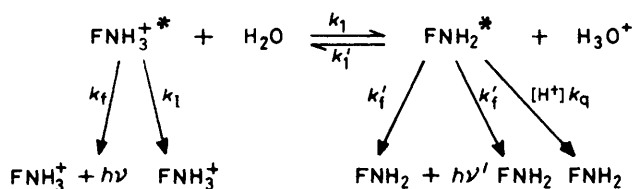


Figure 2. Plot of relative fluorescence intensities of 3-amino-fluoranthene versus $H_0 - \text{pH} - H_-$.



Scheme.

shown, by theoretical calculations,²⁰ from i.r. data²¹ and $\text{p}K_a$ measurements⁹ that the conjugative power (*i.e.* charge-transfer interaction) of the amino-group in fluoranthene at position 3 is a maximum, thus indicating that fluoranthene differs from the usual benzenoid hydrocarbons and is non-alternant even in the ground state. In other words, there is significant interaction between the benzene and naphthalene portions of the molecule. Though data about the charge densities at the nitrogen atom, carbon atoms, and the vibrational frequencies in the S_1 state for the FNH_2 molecule are not available, $\text{p}K_a^*(1)$ has shown that arylammonium ion is a stronger acid in the S_1 than in the S_0 state, indicating that charge migration is greater than in the excited state, thereby fulfilling the first condition. On the other hand, our studies have also indicated that the proton-induced quenching rate of the fluorescence intensity of FNH_2 is much smaller than the rate of protonation, showing that the interaction between the benzene and naphthalene rings is also strong even in the S_1 state. Owing to this, the charge density at the appropriate carbon atom of the fluoranthene will not be large since the migrating charge will be widely distributed over the carbon atoms of the ring. This means that electrophilic protonation at one of the carbon atoms of FNH_2 will be locally restricted. As a result, the value of k_q for FNH_2^* become smaller than those (10^8 – 10^9 $\text{l mol}^{-1} \text{s}^{-1}$) of naphthylamines.² In our study, the values $k_q\tau_0'$ cannot be calculated separately, using the Stern-Volmer plot (as in case of other arylamines), as the quenching and protonation of FNH_2^* takes place more or less simultaneously.

As suggested by Tsutsumi *et al.*,¹ the above experimental results can be accounted for by the Scheme where k_f and k_f' are the rate constants for the emission of fluorescence, k_1 and k_1' describe radiationless decay of the excited state, k_q refers to the quenching of FNH_2^* by the protons, and k_i and k_i' are the forward and reverse rate constants for deprotonation. Unprimed quantities refer to FNH_3^+ and primed quantities to FNH_2^* . If all the exciting radiation is absorbed only by the

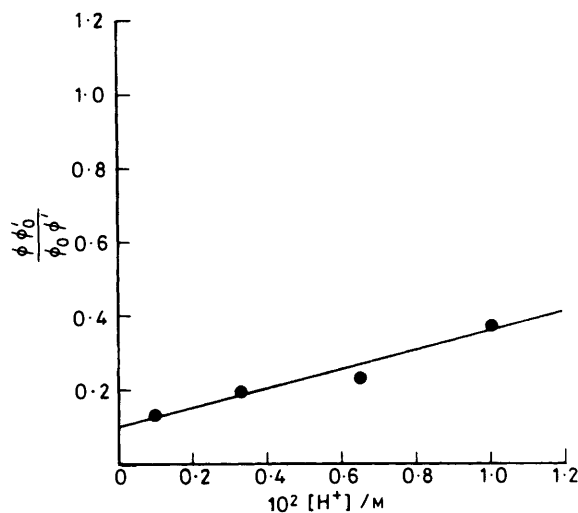


Figure 3. Plot of $\varphi\varphi_0'/\varphi_0\varphi_0'$ versus hydrogen ion concentration

photodissociating acid, then by applying the steady-state approximation, equations (3)–(5) can be obtained where τ_0

$$\frac{\varphi}{\varphi_0} = \frac{1 + [k_1' + k_q'(1 + k_1\tau_0)]\tau_0'[H^+]}{1 + k_1\tau_0 + [k_1' + k_q'(1 + k_1\tau_0)]\tau_0'[H^+]} \quad (3)$$

$$\frac{\varphi'}{\varphi_0'} = \frac{k_1\tau_0}{1 + k_1\tau_0 + [k_1' + k_q'(1 + k_1\tau_0)]\tau_0'[H^+]} \quad (4)$$

$$\frac{\varphi\varphi_0'}{\varphi_0\varphi_0'} = \frac{1}{k_1\tau_0} + \frac{[k_1' + k_q'(1 + k_1\tau_0)]\tau_0'}{k_1\tau_0} [H^+] \quad (5)$$

and τ_0' are the lifetimes of FNH_3^+ and FNH_2 , respectively, in the S_1 state. $\varphi\varphi_0'/\varphi_0\varphi_0'$ is plotted against $[H^+]$ in Figure 3 and as expected the plot is fairly linear. $[H^+]$ (in reality a_{H^+}) has been calculated from Hammett H_0 values,¹⁰ which is actually a measure of the available H^+ in a given aqueous solution. The intercept gave $k_1\tau_0$ 10 and the slope $[k_1' + k_q'(1 + k_1\tau_0)]\tau_0'/k_1\tau_0 = 0.0031$, giving $(k_1' + 11k_q')\tau_0' = 0.031$. The lifetime of FNH_2 (τ_0') was calculated by using the Strickler–Berg²² equation and found to be 3.5 ns, whereas that of FNH_3^+ could not be calculated by this equation as the longest absorption band of FNH_3^+ could not be isolated. But it has been observed for naphthylamine cation and naphthalene²³ and chrysene and 6-aminochrysene²⁴ cation that the lifetimes of the protonated arylamines are nearly equal to that of the parent hydrocarbon. The radiative lifetime of the fluoranthene molecule is 210 ns.²⁵ Multiplying this by the quantum yield of fluorescence of FNH_2 in water (0.15) gives an approximate molecular fluorescence lifetime of 35 ns. Taking τ_0' to be 35 ns and as a first approximation neglecting k_q' the value of k_1' obtained is 8.9×10^6 $\text{l mol}^{-1} \text{s}^{-1}$, whereas that of k_1 is 2.9×10^8 s^{-1} . The value of $\text{p}K_a^*(1) = -\log k_1/k_1'$ thus calculated is -1.51 . The agreement between the values of $\text{p}K_a^*(1)$ obtained by the latter method and that obtained from the mid-point of the formation curve of FNH_3^+ is too good to believe, considering the inaccuracies in τ_0 and τ_0' , but one thing is certain and that is $k_q \ll k_1'$.

The fluorescence of the neutral molecule is again quenched when the pH is increased above 13 and quenching is complete at H_- 16. This could be due to the formation of FNH^- as the iminoanions of aminoquinolines,²⁶ 9-phenanthrylamine,¹⁸ and 5-aminoindazole¹⁷ are observed to be non-fluorescent. The middle point of this quenching occurs at pH 13.8, which is

$pK_a^*(2)$ for the equilibrium between the neutral form and monoanion of FNH₂. This indicates that the FNH₂ is more acidic in the S₁ than in the S₀ state, as for other arylamines.

In conclusion, the effect of pH on the fluorescence intensity of FNH₂ has indicated that this molecule behaves differently from other arylamines.

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