Deactivation of Excited 1-Amino-5,6,7,8-tetrahydronaphthalene in Various Solvents

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Fluorescence emission of 1-amino-5,6,7,8-tetrahydronaphthalene is quenched by pyridine at 300 and 77 K and the mechanism involves π-electron delocalization *via* a hydrogen bond. The probable effect of conformational changes in the molecule also needs to be considered. In polar solvents ethanol and methanol which form hydrogen-bonding chains a significant role is played by resonance transfer from the aminotetrahydronaphthalene and its methyl derivative *NN*-dimethylaminotetrahydronaphthalene to pyridine in quenching the fluorescence emission of the molecules. Triethylamine quenches fluorescence of aminotetrahydronaphthalene at 300 K but not at 77 K. Possible deactivation process may involve ion-pair formation. Reaction schemes for quenching by pyridine and triethylamine are described. From the non-exponential nature of phosphorescence decay at 77 K formation of hydrogen bond complex between aminotetrahydronaphthalene in the triplet state and the quenchers is inferred.

When an electronically excited molecule (a fluorescer) interacts with a molecule of another species in the ground state, interesting photochemical and photophysical processes arise. These lead to changes in the fluorescence emission of the fluorescer, including fluorescence quenching.[1–20] Non-radiative de-excitation of a molecule in solution, in a rigid glass, or in crystals may be due to resonance transfer, exciton transfer, or other processes. Intermolecular interactions, which may include hydrogen bonding, also brings about changes in the phosphorescence spectrum.[21–23] The biexponential nature of the phosphorescence decay curve prompted some authors[21,24] to put forward the idea of the formation of a short-lived complex in the triplet state. In this paper, which deals with the luminescence spectra of 1-amino-5,6,7,8-tetrahydronaphthalene (ATHN) in different solvents in the presence of non-fluorescent molecules pyridine (Py) and triethylamine (TEA) acting as quenchers at 300 and 77 K, spectral changes consequent on molecular interactions in different environments are described. The phosphorescence decay curves of ATHN–Py and ATHN–TEA systems at 77 K are also examined.

Experimental

1-Amino-5,6,7,8-tetrahydronaphthalene (ATHN), m.p. 38 °C, obtained from Aldrich, was carefully distilled under reduced pressure before use. The purity was tested by g.l.c. using a Hewlett–Packard model 5730A chromatograph attached to a 7127A collecting unit, with nitrogen as the carrier gas; detection was by flame ionization. The chromatographic procedure gave a purity of *ca.* 99.96%. Solvents, n-hexane, n-heptane, benzene, methylcyclohexane (MCH), acetonitrile, ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), tetrahydrofuran (THF), triethylamine (TEA), and pyridine (Py), (E. Merck), were of spectroscopic grade. They were repeatedly distilled under vacuum before use and each was tested for the absence of any emission in the wavelength region studied. At 77 K MCH was used as an inert solvent to obtain a glassy matrix.

NN-Dimethylaminotetrahydronaphthalene (DMTHN)[25] was prepared from ATHN and methyl iodide as light yellow needles (from ether–light petroleum), followed by sublimation, m.p. 170 °C. The n.m.r. spectrum confirmed the structure.

The emission spectra were recorded with a Perkin-Elmer model MPF 44A fluorescence spectrophotometer attached to a corrected spectra unit, and the absorption spectra with a Shimadzu UV-VIS 210A spectrophotometer.

The ATHN concentration was fixed at *ca.* 2.86×10^{-4}M at both 300 and 77 K. In ternary mixtures, the concentration of Py in different solvents varied from 10^{-4} to 10^{-2}M and that of TEA from 10^{-4} to 10^{-1}M. The excitation wavelength chosen was 290 nm (absorption maximum of ^1L_b band system of ATHN) and the emission wavelength for studying phosphorescence decay was 395 nm. After the phosphorescence intensity achieved a steady state, the exciting radiation was cut off to obtain the dark decay on the recorder. The relative fluorescence quantum yields of ATHN and fluorescence lifetimes (τ) in different solvents were measured by the same procedure as described elsewhere.[19]

Results and Discussion

Pyridine (Py) or triethylamine (TEA) does not produce any noticeable change in position or intensity of absorption bands of 1-amino-5,6,7,8-tetrahydronaphthalene (ATHN) in n-hexane and acetonitrile at 300 K. Apparently, there is little or no hydrogen bonding interaction between ATHN in the ground state and Py or TEA. On the other hand, when Py is added in steps to ATHN–hexane solution at 300 K, the fluorescence intensity falls off remarkably without any shift in the position of fluorescence bands of ATHN (Figure 1a). Quenching due to Py is smaller for ATHN in solution in the polar acetonitrile than in hexane. The fluorescence intensity of ATHN in n-hexane also decreases in the presence of TEA but only slowly and a gradual red shift of the spectrum is observed (Figure 1b). But TEA produces larger quenching of the fluorescence of ATHN in acetonitrile. Fluorescence of *NN*-dimethylaminotetrahydronaphthalene (DMTHN) in benzene and acetonitrile was also measured in the presence of Py and TEA. Since the solubility of DMTHN in n-hexane is very low, benzene whose dielectric constant (ε_0 *ca.* 2.2) is comparable with that of n-hexane (ε_0 *ca.* 1.89) was used. It is seen that in both benzene and acetonitrile no change in intensity or position of the fluorescence bands of DMTHN is produced by either Py or TEA (Figures 2a and b). It is thus apparently reasonable to ascribe the changes in the fluorescence emission of ATHN to hydrogen bonding of the molecule with Py or TEA.

In the case of ATHN and Py both the donor and the acceptor have conjugate π-electron systems. It is generally accepted[21,26–28] that, for such systems, the internal conversion rate is enhanced and causes quenching of fluorescence, while the intersystem crossing is not affected. The deactivation of excited ATHN by loss of energy to non-fluorescent Py is known to be through π-electron delocalization *via* a hydrogen bond. It is observed that both fluorescence and phosphorescence emissions

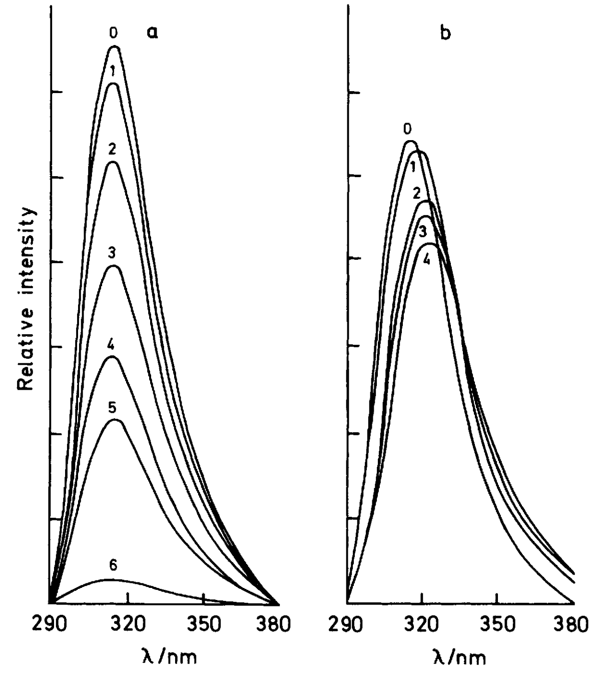


Figure 1. a, Fluorescence spectra of ATHN at 300 K (2.86 × 10^{-4}M in n-hexane) (excitation wavelength 290 nm): Concentration (M) of Py in 0, 0; 1, 2.48 × 10^{-4}; 2, 1.5 × 10^{-3}; 3, 6.2 × 10^{-3}; 4, 7.5 × 10^{-3}; 5, 1.24 × 10^{-2}; 6, 9.9 × 10^{-2}. b, Fluorescence spectra of ATHN at 300 K (2.86 × 10^{-4}M in n-hexane) (excitation wavelength 290 nm). Concentration (M) of TEA in 0, 0; 1, 1 × 10^{-1}; 2, 3 × 10^{-1}; 3, 5 × 10^{-1}; 4, 7 × 10^{-1}

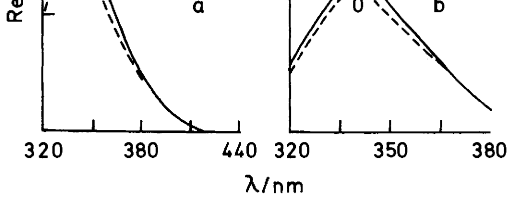


Figure 2. Fluorescence spectra of DMTHN at 300 K (4.6 × 10^{-4}M in acetonitrile). a, Concentration (M) of Py in 0, 0; 1, 4.14 × 10^{-2}. b, Concentration (M) of TEA in 0, 0; 1, 2.9 × 10^{-1}

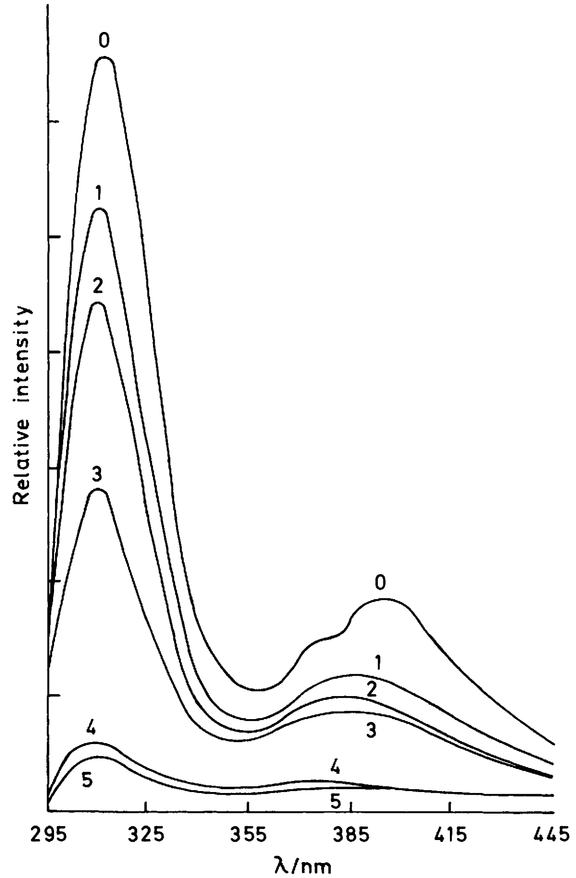


Figure 3. Emission spectra of ATHN at 77 K (2.86 × 10^{-4}M in MCH) (excitation wavelength 290 nm). Concentration (M) of Py in 0, 0; 1, 6.21 × 10^{-5}; 2, 1.24 × 10^{-4}; 3, 3.11 × 10^{-4}; 4, 6.21 × 10^{-4}; 5, 1.24 × 10^{-3}

Table 1. Change of I_P/I_f value and phosphorescence decay time τ_P of ATHN (2.86 × 10^{-4}M) in MCH with Py at 77 K

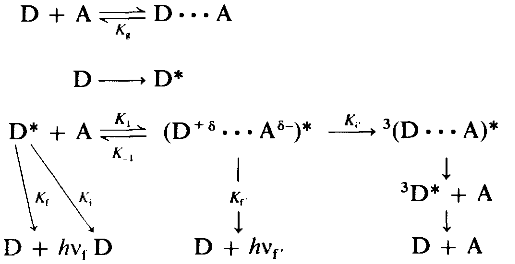
[Py]/M	I_P/I_f	τ_P/s
0	0.278	2.45
3.11 × 10^{-4}	0.313	
6.21 × 10^{-4}	0.370	
1.24 × 10^{-3}	0.455	0.68

of ATHN in MCH at 77 K fall off in intensity on addition of Py (Figure 3), the change in intensity of phosphorescence being smaller than that of fluorescence. Further, with an increase in concentration of Py, the phosphorescence band gradually undergoes a blue shift. From Table 1 it can be seen that as the concentration of Py increases. I_p/I_f increases. Presumably deactivation of the excited singlet state S_1 is followed by an increase in the population of the triplet state through spin–orbit coupling. It should be noted that the phosphorescence decay time of ATHN on complex formation with Py is smaller than that for free ATHN (Table 1).

In this connection, the effect of conformational changes on spin-forbidden electronic transitions studied by previous authors[29–32] in aniline and related compounds may be considered. The NH_2 group in aniline molecule is known to make an angle of *ca.* 46° with the benzene ring in the ground state. It has been suggested by some authors[29–32] that spin-forbidden electronic transition rates in aromatic amines are sensitive to the orientation of NH_2 group. According to Dubroca and Lozano,[32] in several aromatic amines the lone-pair orbital situated on the nitrogen atom tends at 77 K to belong to the aromatic ring. This increases the n,π^* character of the second excited singlet state S_2. As a result, intersystem crossing (i.s.c.) is increased because the spin–orbit matrix element is taken between $n\pi^*$ and $\pi\pi^*$ states of different multiplicities.[33] In the same way the triplet state corresponding to the singlet state $^1 1,a_\pi(S_2)$ will acquire $^3n\pi^*$ or $^3\pi\pi^*$ character.

Here ^{1}1,a_π denotes the state produced by the transition of the lone pair orbital to the antibonding π-orbital of the aromatic ring. Moreover, the i.s.c. from the first singlet excited state S_1 which is the ππ* state to ^{3}1,a_π may be enhanced by spin–orbit coupling if ^{3}1,a_π possesses $^3n\pi^*$ character and due to this the fluorescence may decrease. Hydrogen bonding is known to bring about a change in the conformation of some bicyclic molecules such as 1,2,3,4-tetrahydroquinoline.[34] For the molecule of ATHN it is probable that when the molecule enters into hydrogen bond formation with Py there is a suitable conformation change such that the NH_2 group tends to become more coplanar with the aromatic ring so that ^{3}1,a_π may acquire $n\pi^*$ character. Deactivation of the ππ* first singlet excited state can occur due to enhanced i.s.c. to the ^{3}1,a_π state through spin–orbit coupling. The observed blue shift of the phosphorescence spectrum due to hydrogen bonding with Py seems to be indicative of the acquired $n\pi^*$ character of the triplet state.

The path of deactivation of ATHN in the presence of Py is described in Scheme 1. Here, K_1 and K_{-1} are the bimolecular rate constant of exciplex formation and unimolecular rate constant of decomposition reaction respectively ($K_1 \approx K_d$, the diffusion-controlled rate constant); K_f and K_i are radiative and radiationless transition rate constants of the electronically excited free D molecule. $K_{f'}$ and $K_{i'}$ are the corresponding rate constants for the excited complex.



Scheme 1. $\tau = 1/(K_i + K_f), \tau' = 1/(K_{i'} + K_{f'})$

It was mentioned before that, for the systems studied, there is no significant hydrogen bonding in the ground state. Since, in the case of ATHN–Py, there is remarkable quenching of fluorescence, *i.e.* $K_{i'} \gg K_{f'}$ and also $K_{i'} \gg K_{-1}$, the simple Stern–Volmer equation (1) may be used for determining the quenching

$$f_0/f = 1 + K_{sv}[Q] \qquad (1)$$

rate constant. Here K_q is given by $K_{sv} = K_q\tau$, τ being the fluorescence decay time in the absence of quencher. The Stern–Volmer plots for the ATHN–Py system in different solvents are given in Figure 4.

Some interesting facts emerge on comparing the bimolecular rate constant of fluorescence quenching K_q for the ATHN–Py system measured in different non-polar, polar aprotic, and polar protic solvents given in Table 2, in which diffusion-controlled rate constants K_d for the same solvents, calculated from $K_d = 8RT/3000\eta$, are also included. It is seen that for ATHN in non-

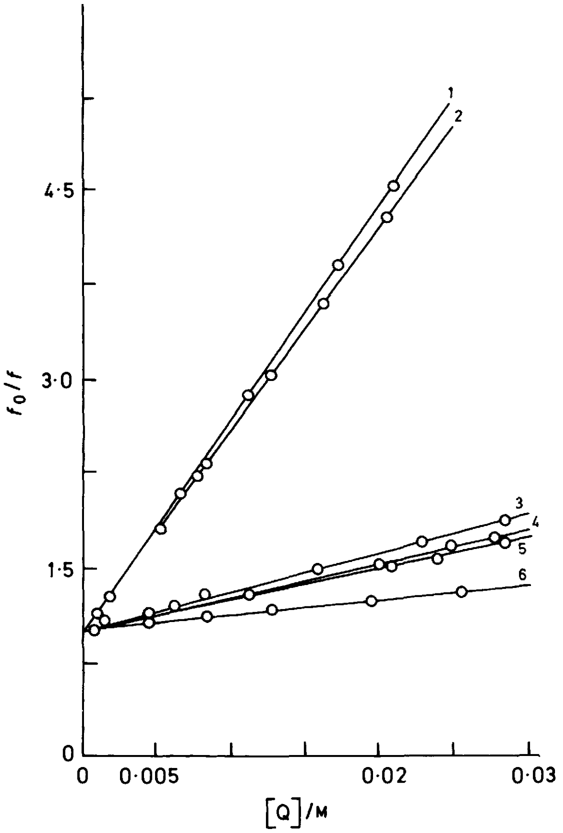


Figure 4. Stern–Volmer plots for ATHN–Py system in different solvents. 1, n-heptane; 2, n-hexane; 3, EtOH; 4, MeOH; 5, acetonitrile; 6, DMF

Table 2. The bimolecular fluorescence quenching rate constant K_q in different solvents for ATHN–pyridine at 300 K

Solvent	ε	Φ_f	10^7K_f	τ/ns	K_{SV}/l mol^{-1}	K_q/l mol^{-1} s^{-1}	K_d/l mol^{-1} s^{-1}	K_q/K_d
n-Hexane	1.9	0.39	2.52	15	164 (±6)	1.1 (±0.02) × 10^{10}	2.25 × 10^{10}	0.5
n-Heptane	2.07	0.50	2.5	20	179 (±6)	0.9 (±0.02) × 10^{10}	1.71 × 10^{10}	0.5
EtOH	24.55	0.28	3.15	9	30 (±2)	3.3 (±0.09) × 10^9	6.01 × 10^9	0.5
MeOH	32.7	0.24	2.48	10	27 (±2)	2.73 (±0.2) × 10^9	1.21 × 10^{10}	0.2
Acetonitrile	37.5	0.35	2.41	18	24 (±2)	1.6 (±0.11) × 10^9	1.9 × 10^{10}	0.08
DMF	36.7	0.39	2.89	14	9 (±1)	6.00 (±0.10) × 10^8	8.2 × 10^9	0.07
THF	7.58	0.92	3.0	31	65 (±2)	2.10 (±0.07) × 10^9	2.22 × 10^{10}	0.09

The standard deviations are given in parentheses.

polar solvents, quenching by Py is mostly diffusion-controlled. In polar solvents like acetonitrile, DMF, and THF, the measured K_q values are much smaller than those in non-polar solvents like n-hexane or n-heptane. From Scheme 1, the flourescence quenching rate constant K_q is given by equation (2).

$$K_q = \frac{K_{i'} K_1}{K_{i'} + K_{-1}} \qquad (2)$$

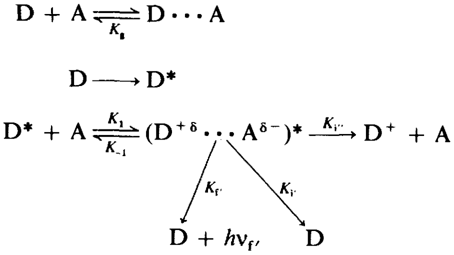
It is known that high stability of the complex favours the forward reaction while the weak complex decomposes easily and the back reaction K_{-1} is large. When $K_{-1} \ll K_{i'}$, $K_q \approx K_1$ *i.e.*, the observed quenching rate constant K_q is nearly equal to the diffusion-controlled rate constant which is actually observed in non-polar solvents. From equation (2), when $K_{-1} \gg K_{i'}$, K_q is less than K_1, the diffusion-controlled value which is observed in polar aprotic solvents like acetonitrile, DMF, and THF. Probably the hydrogen-bonding interaction is hindered due to solvation of both donor and acceptor molecules in these polar solvents and consequently only a very weak complex is formed. But in the polar protic solvents MeOH and EtOH which are capable of forming hydrogen-bonding chains, the quenching efficiency K_q/K_d is higher than the efficiency in polar aprotic solvents (Table 2).

Since in non-polar and polar aprotic solvents Py quenches the fluorescence of ATHN but does not affect the fluorescence of DMTHN, it may be inferred that the hydrogen-bonding interaction is crucial for quenching to occur. Some further interesting features are observed when EtOH and MeOH are used as solvents. Contrary to expectation, the fluorescence intensity of both ATHN and DMTHN in these solvents falls off rapidly in the presence of Py. When EtOH or MeOH is added to the binary solution of DMTHN–benzene, the intensity of fluorescence of DMTHN is not quenched. Also, in binary solutions in pure EtOH or MeOH, no fall off of the emission intensity is observed for both ATHN and DMTHN. Thus, the deactivation of the excited molecules should involve transfer of energy to Py which plays the role of quencher. It seems that some interaction other than hydrogen bonding must be considered. Presumably, the hydrogen-bonding chain in EtOH or MeOH assists the interaction of ATHN and DMTHN with Py, leading to radiationless transfer of excitation energy causing quenching of fluorescence of the two fluorescers. A possible mechanism may conceivably be resonance-type transfer[35–37] from the fluorescer to the acceptor Py. Particularly for DMTHN, which does not enter into hydrogen bonding with Py, this transfer mechanism will be instrumental in quenching the fluorescence. In the case of ATHN, this process will contribute and lead to a larger value for the quenching efficiency. The fluorescence transitions of ATHN and DMTHN, and the absorptive transitions of Py, are in energy ranges suitable for such a transfer of excitation energy. A further point of interest is that no quenching is produced in the fluorescence emission of DMTHN in EtOH when TEA is the quencher, because the energy level is unfavourable for resonance transfer.

In ATHN–TEA systems, the K_q values calculated by using Stern–Volmer equation are somewhat smaller than diffusion-controlled rates in different solvents (Table 3). In the case of ATHN–Py systems solvent polarity does not play an important role whereas in the case of ATHN–TEA solvent polarity clearly enhances quenching as can be seen from Table 3. So the quenching mechanism must be different for TEA as quencher and Scheme 2 can be adopted. The observed quenching rate constant K_q can be written as in equation (3). In non-polar

$$K_q = \frac{K_1(K_{i'} + K_{i''})}{K_{-1} + (K_{i'} + K_{i''})} \qquad (3)$$

solvents $K_{i''}$ is zero but in polar solvents it has a non-zero value. The numerator increases more rapidly with $K_{i''}$ than the demonimator and consequently K_q increases. Since $K_{i''}$ is directly related to the dielectric constant of the solvent, K_q is expected to



Scheme 2.

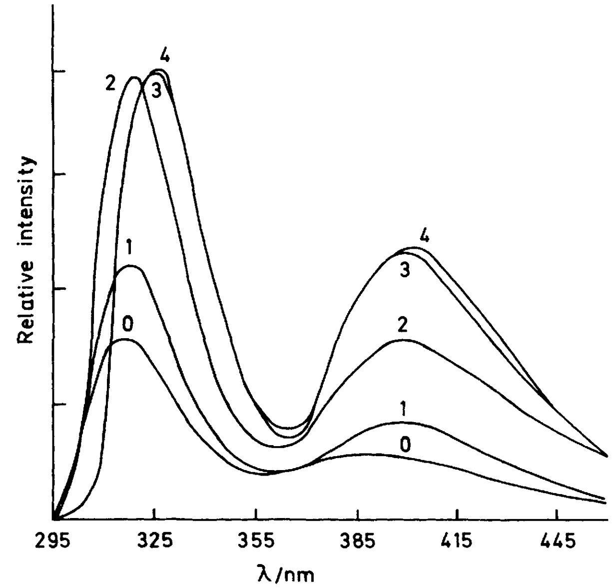


Figure 5. Emission spectra of ATHN at 77 K (2.86 × 10^{-4}M in MCH) (excitation wavelength 290 nm). Concentration (M) of TEA in 0, 0; 1, 3.55 × 10^{-4}; 2, 1.8 × 10^{-3}; 3, 3.57 × 10^{-1}; 4, 7.1 × 10^{-1}

Table 3. Bimolecular fluorescence quenching rate constants K_q of ATHN–TEA in different solvents at 300 K

Solvent	ε	τ/ns	K_q/l mol^{-1} s^{-1}
n-Hexane	1.89	15	2.5 × 10^7
EtOH	24.55	9	4.0 × 10^7
Acetonitrile	37.50	18	~ 10^8

Table 4. Effect of Py and TEA on the fluorescence spectrum of DMTHN in different solvents at 300 K

Solvent	ε	PY	TEA
Benzene	2.28	No quenching	No quenching
EtOH	24.55	quenching	No quenching
Acetonitrile	37.50	No quenching	No quenching

Table 5. Effect of pyridine and TEA on the various fluorescence and phosphorescence photophysical parameters of ATHN at 77 K (Φ_f 0.14, Φ_T 0.86[a]) (C_{ATHN} 2.86 × 10^{-4}M; C_{PY} 1.24 × 10^{-3}M; C_{TEA} 1.8 × 10^{-3}M)

System	I_F/I_F^0	I_P/I_P^0	τ_P/s	τ'_P/s	β	α[b]	K'_i/K_i	$K_{P'}/K_P$	$K_{iP'}/K_{iP}$	Φ_T	Φ'_T	Φ_P	Φ'_P
ATHN + MCH	1	1	2.08 ± 0.05		1	1	1	1	1	0.86		0.08	
ATHN + MCH + Py	0.42 (±0.02)	0.47 (±0.02)		0.68 (±0.05)	0.48 (±0.01)	0.224 (±0.007)	4.37 (±0.33)	0.87 (±0.04)	3.301 (±0.004)		0.964 (±0.003)		0.025 (±0.001)
ATHN + MCH + TEA	1.34 (±0.07)	1.56 (±0.03)		2.94 (±0.05)	0.21 (±0.01)	0.321 (±0.006)	0.61 (±0.06)	1.41 (±0.06)	0.636 (±0.006)		0.79 (±0.02)		0.146 (±0.004)

[a] Considering $\Phi_f + \Phi_T = 1$[39]. [b] $\alpha/\beta = I_P/I_P^0$. Standard deviations are in parentheses.

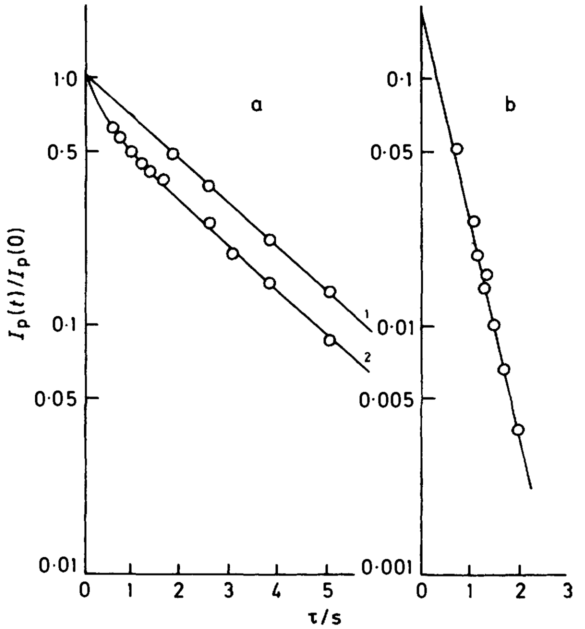


Figure 6. a, Phosphorescence decay functions of ATHN (2.86 × 10^{-4}M in MCH) at 77 K, (1) without any perturber, (2) with Py 1.24 × 10^{-3}M. b, Phosphorescence decay functions of ATHN–Py complex in MCH at 77 K

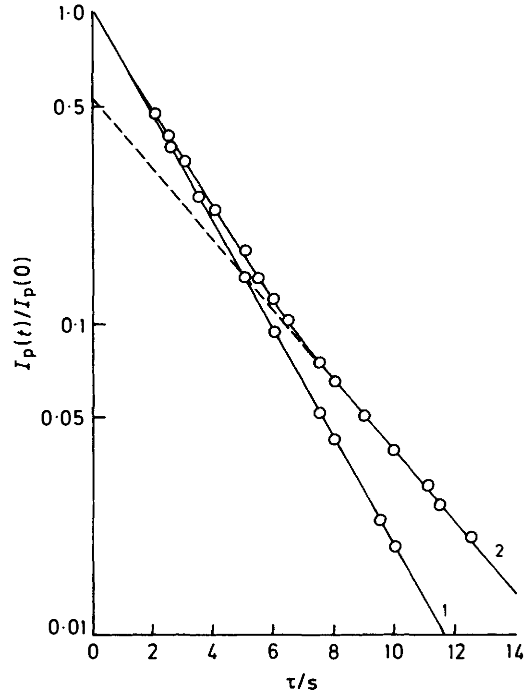


Figure 7. Phosphorescence decay functions of ATHN (2.86 × 10^{-4}M in MCH) at 77 K, (1) without any perturber, (2) with TEA 3.57 × 10^{-1}M

be larger in a solvent of larger dielectric constant. The data are in accord with this expectation. When TEA is used as quencher, a free solvated ion-pair, as shown in Scheme 2, may be formed and formation of ion-pair will be favoured in polar solvents. The dependence of K_q on dielectric constant has been reported by Gebiaki[38] for anthracene. Masuhara *et al.*[26] had observed that in carbazole–amine systems no transient species could be detected with Py as quencher. However, when TEA was used as quencher, proton transfer in the excited state could be observed. On the other hand, fluorescence of DMTHN is not at all affected by TEA in the non-polar solvent benzene, a polar solvent like acetonitrile, and a protic solvent like EtOH (Table 4).

At 77 K the emission intensity of ATHN is intensified slowly with gradual fluorescence red shift with increase in concentration of TEA (Figure 5). The I_p/I_f value is seen not to increase with addition of TEA unlike the case of the other quencher Py.

An examination of phosphorescence decay at 77 K shows that the experimental decay curves for ATHN–MCH–Py and ATHN–MCH–TEA systems are non-exponential tending to become linear in semi-log plot, with passage of time (Figure 6a and 7). In the former system (Figure 6a), the linear portion of the decay curve is similar to 'free' ATHN phosphorescence decay. Subtraction of the exponential decay from the non-exponential decay in the case of complexation of ATHN with Py yields a decay curve (Figure 6b) for which a phosphorescence lifetime of 0.68 s is calculated. This is lower than the lifetime of 'free' ATHN molecule in 'neutral' solvents, which is *ca.* 2.08 s so that depletion of triplet state of ATHN on complexation with Py is somewhat more rapid. In the other case of solution in TEA which does not have a conjugate π-electron system like Py the long-lived portion of the decay component does not correspond to free ATHN decay curve (Figure 7) and a lifetime of 3.89 s is obtained for the complex between ATHN in the triplet state and TEA. The phosphorescence intensity which is composed of two exponential decays (Figures 6 and 7) may be represented by equation (4).[24]

$$I_P(t)/I_P(0) = \beta e^{-t/\tau_P} + (1 - \beta)e^{-t/\tau_P'} \qquad (4)$$

$I_P(0)$ and $I_P(t)$ denote stationary-state and time-dependent phosphorescence intensity.

In Figures 6 and 7, $I_P(t)/I_P(0)$ is plotted as a semi-logarithm curve against time. The values of β were obtained from the extrapolation of the long-lived portion of the phosphorescence decay curves to zero time. The photophysical parameters given in Table 5 are derived for both Py and TEA systems from the relations used by Lessard and Durocher.[24]

From Table 5 it is seen that as Py is added to the binary mixture of ATHN–MCH the i.s.c. rate ($K_{i'}/K_i$) and consequently triplet yield ($\Phi_{T'}$) increases. The radiative rate constant $K_{P'}/K_P$ decreases while the non-radiative rate $K_{iP'}/K_{ip}$ increases as a result of which phosphorescence intensity is lowered. With addition of TEA to ATHN–MCH mixture the ratio $K_{i'}/K_i$ and triplet yield ($\Phi_{T'}$) decreases relative to the magnitude of the corresponding quantities in the free molecule. Contrary to the case of Py, the radiative rate $K_{P'}/K_P$ increases while $K_{iP'}/K_{iP}$ decreases, and the phosphorescence intensity is enhanced.

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