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Excimer fluorescence from acridine and diaza-heterocyclic hydrocarbons in non-polar media at low temperatures

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Abstract

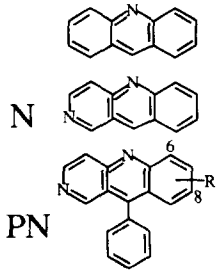
The fluorescence of excited acridine, benzo[b][1,6]naphthyridine (N), 10-phenyl-benzo[b][1,6]naphthyridine (PN) and a series of 6- and 8-substituted derivatives was studied by stationary and transient techniques in two non-polar solvents: methylcyclohexane and a mixture of 2,2′-dimethylbutane and *n*-pentane. The emission spectrum observed at 77 K for all the investigated compounds using concentrations of 0.03–0.5 mM, in comparison with the fluorescence spectrum at room temperature, is dominated by a red-shifted structureless band with a maximum above 500 nm, i.e. 500 nm for acridine, 515 nm for N and 540 nm for parent PN. Owing to the lifetimes of 40–80 ns and the concentration dependence of the two bands, this new emission is attributed to excimer fluorescence. The quantum yields of excimer fluorescence are in the range $\Phi_f^E = 0.01$–0.3, depending on the structure and substituent. Although Φ_f^E is largest at 77 K, the excimer fluorescence can be examined in most cases up to approximately 200 K. This shows that a glass is not necessary for excimer formation. The photophysical processes, the effect of temperature and some mechanistic consequences are discussed.

Keywords: Acridine; Excimer; Fluorescence; Heteroaromatics

1. Introduction

The properties of the excited states of acridine [1–6] and 9-phenylacridine [7] have been studied under various conditions. These heteroaromatics are of special interest because of the presence of a low-lying n,π singlet state [1–9] and the possibility of various deactivation pathways. They are widely used as photoinitiators for polymerization. A further class of related compounds is represented by diaza analogues, e.g. benzo[b][1,6]naphthyridine (N) and 10-phenyl-benzo[b]-[1,6]naphthyridine (PN) and its derivatives [10,11], which also suit the requirements for potential candidates as photoinitiators for polymerization. PN and a series of 6- and 8-substituted derivatives have previously been investigated in solvents of different polarity at 297 and 77 K [11]. It was shown that the main characteristics of their electronic structure differ slightly from those described for acridine and 9-phenylacridine.

The compounds investigated in this work are shown in Scheme 1. We report the specific photophysical behaviour of these diaza-heterocyclic compounds, as well as that of acridine, in non-polar glasses, i.e. excimer fluorescence. The properties of excimer formation and decay have been discussed for various polyaromatic systems [12–25] and reviewed by Birks [12–14]. It is worth mentioning that extensive studies have been carried out devoted to intramolecular excimer formation [26]. However, little is known about excited complexes of acridines [4,5]. No proof could be found in the literature for excimer formation of heterocyclic compounds in the non-crystalline state, with the exception of 9-aminoacridine hydrochloride in aqueous solution [8].



Scheme 1.

In agreement with the literature data for polyaromatic hydrocarbons, such as naphthalene, anthracene, perylene and pyrene [12–20], the excimer lifetime (τ_f^E) of the investigated

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aza- and diaza-heterocyclic compounds in rigid, non-polar media at 77 K is considerably larger than the lifetime (τ_f^M) of monomer fluorescence in the temperature range 300–77 K. The effect of the presence of a phenyl ring at the 10-position in PN and the effects of donor (CH_3, OCH_3, OC_2H_5) and acceptor (CF_3, Br, Cl, F) substituents in the 6- and 8-positions of PN are examined. A comparison of the spectral properties with those of aromatic hydrocarbons is performed, and the relationship between the monomer and excimer fluorescence of acridine and the diaza-heterocyclic analogues is discussed.

2. Experimental details

PN and 11 derivatives were synthesized from 3-benzoyl-4-chloropyridine by regioselective two-step cyclocondensation with substituted anilines [10]. The PNs, N and acridine were the same as used previously [11]. The solvents (Merck) were distilled, e.g. methylcyclohexane (MCH) and ethanol, or used as received, e.g. cyclohexane and 2,2′-dimethylbutane–*n*-pentane (8 : 3) (abbreviated to D–P). The samples were freshly prepared and measured in 4 mm quartz cells.

The absorption spectra were recorded on a Perkin–Elmer 554 spectrophotometer. Fluorescence measurements were carried out using Fluorolog (for corrected spectra and quantum yields Φ_f) and Perkin–Elmer (LS-5) fluorometers. In various solvents at room temperature the PNs exhibit absorption maxima (long-wavelength band) at 375–411 nm and fluorescence maxima in the 450–500 nm range [1]; the molar absorption coefficients at 353 nm in cyclohexane range from $\varepsilon_{353} = 1.8 \times 10^3\ M^{-1}\ cm^{-1}$ for 8-OCH_3-PN to $5.5 \times 10^3\ M^{-1}\ cm^{-1}$ for 6-CF_3-PN and, further, to $9.8 \times 10^3\ M^{-1}\ cm^{-1}$ for acridine. The fluorescence decay measurements at 77 K were carried out as described elsewhere [27]. The measurements of τ_f^E at higher temperatures were carried out using a photolysis set-up with 353 nm laser excitation (without analysing light, limit of resolution was approximately 12 ns); it should be noted that this method is less precise ($\pm 15\%$) than the single-photon counting method ($\pm 5\%$). The Φ_f values were determined using optically matched solutions and 9,10-diphenylanthracene in ethanol ($\Phi_f = 1.0$ at 77 K) as reference; for excimer fluorescence, typical absorbances at 353 nm (A_{353}) in the 4 mm cell were 0.2 or 0.4.

3. Results and discussion

The main spectral characteristics of the PN compounds in several solvents at approximately 300 and 77 K have been discussed previously [11]. The fluorescence quantum yield (Φ_f^M, M denotes monomer) and the lifetime at room temperature are rather small for parent PN, i.e. $\Phi_f^M = 0.003$, 0.03 and 0.02 and $\tau_f^M < 0.2$, 0.3 and 0.2 ns in MCH, acetonitrile and ethanol respectively. These values are very similar for derivatives with electron-accepting substituents, whereas the introduction of an electron-donating substituent leads to an increase in both Φ_f^M and τ_f^M. In addition, these values increase with increasing polarity of the solvent. In polar glasses at 77 K, Φ_f^M increases even further, e.g. 0.2–0.9 in ethanol and butyronitrile. Intersystem crossing is quite substantial throughout, the yield (Φ_{isc}) in acetonitrile at 297 K being in the 0.03–0.4 range; phosphorescence was detected at 77 K; the maxima are typically observed at $\lambda_p = 650$ nm and the lifetimes (τ_p) are in the millisecond range.

Table 1
Fluorescence maxima (in nm) of the monomer and excimer for heterocyclic compounds in non-polar fluid solutions and glasses[a]

Compound/substituent	λ_f^M At 297 K	λ_f^M At 77 K	λ_f^E
Acridine	446	426	498
N	434	425, 450	515
PN	442	427, 445	540
6-CF_3	460	452	485[b]
6-Br	440	458	540
8-Br	440	441	535
6-Cl	446	449	550
8-Cl	440	440	542
6-F	443	443	558
6-CH_3	442	445	525
8-CH_3	440	448	540
6-OCH_3	475	450	560
8-OCH_3	444	444	533
8-OC_2H_5	444	446	540

[a] $\lambda_{exc} = 350$–390 nm; the values are practically the same in D–P and MCH.
[b] No spectral distinction between the two bands in MCH.

3.1. Monomer and excimer fluorescence of parent PN and derivatives at 77 K

The fluorescence spectra of all investigated PNs at low concentrations (0.013 mM or less, corresponding to $A_{353} \leq 0.08$ in a 1 cm cell) are structured in D–P at 77 K and exhibit a maximum around 450 nm. In some cases, λ_f^M is slightly blue or red shifted when compared with that at room temperature. With increasing concentration of a given PN, a new structureless emission band with a maximum (λ_f^E) in the 520–560 nm region appears at 77 K (Table 1). Examples are shown in Fig. 1 for parent PN and in Fig. 2 for 8-Br-PN. For concentrations higher than 0.08 mM ($A_{353} \geq 0.5$), the new red-shifted band dominates the emission spectrum. Similar results were obtained in MCH. The radiative process cannot be due to phosphorescence because of energetic and kinetic reasons. For instance, the values for the phosphorescence maximum and lifetime of PN in ethanol at 77 K are $\lambda_p = 650$ nm and $\tau_p = 20$ ms respectively [11]. Thus the new structureless emission band with a maximum in the 520–560 nm region is attributed to excimer fluorescence.

The addition of small amounts of ethanol (0.1 M) to a given PN (0.2 mM) in D–P leads to a decrease in the intensity of the excimer fluorescence and an increase in the intensity

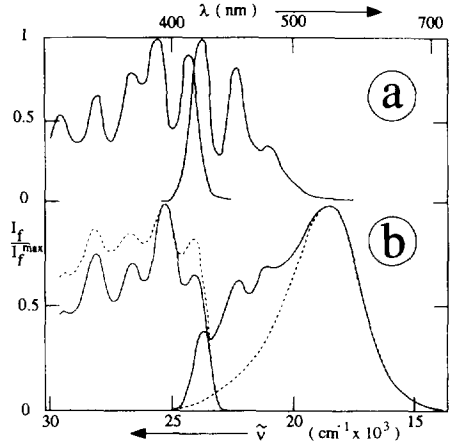


Fig. 1. Fluorescence excitation (left) and emission (right, $\lambda_{exc}=353$ nm) spectra of PN at 77 K in MCH (0.02 mM; $\lambda_{obs}=450$ nm) (a) and in D–P (0.12 and 0.45 mM, full and broken lines respectively; $\lambda_{obs}=580$ nm) (b).

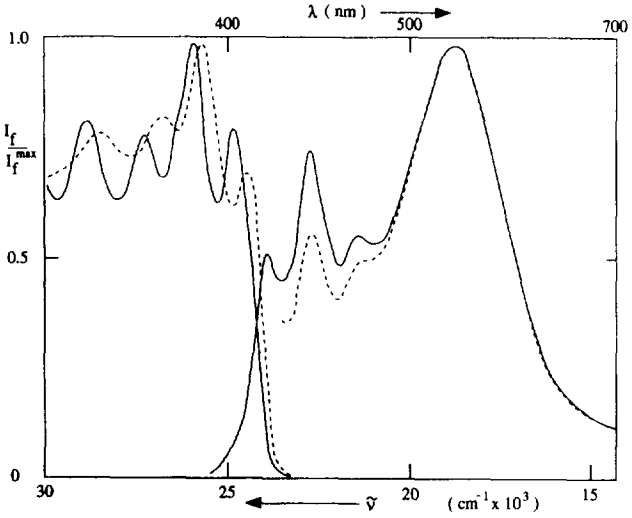


Fig. 2. Fluorescence excitation (left) and emission (right) spectra of 8-Br-PN (0.15 mM) in D–P at 77 K: full lines, $\lambda_{exc}=353$ nm, $\lambda_{obs}=450$ nm; broken lines, $\lambda_{exc}=410$ nm, $\lambda_{obs}=550$ nm.

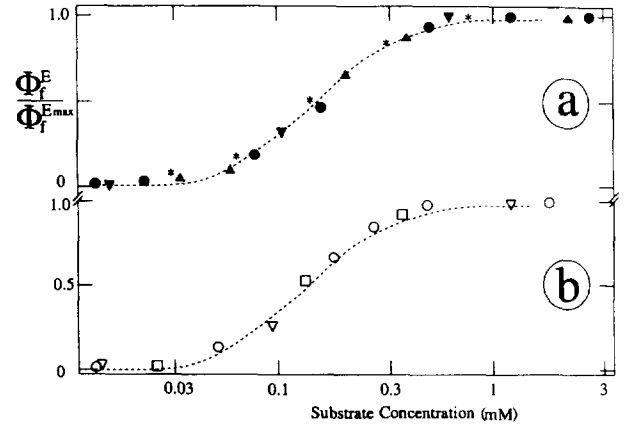


Fig. 3. Plots of the relative quantum yield of excimer fluorescence as a function of concentration at 77 K in D–P (a) and MCH (b) for PN (circles), 6-CH_3-PN (▲), 8-OC_2H_5-PN (▽, ▼), N (*) and acridine (□); $\lambda_{exc}=353$ nm.

of the monomer fluorescence. The monomer is the only fluorescent species at higher ethanol concentrations (above 1 M). The effect of PN concentration on the excimer fluorescence is illustrated in Fig. 3(a) and (b) for several PNs in D–P and MCH respectively. The excimer fluorescence is not detectable with steady state methods for concentrations of less than 0.01 mM but, with increasing [PN], the intensity of the excimer fluorescence increases and, correspondingly, that of the monomer fluorescence decreases.

The decay of the excimer fluorescence observed in the two rigid matrices (using $\lambda_{exc}=353$ nm and $\lambda_{obs}=615$ nm) can be reasonably fitted by a monoexponential curve in most cases. The lifetime of parent PN in D–P is $\tau_f^E=53$ ns and the lifetimes of most of the derivatives are also in the 40–80 ns range (Table 2). The exceptions, due to the internal heavy atom effect, are the two bromine compounds with $\tau_f^E\approx4.5$ ns. In some cases, e.g. for 6-F-PN or 6-OCH_3-PN, a biexponential fit (with a longer lived component in the 50–90 ns range) is significantly better.

The excitation spectra of both monomer and excimer fluorescence overlap essentially with the absorption spectrum. However, close inspection reveals slightly different excitation spectra on detection at either 450 or 550–600 nm and as a function of concentration. The former effect is illustrated in Fig. 2 for 8-Br-PN. The excitation spectrum of the excimer fluorescence (using $\lambda_{obs}=550$ nm) is slightly red-shifted from that of the monomer fluorescence (using $\lambda_{obs}=450$ nm). For all PNs, a long-wavelength band appears in the excitation spectrum at 77 K which is absent at room temperature. Its intensity decreases with decreasing concentration with respect to the main maximum (Fig. 1(b)). This concentration dependence corresponds to the behaviour of the

Table 2
Characteristic concentration of heterocyclic compounds and lifetime of excimer fluorescence in non-polar glasses at 77 K[a]

Compound/substituent	$[A]_c$ (mM)[b]	τ_f^E (ns)[c]
Acridine	0.12	73 (70)[d]
N	0.14	23/56[e] (55)
PN	0.15	53 (65)
6-CF_3		40 (45)
6-Br	≤0.2	4.8
8-Br	≤0.2	4.4
6-Cl	0.2	42 (45)
8-Cl	0.15	40
6-F	0.15	59
6-CH_3	0.2	82 (80)
8-CH_3	≤0.25	72
6-OCH_3	0.2	90 (80)
8-OCH_3	0.2	69 (70)
8-OC_2H_5	≤0.25	72

[a]In aerated solution.
[b]Concentration for which the excimer yield is 50% of the maximum value.
[c]$\lambda_{exc}=353$ nm ($A_{353}=1.0\,cm^{-1}$); $\lambda_{obs}=615$ nm; experimental error, ±5%.
[d]Values in parentheses refer to laser excitation; error, ±15%.
[e]Ratio of amplitudes of the two components, 4 : 6; in the other cases, the short-lived component represents 20% or less.

absorption spectrum, which contains a new peak, centred at the same position as in the excitation spectrum, e.g. for parent PN in D–P at 77 K at 408 nm. Such a red shift in the excitation spectrum has been reported for pyrene in cyclohexane at 77 K [18] and for 9-aminoacridine hydrochloride in aqueous solution at 288 K [8].

The Φ_f^M values of most PNs in non-polar solvents at room temperature are smaller than 0.01 and larger only for the derivatives with OCH_3 and OC_2H_5 substituents. The total quantum yield of fluorescence in D–P at 77 K can be separated into Φ_f^M and Φ_f^E; the former values are very low, whereas the latter depend significantly on the nature of the substituent in the 6- or 8-position, showing roughly the same trend as Φ_f^M at 300 K (Table 3). For parent PN, no remarkable effects on the spectral characteristics, Φ_f values and decay kinetics were detected in aerated or argon-saturated solutions, i.e. the results at 77 K are independent of the oxygen concentration. Φ_f^E varies from approximately 0.01 for the two Br-PNs to 0.1 for PN and, further, to 0.2–0.4 for derivatives with electron-donating substituents (Table 3). In MCH, due to the 50% lower concentrations, the contributions from the monomer and excimer fluorescence are larger and smaller respectively, with the same tendency regarding the substituent effect.

3.2. Monomer and excimer fluorescence observed for related heterocyclic compounds

A similar spectral behaviour, $\lambda_f^E = 515$ nm, $\Phi_f^E = 0.14$ and $\tau_f^E = 56$ ns (longer lived component), was observed for N (0.05 mM or more) in D–P at 77 K (Fig. 4(a) and Tables 1–3). This may be compared with $\lambda_f^M = 450$ nm and $\Phi_f^M = 0.003$ at room temperature. For acridine in D–P at 77 K, the excimer fluorescence has a maximum at 498 nm (Fig. 4(b)) and a lifetime of approximately 70 ns (Table 2). It is well known from the literature that acridine, because of the strong deactivation processes through the $S_2(n,\pi^*)$ level, shows little fluorescence in hydrocarbons at 300 K (see, for example, Refs. [2,6]).

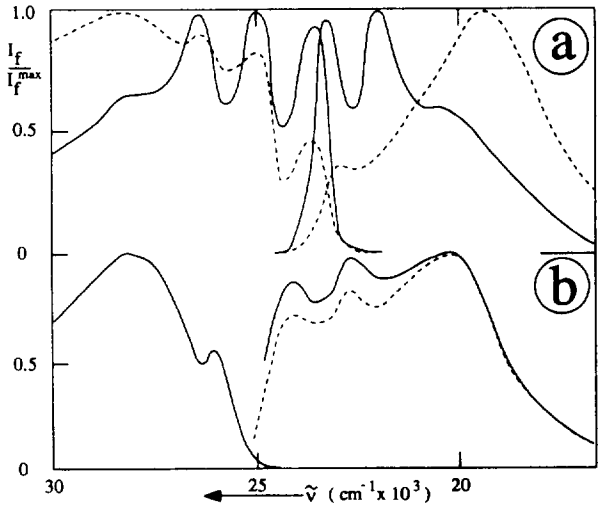


Fig. 4. Fluorescence excitation (left) and emission (right) spectra in D–P at 77 K of N (0.08 and 0.30 mM, full and broken lines respectively) (a) and acridine (0.15 mM; full lines refer to $\lambda_{exc} = 353$ nm and $\lambda_{obs} = 450$ nm and broken line to $\lambda_{exc} = 400$ nm) (b).

The main features of the excimer in the PN series described above were also observed for N and acridine at 77 K, e.g. increase in the excimer fluorescence intensity with increasing concentration (Fig. 3) and a lack of dependence of the results on the oxygen concentration. In the presence of small amounts of ethanol, the intensity of the excimer fluorescence of acridine or N decreases and, as for the PNs, in frozen ethanol solutions, only the short-lived structured monomer

Table 3
Quantum yields of monomer and excimer fluorescence for heterocyclic compounds in non-polar fluid solutions and glasses[a]

Compound/substituent	Φ_f^M		Φ_f^M	Φ_f^E	
	At 297 K		At 77 K		
Acridine			≈0.002	0.03	(0.04)[b,c]
N			<0.003	0.14	(0.12)
PN	0.003	(0.003)[b]	<0.003	0.12	(0.04)
6-CF_3	0.002	(<0.001)	<0.01	<0.1	(<0.06)
6-Br	<0.001	(0.001)	≈0.001	0.007	(0.008)
8-Br	0.009	(0.007)	0.001	0.012	(0.01)
6-Cl	0.01	(0.01)	0.03	0.07	(0.04)
8-Cl	0.006	(0.006)	≈0.005	0.1	(0.06)
6-F	0.03	(0.03)	≈0.005	0.1	(0.04)
6-CH_3	0.012	(0.016)	≈0.03	0.29	(0.15)
8-CH_3	0.009	(0.008)	≈0.01	0.23	(0.12)
6-OCH_3	0.2	(0.2)	<0.01	0.13	(0.09)
8-OCH_3	0.3	(0.3)	<0.02	0.36	(0.14)
8-OC_2H_5	0.3	(0.3)	<0.02	0.29	(0.20)

[a]In aerated D–P solution, concentration of 0.01 mM or less at 297 K and 0.1–0.5 mM (corresponding to $A_{353} = 1.0$ cm^{-1}) at 77 K; $\lambda_{exc} = 353$ nm. Experimental errors of ±15% and ±40% for $\Phi_f > 0.02$ and $\Phi_f < 0.02$ respectively.
[b]Values in parentheses refer to MCH.
[c]Concentration, 0.05–0.25 mM ($A_{353} = 0.5$ cm^{-1}).

fluorescence remains. Qualitatively the same effects as in D–P or MCH were found in cyclohexane which is non-transparent at 77 K.

3.3. Comparison of the excimer fluorescence data with the literature

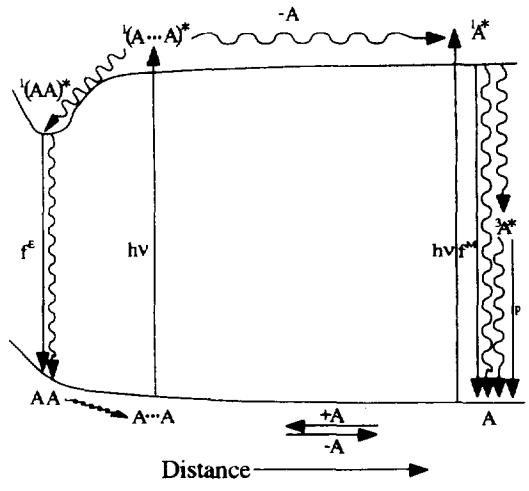
Excimer fluorescence in a rigid cyclohexane matrix has been described in the literature for several polyaromatic hydrocarbons, e.g. pyrene, perylene, anthracene, 1,2-benzanthracene and naphthalene and their derivatives [12–20]. The characteristics of the observed excimers of the investigated heterocyclic compounds are, to a certain extent, similar. Emission in the region above 415 nm has been observed for acridine in frozen *n*-octane at 77 K, but no experimental details or comments on this phenomenon have been given [5]. Crystalline modifications of acridine have been reported to show excimer emission with a maximum at 500 nm and a lifetime of 80 ns [4]. Our experimental data for acridine (e.g. above 0.1 mM) clearly show that, similar to the diaza analogues N and PN, the emission in frozen non-polar matrices is due to excimer fluorescence. An excimer emission has also been reported for acridine crystals at 298 K [4]; for the "type III modification", where acridine pairs are antiparallel within a distance of 0.349 nm, fluorescence properties were found, e.g. a maximum at 500 nm and a 40 ns decay component, which are similar to those presented here. A further relevant case reported in the literature is 9-aminoacridine hydrochloride in aqueous solution, where the excimer fluorescence at 288 K has a maximum at 555 nm [8].

For all the investigated PNs, the lifetime of the excimer at 77 K is considerably longer (greater than 40 ns, except for the bromine derivatives) than that of the monomer fluorescence. Generally, the monomer lifetimes are 1 ns or shorter at both 300 and 77 K (except for $R \equiv OCH_3$ and OC_2H_5) [11], e.g. for 6-F-PN in D–P, $\tau_f^E = 59$ ns, whereas $\tau_f^M \leq 1$ ns at 300–77 K. These excimer and monomer lifetimes are in the same ranges as the corresponding data for perylene (77 and 5 ns) [16,21], anthracene (215 and 9 ns) [16] and pyrene in cyclohexane at 77 K ($\tau_f^E = 200$ ns) [21]. It has been concluded [16] that this significant difference in the fluorescence lifetimes indicates that the transition from the excimer is symmetry forbidden. The excimers of pyrene and anthracene have an overlapping sandwich configuration [12,20]. For the heterocyclic compounds under investigation, we also assume sandwich-type complexes.

3.4. Mechanistic considerations

Excimer fluorescence in fluid solution at ambient temperature is due to a diffusion process between two molecules in the S_1 and S_0 states [12–14]

$$^1A^* + A \rightarrow {}^1(AA)^* \xrightarrow{h\nu^E} 2A \quad (1)$$



Scheme 2.

Obviously, in rigid glasses, Eq. (1) cannot be the origin of excimer formation because the monomer lifetime is much too short with respect to the time required for the formation of a collision complex. The formation of a complex in glassy media at low temperature must take place in the ground state

$$A + A \rightleftarrows A...A \quad (2)$$

The establishment of equilibrium (2) may occur during dissolution or freezing. The ground state complex A...A is probably loosely bound; some indication is given by the red shift of the absorption spectrum at 77 K relative to that at 200–300 K (see above). Its existence can be concluded from the concentration dependence of the monomer vs. excimer fluorescence (Fig. 3). On excitation of A...A, a reorientation in the S_1 state is suggested

$$A...A \xrightarrow{h\nu} {}^1(A...A)^* \quad (3)$$

This leads with a certain probability to the excimer

$$^1(A...A)^* \rightarrow {}^1(AA)^* \quad (4)$$

which should have a smaller average distance between the two molecules, typical for excimers of aromatic compounds, e.g. 3–4 Å [12–15]. This process on the S_1 coordinate should lower the energy significantly, giving rise to the red-shifted fluorescence in the repulsive ground state

$$^1(AA)^* \xrightarrow{h\nu^E} AA \rightarrow A...A \quad (5)$$

The disappearance of the excimer fluorescence on addition of ethanol to the PNs in non-polar glasses is tentatively ascribed to a shift in equilibrium (2), rendering ground state complexation unfavourable.

The proposed reaction mechanism is shown in Scheme 2. With regard to the radiationless processes, only intersystem crossing from the monomer is known, but it is conceivable that the same could occur from the excited complex. An indication for this is that the triplet yield of parent PN in D–P at 100 K, i.e. under conditions of efficient excimer fluores-

cence, is not very different (not shown) from that in acetonitrile [12] or MCH at room temperature.

In the simplest case, i.e. when all processes in the excited states are independent of the concentration, the concentration dependence of Φ_f^M and Φ_f^E can be described by Eq. (6a) and (6b)

$$\Phi_f^M/\Phi_f^{M_0} = 1/(1+[A]/[A]_c) \quad (6a)$$

$$\Phi_f^E/\Phi_f^{E_{max}} = [A]/([A]+[A]_c) \quad (6b)$$

where $\Phi_f^{M_0}$ is the yield of the monomer when sufficiently diluted, $\Phi_f^{E_{max}}$ is the maximum yield of the excimer and $[A]_c$ is a characteristic concentration (half-concentration), i.e. where $\Phi_f^E = 0.5 \times \Phi_f^{E_{max}}$ (Table 2).

3.5. Effects of substitution and solvent polarity

The Φ_f^E values for acridine and N are difficult to interpret without further information on the competing processes. Obviously, the introduction of a second nitrogen atom in the π system increases Φ_f^E (0.14 vs. 0.03 for N vs. acridine). On the other hand, the presence of a phenyl ring in the 10-position has only a small effect on Φ_f^E (0.1 vs. 0.14 for PN vs. N).

The results for the PNs indicate that the nature of the substituent and the surrounding medium have a pronounced influence on the yield and lifetime of the excimer fluorescence. With regard to the properties of the monomer, it has been suggested, based essentially on spectroscopic data for 9-phenylacridine [7], that the energy of the fluorescing $S_1(\pi,\pi^*)$ state is increased for PN as the solvent polarity is decreased [11]. Thus the energy difference between the $S_1(\pi,\pi^*)$ and the lowest lying (n,π^*) singlet states is at a minimum in non-polar solvents. The competing radiationless processes involving the $S_2(n,\pi^*)$ state are substantial at ambient temperature and Φ_f^M is small (Table 3). At low temperatures, the thermal radiationless deactivation step becomes less efficient and thus Φ_f is enhanced and largest at 77 K [11].

The gap between the $S_1(\pi,\pi^*)$ and the $S_2(n,\pi^*)$ states also increases with increasing electron-donating strength of the substituent in the 6- or 8-position for PN [11]. This leads to a suppression of the competing radiationless processes via $S_2(n,\pi^*)$ and explains the substantial Φ_f^M values even in non-polar solvents at room temperature. Electron-donating substituents increase not only Φ_f^M [11], but also, significantly, Φ_f^E (Table 3), indicating that, for the monomer as well as for the excimer, the competing radiationless processes are less important than for parent PN. Once the requirements for excimer formation at 77 K are fulfilled, Φ_f^M is small (Table 3), i.e. even when the $S_1(\pi,\pi^*)$–$S_2(n,\pi^*)$ gap is larger ($R \equiv OCH_3$ or OC_2H_5), excimer fluorescence competes efficiently.

The rather small Φ_f^E values for the two bromo derivatives can be ascribed to efficient intersystem crossing, as described in the literature for polyaromatic hydrocarbons with heavy atom substituents [12–14]. This is confirmed by the short excimer lifetime in these two cases (Table 2). Interestingly, the position (6- or 8-) of the substituent, which has a very strong influence on the quantum yield of photoreduction at room temperature in the presence of H-atom donors such as 2-propanol [11], has only a small effect on Φ_f^M and Φ_f^E (Table 3). The photoreduction, at least in those cases in which the quantum yield is large, i.e. substitution in the 8-position, is suggested to involve a non-emitting $^1(n,\pi)^*$ state.

There are cases in the literature where the radiationless deactivation processes of the excimer are activated and their rate constants increase at room temperature with increasing solvent polarity [12]. Therefore, in the high temperature range, i.e. for the "dynamic" case (Eq. (1)), the excimer lifetime may decrease with increasing polarity because the radiationless processes from $^1(AA)^*$ are enhanced in polar media. In the low temperature range, i.e. for the "static" case (Eqs. (2)–(5)), however, other parameters are relevant, e.g. the nature of the solvent governs equilibrium (2). We suggest that, for a given concentration, this ground state equilibrium is shifted to the monomer side with increasing solvent polarity (the amount may be different for each compound).

3.6. Effects of temperature

Relatively little information is available in the literature regarding the specific effect of temperature on Φ_f^E and τ_f^E [12–14,22–25]. The long-wavelength peak in the absorption and fluorescence excitation spectra is not only dependent on the concentration at 77 K, but is also dependent on the temperature. The absorption peak increases significantly with decreasing temperature below 130 K; this was observed for PN in both media, for several derivatives, N and acridine. We propose that, under these conditions, absorption occurs at least partly from the A...A species. Similar features have been reported for perylene [22].

In order to obtain information concerning the requirements of the rigidity of the glass for excimer fluorescence, we measured the influence of temperature on the spectra and both τ_f^E and Φ_f^E. The excimer fluorescence can be recorded over a broad temperature range, e.g. up to approximately 200 K for PNs in D–P or MCH and for N and acridine in D–P (Fig. 5). This indicates that, although the lifetime for a given compound is longest at 77 K, a glass is not a prerequisite for excimer formation. Indeed, as long as the temperature is sufficiently low (e.g. lower than 200 K for acridine in D–P under our conditions), there is only a gradual change on going from highly viscous to fluid MCH or D–P. For 6-CF_3-PN in MCH, which is the only case where no definite separation between the monomer and excimer bands was observed at 77 K, the long lifetime (Fig. 5(b)) clearly reveals the excimer origin of the fluorescence.

Despite the failure to record excimer fluorescence at room temperature in various cases tested, it is possible to extend the range for the spectral method quite substantially. The effect of temperature on Φ_f^E is illustrated in Fig. 6 for PN and for several derivatives and in the inset of Fig. 6 for N and

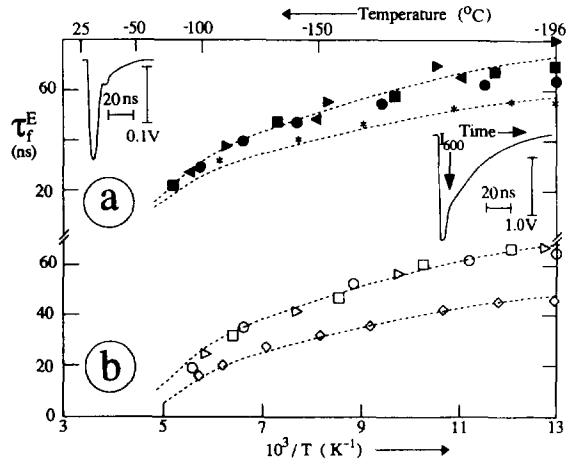


Fig. 5. Plots of the excimer lifetime as a function of $1/T$ in D–P (a) and MCH (b) for PN (circles), 6-CF_3-PN (diamonds), 6-OCH_3-PN (◁,▶), 8-OCH_3-PN (◀), N (*) and acridine (squares); λ_{exc} = 353 nm. Inset: excimer decay for PN in D–P at 200 and 77 K (left and right respectively).

acridine. It is interesting to note that the temperature at which Φ_f^E is 50% of the maximum value does not vary strongly with the structure and substituent (Fig. 6); a typical value is 110 K. Concerning the high temperature behaviour, we propose that one of the reasons why no excimer can be detected by the steady state technique is that the excimer fluorescence is hidden under the tail of the monomer band (see Fig. 7).

The processes which reduce the excimer formation compete with Eqs. (2) and (4), and the processes which limit the excimer lifetime compete with Eq. (5). The latter, which selectively affect τ_f^E, are rather small, both on changing the substituent at 77 K (Table 2) or by variation of the temperature (Fig. 5). In contrast, all the competing effects act on the steady state measurements which show a larger change with temperature (Fig. 6).

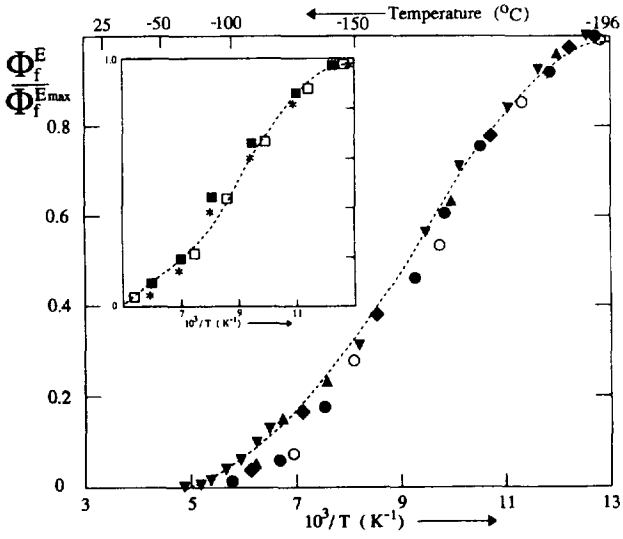


Fig. 6. Plots of the relative quantum yield of excimer fluorescence as a function of $1/T$ in D–P and MCH (filled and open symbols respectively) for PN (circles), 8-Cl-PN (◆diamonds), 6-CH_3-PN (▲) and 8-CH_3-PN (▼); λ_{exc} = 353 nm. Inset: results for N in D–P (*) and acridine (squares).

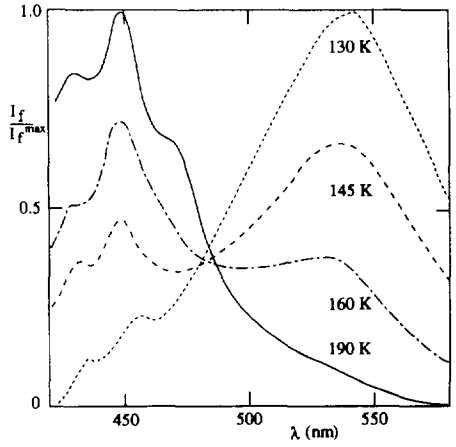


Fig. 7. Fluorescence spectra (non-corrected) for 8-CH_3-PN in D–P at 130, 145, 160 and 190 K.

4. Conclusions

The excimer fluorescence, reported in this work for acridine, benzonaphthyridine, 10-phenyl-benzonaphthyridine and derivatives, shows, in non-polar media, features which are, to a certain extent, similar to those known for polyaromatic hydrocarbon analogues. The specific differences have been discussed and the influence of the environment on the excimer fluorescence has been outlined. The temperature at which the excimer fluorescence of the diaza-heterocyclic compounds can be detected extends from 77 to approximately 200 K, corresponding to a change from a highly viscous glass to a nearly fluid solvent.

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References

[1] A. Kellmann and L. Lindqvist, in A.B. Zahlan (ed.), *The Triplet State*, Cambridge University Press, New York, 1967, p. 439. A. Kellmann, *J. Phys. Chem., 81* (1977) 1195.
[2] D.G. Whitten and Y.J. Lee, *J. Am. Chem. Soc., 93* (1971) 961.
[3] K. Kasama, K. Kikuchi, Y. Nishida and H. Kokubun, *J. Phys. Chem., 85* (1981) 4148. K. Kasama, K. Kikuchi, K. Uji-ie, S.-A. Yamamoto and H. Kokubun, *J. Phys. Chem., 86* (1982) 4733. N. Periasamy, *Chem. Phys. Lett., 99* (1983) 322. K. Kikuchi, K. Kasama, A. Kanemoto, K. Uji-ie and H. Kokobun, *J. Chem. Phys., 89* (1985) 868.
[4] B.P. Clarke, J.M. Thomas and J.O. Williams, *Chem. Phys. Lett., 35* (1975) 251 J.O. Williams and B.P. Clarke, *J. Chem. Soc., Faraday Trans. 1, 73* (1977) 514.
[5] L.A. Klimova, G. Nersesova, V. Prozorovskaja and G. Ter-Sarkisyan, *Theor. Eksp. Khim., 12* (1976) 233.

[6] K. Kasama, K. Kikuchi, S. Yamamoto, K. Uji-ie, Y. Nishida and H. Kokobun, *J. Phys. Chem., 85* (1981) 1291.
[7] K. Kikuchi, Y. Hattori, C. Sato and H. Kokubun, *J. Phys. Chem., 94* (1990) 4039.
[8] P. Gangola, N.J. Joshi and D.D. Pant, *Chem. Phys. Lett., 80* (1981) 418.
[9] K. Kikuchi, H. Kokobun and M. Koizumi, *Bull. Chem. Soc. Jpn., 44* (1971) 1527. H. Groppeterper and F. Dörr, *Ber. Bunsenges. Phys. Chem., 67* (1963) 46.
[10] M.G. Hicks, G. Jones and D.C. York, *J. Chem. Soc., Perkin Trans. 1* (1988) 69.
[11] H. Görner, P. Nikolov and R. Radinov, *J. Photochem. Photobiol. A: Chem., 85* (1995) 23.
[12] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970, p. 301.
[13] J.B. Birks, in J.B. Birks (ed.), *Organic Molecular Photophysics*, Wiley, London, 1975, p. 494. J.B. Birks, *Progr. React. Kinet., 5* (1970) 181.
[14] J.B. Birks, in M. Gordon and W.R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975, p. 39.
[15] Th. Förster, *Angew. Chem. Int. Ed. Engl., 81* (1969) 333.
[16] R. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley Interscience, New York, 1969. N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra*, Marcel Dekker, New York, 1970.
[17] E.A. Chandross, *J. Chem. Phys., 43* (1965) 4175.
[18] J. Ferguson, *J. Chem. Phys., 43* (1965) 306.
[19] J. Ferguson, *J. Chem. Phys., 44* (1966) 2677.
[20] E.A. Chandross, J. Ferguson and E.G. McRae, *J. Chem. Phys., 45* (1966) 3546.
[21] N. Mataga, Y. Torihashi and Y. Ota, *Chem. Phys. Lett., 1* (1967) 385.
[22] P.C. Johnson and H.W. Offen, *Chem. Phys. Lett., 18* (1973) 258.
[23] M.D. Lumb and I.H. Munro, *Proc. R. Soc. London, Ser. A, 280* (1964) 289. J.B. Aladekomo and J.B. Birks, *Proc. R. Soc. London, Ser. A, 284* (1965) 551. R.L. Barnes and J.B. Birks, *Proc. R. Soc. London, Ser. A, 291* (1966) 570.
[24] J.B. Birks and A.J.H. Alwattar, *Chem. Phys. Lett., 11* (1971) 89.
[25] R.B. Cundall and L.C. Pereira, *Chem. Phys. Lett., 15* (1972) 383.
[26] M. Van der Auweraer, A. Gilbert and F. de Schryver, *J. Am. Chem. Soc., 102* (1980) 4007. K.A. Zachariasse, G. Duveneck and R. Busse, *J. Am. Chem. Soc., 106* (1984) 1045. K.A. Zachariasse, R. Busse, G. Duveneck and W. Kühnle, *J. Photochem. Photobiol. A: Chem., 28* (1985) 237. K.A. Zachariasse, W. Kühnle, U. Leinhos, P. Reynders and G. Striker, *J. Phys. Chem., 95* (1991) 5476, and references cited therein.
[27] K. Hildenbrand and C. Nicolau, *Biochim. Biophys. Acta, 553* (1979) 365.