

Excited state properties of 10-phenyl-benzo[b][1,6]naphthyridines in solution

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Abstract

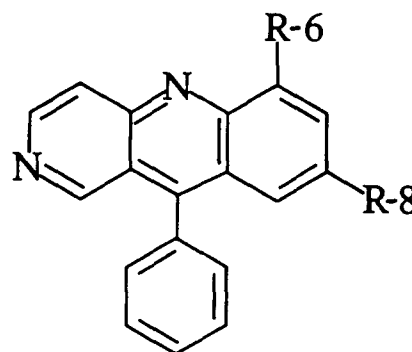
The relaxation pathways of excited 10-phenyl-benzo[b][1,6]naphthyridine (PN), an analogue of acridine, and a series of 12 derivatives (R-6: CF₃, Br, Cl, F, CH₃, OCH₃; R-8: SO₂NH₂, Br, Cl, CH₃, OCH₃, OC₂H₅) were studied in several solvents at 297 and 77 K. Fluorescence, intersystem crossing and photodecomposition processes were examined by stationary and transient techniques. At 297 K, the quantum yield of fluorescence (Φ_f) increases significantly with solvent polarity and with electron-donating substitution, intersystem crossing partly compensating this effect. The triplet is characterized by T-T absorption at 297 and 77 K and by phosphorescence at 77 K. Generally, intersystem crossing is less sensitive to environment and substitution than Φ_f . Photodecomposition is negligible for PNs in acetonitrile at room temperature, but effective for PN and most of its R-8 derivatives in alcohols, e.g. 2-propanol, ethanol or methanol. This is ascribed to photoreduction, involving a spectroscopically hidden, probably (n, π^*) singlet state.

Keywords: Excited state; 10-Phenyl-benzo[b][1,6]naphthyridines

1. Introduction

The photophysical and photochemical properties of acridines depend strongly on the nature of the solvent [1–12]. The quantum yields of fluorescence (Φ_f) and intersystem crossing (Φ_{isc}) of acridine are sensitive to changes in solvent polarity, temperature, substitution and the presence of hydrogen-atom donors. For example, $\Phi_{isc} \approx 0.3$ for acridine in methanol, but $\Phi_{isc} \approx 1$ in benzene [7]. Substituents, such as a phenyl group in the 9 position of acridine, lead to interesting effects. Some photochemical properties of 9-phenylacridine, e.g. the electronic structure and the deactivation processes, have been reported recently [12]. Among the diaza-aromatics, e.g. phenazine or quinoxaline, the importance of (n, π) states for the fluorescence and phosphorescence behaviour has been discussed [13–15].

The compounds under examination are the parent 10-phenyl-benzo[b][1,6]naphthyridine (PN), an aza analogue of acridine, and several 6- and 8-substituted derivatives.



The photophysical and photochemical properties of PNs have not been studied previously. Acridines and 9-phenylacridine are widely used as photoinitiators of polymerization processes [16–18]. Their structural analogues may also be of interest for such applications. The introduction of substituents in PN provides a method to vary strongly the efficiencies of radiative vs. non-radiative and photophysical vs. photochemical relaxation pathways with little alteration of their spectroscopic behaviour.

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2. Experimental details

PN and its derivatives were synthesized from 3-benzoyl-4-chloropyridine by regioselective two-step cyclocondensation with substituted anilines [19–23]. The first step is nucleophilic substitution of the halogen in 3-benzoyl-4-chloropyridine with anilines. The resulting 4-anilino-3-benzoylpyridines were obtained in dimethylformamide at room temperature (yield, 80%–98%). The second step is cyclization of the 4-anilino-3-benzoylpyridines in phenylphosphoric acid at 100 °C; the yields after 10 min were 40%–85%. Benzo[b][1,6]-naphthyridine (N) was synthesized according to Ref. [23]. Acridine was sublimated under vacuum; 4-methylanisole (MA) was used as received (EGA); butyronitrile (Fluka) was distilled; the other solvents (Merck) were distilled (methylcyclohexane (MCH), 2-methyltetrahydrofuran (MTHF), methanol and ethanol) or used as received (acetonitrile (MeCN, Uvasol quality), benzene (EGA, gold label), 2-propanol and tert-butanol).

The absorption spectra were recorded on a Perkin-Elmer 554 spectrophotometer; for irradiation a 200 W Hg lamp and interference filters (for 366 or 405 nm) were used [24]. Potassium iron(III)oxalate was used as actinometer [25]. Fluorescence decay measurements were carried out as described elsewhere [26]. Fluorescence and phosphorescence measurements were carried out using Fluorolog and Perkin-Elmer fluorimeters (LS-5). The procedures, e.g. determination of Φ_f using 9,10-diphenylanthracene in ethanol ($\Phi_f=1.0$ at 77 K) as standard, have been described elsewhere [27,28]. Laser excitation at 248 or 353 nm was performed using an excimer laser and Nd laser respectively [24,29].

The triplet yield (Φ_T) of the PNs in acetonitrile was measured using acridine (A) in benzene as reference

$$\Phi_T(\text{PN}) = \Phi_T(\text{A}) \times \{s(\text{PN}) \times \epsilon(\text{A}) / s(\text{A}) \times \epsilon(\text{PN})\}$$

where $s(\text{PN})$ and $s(\text{A})$ are the slopes of the linear dependences of the strength of the transient absorption (ΔA) at the maximum (λ_T) and end of the 353 nm pulse as a function of the incident laser intensity for PN and acridine respectively. For acridine, $\epsilon(\text{A}) = 2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 442 nm and $\Phi_T(\text{A}) = 0.73$ were used [5,30,31]. The solutions had the same absorption ($A_{353} = 0.8 \text{ cm}^{-1}$) and $\epsilon(\text{PN}) = 2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at λ_T was assumed for PN ($\lambda_T = 445 \text{ nm}$) and, due to the similarity of the T-T absorption spectra, for the derivatives also, i.e. $\epsilon(\text{A})/\epsilon(\text{PN}) = 1$.

3. Results

3.1. Absorption and photolysis

The PNs exhibit two main absorption bands with maxima around 250 and 390 nm. The latter is structured,

showing several peaks (Fig. 1). The molar extinction coefficients of the 13 compounds studied in acetonitrile at $\lambda_a = 247\text{--}263 \text{ nm}$ (second maximum) and $376\text{--}411 \text{ nm}$ (first maximum) are compiled in Table 1. The ϵ values are similar in most cases and smaller at both λ_a bands for $\text{R} \equiv 8\text{-SO}_2\text{NH}_2$ and 6-OCH_3 .

To study the role of solvent polarity on λ_a , the spectra were also recorded in MCH and ethanol. The respective values for the first maximum of PN itself are 372 and

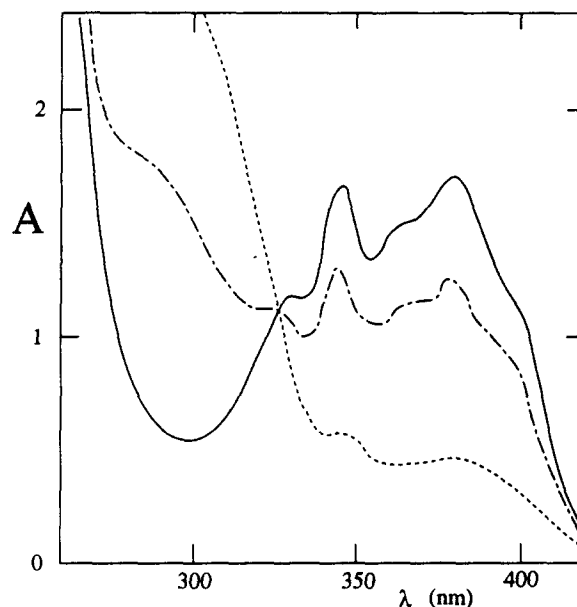


Fig. 1. Absorption spectra of PN in argon-saturated 2-propanol at 297 K prior to (full line) and after 366 nm irradiation ($t=1 \text{ min}$ (---) and 3 min (-.-)).

Table 1
Absorption maxima and molar extinction coefficients of PNs^a

| Substituent | λ_a (nm) | $\epsilon \times 10^3$ ($\text{M}^{-1} \text{ cm}^{-1}$) | λ_a (nm) | $\epsilon \times 10^3$ ($\text{M}^{-1} \text{ cm}^{-1}$) |
|-----------------------------------|---------------------|---|---------------------|---|
| 8-SO ₂ NH ₂ | 256 | 66.3 | 376 | 4.29 |
| 6-CF ₃ | 247 | 88.6 | 379 | 6.60 |
| 6-Br | 256 | 85.9 | 389 | 6.96 |
| 8-Br | 256 | 100 | 382 | 6.55 |
| 6-Cl | 254 | 90.8 | 388 | 6.95 |
| 8-Cl | 235 | 102 | 381 | 6.48 |
| 6-F | 252 | 87.1 | 384 | 5.15 |
| H | 250 | 93.5 | 379 | 5.98 |
| 6-CH ₃ | 256 | 87.0 | 384 | 5.72 |
| 8-CH ₃ | 254 | 100 | 382 | 6.14 |
| 6-OCH ₃ | 263 | 62.0 | 399 | 5.03 |
| 8-OCH ₃ | 260 | 82.5 | 409 | 6.35 |
| 8-OC ₂ H ₅ | 260 | 83.4 | 411 | 6.39 |

^aIn acetonitrile at room temperature.

376 nm. For electron-donating substituents, the solvent shift is similar or smaller, while in MCH, for electron-accepting substituents, a blue shift is observed of typically 5–8 nm compared with polar solvents. For comparison, $\lambda_a = 342$ and 345 nm for N in MCH and ethanol respectively.

Irradiation at 366 or 405 nm of parent PN in acetonitrile has virtually no chemical effect, corresponding to a quantum yield of decomposition $\Phi(-\text{PN})$ (i.e. of bleaching in the 350–420 nm range) of smaller than 10^{-3} . However, when the inert solvents (benzene or acetonitrile) are replaced by 2-propanol, photobleaching is significant (Fig. 1). $\Phi(-\text{PN})$ was obtained from the initially linear dependence of the logarithm of the absorbance at 390 nm (A_{390}) vs. the fluence (Fig. 2). A change in irradiation wavelength (λ_{irr}) from 366 to 405 nm has virtually no effect on $\Phi(-\text{PN})$.

Values of $\Phi(-\text{PN})$ are compiled in Table 2 for the PNs in several solvents. Remarkably, in 2-propanol, ethanol or methanol, $\Phi(-\text{PN})$ is large for parent PN and most of its 8 derivatives (with the exception of OCH_3 and OC_2H_5), but small for the 6 derivatives. For PN and the 8- SO_2NH_2 , 8-Br, 8-Cl and 8- CH_3 derivatives, $\Phi(-\text{PN})$ is much smaller in tert-butanol. Much smaller quantum yields of photobleaching in tert-butanol than in 2-propanol have also been reported for acridine [5].

A plot of $1/\Phi(-\text{PN})$ as a function of the inverse 2-propanol concentration in argon-saturated acetonitrile at room temperature is shown in Fig. 3 for PN-8-Cl, i.e. for a derivative with large $\Phi(-\text{PN})$. From the linear dependence, an intercept to slope value of 0.17 M^{-1} is obtained. In order to study the dependence of $\Phi(-\text{PN})$ on the concentration of a hydrogen-atom donor which is not an alcohol, PN-8-Cl in argon-saturated acetonitrile at room temperature in the presence of MA was irradiated at 366 nm. A plot of $1/\Phi(-\text{PN})$ as a function of the inverse MA concentration is shown

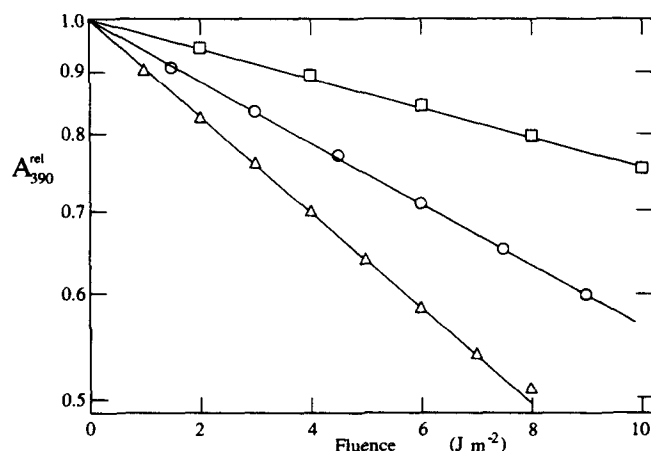


Fig. 2. Plots of $\log A_{390}$ as a function of the fluence at 366 nm for PN (O), PN-8-Cl (Δ) and PN-8- CH_3 (\square) in argon-saturated 2-propanol.

Table 2
Quantum yields of decomposition of PNs^a

| Substituent | $\Phi(-\text{PN}) \times 10^2$ | | | | |
|-----------------------------|--------------------------------|------|------|-----------|------|
| | 2-Propanol | EtOH | MeOH | tert-BuOH | MeCN |
| 8- SO_2NH_2 | 33 | 30 | 25 | | <0.2 |
| 6- CF_3 | 0.05 | <0.5 | | | |
| 6-Br | 0.03 | 0.3 | | | |
| 8-Br | 34 | 32 | 22 | 6.5 | <0.3 |
| 6-Cl | 1.2 | 2 | | | |
| 8-Cl | 32 | 30 | 19 | 5.8 | 0.13 |
| 6-F | 5.4 | 4.1 | | | |
| H | 20 | 19 | 8.6 | 2.7 | 0.07 |
| H ^b | 19 | | 8 | | 0.07 |
| 6- CH_3 | 0.16 | <1 | | | |
| 8- CH_3 | 10 | 9.1 | 5.2 | | |
| 6- OCH_3 | 0.2 | <0.3 | | | |
| 8- OCH_3 | 0.2 | <0.3 | | | |

^aIn argon-saturated solution at room temperature, $\lambda_{\text{irr}} = 366 \text{ nm}$.

^bUsing $\lambda_{\text{irr}} = 405 \text{ nm}$.

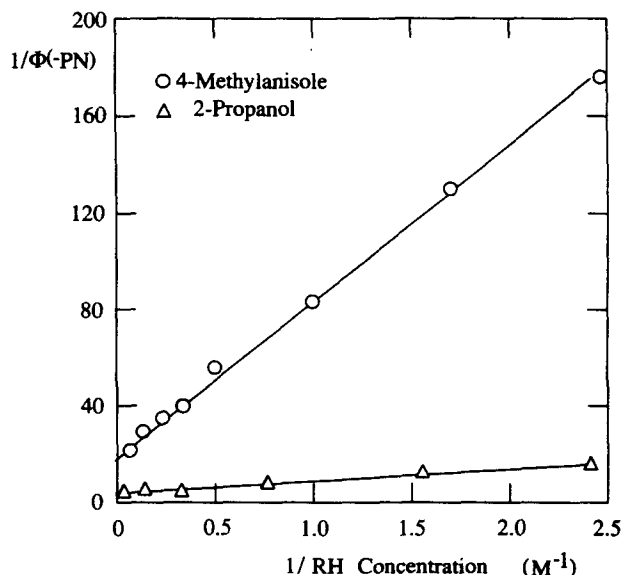


Fig. 3. Plots of $1/\Phi(-\text{PN})$ as a function of the inverse MA (O) and 2-propanol (Δ) concentrations for PN-8-Cl in argon-saturated acetonitrile ($\lambda_{\text{irr}} = 366 \text{ nm}$).

in Fig. 3. An intercept to slope value of 0.26 M^{-1} is obtained from the almost linear dependence of $1/\Phi(-\text{PN})$ vs. $1/[\text{MA}]$.

3.2. Emission properties

3.2.1. Fluorescence spectra

The fluorescence spectrum of parent PN in MCH at room temperature has a maximum (λ_f) at 440 nm; λ_f is similar in MTHF (Fig. 4(a)) and acetonitrile (or butyronitrile), examples of slightly and strongly polar solvents respectively, but red shifted by 18 nm in ethanol (Fig. 4(b)). In MCH, substitution by electron-accepting or electron-donating groups has little effect (Table 3).

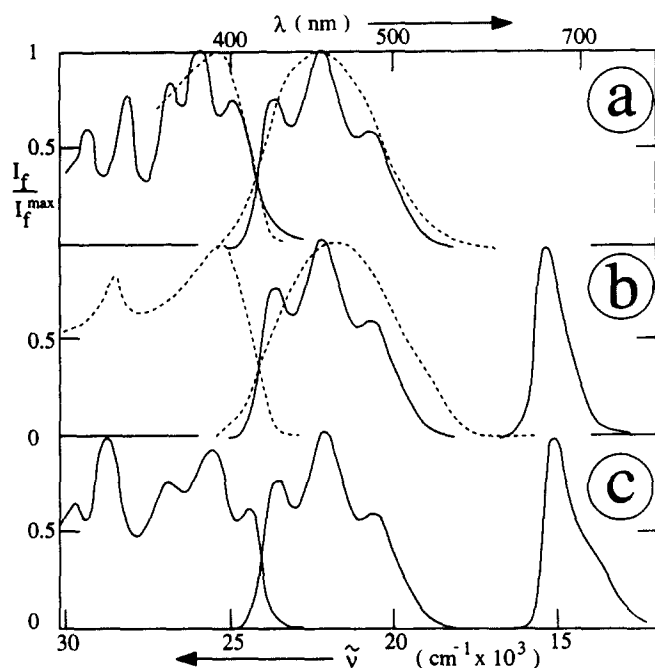


Fig. 4. Fluorescence excitation (left, $\lambda_f = 480$ nm) and emission (mid, $\lambda_{exc} = 390$ nm) and phosphorescence spectra (right): (a) PN in MTHF; (b) PN in ethanol; (c) PN-8-Br in ethanol; at 297 K (broken lines) and 77 K (full lines).

On going from non-polar to polar solvents, λ_f of the PN derivatives is red shifted. This effect is strongest (about 40 nm) for $R \equiv OCH_3$ and OC_2H_5 .

In slightly and strongly polar glasses at 77 K (MTHF, butyronitrile and ethanol), the fluorescence spectrum is structured with similar λ_f (in the 440 nm region) as at 297 K (Figs. 4(a) and 4(b)); λ_f of some derivatives ($R \equiv 8-SO_2NH_2$, 6-F or 6- OCH_3) is blue shifted (typically 20–40 nm) compared with the room temperature values.

The fluorescence excitation spectra in fluid solution are similar to the absorption spectra. This is in line with the independence of the fluorescence spectra of λ_{exc} (in the range 320–400 nm). At 77 K, the excitation spectra are slightly red shifted, an effect which is common for many aromatic compounds.

3.2.2. Fluorescence quantum yield

For the parent compound at room temperature, Φ_f is small (0.003) in MCH and MTHF and increases in ethanol (0.02) and MeCN (0.03). Somewhat larger values were found for derivatives with moderately polar groups (6-Br, 8-Br or 6- CF_3) (Table 4). In a given solvent, Φ_f shows an increasing trend on substitution with electron donors, the values being largest for $R \equiv 6-OCH_3$, 8- OCH_3 and 8- OC_2H_5 . In these cases, Φ_f is also substantial in non-polar solvents. The presence of oxygen reduces the fluorescence intensity in those cases where Φ_f is larger than about 0.05; for example, the ratio of the intensities in the absence of oxygen and in air-saturated (oxygen-saturated) ethanol is 1.2 (1.8) for PN-8- OCH_3 . On the other hand, at 77 K, oxygen has virtually no effect on Φ_f (e.g. for PN in ethanol).

In polar glasses at 77 K, Φ_f is 0.2 or larger throughout, and close to unity for $R \equiv 6-OCH_3$, 8- OCH_3 and 8- OC_2H_5 (Table 4). The values are in all cases larger than at 297 K and the largest increases in Φ_f result for $R \equiv 6-Br$, 8-Br, 6- CF_3 and 8- SO_2NH_2 . In MTHF the tendency is similar. A comparison of the fluorescence properties of PN and N shows close similarities, e.g. for N in ethanol, $\lambda_f = 440$ and 430 nm and $\Phi_f = 0.015$ and 0.65 at 297 and 77 K respectively.

To compare the results for the photoreduction in the presence of MA with those of fluorescence quench-

Table 3
Fluorescence maxima of PNs in fluid solutions and glasses^a

| Substituent | MCH ^b | MTHF ^b | MeCN ^b | EtOH ^b | MTHF ^{c,d} | EtOH ^c |
|---------------|------------------|-------------------|-------------------|-------------------|---------------------|-------------------|
| 8- SO_2NH_2 | – | 460 | 457 | 462 | 450 | 425, 448, 477 |
| 6- CF_3 | 450 | 460 | 459 | 475 | 444 | 423, 444, 472 |
| 6-Br | 440 | 460 | 462 | 470 | 460 | 435, 460, 488 |
| 8-Br | 440 | 460 | 444 | 454 | 450 | 425, 448, 475 |
| 6-Cl | 446 | 457 | 460 | 470 | 453 | 435, 458, 485 |
| 8-Cl | 440 | – | 444 | 456 | – | 430, 447, 473 |
| 6-F | 443 | 450 | 458 | 466 | 447 | 442, 462, 484 |
| H | 440 | 444 | 444 | 458 | 442 | 428, 450, 480 |
| 6- CH_3 | 442 | 452 | 459 | 467 | 447 | 429, 454, 480 |
| 8- CH_3 | 440 | 450 | 447 | 462 | 446 | 432, 458, 485 |
| 6- OCH_3 | 485 | 490 | 500 | 515 | 490 | 475, 500 |
| 8- OCH_3 | 444 | 458 | 463 | 480 | 450 | 444, 465, 500sh |
| 8- OC_2H_5 | 444 | 460 | 466 | 482 | 454 | 445, 466, 500sh |

^a $\lambda_{exc} = 366$ nm.

^bAt 297 K.

^cAt 77 K.

^dMain peak in MTHF.

Table 4
Quantum yields of fluorescence of PNs in fluid solutions and glasses^a

| Substituent | MCH ^b | MTHF ^b | MeCN ^b | EtOH ^b | MTHF ^c | R'CN ^{c,d} | EtOH ^c |
|-----------------------------------|------------------|-------------------|-------------------|-------------------|-------------------|---------------------|-------------------|
| 8-SO ₂ NH ₂ | | <0.01 | 0.004 | 0.008 | 0.05 | 0.4 | 0.2 |
| 6-CF ₃ | <0.001 | <0.001 | 0.003 | 0.007 | 0.2 | 0.4 | 0.3 |
| 6-Br | <0.001 | 0.001 | 0.004 | 0.01 | 0.3 | 0.3 | 0.3 |
| 8-Br | 0.008 | <0.01 | 0.03 | 0.02 | 0.2 | 0.5 | 0.3 |
| 6-Cl | 0.01 | <0.01 | 0.09 | 0.10 | 0.2 | 0.4 | 0.4 |
| 8-Cl | 0.006 | <0.01 | 0.03 | 0.03 | 0.3 | 0.5 | 0.3 |
| 6-F | 0.03 | 0.03 | 0.13 | 0.12 | 0.5 | 0.6 | 0.2 |
| H | 0.003 | 0.003 | 0.03 | 0.02 | 0.2 | 0.5 | 0.6 |
| 6-CH ₃ | 0.01 | 0.02 | 0.06 | 0.12 | 0.46 | 0.3 | 0.6 |
| 8-CH ₃ | 0.009 | 0.02 | 0.1 | 0.10 | 0.25 | 0.6 | 0.6 |
| 6-OCH ₃ | 0.2 | 0.2 | 0.3 | 0.44 | 0.3 | 0.8 | 0.9 |
| 8-OCH ₃ | 0.3 | 0.2 | 0.4 | 0.66 | 0.25 | 0.9 | 0.9 |
| 8-OC ₂ H ₅ | 0.3 | 0.3 | 0.4 | 0.60 | 0.3 | 0.9 | 0.9 |

^a Φ_f was obtained in aerated solution and corrected for deoxygenated solution, $\lambda_{exc} = 366$ nm.

^bAt 297 K.

^cAt 77 K.

^dButyronitrile, R': CH₃CH₂CH₂.

ing, the fluorescence of PN and PN-8-Cl in argon-saturated acetonitrile at 297 K was studied. In the concentration range below 10 M MA, the fluorescence spectrum does not change. The Stern–Volmer constants, obtained from the linear dependence of $1/\Phi_f$ vs. the MA concentration, are 0.50 and 0.63 M⁻¹ for PN and PN-8-Cl respectively. This corresponds to rate constants for fluorescence quenching of 1.7×10^9 and 1.6×10^9 M⁻¹ s⁻¹ respectively, using the fluorescence lifetimes in Table 5.

Table 5
Fluorescence lifetimes of PNs in fluid solutions and glasses^a

| Substituent | τ_f (ns) | | | |
|-----------------------------------|------------------|-------------------|-------------------|-------------------|
| | MCH ^b | MeCN ^b | EtOH ^b | EtOH ^c |
| 8-SO ₂ NH ₂ | <0.2 | <0.2 | <0.2 | 9 |
| 6-CF ₃ | | <0.2 | <0.2 | |
| 6-Br | | <0.2 | 0.3 | 3/9 ^d |
| 8-Br | | 0.5 | 0.5 | 4/11 ^d |
| 6-Cl | | 2 | 2 | |
| 8-Cl | | 0.4 | 0.6 | |
| 6-F | 0.5 | 4 | 4 | 4/16 ^d |
| H | <0.2 | 0.3 | 0.2 | |
| 6-CH ₃ | | 2 | 3 | |
| 8-CH ₃ | 0.2 | 3 | 3 | |
| 6-OCH ₃ | 1/8 ^d | | | 25 |
| 8-OCH ₃ | 1/8 ^d | 11 | 14 | |
| 8-OC ₂ H ₅ | 1/8 ^d | 12 | 15 | |

^aObserved at 450–480 nm in aerated solution using $\lambda_{exc} = 353$ nm.

^bAt 297 K.

^cAt 77 K.

^dTwo decay components.

3.2.3. Fluorescence decay

The fluorescence decays of the samples in solution at 297 K were fitted by a monoexponential function, except for the methoxy and ethoxy derivatives in MCH where two exponentials were necessary. The reason for the two lifetimes was not revealed; an impurity is unlikely due to the monoexponential decay in acetonitrile and ethanol. The fluorescence lifetime (τ_f) ranges from 0.2 ns or less to 15 ns (Table 5). At 77 K, τ_f of most PNs is significantly longer than at room temperature; a biexponential fit was required for several compounds. (There seems to be no apparent trend for the amplitude ratios.) The possible reason for the two lifetimes in glassy ethanol may be the existence of two non-equilibrated (π , π^*) singlet states, e.g. due to rotamers.

3.2.4. Phosphorescence

For several compounds in MTHF, butyronitrile and ethanol at 77 K, a new weak band appeared with λ_p around 650 nm (Table 6) and an onset at about 630 nm (Figs. 4(b) and 4(c)). For R \equiv 6-Br and 8-Br it was shown that the excitation spectrum at 77 K essentially matches the absorption spectrum at 297 K. This emission is attributed to phosphorescence of PN. This is consistent with the relatively long lifetime; the phosphorescence lifetime (τ_p) is in the 10–20 ms range (Table 6). Owing to the internal heavy atom effect, τ_p (as well as τ_T , see below) is significantly shorter for the two bromo derivatives. In several cases phosphorescence could not be detected in the absence of additives but was observed in the presence of ethyl iodide (3–5 vol.%). Since Φ_T is substantial in fluid solution (Table 7) and is probably only partly reduced in rigid glasses, the main effect of ethyl iodide is suggested to be an increase in the rate

Table 6
Phosphorescence maxima and triplet lifetimes of PNs at 77 K^a

| Substituent | Solvent | λ_p (nm) | τ_p (ms) | τ_T (ms) |
|-----------------------------------|---------------------|---------------------|-------------------------|------------------|
| 8-SO ₂ NH ₂ | MTHF | 636 | 10, $\leq 2^b$ | 15 |
| | EtOH | 635 | 20 | 15 |
| 6-CF ₃ | MTHF | 625 | 20 | 20 |
| | EtOH | 630 | 20 | 20 |
| 6-Br | MTHF | 656 | 0.45, 0.45 ^b | 0.5 |
| 8-Br | MTHF | 655 | 0.45 | 0.5 |
| 6-F | EtOH | 650 ^b | 2 ^b | 40 |
| H | MTHF | 648 | $\leq 2^b$ | 20 |
| | R'CN ^{b,c} | 650 | ≤ 3 | |
| | EtOH | 650 | 20 | 16 |
| 6-CH ₃ | MTHF | 652 ^b | $\leq 2^b$ | 14 |
| 8-CH ₃ | MTHF | 660 ^b | $\leq 3^b$ | 15 |
| 8-OC ₂ H ₅ | EtOH ^b | 656 | ≤ 2 | |

^aIn aerated solution using $\lambda_{irr} = 390$ nm for phosphorescence measurements and in argon-saturated solution using $\lambda_{exc} = 353$ nm for τ_T .

^bIn the presence of 3–5 vol.% ethyl iodide.

^cR': CH₃CH₂CH₂.

Table 7
T–T absorption maxima, triplet lifetimes and yields for PNs at 297 K^a

| Substituent | λ_T (nm) | τ_T^b (μ s) | Φ_T^c |
|-----------------------------------|---------------------|--------------------------|--------------------------|
| 8-SO ₂ NH ₂ | 320, 450 | > 25 (30) ^d | 0.54 (0.32) ^d |
| 6-CF ₃ | < 310, 455 | > 20 (35) | 0.35 |
| 6-Br | 470 | > 20 (25) | 0.39 |
| 8-Br | < 300, 450 | 20 (30) | 0.43 |
| 6-Cl | < 300, 465 | 20 (35) | 0.16 |
| 8-Cl | < 300, 445 | 25 (30) | 0.32 (0.26) |
| 6-F | < 320, 450 | > 25 | 0.09 |
| H | < 300, 445 | 20 (40) | 0.38 (0.26) |
| 6-CH ₃ | < 300, 460 | 20 (40) | 0.27 |
| 8-CH ₃ | < 300, 450 | > 25 (45) | 0.34 |
| 6-OCH ₃ | 460 | > 10 | 0.03 |
| 8-OCH ₃ | 450 | > 10 | 0.04 |
| 8-OC ₂ H ₅ | 450 | > 10 | 0.05 |

^aIn argon-saturated acetonitrile.

^bNot corrected for self-quenching.

^cFor estimation, see Section 2.

^dValues in parentheses refer to 2-propanol.

of the radiative $T_1 \rightarrow S_0$ transition. A consequence of the presence of the heavy atom effect is a strong reduction of τ_p .

3.3. T–T absorption

A transient with two maxima (λ_T), one around 450 nm and the second at 300 nm or below, was observed on laser flash photolysis of PNs in acetonitrile at room temperature (Table 7). On the basis of energy transfer and quenching results (see below), the observed transient is assigned to the triplet state. Examples of the T–T absorption spectra are shown in Fig. 5. The T–T

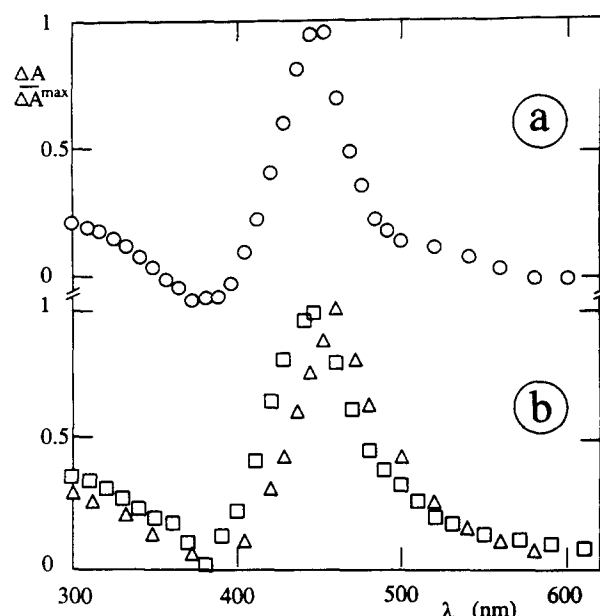


Fig. 5. T–T absorption spectra of PN (a) and PN-6-Br (Δ) and PN-8-CH₃ (\square) (b) in argon-saturated acetonitrile at 297 K, 1 μ s after the 248 nm pulse.

absorption maxima vary only slightly with substituent (Table 7). A change in λ_{exc} from 353 to 248 nm has no discernible effect on the T–T absorption spectrum (in the visible range).

The triplet is formed within the duration of the laser pulse (width, 15–20 ns; the maximum formation at the end of the pulse is distorted by saturation of the photomultiplier in cases of strong fluorescence). The decay of the triplet of any given PN in argon-saturated acetonitrile follows both first- and second-order kinetics. The latter component can be reduced significantly by reducing the laser intensity, as is usually the case with efficient T–T annihilation. Triplet decay in the presence of oxygen is generally first order; a typical rate constant for quenching by oxygen is $k_{ox} = 2 \times 10^9$ M⁻¹ s⁻¹ for PN in acetonitrile. This is comparable with $k_{ox} = 2.41 \times 10^9$ M⁻¹ s⁻¹, reported for acridine in benzene [31].

The triplet yield (Φ_T), obtained from ΔA values in acetonitrile using acridine in benzene as reference (see Section 2), is substantial for PN and several derivatives, but smaller for R \equiv 6-Cl and 6-F, and reduced even further for R \equiv OCH₃ and OC₂H₅ (Table 7).

Essentially the same spectrum, decay kinetics and effect of oxygen were observed for several PNs in 2-propanol at room temperature. In particular, Φ_T , although smaller than in acetonitrile, is not drastically reduced by this alcohol (Table 7). The observation that τ_T has virtually the same value in 2-propanol and acetonitrile excludes the possibility that photobleaching originates from the observed triplet. Such a reaction would also be incompatible with the strong triplet quenching by oxygen (see above) and the rather small effect on $\Phi(-PN)$ (not shown).

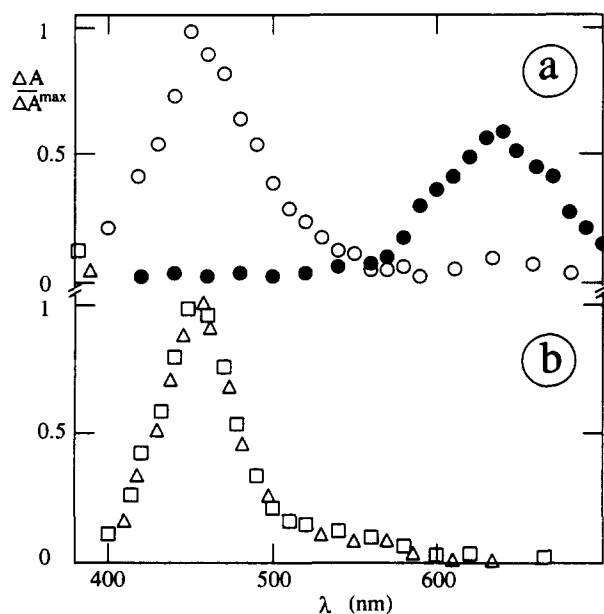


Fig. 6. Triplet absorption spectra of PN-8-OCH₃ in argon-saturated acetonitrile at 297 K under xanthone-sensitized conditions at 0.2 (○) and 1 μs (●) after the pulse (a) and PN (□) and PN-6-Br (Δ) in argon-saturated ethanol at 77 K about 5 μs after the pulse (b) ($\lambda_{\text{exc}} = 353$ nm).

For those cases in which Φ_T is low, energy transfer from sensitizers allowed better observation of the T–T absorption spectra. The example of xanthone-sensitized energy transfer to PN-8-OCH₃ in argon-saturated acetonitrile at room temperature is shown in Fig. 6(a). The ϵ_{TT} value for PN-8-OCH₃ of $2.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, obtained from Fig. 6(a) for about 60% energy transfer using $\epsilon_{TT} = 8.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 620 nm for the xanthone triplet [30], is in reasonable agreement with the above assumption of $2.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for PNs. It should be noted that, for 9-phenylacridine in methanol, a value of $1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ has been reported [12]. (A consequence of a somewhat smaller $\epsilon(\lambda_T)$ value for PNs would be a larger Φ_T value than that given in Table 7.)

The T–T absorption spectra at 77 K (examples shown in Fig. 6(b)) are similar to those obtained at 297 K. However, τ_T in frozen glasses is much longer than in fluid solution (Tables 6 and 7). The triplet lifetimes, obtained from T–T absorption and phosphorescence under otherwise comparable conditions (no heavy atom effect) are the same within experimental error (Table 6).

4. Discussion

4.1. Energy levels

A comparison of our experimental results for PN (Tables 1 and 3) with the literature data for 9-phen-

ylacridine [11], which has the same π -electronic structure, shows a close similarity of the electronic spectra, i.e. the energy of the Franck–Condon transitions, the vibrational structure, the bands and the energy of S_1 are similar. Moreover, the literature data show that the energy of the lowest lying singlet state is virtually the same for acridine [7,11] and 9-phenylacridine [12] and close to that of some diaza compounds [13]. Consequently, we can assume that the energy level diagram of PN resembles that of 9-phenylacridine [12] and that the lowest lying singlet state in PN is of (π, π^*) character in all solvents studied, while the S_2 state is of (n, π^*) character.

The lowest triplet state of 9-phenylacridine also has (π, π^*) character [11]. The phosphorescence spectra of PNs with λ_p in the 625–660 nm range (Table 6) and a 0–0 band of PN at about 630 nm are consistent with a $T_1 \rightarrow S_0$ transition for acridine at 634 nm, corresponding to $E_T = 189 \text{ kJ mol}^{-1}$ [30].

4.2. Calculations

Theoretical PPP-SCF-CI calculations for PN, performed with a standard parametrization [32] and taking into account all singly excited configurations, are in good agreement with the absorption spectrum. The calculated wavelengths of the first nine singlet (π, π^*) transitions are 396, 333, 292, 289, 288, 253, 250, 247 and 237 nm; the corresponding oscillator strengths are 0.589, 0.064, 0.002, 0.087, 0.026, 0.036, 1.0, 0.327 and 0.715 respectively. Accordingly, the lowest wavelength absorption band of PN is due to the overlap of the $S_0 \rightarrow S_1(\pi, \pi^*)$ and $S_0 \rightarrow S_2(\pi, \pi^*)$ transitions, while the strong absorption in the region of about 250 nm is mainly due to the $S_0 \rightarrow S_7(\pi, \pi^*)$ transition.

The calculated dipole moments of PN in the ground and first excited singlet states are 2.46 and 2.27 D respectively. They are comparable with those of the singlet ground state of other aza heterocyclic compounds, e.g. 4.2 D for 3,4-benzquinoline, 4.12 D for quinoline and 4.23 D for pyridazine [33]. The low dipole moments of PN in the ground and first excited singlet states agree well with the small effect of solvent polarity on the absorption and fluorescence maxima (Tables 1 and 3).

4.3. Effects of temperature and solvent polarity

The temperature dependences of Φ_f and Φ_T of 9-phenylacridine in methanol have been ascribed to deactivation processes involving $S_1(\pi, \pi^*) \rightarrow T_3(\pi, \pi^*)$ and $S_1(\pi, \pi^*) \rightarrow S_2(n, \pi^*)$ transitions [12]. Furthermore, the quantum yield of formation of the observed radical (Φ_R), which decreases with decreasing temperature, has been suggested to be due to a reaction starting from the $S_2(n, \pi^*)$ state [12]. The strong increase in

Φ_f with decreasing temperature for PNs, even in “inert” solvents such as acetonitrile at 297 K and butyronitrile at 77 K (Table 4), can in principle be attributed to competition of these activated processes with fluorescence from the $S_1(\pi, \pi^*)$ state. Since the photoreduction of PNs in hydrogen-donating solvents, e.g. MTHF or ethanol, can be neglected at 77 K, the enhancement of Φ_f and τ_f (Tables 4 and 5) with respect to the values at room temperature can be attributed to the freezing out of the activated, radiationless deactivation processes. If we take Φ_T at 297 K (Table 7) as the maximum yield for intersystem crossing at 77 K, the sum of Φ_f and Φ_{isc} in polar media (butyronitrile and ethanol) is close to unity for PNs with electron-donating substituents but lower for PNs with electron-accepting substituents and for PN itself. In the last two cases internal conversion should not be neglected.

For 9-phenylacridine, when the solvent polarity at room temperature is increased or when hydrogen bonds are formed with the nitrogen lone pair, the energy of the lowest lying (n, π^*) singlet state increases [12]. Under these conditions, the energy of the $S_1(\pi, \pi^*)$ state is reduced so that the energy difference between the $S_1(\pi, \pi^*)$ and $S_2(n, \pi^*)$ states increases with increasing polarity. Therefore, the thermal radiationless deactivation step becomes less efficient in polar solvents and thus Φ_f is enhanced. The same pattern, resulting in a larger Φ_f in polar solvents (Table 4), is suggested for PNs.

4.4. Effect of substituents

The absorption spectra of N and PN are similar in shape and the vibrational structure in the 300–400 nm region is the same (Section 3.1). The fluorescence properties are also very similar (Section 3.2.2). Consequently, the phenyl group in position 10 has no decisive influence on the spectral characteristics of PN. For PNs at room temperature, the sum of Φ_f , Φ_T and $\Phi(-PN)$ is generally smaller than unity (Tables 2, 4 and 7), and thus internal conversion probably contributes to a certain extent.

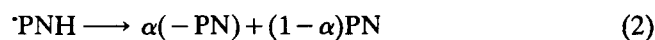
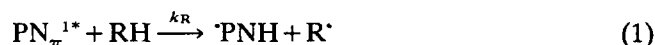
Spectral results, e.g. λ_f at 297 K (Table 3), show that electron-accepting substituents in positions 6 and 8 of PN affect the spectral characteristics only slightly, while electron-donating substituents have a substantial influence. The introduction of an electron-donating substituent leads to an increase in the energy gap between $S_2(n, \pi^*)$ and $S_1(\pi, \pi^*)$ states. As a consequence, with increasing Hammett constant (σ), Φ_f increases (Table 4) and Φ_T decreases (Table 7). However, this view is too simple to describe the complex effects of environment on the relevant yields, especially on $\Phi(-PN)$.

4.5. Photoreduction

The photoreduction of acridine in the presence of hydrogen-atom donors is well known [1–6]. The quantum yields of decomposition of acridine in 2-propanol and methanol at room temperature are 0.10 [5] and 0.043 [11] respectively. This may be compared with $\Phi_R = 0.17$ for acridine in methanol [11]. The values for 9-phenylacridine in ethanol at room temperature are $\Phi(-PN) = 0.005$ and $\Phi_R = 0.044$ [12]. The reduction products of acridine are diacridane, 9-substituted acridanes and 9,10-dihydroacridine [1,5].

To account for the photoreduction of acridine, Whitten and Lee [5] have suggested that a low-lying, non-emitting (n, π^*) singlet state (rather than the fluorescing singlet state or a triplet state) is involved in the presence of a hydrogen-atom donor. For the photoreduction of PN and its derivatives in the presence of alcohols, it can be presumed, analogously, that hydrogen-atom abstraction in the fluorescing singlet state is not efficient enough. For those cases in which $\Phi(-PN)$ is large, e.g. PN or PN-8-Cl, we would expect significantly smaller Φ_f and τ_f values in ethanol compared with those in acetonitrile. However, in these cases, Φ_f is similar in the two solvents (Table 4). The observed triplet state can also be excluded as the reactive intermediate in the photoreduction of PNs. This follows from the result that the triplet lifetime in 2-propanol is similar to that in acetonitrile or even larger (Table 7). Otherwise we would expect that τ_T would decrease for PN and the 8-derivatives when acetonitrile is replaced by 2-propanol. Moreover, there is virtually no dependence of τ_T on the substitution of PN.

From the linear Stern–Volmer behaviour (see Section 3.2.2), it can be assumed that reaction (1), i.e. quenching of the fluorescence of the PN_{π}^{1*} state by MA (RH), is the main reaction for the photoreduction of PNs



The intermediate acridanyl-type radical ($\cdot PNH$) decomposes with the probability α and restores acridine with the probability $1-\alpha$ (reaction (2)). If reactions (1) and (2) are the only steps for hydrogen-atom abstraction, the effect of decomposition is predicted by

$$\Phi(-PN) = \frac{\alpha \tau_f k_R [RH]}{1 + \tau_f k_R [RH]} \quad (3)$$

where $\tau_f = 1/(k_f + k_{ic} + k_{isc})$ is the lifetime of the fluorescing PN_{π}^{1*} state. The intercept and slope of the plot of $1/\Phi(-PN)$ vs. $1/[RH]$ are given by $1/\alpha$ and $1/(\alpha \tau_f k_R)$ respectively. The experimental intercept to slope ratio of 0.26 M^{-1} from Fig. 3 is markedly smaller than the Stern–Volmer constant $\tau_f k_R$ of 0.63 M^{-1} , obtained

from the fluorescence quenching of PN-8-Cl by MA. This points to a more complicated pattern.

The photoreduction of PNs by alcohols (RH), e.g. 2-propanol, ethanol and methanol, follows a different reaction scheme. For example, fluorescence quenching by ethanol plays no role (Table 4), whereas $\Phi(-\text{PN})$ is substantial for PN and the 8-substituted derivatives (except for R-8 \equiv OCH₃ and OC₂H₅, Table 2). Therefore, in analogy with acridine [5], we postulate the involvement of the non-emitting (n, π^*) singlet state (PN_n^{1*}), i.e. reaction (4), and suggest reaction (5) as the key step for hydrogen-atom abstraction from alcohols



From reaction sequence (4), (5) and (2), it follows that

$$\Phi(-\text{PN}) = \frac{\alpha\tau_f k_n \tau_n k_{R'} [\text{RH}]}{1 + \tau_n k_{R'} [\text{RH}]} \quad (6)$$

where τ_n is the lifetime of the PN_n^{1*} state and $\tau_f = 1/(k_f + k_{ic} + k_{isc} + k_n)$. In this case, the slope and intercept of the plot of $1/\Phi(-\text{PN})$ vs. $1/[\text{RH}]$ are given by $1/(\alpha\tau_f k_n)$ and $1/(\alpha\tau_f k_n \tau_n k_{R'})$ respectively, and the intercept to slope ratio equals $\tau_n k_{R'}$. Using the experimental intercept to slope value of $\tau_n k_{R'} = 0.17 \text{ M}^{-1}$ from Fig. 3 for the photoreduction of PN-8-Cl by 2-propanol and assuming $k_{R'} = k_R = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the lifetime of the PN_n^{1*} state is 0.1 ns.

5. Concluding remarks

The spectroscopic features of PN were found to be close to those of acridine and N, a diaza analogue. The introduction of substituents to PN in the 6 and 8 positions and variation of the environment cause substantial changes in the quantum yields of fluorescence, triplet formation and photoreduction. PN and its 8-substituted derivatives are potential candidates as initiators of polymerization.

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