

Photophysics, Molecular Reorientation in Solution and X-Ray Structure of a New Fluorescent Probe, 1,7-Diazaperylene

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A new fluorescent molecule 1,7-diazaperylene (DP) has been investigated by means of time-resolved and steady-state polarized fluorescence spectroscopy, as well as X-ray spectroscopy. Absorption and fluorescence spectra of DP in solution are similar to those of perylene. However, absorption and fluorescence spectra of 2,8-dimethoxy DP and 2,8-dipentyloxy DP in solution are red-shifted by *ca.* 55 nm relative to perylene. The fluorescence decay of DP is exponential with a lifetime of 5.1 ns in ethanol, 4.9 ns in glycerol and 4.3 ns in paraffin oil. The radiative lifetime in ethanol was calculated to be 6.3 ns for DP, 8.0 ns for 2,8-dimethoxy DP and 7.6 ns for 2,8-dipentyloxy DP. The calculated fluorescence quantum yields of 0.8 for DP and its alkoxy derivatives in ethanol, are in good agreement with those obtained from measurements. The calculated Förster radius is $37.2 \pm 1 \text{ \AA}$ for DP and $41.9 \pm 1 \text{ \AA}$ for its alkoxy derivatives in ethanol. Examining the $S_0 \leftrightarrow S_1$ transition, we obtain a limiting fluorescence anisotropy of $r_0 \approx 0.38$ for DP and its alkoxy derivatives. The rotational rates of DP in paraffin oil and glycerol were compared to that of perylene. In paraffin oil both molecules show an almost identical biexponential decay of the fluorescence anisotropy, which is compatible with a rotational motion like an oblate ellipsoid. The fluorescence anisotropy is monoexponential for DP in glycerol, and DP appears to rotate like a spherical particle while perylene in glycerol appears to rotate like an oblate ellipsoid. Moreover, the rotational diffusion constant, corresponding to rotation about an axis in the aromatic plane (D_{\perp}), is the same for both DP and perylene in glycerol.

Perylene and its derivatives are of interest in various applications and are topics of research as, for example, chemically and light-stable pigments,¹ laser dyes,²⁻⁴ fluorescent solar antennas,⁵ fluorescence immunoassays,⁶ reporter molecules in membrane research,^{7,8} probe molecules in membranes⁹ as well as in the modelling of electronic energy transfer in lipid bilayers.¹⁰

In this article we report on fluorescence spectroscopic studies of a new derivative of perylene, 1,7-diazaperylene (DP; benz[*de*]isoquinolino[1,8-*gh*]quinoline) and two of its derivatives, 2,8-dimethoxy-1,7-diazaperylene and 2,8-dipentyloxy-1,7-diazaperylene. The fluorescence lifetime and quantum yield were determined by means of time-resolved and steady-state fluorescence spectroscopy. From the fluorescence anisotropy of DP in glycerol and paraffin oil we analyse the rotational motions which we compare to results previously obtained for perylene.^{11,12}

The DP molecule has about the same molecular mass as perylene (see Fig. 1) but, owing to the sp^2 hybridization of two nitrogens, these can form hydrogen bonds with protic solvents. Furthermore, the aromatic plane of perylene is probably not planar because of steric repulsion between the hydrogen atoms bound to C-atoms 1 and 12, as well as 6 and

7. Recently, Zannoni and co-workers¹³ reported that the two naphthalene rings of perylene are mutually tilted at an angle of *ca.* 11°. This steric hindrance is eliminated in DP. Hence DP is expected to be a 'planar perylene'.

Experimental

1,7-Diazaperylene and 2,8-dimethoxy-1,7-diazaperylene were synthesized as described in ref. 14.

2,8-Dipentyloxy-1,7-diazaperylene

2,8-Dihydroxy-1,7-diazaperylene disodium salt¹⁴ (1 g; 3 mmol) was dissolved in DMF (100 ml) and after addition of potassium carbonate (2.5 g) and 1-bromopentane (1.7 ml; 10 mmol) heated to 445 K for 3 h and then quenched by the addition of ice water (150 ml) and filtered (0.8 g). The raw material was purified twice by column separation with toluene and silica gel and then recrystallized from toluene. Yield 0.15 g (12%) orange crystals, m.p. 430–431 K; r_f (silica gel/toluene) = 0.84; IR (KBr): ν/cm^{-1} = 3070 (w), 2945 (m), 2927 (m), 2870 (m), 1604 (s), 1581 (s), 1464 (w), 1446 (m), 1431 (m), 1399 (m), 1344 (m), 1319 (s), 1280 (m), 1227 (m), 1151 (s), 1109 (s), 1072 (m), 843 (m), 692 (m). UV (toluene): λ_{max}/nm [$\log(\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1})$] = 437 nm (3.979), 465 (4.348), 488 sh, 496 (4.501); UV ($CHCl_3$): λ_{max}/nm [$\log(\epsilon/l \text{ mol}^{-1} \text{ cm}^{-1})$] = 430 nm sh, 459 (4.297), 488 (4.411). MS (70 eV): m/z (%) = 428 (4.6), 427 (31.5), 426 [M^+] (100), 383 (4.3), 370 (5.1), 369 (16.2), 357 (6.4), 356 (16.9), 327 (3.3), 313 (1.9), 300 (3), 299 (8.9), 287 (6.8), 286 (27.8), 269 (4.8), 259 (3), 258 (15.9), 257 (5.7), 241 (4.5), 230 (7.4), 224 (7.3), 203 (3.5), 91 (2.4), 43 (2.2). $C_{28}H_{30}N_2O_2$ (426.5), calc. C, 78.84%; H, 7.09%; N, 6.57%; found C, 78.85%; H, 7.03%; N, 6.46%.

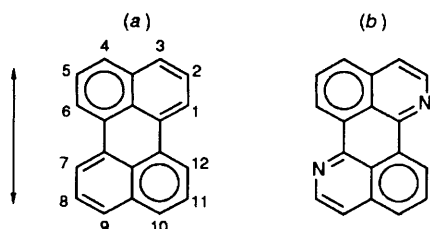


Fig. 1 Structure formulae of perylene (a) and 1,7-diazaperylene (b). The arrow indicates the transition dipole moment of the electronic $S_0 \leftrightarrow S_1$ transition of perylene

Crystal Structures†

Diffraction: ENRAF-Nonius CAD4, radiation: Mo-K α
Monochromator: Highly oriented graphite crystal.

1,7-Diazaperylene

C₁₈H₁₀N₂, $M_r = 254.3$, $a = 8.020$ (2) Å; $b = 6.378$ (2) Å; $c = 12.206$ (3) Å; $\beta = 107.70$ (2)°; volume 594.8 Å³; $Z = 2$, density (calc.) = 1.420 Mg m⁻³, $\mu = 0.79$ cm⁻¹, crystal system monoclinic, space group $P2_1/c$ (no. 14). Data collection: single crystal: $0.2 \times 0.33 \times 0.4$ mm³, ω - 2θ scan, measured 2θ range: 4.0–44.0° in $hk \pm l$, signal width $1.00^\circ \pm 0.35 \tan \theta$, background measurement: stationary counter at beginning and end of scan, each for 25.0% of total scan time. Standard reflexions: three measured every 100 reflexions, index ranges $-8 \leq h \leq 8$, $0 \leq k \leq 6$, $0 \leq l \leq 12$; 774 reflexions collected, 676 independent reflexions ($R_{\text{int}} = 2.77\%$), 592 considered as observed [$I \geq 2\sigma(I)$]. No absorption correction. Solution of structure: direct methods, anisotropic description of the non-hydrogen atoms, isotropic description of the H-atoms, 91 parameters, $R = 0.0752$, $R_w = 0.0689$, $w^{-1} = F + 0.0F^2$, residue of max. and min. electron density (10^6 e pm⁻³) 0.20–0.24; a model with N on the position of C(6) can be excluded ($R = 0.1068$, $R_w = 0.0979$). Further data are given in Table 1.

2,8-Dipentyloxy-1,7-diazaperylene

C₂₈H₃₀N₂O₂ (orange plate), $M_r = 426.6$, $a = 10.894$ (2) Å; $b = 5.005$ (1) Å; $c = 21.430$ (4) Å; $\beta = 104.48$ (2)°; volume = 1131.3 Å³; $Z = 2$, density (calc.) = 1.252 Mg m⁻³, $\mu = 0.73$ cm⁻¹, crystal system monoclinic, space group $P2_1/n$ (no. 14). Data collection: single crystal: $0.13 \times 0.53 \times 0.6$ mm³, ω - 2θ scan, measured 2θ range: 4.0–46.0° in $\pm hkl$, signal width $0.90^\circ + 0.35 \tan \theta$, background measurement: stationary counter at beginning and end of scan, each for 25.0% of total scan time. Standard reflexions: three measured every 100 reflexions, index ranges $0 \leq h \leq 8$, $0 \leq k \leq 4$, $-22 \leq l \leq 22$; 1886 reflexions collected, 1522 independent reflexions ($R_{\text{int}} = 2.77\%$), 1352 considered as observed [$I \geq 2\sigma(I)$]. No absorption correction. Solution of structure: direct methods, anisotropic description of the non-hydrogen atoms, isotropic description of the H-atoms, 145 parameters, $R = 0.0530$, $R_w = 0.0449$, $w^{-1} = F + 0.0F^2$, residue of max. and min. electron density (10^6 e pm⁻³) 0.15–0.21. ω -gemini delta $\omega = 0.29^\circ$.

Table 1 Atomic coordinates ($\times 10^4$) of 1,7-diazaperylene

atom	x	y	z	U (eq)
N(1)	3357 (5)	1251 (7)	1235 (3)	66 (2)
C(1)	3569 (8)	2992 (10)	1897 (5)	76 (3)
C(2)	2238 (9)	4224 (9)	1977 (4)	74 (3)
C(3)	502 (7)	3688 (8)	1350 (4)	56 (2)
C(4)	-973 (10)	4858 (9)	1405 (5)	75 (3)
C(5)	-2589 (9)	4156 (10)	818 (5)	77 (3)
C(6)	-2877 (7)	2368 (8)	159 (4)	58 (2)
C(7)	-1496 (6)	1185 (7)	63 (4)	46 (2)
C(8)	237 (6)	1852 (7)	677 (3)	44 (2)
C(9)	1737 (6)	679 (7)	632 (4)	47 (2)
H(1A)	4738	3377	2337	80
H(2A)	2473	5450	2456	80
H(4A)	-828	6124	1849	80
H(5A)	-3584	4945	865	80
H(6A)	-4054	1941	-239	80

† Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre; further information available from the Editorial office.

Table 2 Atomic coordinates ($\times 10^4$) of 2,8-dipentyloxy-1,7-diazaperylene

N(1)	230 (2)	2380 (5)	3897 (1)	58 (1)
O(1)	-435 (2)	1715 (4)	2800 (1)	72 (1)
C(1)	86 (3)	3678 (6)	4419 (1)	52 (1)
C(2)	-841 (2)	5640 (6)	4401 (1)	50 (1)
C(3)	-957 (2)	6998 (6)	4962 (1)	52 (1)
C(4)	-1867 (3)	8942 (6)	4909 (1)	65 (1)
C(5)	-2688 (3)	9556 (6)	4307 (1)	70 (1)
C(6)	-2604 (3)	8247 (6)	3768 (1)	66 (1)
C(7)	-1684 (3)	6238 (6)	3792 (1)	56 (1)
C(8)	-1532 (3)	4829 (6)	3257 (1)	63 (1)
C(9)	-576 (3)	2995 (6)	3336 (1)	61 (1)
C(10)	548 (3)	-246 (6)	2878 (1)	71 (1)
C(11)	495 (3)	-1386 (6)	2223 (1)	75 (1)
C(12)	982 (3)	496 (7)	1790 (1)	77 (1)
C(13)	929 (3)	-615 (7)	1133 (2)	97 (2)
C(14)	1448 (4)	1182 (8)	716 (1)	115 (2)
H(4A)	-1942	9893	5287	80
H(5A)	-3316	10926	4279	80
H(6A)	-3179	8685	3363	80
H(8A)	-2089	5143	2840	80
H(10A)	422	-1629	3166	80
H(10B)	1360	563	3053	80
H(11A)	-370	-1831	2020	80
H(11B)	981	-3006	2271	80
H(12A)	1846	942	1994	80
H(12B)	495	2115	1743	80
H(13A)	61	-1000	923	80
H(13B)	1388	-2270	1181	80
H(14A)	1379	341	306	80
H(14B)	981	2828	655	80
H(14C)	2324	1543	916	80

Time-resolved Fluorescence Measurements

A PRA 3000 system (Photophysical Research Ass. Inc., Canada) was used for single-photon-counting measurements of the fluorescence decay. The excitation source was a thyratron-gated flash lamp (Model 510C, PRA) filled with deuterium gas and operated at ca. 30 kHz. The excitation wavelengths were selected by interference filters (Omega/Saven AB, Sweden) centred at 409.4 nm (HBW = 13.0 nm) and 497.1 nm (HBW = 31 nm). The fluorescence emission was observed above 470 and 550 nm through long-pass filters Schott KV 470 and KV 550 (Schott, West Germany), respectively. The maximum absorbance of all samples was kept below 0.08.

The time-resolved polarized fluorescence decay curves were measured by repeated collection of photons during 200 s, for each setting of the polarizers. The emission polarizer was fixed and the excitation polarizer rotated periodically. In each experiment the decay curves $F_{\parallel}(t)$ and $F_{\perp}(t)$ were collected. The suffices \parallel and \perp refer to an orientation of the emission polarizer parallel and perpendicular with respect to the excitation polarizer. From these a sum curve

$$S(t) = F_{\parallel}(t) + 2GF_{\perp}(t)$$

and a difference curve

$$D(t) = F_{\parallel}(t) - GF_{\perp}(t)$$

were calculated. The correction factor, G , was obtained by normalizing the total number of counts F_{\parallel} and F_{\perp} collected in $F_{\parallel}(t)$ and $F_{\perp}(t)$, respectively, to the steady-state anisotropy, r_s , as

$$G = (1 - r_s)(1 + 2r_s)F_{\parallel}(F_{\perp})^{-1}$$

The data were analysed with a MINC-11/03 computer using the deconvolution software (DECAY V3.0a, ATROPY V1.0) developed by PRA.

Fluorescence Quantum Yield, Φ

Perylene in ethanol and fluorescein in 0.1 mol dm⁻³ NaOH were used as reference standards with reported quantum yields of 0.92¹⁵⁻¹⁷ and 0.93,¹⁸ respectively. The quantum yield to be determined, Φ_{sample} , was calculated from

$$\Phi_{\text{sample}} = \Phi_{\text{ref}} \frac{F_{\text{ref}}}{F_{\text{sample}}} \frac{1 - \exp(-A_{\text{ref}} \ln 10)}{1 - \exp(-A_{\text{sample}} \ln 10)} \frac{n_{\text{sample}}^2}{n_{\text{ref}}^2}$$

where, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength and n is the refractive index.

Radiative Lifetime, τ_0

The corrected fluorescence $F(\nu)$, of the chromophore dissolved in ethanol was determined at 298 K. Here ν stands for the wavenumber. The molar absorptivity as a function of wavenumber, $\epsilon(\nu)$, was determined from the absorption spectrum recorded on the chromophore solution. From $\epsilon(\nu)$, $F(\nu)$ and the modified Strickler-Berg equation¹⁹

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \frac{\int F(\nu) d\nu}{\int F(\nu) \nu^{-3} d\nu} \int \epsilon(\nu) \nu^{-1} d\nu$$

the radiative lifetime τ_0 is obtained. Since the fluorescence lifetime is known from the time-resolved fluorescence decay, the quantum yield is obtained from $\tau = \phi \tau_0$. The value of ϕ is compared with that determined independently as described above.

Förster Radius

The Förster radius as, defined by Kawski,²⁰ is

$$R_{\text{OF}} = \left| \frac{900 (\ln 10) \langle \kappa^2 \rangle \phi J}{128 \pi^5 n^4 N_A} \right|^{1/6}$$

where

$$J = \int \epsilon(\nu) f(\nu) \nu^{-4} d\nu$$

and

$$f(\nu) = \frac{F(\nu)}{\int F(\nu) d\nu}$$

where N_A and n denote the Avogadro constant and the refractive index of the medium. $\langle \kappa^2 \rangle$ is a mean value of the orientational part of a dipole-dipole interaction. In order to calculate an explicit value on the Förster radius it is convenient to choose $\langle \kappa^2 \rangle = 2/3$ as reference state which corresponds to the mean value for an interaction between rapidly rotating dipoles in a three-dimensional system. This case is often referred to the dynamic limit or the fast case. We denote this Förster radius by R_0 . For ethanol $n = 1.36$.

Results and Discussion

Geometry by Crystal Structure Analysis

The geometry of 1,7-diazaperylene has been examined by crystal structure analysis. 1,7-Diazaperylene crystallizes in two or more modifications. The reported¹⁴ yellow needles have a melting point of 529–530 K and correspond to a metastable modification. Owing to lattice displacements a crystal structure analysis of this modification could not be obtained. However, recrystallization from toluene-acetone

(4 : 1) yields a more stable modification. This modification has a melting point of 537–538 K, an orange colour and it forms crystals suitable for structure analysis. The structure of 1,7-diazaperylene is given in Fig. 2(a). The structure of aromatic systems may be appreciably deformed by lattice forces.²¹ In order to exclude that the planarity of 1,7-diazaperylene is just a consequence of these forces, the crystal structure of the derivative 2,8-dipentyloxy-1,7-diazaperylene was additionally determined and displayed in Fig. 2(b). Both structures confirm the planarity of the aromatic heterocycle.

Spectral and Photophysical Properties

Fig. 3 shows the absorption and fluorescence (corrected) spectra of 1,7-diazaperylene (DP) and 2,8-dimethoxy-1,7-diazaperylene in ethanol. The spectral shapes are similar to that of perylene with its characteristic vibronic structure. However, absorption and fluorescence spectra of DP and its alkoxy derivatives are red-shifted relative to those of perylene by 8 and 55 nm, respectively. The molar absorptivities of the 0–0' vibronic peak are 28 100 ± 200 l mol⁻¹ cm⁻¹ for DP, 29 500 ± 200 l mol⁻¹ cm⁻¹ and 30 350 ± 200 l mol⁻¹ cm⁻¹ for 2,8-dimethoxy DP and 2,8-dipentyloxy DP, respectively, which are to be compared with the corresponding value of 37 270 l mol⁻¹ cm⁻¹ for perylene in ethanol. By using the absorption and fluorescence spectra as well as the modified Strickler-Berg equation we calculate the radiative lifetimes (τ_0) to be 6.3 ns for DP, 8.0 ns for 2,8-dimethoxy DP and 7.6 ns for 2,8-dipentyloxy DP. Time-resolved fluorescence experiments yield monoexponential decays of the photophysics with a lifetime of $\tau = 5.1$ ns for DP and 6.2 ns for the derivatives in ethanol at 298 K. Since the fluorescence quantum yield is given by $\Phi = \tau/\tau_0$ we calculate that $\Phi(\text{DP}) = \Phi(2,8\text{-dipentyloxy DP}) = 0.81$ and $\Phi(2,8\text{-dimethoxy DP}) = 0.78$. Independent measurements of the quantum yield of fluorescence give $\Phi(\text{DP}) = 0.83 \pm 0.05$ and $\Phi(\text{alkoxy-DP}) = 0.80 \pm 0.05$. Note that the samples were not degassed.

The fluorescence lifetime of DP in glycerol and paraffin oil is monoexponential, 4.9 and 4.6 ns, respectively, and independent of temperature in the range 260–305 K as investigated in this work.

The Förster radii of DP and the dialkoxy derivatives of DP in ethanol were found to be 37.2 ± 1 and 41.9 ± 1 Å, respectively. These values are greater than 33.6 ± 0.2 Å reported for 2,5,8,11-tetra-*tert*-butylperylene (TBPe, see ref. 10 and papers cited therein). The greater R_0 values of DP and the dialkoxy derivatives, as compared to that of TBPe, are mainly due to their more efficient overlap between absorption and fluorescence spectra.

Fluorescence Anisotropy

In order to obtain information about the polarization of the electronic transition dipoles of the $S_0 \leftrightarrow S_1$ transition, we examined the fluorescence excitation and emission anisotropies at low temperatures, where rotational motions of the fluorophores can be neglected. Both excitation and emission anisotropies are constant with excitation and emission wavelengths, respectively, which shows that the band corresponds to one direction of the electronic transition dipole moment. The steady-state anisotropy of DP and alkoxy-DP in glycerol approaches a constant value below *ca.* 260 K. This means that indeed the influence of rotational motions is negligible, and that the value of the limiting fluorescence anisotropy, r_0 , is reached. The obtained values of r_0 are 0.375 ± 0.005 for DP and 0.382 ± 0.005 for its derivatives. These values of r_0 are somewhat larger than those found for perylene and its alkyl derivatives,²¹ but they are still significantly smaller than

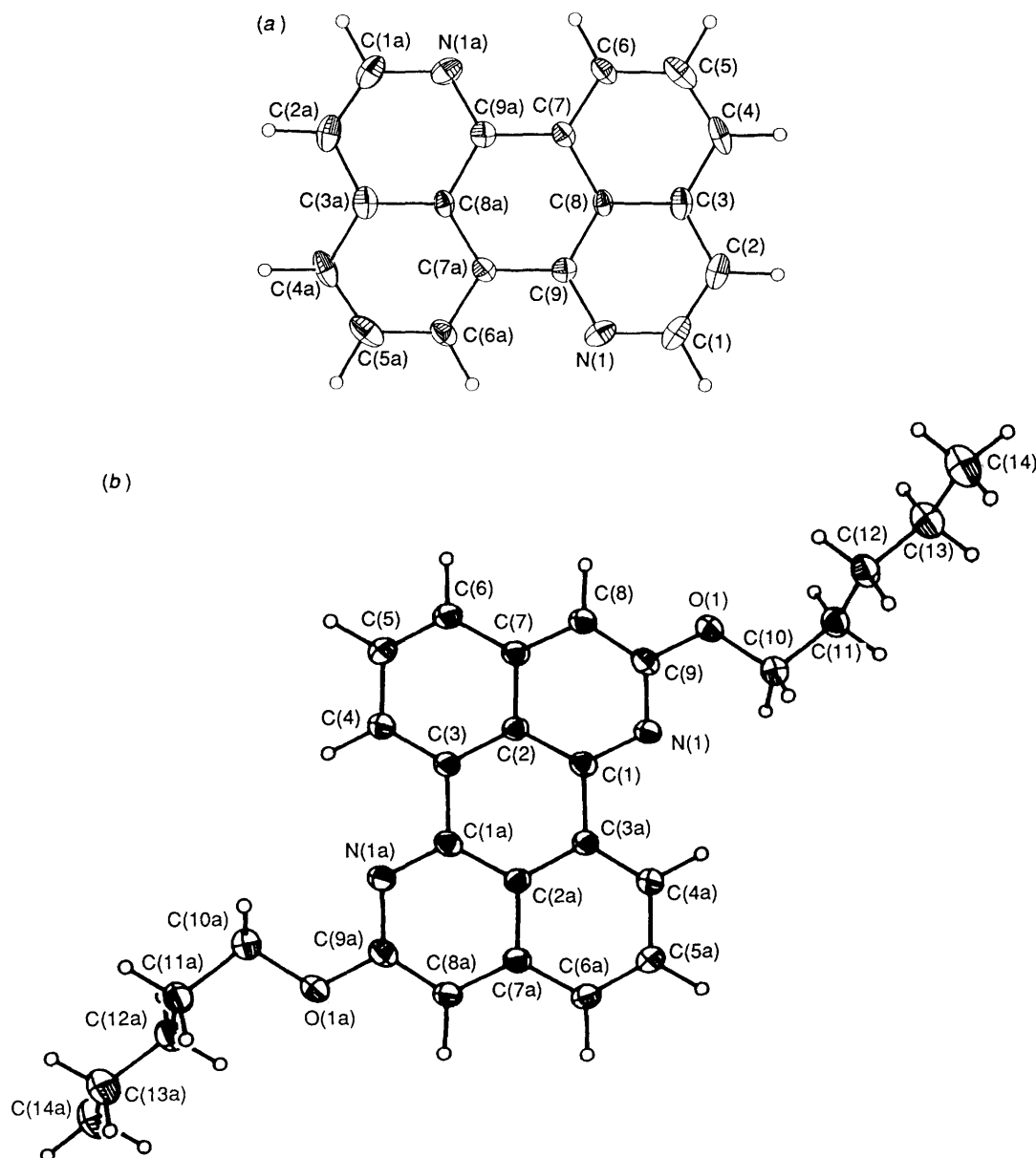


Fig. 2 Structures of 1,7-diazaperylene (a) and 2,8-dipentyloxy-1,7-diazaperylene (b). The structure is similar to the one of perylene, but the ring system is planar. The molecules are packed in the herringbone structure which is typical for polycyclic aromatic hydrocarbons

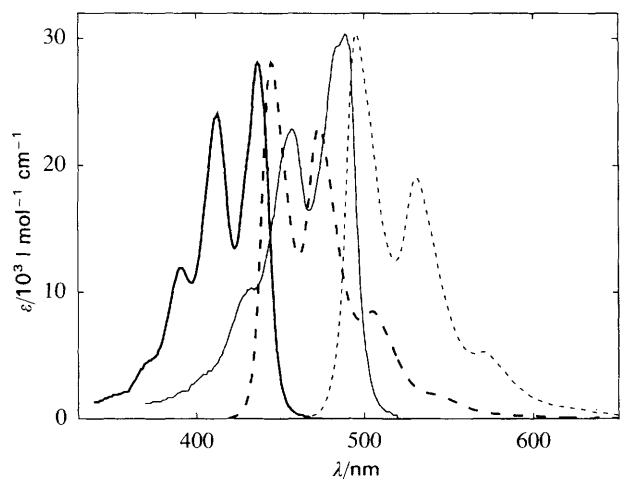


Fig. 3 Absorption (—) and fluorescence (---) (corrected) spectra of 1,7-diazaperylene (bold lines) and 2,8-dipentyloxy-1,7-diazaperylene (feint lines) in ethanol

the theoretical value of $2/5$, expected for parallel absorption and emission dipoles. Since the DP chromophore is planar, as shown by X-ray spectroscopy, the deviation between the observed and theoretical values of r_0 cannot be ascribed to the non-planarity of the perylene molecule in its ground state. However, the deviations between r_0 and $2/5$ found for DP can still be due to a distortion of the excited-state geometry.

The rotational motion of DP in paraffin oil and glycerol has been studied by means of time-resolved fluorescence anisotropy. The viscosity of paraffin oil followed the relation¹

$$\eta = \eta_0 \exp(\Delta E_\eta / RT)$$

with $\Delta E_\eta = 45.3 \text{ kJ mol}^{-1}$ and $\eta_0 = 1.26 \text{ cP}$. The steady-state anisotropies of DP and perylene in paraffin oil are very similar at different temperatures (data not shown). This indicates that both molecules rotate in much the same way which is also supported by the time-resolved fluorescence anisotropy $[r(t)]$. The decay of $r(t)$ fits nicely to a sum of two exponential functions, as expected if the molecules undergo

rotational diffusion like an oblate ellipsoid, that is^{22,23}

$$r(t) = a_1 \exp(-t/\phi_1) + a_2 \exp(-t/\phi_2) \quad (1a)$$

$$\phi_1 = (6D_{\perp})^{-1} \quad (1b)$$

$$\phi_2 = (2D_{\perp} + 4D_{\parallel})^{-1} \quad (1c)$$

In eqn. (1b) and (1c) D denotes the diffusion coefficient for rotation about (\perp) and perpendicular (\parallel) to the C_{∞} symmetry axis of an oblate molecule. For mutually parallel absorption and emission dipoles polarized perpendicular to the C_{∞} axis, $a_1 = 0.1$ and $a_2 = 0.3$. The pre-exponential factor a_1 is insensitive to librational motions about the C_{∞} axis while such motions, as well as a small inherent angle between the absorption and emission dipoles, will effectively decrease a_2 so that, for example, $a_2 \approx 0.26$ for an angle of 5° (see ref. 12).

We find that $r(t)$ for DP, as well as for perylene in paraffin oil can be analysed with eqn. (1a) for essentially the same values of $a_1 \approx 0.1$ and $a_2 < 0.3$. As can be seen from Fig. 4, the rotational correlation times ϕ_1 and ϕ_2 are very similar for DP and perylene. Consequently, the rotational diffusion coefficients, calculated from eqn. (1b) and (1c), also become very similar. The ratio of $D_{\parallel}/D_{\perp} \approx 10$ is essentially the same as that previously obtained for perylene in propylene glycol²⁴ as well as glycerol.¹¹ Zinsli interpreted this result as indicating boundary conditions between slipping and sticking.²⁵

Let us proceed to the anisotropy data obtained for DP in glycerol, and compare these data with those of perylene. The steady-state anisotropy of DP as a function of temperature is significantly larger than that of perylene, which strongly suggests a slower rotational relaxation of DP (data not shown). Moreover, $r(t)$ of DP is a monoexponential function in contrast to perylene, where $r(t)$ is biexponential. For DP the pre-exponential factor is ca. 0.38 at all temperatures studied, i.e. between 264 and 303 K. This is compatible with a diffusion coefficient of $D_{\parallel} \approx D_{\perp} = D$ in eqn. (1), yielding

$$r(t) = r_0 \exp(-t/\phi) \quad (2a)$$

$$\phi = (6D)^{-1} \quad (2b)$$

and it means that the rotational motion of DP in glycerol resembles that of a spherical particle. Comparison with the data on perylene in glycerol¹¹ demonstrates that the diffusion coefficient of the diazaperylene is equal to D_{\perp} of perylene, within the accuracy of the experiment. This is illustrated in Fig. 5. Thus, the rotational rate about an axis in the aromatic

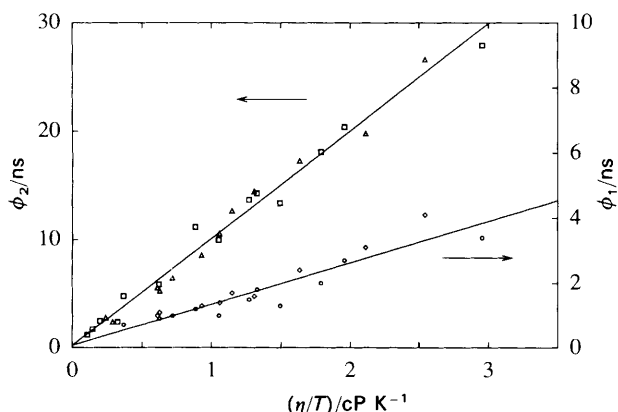


Fig. 4 Rotational correlation times (ϕ_1 and ϕ_2) of 1,7-diazaperylene (ϕ_1 , \square ; ϕ_2 , \circ) and perylene (ϕ_1 , \triangle ; ϕ_2 , \diamond) in paraffin oil as a function of the ratio between solvent viscosity (η in cP) and temperature

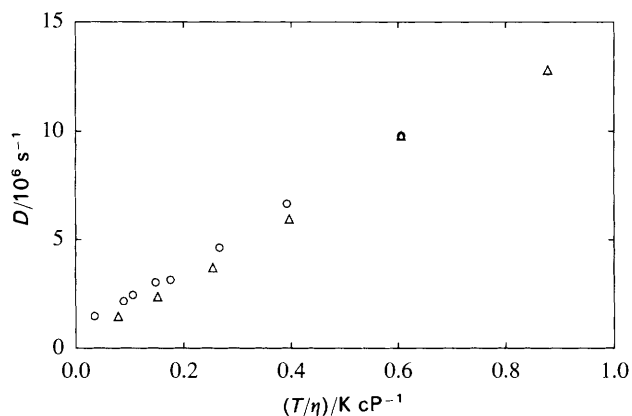


Fig. 5 Rotational diffusion coefficient (D) of 1,7-diazaperylene (\circ) and perylene (\triangle) in glycerol as a function of the ratio between temperature and solvent viscosity (η in cP). For perylene $D = D_{\perp}$, that is, the rotational diffusion perpendicular to the assumed C_{∞} axis. Data on the viscosity of glycerol were taken from ref. 26

plane of DP and perylene are equal. This could also be expected, since the size and mass of DP is nearly equal to that of perylene, suggesting that such a rotation involves the same energy of displacing the same number of solvent molecules. However, the reason that $D_{\parallel} \approx D_{\perp}$ for DP must be ascribed to hydrogen bonding between the nitrogens of DP and the OH groups of glycerol. Because of these bonds, the solvent will stick to DP and hamper the rotational rate about the C_{∞} axis. Furthermore, the finding of nearly identical rotational motions of DP and perylene in paraffin oil, where no hydrogen bonds can be formed, supports this explanation.

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