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 DP are 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 ± 1 Å for DP and 41.9 ± 1 Å for its alkoxy derivatives in ethanol. Examining the S₂ → S₁ transition, we obtain a limiting fluorescence anisotropy of r₀ ≈ 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 monoeponential 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 (D₁), 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, laser dyes, fluorescent solar antennas, fluorescence immunoassays, reporter molecules in membrane research, probe molecules in membranes as well as in the modelling of electronic energy transfer in lipid bilayers.

In this article we report on fluorescence spectroscopic studies of a new derivative of perylene, 1,7-diazaperylene (DP; benzen[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. The DP molecule has about the same molecular mass as perylene (see Fig. 1) but, owing to the sp² 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-workers 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 salt (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; τ₁ (silica gel/toluene) = 0.84; IR (KBr): ν/cm⁻¹ = 3070 (w), 2945 (m), 2870 (m), 1604 (s), 1581 (s), 1464 (w), 1446 (m), 1341 (m), 1399 (s), 1344 (m), 1280 (m), 1272 (m), 1115 (s), 1109 (s), 1072 (m), 843 (m), 692 (m). UV (toluene): λ_{max}/nm [log (ε/l mol⁻¹ cm⁻¹)] = 437 nm (3.979), 465 (4.348), 488 sh, 496 (4.501); UV (CHCl₃): λ_{max}/nm [log (ε/l mol⁻¹ 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). C₉₈H₈₈N₂O₂ (426.5), calc. C, 78.84%; H, 7.09 %; N, 6.57%; found C, 78.85%; H, 7.03%; N, 6.46%.
Crystal Structures

Diffraclorntor: ENRAF-Nionius CAD4, radiation: Mo-Kα
Monochromator: Highly oriented graphite crystal.

1,7-Diazeplyrene

\[ C_{18}H_{14}N_{2} \]

Monochromator: Highly oriented graphite crystal.

Diffractometer: ENRAF-Nonius CAD4, radiation: Mo-Kα

Density: 1.420 Mg m\(^{-3}\), \( \mu = 0.79 \) cm\(^{-1}\), crystal system monoclinic, space group P2\(_1\) (no. 14).

Data collection: single crystal; 0.2 \( \times \) 0.33 \( \times \) 0.4 mm\(^3\), \( \omega \)-2θ scan, measured 20 range: 4.0–44.0° in \( h+k+l \), signal width 1.00° \( \pm \) 0.35 tan \( \theta \).

Background measurement: stationary counter at beginning and end of scan, each for 25.0% of total scan time.

Standard reflections: three measured every 100 reflections, index ranges \(-8 \leq h \leq 8, 0 \leq k \leq 6, 0 \leq l \leq 12; 774\) reflexions collected, 676 independent reflexions (\( R_{int} = 2.77\% \)), 592 considered as observed \([ I \geq 2\sigma(I)]\).

Absorption correction: \( \mu = 0.0752 \), \( R_a = 0.0689, w^{-1} = F + F0^2 \), residue of max. and min. electron density \( (10^3 \text{ e pm}^{-3}) \) 0.20-0.24; \( \omega \)-2θ scan, measured 20 range: 4.0–46.0° in \( h+k+l \), signal width 0.90° \( \pm \) 0.35 tan \( \theta \), background measurement: stationary counter at beginning and end of scan, each for 25.0% of total scan time.

Solution of structure: direct methods, anisotropic description of the non-hydrogen atoms, isotropic description of the H-atoms, 91 parameters, \( R = 0.1068, R_w = 0.0979 \).

Further data are given in Table 1.

### Table 1

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*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

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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) at 480.4 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 polarized rotated periodically. In each experiment the decay curves \( I(t) \) and \( D(t) \) were collected. The suffixes \( \parallel \) and \( \perp \) refer to an orientation of the emission polarizer parallel and perpendicular with respect to the excitation polarizer. From these a sum curve

\[
S(t) = F(t) + 2GF(\parallel)(t)
\]

and a difference curve

\[
D(t) = F(\parallel)(t) - GF(\parallel)(t)
\]

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

\[
G = \left(1 - r_s \right) K \left(1 + 2r_s F(\parallel)(t)^{-1}ight)
\]

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, $\Phi$

Perylene in ethanol and fluorescein in 0.1 mol dm$^{-3}$ NaOH were used as reference standards with reported quantum yields of 0.92$^{15-17}$ and 0.93$^{18}$, respectively. The quantum yield to be determined, $\Phi_{\text{sample}}$, was calculated from

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

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, $\tau_0$

The corrected fluorescence $F(v)$, of the chromophore dissolved in ethanol was determined at 298 K. Here $v$ stands for the wavenumber. The molar absorptivity as a function of wavenumber, $e(v)$, was determined from the absorption spectrum recorded on the chroomophore solution. From $e(v)$, $F(v)$ and the modified Strickler-Berg equation$^{19}$

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9} n^2 \int \frac{F(v) \ln F(v)}{F(v) - 1} dv$$

the radiative lifetime $\tau_0$ 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 $\phi$ is compared with that determined independently as described above.

 Förster Radius

The Förster radius, as defined by Kawski,$^{20}$ is

$$R_{\text{F}} = \frac{900 \ln(10) \langle \tau^2 \rangle}{128 \pi^2 n^4 N_A}$$

where

$$J = \int \frac{e(v)f(v)\ln v}{v^4} dv$$

and

$$f(v) = \frac{F(v)}{\int F(v) dv}$$

where $N_A$ and $n$ denote the Avogadro constant and the refractive index of the medium. $\langle \tau^2 \rangle$ 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 $\langle \tau^2 \rangle = 2/3$ 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 reported$^{14}$ 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 vibrionic 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’ vibrionic peak are 28 100 ± 200 l mol$^{-1}$ cm$^{-1}$ for DP, 29 900 ± 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 ($\tau_0$) 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 monoeponential decays of the photophysics with a lifetime of $\tau = 5.1 \pm 0.1$ 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 $\Phi$(DP) = 0.81 and $\Phi$(2,8-dimethoxy DP) = 0.78. Independent measurements of the quantum yield of fluorescence give $\Phi$(DP) = 0.83 ± 0.05 and $\Phi$(alkoxy-DP) = 0.80 ± 0.05. Note that the samples were not degassed.

The fluorescence lifetime of DP in glycerol and paraffin oil is monoeponential, 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-butyrylperylene (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 wavelength, respectively, which shows that the band corresponds to one direction of the electronic transition dipole moment. The steady-state anisotropy of DP and dialkoxy-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 relation:

\[
\eta = \eta_0 \exp(\Delta E_a / RT)
\]

with \( \Delta E_a = 45.3 \text{ kJ mol}^{-1} \) 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:\(^{22,23}\)
\[
\begin{align*}
\phi(t) &= a_1 \exp(-t/\phi_1) + a_2 \exp(-t/\phi_2) \\
\phi_1 &= (6D_1)^{-1} \\
\phi_2 &= (2D_1 + 4D_2)^{-1}
\end{align*}
\] (1a)

In eqn. (1b) and (1c) \(D\) denotes the diffusion coefficient for rotation about (\(L\)) and perpendicular (\(L\)) to the \(C_\infty\) symmetry axis of an oblate molecule. For mutually parallel absorption and emission dipoles polarized perpendicular to the \(C_\infty\) axis, \(a_1 = 0.1\) and \(a_2 = 0.3\). The pre-exponential factor \(a_1\) is insensitive to librational motions about the \(C_\infty\) axis while such motions, as well as a small inherent angle between the absorption and emission dipoles, will effectively decrease \(\phi_2\) 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 \(\phi_1\) and \(\phi_2\) 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 glycol\(^{24}\) 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 exponential factor is \(\exp(-t/\phi)\) (2a)
\[
\phi = (6D)^{-1}
\] (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 glycerol\(^{11}\) demonstrates that the diffusion coefficient of the diazaperylene is equal to \(D_\parallel\) of perylene, within the accuracy of the experiment. This is illustrated in Fig. 5. Thus, the rotational rate about an axis in the aromatic 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 \(D_\parallel\) for DP must be ascribed to hydrogen bonding between the nitrogens of DP and the \(\mathrm{OH}\) groups of glycerol. Because of these bonds, the solvent will stick to DP and hamper the rotational rate about the \(C_\infty\) 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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References


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