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Excimer fluorescence from phenanthrene-9-carboxylate derivatives

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Abstract

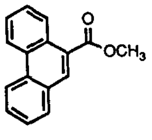
Phenanthrene and most of its known derivatives do not form stable, fluorescent excimers. Moderately intense, long-lived excimer fluorescence has been observed for lactone and lactam derivatives of phenanthrene. The solvatochromic shift of this excimer fluorescence is similar to that previously reported for the pyrene excimer. Stabilization of the excimer is attributed to the increased polarizability of phenanthrene by a coplanar carbonyl substituent. Excimer formation is not observed for a coplanar cyano substituent or an orthogonal carbonyl substituent.

Keywords: Excimer fluorescence; Phenanthrene-9-carboxylate derivatives; Solvatochromic shift

1. Introduction

The singlet excimer of phenanthrene remains an elusive species [1–6]. The absence of self-quenching of the singlet state of phenanthrene indicates that the enthalpy of excimer formation is too small to overcome the entropy of association [1]. Attempted approaches to overcome this fundamental problem have included covalent attachment of two phenanthrenes and the use of substituted phenanthrenes. Several isomers of 1,3-diphenanthrylpropane [2] and 9-phenanthroic anhydride [3] have been investigated and found to exhibit either very weak or non-existent excimer fluorescence. Two isomers of [2.2]phenanthrenophane have been synthesized, but neither is reported to display excimer fluorescence in solution [4]. Substituted phenanthrenes have proven to be equally uncooperative. Very weak excimer fluorescence has been observed for 9-cyano-10-methoxyphenanthrene [5], but no monosubstituted phenanthrene has been reported to display excimer fluorescence [5–7].

We are interested in the photochemical behavior of ester and amide derivatives of phenanthrene-9-carboxylic acid [7–9]. An earlier investigation of methyl- phenanthrene-9-carboxylate (**1**) revealed the occurrence of self-quenching and moderately efficient photodimerization; however, no excimer fluorescence was observed [7]. We proposed that dimer formation occurred via a weakly bound, non-fluorescent singlet excimer. No self-quenching was observed for *N*,*N*-dimethylphenanthrene-9-carboxamide (**2**). The different behavior for the ester vs. amide was attributed to different singlet state geometries, the ester adopting a nearly coplanar arene-carbonyl geometry and the amide a nearly perpendicular geometry. In this paper, we report an investigation of the photochemical behavior of the lactone **3** and lactam **4** which serve as planar models of **1** and **2**. Both **3** and **4** display strong excimer emission, permitting investigation of excimer formation and behavior in these phenanthrene derivatives.



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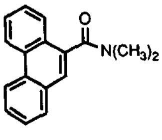

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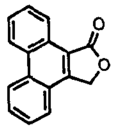

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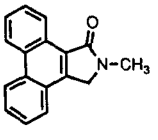

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2. Experimental details

2.1. General methods and materials

^{1}H NMR spectra were recorded on a Gemini 300 MHz spectrophotometer in $CDCl_3$ solution with tetramethylsilane (TMS) as internal standard. IR spectra were recorded using a Matson FT-IR. UV–visible absorption spectra were measured with a Hewlett-Packard model 8452A diode array spectrophotometer in 1 cm path length quartz cuvettes. Fluorescence emission and excitation spectra were recorded using a Spex FluoroMax spectrophotometer in 1 cm path length quartz cells. Fluorescence quantum yields were determined relative to phenanthrene ($\Phi_f = 0.13$ in hexane [10]) for solutions of matched absorbance (approximately 0.1 optical density (OD)). Solutions were approximately 10^{-4} M and purged with nitrogen for more than 5 min in 1 cm path length quartz cuvettes. Front-face geometry was used for

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concentrated solutions (above 5×10^{-3} M). Fluorescence decay times were determined with a PTI LS-1 spectrophotometer using a gated hydrogen arc lamp and single photon counting technique. The decays were deconvoluted using a single multiexponential least- squares analysis. The reduced χ^2 values, randomness of the residuals and autocorrelation functions were used to determine the goodness of the fit. The excimer fluorescence decays of **3** and **4** display both rising and decaying components. The rising components are longer than the lamp profile and are concentration dependent. The decaying components are single exponentials and independent of concentration. Solvents were spectral grade (Aldrich or Fisher). Dichloromethane was distilled over calcium hydride prior to use.

2.2. Phenanthrene-10-hydroxymethyl-9-carboxylic acid lactone (3)

Phenanthrene-9,10-dicarboxylic acid anhydride was prepared via the irradiation of 2,3-diphenylmaleic anhydride (Aldrich) by the method of Sargent and Timmons [11]. Reduction of the resulting anhydride (0.004 mol) with $NaBH_4$ by the method of Bailey and Johnson [12], followed by recrystallization from tetrahydrofuran, afforded **3** as yellow needles (0.8 g, 85% yield): m.p. 230 °C sublimated (259 °C [13]); IR ($CHCl_3$, cm^{-1}) 1754, 1523; ^{1}H NMR ($CDCl_3$) δ9.22 (H8), 8.79 (H5), 8.73 (H4), 7.88 (H1), 5.66 (CH_2).

2.3. Phenanthrene-10-aminomethyl-9-carboxamide lactam (4)

A methanol solution of phenanthrene-9,10-dicarboxylic acid anhydride (0.004 mol) and sodium methoxide (0.01 mol) was saturated with methylamine and stirred for 7 days at 40 °C in a sealed tube. The solvent was removed and water and ethyl acetate were added to the residue. The organic layer was washed with water, dried with $CaCl_2$ and the solvent was removed. Recrystallization from tetrahydrofuran afforded the *N*-methyl imide as brown needles (0.5 g, 45% yield); m.p. 223–225 °C; IR ($CHCl_3$, cm^{-1}) 1709. The imide was partially reduced with $NaBH_4$ to the hydroxyamide by the method of Horii et al. [14]. The crude hydroxyamide was converted to the lactam via irradiation with diethylamine in deoxygenated benzene solution using the method of Kubo et al. [15]. Recrystallization from ethyl acetate and hexanes afforded **4** as yellow cubes (0.2 g, 54% yield); m.p. 142–144 °C; IR ($CDCl_3$, cm^{-1}) 1674, 1525; ^{1}H NMR ($CDCl_3$) δ9.41 (H8), 8.77 (H5), 8.72 (H4), 7.90 (H1), 4.73 (CH_2), 3.34 (CH_3).

3. Results and discussion

3.1. Molecular structure and spectra

We have previously observed that the dihedral angle between phenanthrene and carbonyl substituents at the 9-position is dependent on the bulk of the substituent [8]. An indication of the magnitude of this dihedral angle is provided by the ^{1}H NMR chemical shift of phenanthrene H8. Significant deshielding is observed for ester **1** (9.07 ppm), indicative of a relatively small dihedral angle (less than 10°); in contrast, little deshielding is observed for amide **2** (7.84 ppm), indicative of a large dihedral angle (above 60°). We have recently determined the crystal structure for a derivative of **2** which has a dihedral angle of 86° [16]. Small dihedral angles are expected for the lactone **3** and lactam **4** due to structural constraints. In accord with this expectation, significant deshielding of H8 is observed for both molecules (9.22 and 9.41 ppm respectively).

The absorption and fluorescence spectra of **4** in dichloromethane solution are shown in Fig. 1 and the first vibrational maxima (λ_1) of the absorption and fluorescence bands of **1**–**4** are reported in Table 1 together with Berlman's data [10] for phenanthrene. All four molecules display weak lowest energy absorption bands (S_1) with some vibrational structure, and stronger bands at higher energy (S_2), similar in appearance to the ^1L_b (short-axis polarized) and ^1L_a (long-axis polarized) bands of phenanthrene. There is a distinct red shift in the S_2 bands of **3** and **4** vs. **1** and **2** or phenanthrene; in contrast, the S_1 bands are less sensitive to ground state enone planarity (Table 1). The absorption and fluorescence maxima display small solvent-induced shifts (less than 5 nm) in hexane or methanol solution. The Stokes shifts between the absorption and emission bands of **3** and **4** (Fig. 1) are very small, as expected for rigid molecules. We have previously reported a moderate Stokes shift for **1**, attributed to an increase in planarity in the singlet vs. ground state [8].

The electronic structure and spectra of **1**–**4** have been investigated using the INDO/S model as supplied in the Gaussian 92 package [17]. The frontier orbitals calculated for **4** are shown in Fig. 2 and are similar in appearance to those for **1**–**3**. The carbonyl π orbital coefficients are significant only in the case of the LUMO and the carbonyl lone pair orbitals are calculated to lie below the SHOMO. Excited states were generated using a singly excited configuration interaction method employing 100 singly excited transitions. The S_1 bands of **1**–**4** are found to result from configuration interaction between SHOMO–LUMO and HOMO–SLUMO transitions, whereas the S_2 bands result from a HOMO–LUMO transition with a small degree of configuration interaction with the SHOMO–SLUMO transition.

3.2. Self-quenching and excimer formation

Single-exponential fluorescence decay is observed for **1**–**4** in dilute dichloromethane solution. Singlet lifetimes (τ_s) and fluorescence quantum yields (Φ_f) are reported in Table 1, together with Berlman's data [10] for phenanthrene. The lifetimes for **1**–**4** are shorter than that for phenanthrene. The values of τ_s for **3** and **4** are longer than those for **1** and **2**, suggesting that increased molecular rigidity leads to an increase in lifetime. The fluorescence rate constants calculated

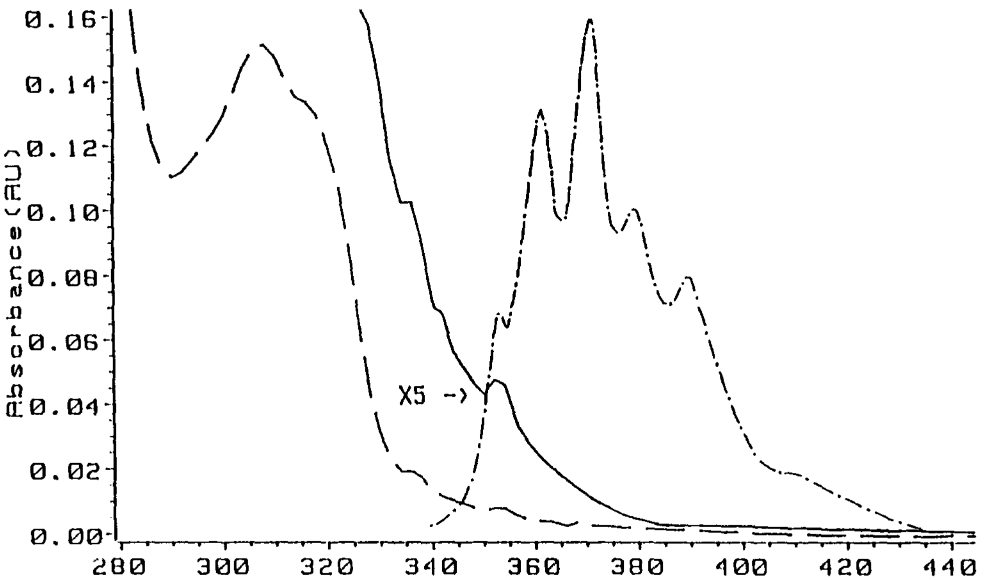

Fig. 1. Absorption (——) and fluorescence (–·–) spectra of lactam **4** (2×10^{-5} M) in nitrogen-purged dichloromethane solution.

Table 1
Absorption and fluorescence spectral data for phenanthrene derivatives [a]

	1	2	3	4	Phenanthrene
S_2 (nm)	304	300	316	316	293 [b]
S_1 (nm)	357	350	352	353	347
Fl (nm)	366	352	354	353	347
τ_s (ns)	10.3	7.7	14.0	20.2	57.5
Φ_f	0.15	0.04	0.22	0.08	0.13

[a] Data for nitrogen-purged dilute dichloromethane solutions (less than 10^{-4} M).
[b] Data from Ref. [10].

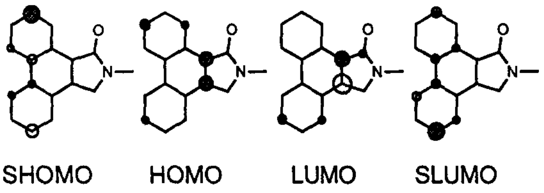

Fig. 2. Calculated frontier molecular orbitals for lactam **4**.

from these measured values ($k_f=\Phi_f\tau_s^{-1}$) are somewhat larger for the esters **1** and **3** (approximately 1.5×10^7 s^{-1}) than for the amides **2** and **4** (approximately 0.5×10^7 s^{-1}) or for phenanthrene (2.3×10^6 s^{-1}). Increasing concentration results in a decrease in singlet lifetime for **1**, **3** and **4**, but not for **2**. Stern–Volmer plots of the measured singlet lifetime (τ) vs. concentration of **3** and **4** (Eq. (1)) are shown in Fig. 3 and values of the self-quenching rate constant (k_{sq}) are reported in Table 2. A value of $k_{sq}=1.2\times10^9$ M^{-1} s^{-1} was previously reported for **1** [7].

$$\tau^{-1}=\tau_0^{-1}+k_{sq}[3] \qquad (1)$$

Self-quenching of **3** and **4** is accompanied by the appearance of moderately intense long-wavelength fluorescence attributed to excimer formation. Fluorescence spectra obtained using front-face geometry for 0.025 M **4** in several solvents are shown in Fig. 4 and the fluorescence maxima for **3** and **4** are reported in Table 2. Assignment of the long-

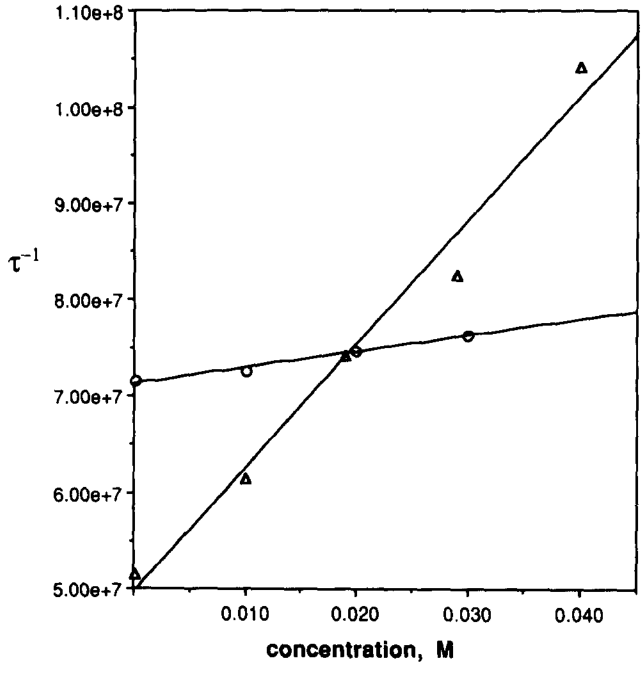

Fig. 3. Stern–Volmer plots for concentration quenching of lactone **3** (○) and lactam **4** (△).

Table 2
Excimer kinetics and fluorescence maxima [a]

$10^{-9}k_{sq}$	0.2	1.3
τ_{ex} (ns)	16	14
λ_{ex} (nm)	449	462
λ_{ex}(EtOAc) (nm)	436	452
λ_{ex}(CH_3CN) (nm)	460	466

[a] Data for nitrogen-purged dichloromethane solutions except as noted.

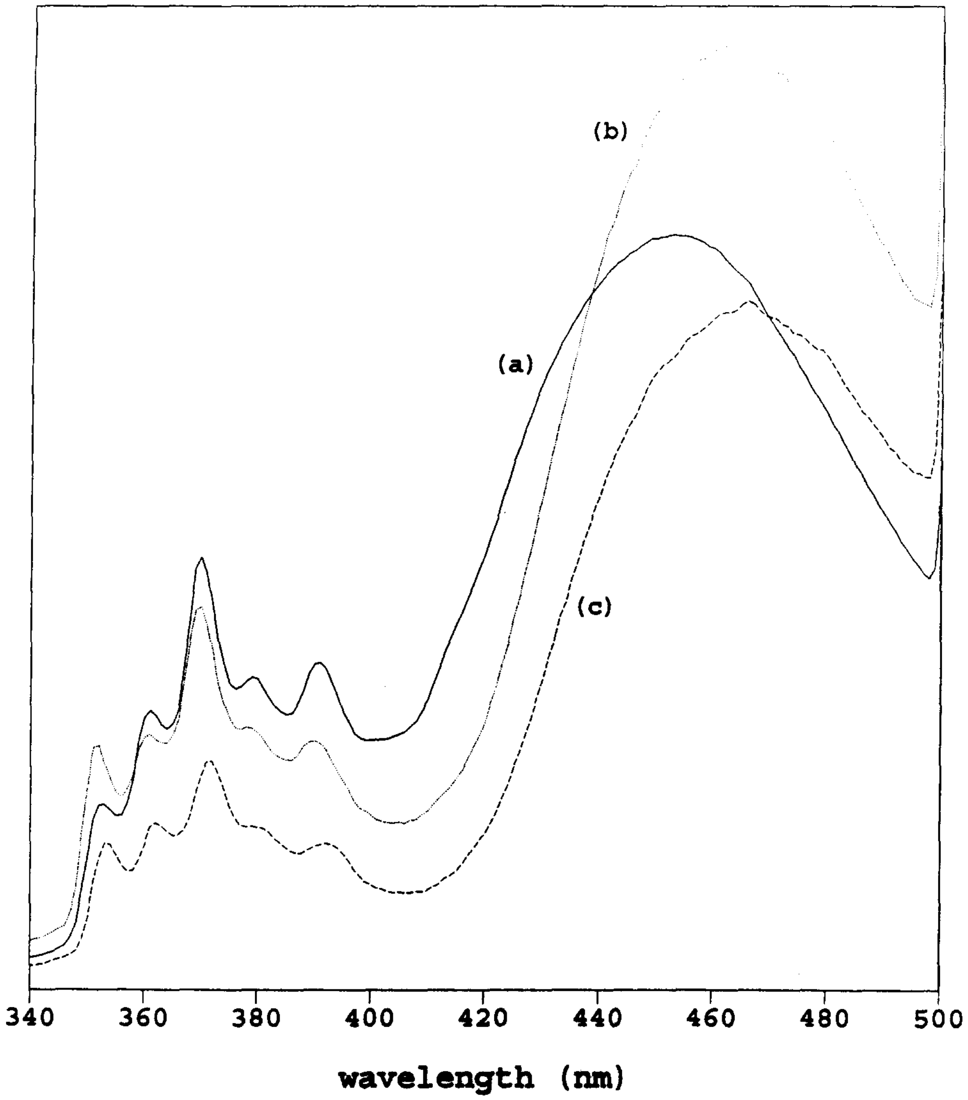

Fig. 4. Fluorescence spectra of lactam **4** (0.025 M) in ethyl acetate (a), dichloromethane (b) and acetonitrile (c) solution.

wavelength fluorescence to excimers formed by diffusional self-quenching, rather than excitation of ground state aggregates, is supported by (a) linear Beer's law plots and the absence of light scattering at the highest concentrations employed, (b) linear Stern–Volmer plots for fluorescence self-quenching (Fig. 3) and (c) the observation of concentration-dependent rising components for excimer fluorescence with rise times similar to the decay times for locally excited fluorescence. The decaying components of excimer fluorescence are independent of concentration and are assigned to the excimer decay time (Table 2). Photodimerization does not accompany self-quenching of **3** and **4**.

The excimer fluorescence maxima of **3** and **4** display modest solvent dependence (Fig. 4). Beens et al. [18] reported that the pyrene excimer fluorescence maximum is independent of solvent polarity in solvents of low to medium polarity. Castanheira and Martinho [19] have recently reported modest solvatochromic shifts for naphthalene and pyrene excimers in polar non-hydroxylic solvents. Larger shifts for pyrene vs. naphthalene were attributed to its larger size and polarizability. The solvent shifts for **3** and **4** are similar in magnitude to those reported for pyrene, suggesting that a coplanar carbonyl substituent may increase the polarizability of phenanthrene with a resulting increase in excimer stability. The large carbonyl-arene dihedral angle in the singlet state of **2** would result in decreased polarizability as well as steric destabilization of a sandwich excimer. It is interesting to note that 9-cyanophenanthrene does not form a fluorescent excimer and has a much smaller self-quenching rate constant ($k_{sq} \leqslant 1 \times 10^8 \mathrm{M}^{-1} \mathrm{s}^{-1}$) than **1**, **3** and **4** (for a detailed kinetic analysis of the self-quenching and photodimerization of 9-cyanophenanthrene, see Ref. [20]). Furthermore, the excimer fluorescence reported for 0.45 M 9-cyano-10-methoxyphenanthrene is much weaker than the residual monomer fluorescence [5]. Thus the coplanar carbonyl group is more effective than the sterically undemanding cyano group in stabilizing the phenanthrene excimer.

In summary, the lowest singlet states of the phenanthrene derivatives **1**–**4** have similar electronic configurations (as shown by INDO/S calculations) and photophysical properties (Table 1). Thus the observation of self-quenching for **1**, **3** and **4** but not for **2** is attributed to the orthogonal amide group in **2** which sterically hinders the formation of a sandwich excimer. Self-quenching of **1** results in the formation of a non- fluorescent excimer which undergoes efficient photodimerization [7]; in contrast, **3** and **4** form fluorescent excimers which do not undergo photodimerization. Photodimerization of **1** yields the syn head-to-tail dimer with a quantum yield of 1.0 ± 0.2, in the limit of high concentration. Thus the absence of excimer fluorescence for **1** and the very weak excimer fluorescence observed for 9-cyano-10-methoxyphenanthrene [5] may be due to rapid photodimerization, as is the case for the anthracene excimer. The increased steric demands for dimerization of **3** and **4** vs. **1** (formation of tetrasubstituted vs. trisubstituted cyclobutanes) could account for the absence of dimer and the observation of excimer fluorescence, as is the case for 9,10-dimethylanthracene [21].

Acknowledgements

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Note added in proof

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