Notes

Intramolecular Excimer Formation in Diastereoisomeric Bis[1-(1-pyrenyl)ethyl] Ethers

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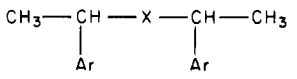
Received November 9, 1982

Introduction

The study of excimer formation in polychromophoric compounds has been an active research area.[1] Recently, the role and importance of configurational and conformational aspects of the ground state in relation to the excited-state behavior of the polychromophoric compound have been demonstrated.[2-14]

The use of diastereoisomeric model compounds of general formula I has been extremely helpful in understanding



I

Ar = phenyl, α- and β-naphthyl, 9-anthroyl, or *N*-carbazolyl
X = CH_2 or O

the emission behavior of polyvinyl aromatic compounds. In the case of 2,4-di(*N*-carbazolyl)pentane, the excimer emission of the racemic and meso isomers could be correlated with the "high-energy" and "normal" excimers, respectively, observed in poly(*N*-vinylcarbazole).[13] In the other systems, the meso isomer has always a relatively larger excimer contribution than the racemic isomer. This difference in excimer-forming efficiency could be, for 2,4-diphenylpentane, explained on the basis of conformational maps.[3,6]

The meso isomer of bis[1-(1-naphthyl)ethyl] ether (B1NEE) has two spectrally different excimers.[11] This is due to strong steric interactions between the H_8, $H_{8'}$ peri hydrogens and the methyl groups. These interactions are also important in bis[1-(9-anthryl)ethyl] ether (B9AEE).[14]

So far, no attention has been given to diastereoisomers of I in which the aryl group is a 1-pyrenyl chromophore. Two reasons prompted us to study this system: first, the statement by Fox[15] in study of the photophysical properties of poly(1-vinylpyrene) that "the maximum of the excimer emission shifts from 492 nm at 200 K to 455 nm at 100 K in CH_2Cl_2", and second, the fact that 1,3-di(1-pyrenyl)-propane is an extensively used probe in the study of organized media.[16]

In this paper we report the spectral behavior of 1-(1-pyrenyl)ethyl ethyl ether (1PEE), which serves as a reference compound, and bis[1-(1-pyrenyl)ethyl] ether (B1PEE).

Experimental Section

B1PEE was synthesized in analogy with the method developed by Becker.[14a] *meso*- and *rac*-BIPEE, obtained upon chromatography on silica with 80/20 toluene–hexane eluent, were assigned on the basis of the upfield absorption of the methine carbon in the ^{13}C NMR spectrum and the downfield absorption of the methine hydrogens in the ^1H NMR spectrum for the meso isomers (Table I). This observation is made for all systems of type I studied so far.

Table I
NMR Spectral Data in $CDCl_3$ at 25 °C with Me_4Si as Reference

	δ(^{1}H)		δ(^{13}C)	
group	meso	racemic	meso	racemic
CH_3	1.75	1.70	23.89	24.82
CH	5.70	5.30	72.49	73.37
pyrene	7.40-8.40	7.50-8.35	122.90-138.37	123.01-131.65

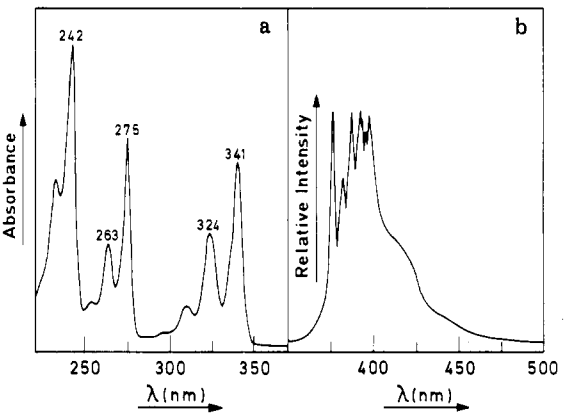


Figure 1. (a) Absorption of 1PEE in isooctane at room temperature. (b) Fluorescence of 1PEE (10^{-6} M) dissolved in isooctane at room temperature.

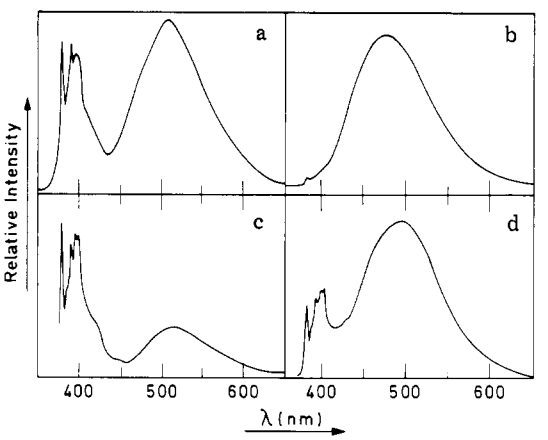


Figure 2. (a) Fluorescence emission of *rac*-B1PEE (10^{-6} M) in isooctane at room temperature. (b) Fluorescence emission of *meso*-B1PEE (10^{-6} M) in isooctane at room temperature. (c) Fluorescence emission of *rac*-B1PEE (10^{-6} M) in isooctane at 180 K. (d) Fluorescence emission of *meso*-B1PEE (10^{-6} M) in isooctane at 180 K.

Absorpion spectra were taken on a Perkin-Elmer 550S UV-vis spectrophotometer. All emission spectra were taken on a Fica spectrofluorometer and on a Spex Fluorolog.

Results and Discussion

Absorption Measurements. The shape of the absorption spectra of B1PEE and 1PEE (Figure 1a) is comparable to the absorption spectum of pyrene itself. No important differences are observed between the three compounds. All absorption spectra were taken in isooctane.

0024-9297/83/2216-1390$01.50/0

Table II
Fluorescence Spectral Data of B1PEE in Isooctane at Room Temperature

	λ_{max}, nm	fwhh, cm^{-1}
meso	472	4800
racemic	510	3700

Emission Measurements. The fluorescence spectra of dilute solutions (10^{-6} M) of B1PEE (Figure 2) and 1PEE (Figure 1b) in isooctane at 298 K show important differences. 1PEE has a structured monomer fluorescence similar to the emission spectrum of pyrene itself. Both isomers of B1PEE have an appreciable excimer contribution at 298 K. In *meso*-B1PEE, the monomer emission is absent and the excimer emission is broader and more hypsochromic in comparison with that of the racemic isomer. Wavelengths of the maximum of the excimer emission (λ_{max}) and frequency widths at half-height (fwhh) are listed in Table II. Temperature-dependent fluorescence spectra of *rac*-B1PEE are characterized by an isoemissive zone in the temperature region from 183 to 298 K. λ_{max} of the excimer emission in *rac*-B1PEE is hardly temperature dependent (512 nm at 183 K and 510 nm at 317 K) over the entire temperature range studied. In contrast, λ_{max} of the excimer emission in *meso*-B1PEE shifts from 492 nm at 181 K to 469 nm at 317 K. Between 181 K and 238 K, there is an isoemissive zone for *meso*-B1PEE.

Preliminary measurements of the fluorescence decay analyzed at 480 nm, using the time-correlated single-photon-counting technique, indicate that the decay of excimer emission of *meso*-B1PEE in isooctane at room temperature can be fit to a sum of two exponentials. Since the emission of the locally excited state is weak at this temperature, this suggests the excimer buildup is very fast, and the two decay components of 93 ns (35%) and 59 ns (65%) reflect the presence of two excimer configurations. Excitation spectra of the ^1L_a transition of *meso*- and *rac*-B1PEE analyzed in the monomer and excimer regions show some small differences compared to the excitation spectrum of 1PEE (Figure 3). These small differences indicate a possible very weak interaction between the pyrene moieties.

Discussion

Comparing the fluorescence data with data for the other diastereoisomeric bichromophores, we find a clear analogy with the B1NEE system.[11] From the viewpoint of steric interactions the 1-pyrenyl chromophore can be regarded as a "substituted" 1-naphthyl chromophore. In B1PEE the steric interactions between the methyl groups and the H_{10}, $H_{10'}$ hydrogens are analogous to the interactions between H_8 and $H_{8'}$ in D1NEE. This interaction, together with the possibility of endo and exo overlap excimers, gives rise to several possible excimer geometries. The analogy with D1NEE is further confirmed in the ^{13}C and ^1H NMR spectra at low temperatures. In the ^{13}C NMR spectrum the absorption of the methine carbon of *meso*-B1PEE is broadened at 183 K, while for *rac*-B1PEE this absorption splits up (into at least two signals) at 178 K. This result indicates that the interconversion of conformers of B1PEE cannot occur on a nanosecond time scale due to the steric hindrance upon the rotation around the $C_{pyrenyl}$–$C_{methine}$ bond.

The temperature-dependent emission of the meso isomer suggests the following explanation for the observation made by Fox.[15] At low temperatures the meso isomer forms excimers more easily and its emission is hypsochromic in comparison with the excimer emission of the racemic isomer.

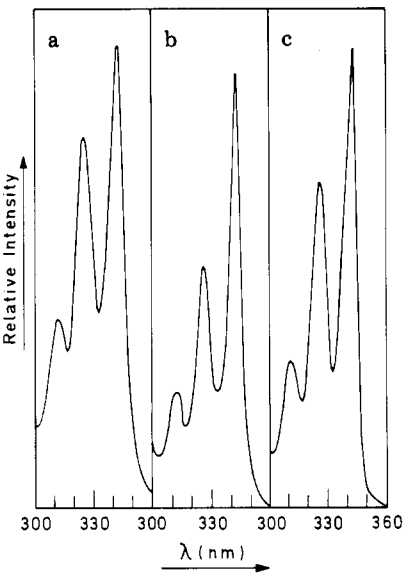


Figure 3. (a) Excitation spectra of *meso*- *rac*-B1PEE analyzed in the excimer region. Peak ratios are 0.80 and 0.40. (b) Excitation spectrum of *rac*-B1PEE. Peak ratios are 0.56 and 0.24. (c) Excitation spectrum of 1PEE. Peak ratios are 0.70 and 0.32.

Acknowledgment. K.D. thanks IWONL for a doctoral fellowship. We thank the NFWO, FKFO, and University Research Fund for financial contributions to the laboratory.

Registry No. 1PEE, 85883-24-5; *rac*-B1PEE, 85883-25-6; *meso*-B1PEE, 85883-26-7.

References and Notes

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