

## LUMINESCENT AND PHOTOCHEMICAL BEHAVIOUR OF DIARYL-ETHYLENES WITH 3-PYRENYL SUBSTITUENTS

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### Summary

A study was made of the photochemical and spectral behaviour of diarylethylenes with 3-pyrenyl side groups in dilute solutions at room temperature. As well as the usual *trans*  $\rightleftharpoons$  *cis* isomerization, dimerization leading to the formation of tetraarylcyclobutanes was observed. Fluorescence spectra, quantum yields and fluorescence lifetimes are reported, together with photochemical quantum yields for the pyrenylethylenes and their dimers.

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### 1. Introduction

The luminescent and photochemical properties of diarylethylenes are well established for stilbene and its derivatives [1 - 3] and somewhat less well established for naphthylethylenes [4 - 10]. In the present communication we report some results obtained on the luminescence and the direct photoisomerization of diarylethylenes with 3-pyrenyl side groups.

### 2. Experimental

The diarylethylenes studied were synthesized from 3-pyrenylaldehyde and the corresponding phosphonate using the Horner procedure [11]. The products were purified by recrystallization from benzene and then chromatographed on an alumina column. The compounds obtained in this way were *trans*-1-(phenyl)-2-(3-pyrenyl)ethylene (m.p. 156°, *cf.* ref. 12) and *trans*-1-(1-naphthyl)-2-(3-pyrenyl)ethylene (m.p. 182 - 183°, *cf.* ref. 12) which will be denoted as *trans*-I and *trans*-II respectively (see Fig. 1).

As described earlier [8], the *cis* isomers were synthesized in two stages: photolysis of dilute ( $10^{-5}$  -  $10^{-4}$  M) solutions of the *trans* isomers down to

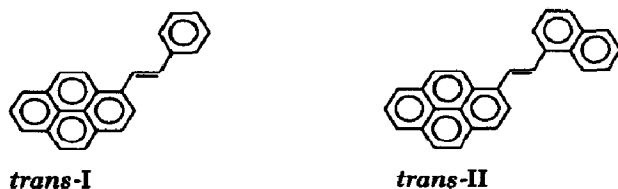


Fig. 1. The structures of the compounds investigated.

the photostationary state (Fig. 2(a)) followed by chromatography on an alumina column. The solution compositions were checked using absorption spectroscopy (Unicam SP-800).

Distilled commercially pure n-hexane, toluene and a 2:1 methanol-ether mixture were used as solvents. Molecular weights were determined by the ebullioscopic method.

Fluorescence spectra excited at an angle of  $90^\circ$  were recorded using the standard SDL-1 spectrofluorimeter with a double-grating monochromator. The fluorescence was excited with monochromatic irradiation from a high pressure 250 W mercury lamp, was stabilized in intensity and was analysed using another monochromator and sets of glass filters. Fluorescence quantum yields were measured at room temperature by comparison with a luminescent standard (anthracene in n-hexane,  $\phi_{f1} = 0.29$  [13]). Fluorescence lifetimes were measured as reported in ref. 14 using a convolution technique with a pulsed nitrogen laser and a stroboscopic oscilloscope.

The quantum yields of *cis*  $\rightleftharpoons$  *trans* photoisomerizations were determined spectrophotometrically as described previously [8].

### 3. Results and discussion

The absorption and fluorescence spectra of *trans-I*, *trans-II* and the corresponding *cis* isomers are presented in Fig. 3. The absorption spectra of the *trans* isomers consist of three structureless bands which are nearly coincident for the two compounds. Compared with stilbene and the naphthylethylenes, the first electronic bands in the spectra of the pyrenylethylenes are shifted towards the red by 50 - 70 nm and the second and the third electronic absorption bands have only slight shifts. The shapes and the extinction coefficient values of the absorption bands of the pyrenylethylenes are similar to those of the previously studied diarylethylenes [1 - 10]. The large Stokes shifts in the *cis*-diarylethylenes are probably caused by the much more pronounced relaxation losses of excitation energy compared with the *trans* molecules; the main reason is the non-planar *cis* configuration [4, 9, 16].

The fluorescence spectra of *trans-I* and *trans-II* have a distinct vibrational structure and are similar to the spectra of other diarylethylenes [1 - 10].

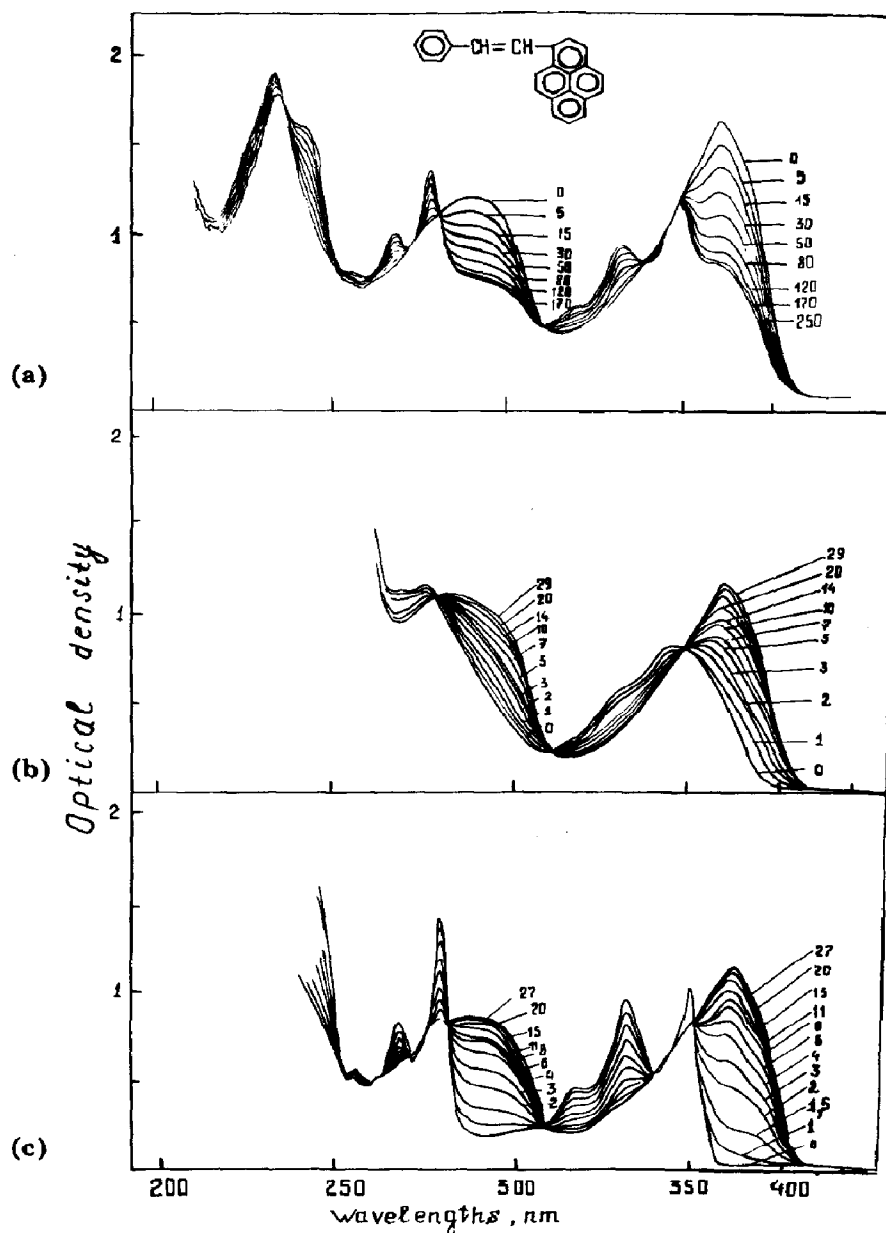


Fig. 2. Changes in the absorption spectra of 1-phenyl-2-(3-pyrenyl)ethylene in argon-flushed n-hexane: concentration =  $(3 - 5) \times 10^{-5}$  M;  $T = 25^\circ\text{C}$ ; the numbers on each curve specify the time of excitation in minutes; (a)  $\lambda = 405$  nm, *trans*  $\rightarrow$  *cis* + dimer; (b)  $\lambda = 366$  nm, *cis*  $\rightarrow$  *trans*; (c)  $\lambda = 366$  nm, dimer  $\rightarrow$  *trans*.

Features of the spectra of *cis*-I and *cis*-II are (1) the absence of vibrational structure in both the absorption and the fluorescence spectra, (2) a blue shift in the absorption spectra and a remarkable red shift in the fluorescence spectra compared with the spectra of the *trans* isomers, (3) an increase in the Stokes shifts compared with the *trans* isomers, (4) a lack of

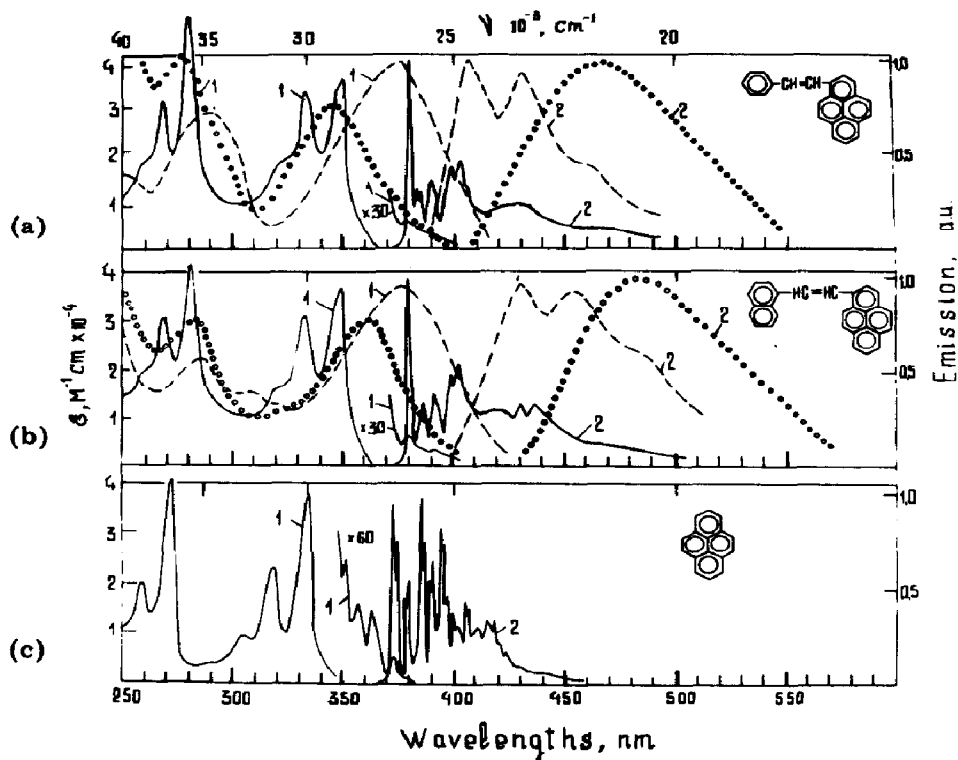


Fig. 3. Absorption (1) and fluorescence (2) spectra of the *trans* isomers (---), the *cis* isomers (o o o) and the dimers (—) of: (a) 1-phenyl-2-(3-pyrenyl)ethylene; (b) 1-(1-naphthyl)-2-(3-pyrenyl)ethylene; (c) pyrene. The solvent was *n*-hexane; concentration =  $(3 - 5) \times 10^{-5}$  M. The absorption spectra and the fluorescence spectra of the *trans* isomers and pyrene were recorded at 300 K; the fluorescence spectra of the *cis* isomers and the dimers were recorded at 77 K.

fluorescence at room temperature and (5) the occurrence of photochemical *cis*  $\rightleftharpoons$  *trans* isomerization (Fig. 2(b)). These features have also been observed for *cis*-stilbene and its naphthyl analogues [2 - 9].

During the separation of the photolysis products of *trans*-I (or *trans*-II), besides the usual *cis* isomers an unidentified product was detected in concentrations of up to 70 - 75% of those of the initial *trans* isomer. The compounds derived from the photolysis of *trans*-I and *trans*-II differ strongly in absorption and luminescence from the initial *trans* isomers (Fig. 3). They have distinct vibrational structure in both the absorption spectra and the luminescence spectra, their absorption spectra are very similar to that of pyrene (all the vibronic frequencies of pyrene, allowing for a small red shift, could be traced) [16] and the fluorescence spectra are very similar to that of 3-ethylpyrene [17]. The solutions only fluoresce at low temperatures. It should be noted that these unknown compounds are fully transformed upon irradiation into the initial *trans*-I or *trans*-II (Fig. 2(c)). The molecular weights of these species were found to be equal to 590 and 675 for the products of

I and II respectively, which are greater by as much as a factor of two than the initial molecular weights. This result leads us to conclude that the unknown products are pyrenylethylene dimers of the cyclobutane type. The high thermal stability and the similarity between the luminescent and photochemical behaviours of these compounds and pyrene support this assumption (Fig. 3, Table 1). In tetraarylcyclobutanes the conjugation chain is expected to be interrupted, which implies that the absorption and fluorescence spectra should be similar to the spectra of the separate aryl side groups. This may be the case for the compounds we investigated.

The fluorescence lifetimes  $\tau_{f1}$  of *trans*-I and *trans*-II (as well as of *cis*-I and *cis*-II) were found to be of the order of several nanoseconds, similar to other diarylethylenes [14], whereas the  $\tau_{f1}$  values for the compounds which are assumed to be dimers of I and II are 224 and 217 ns respectively (Table 1). The fluorescence quantum yields for *trans*-I and *trans*-II at room temperature are 0.6 - 0.7 in the presence of dissolved oxygen and approach unity for the argon-bubbled samples.

It should also be mentioned that the processes of *cis* isomer formation and cyclobutane dimer formation from the *trans* species are readily reversible. Irradiation of the *cis* isomers and the dimers with monochromatic light at wavelengths of 366, 334 and 313 nm results in full recovery of the initial *trans* isomers (Fig. 2). The quantum yields of the forward reactions  $\phi$  (*trans*  $\rightarrow$  *cis* + dimer) = 0.04 - 0.05) are significantly lower than those of the back reactions ( $\phi$  (*cis*  $\rightarrow$  *trans*) = 0.6 - 0.7 and  $\phi$  (dimer  $\rightarrow$  *trans*) = 0.8). Measurement of the dimerization quantum yield on its own was not possible.

It should be pointed out that the formation of dimeric molecules in dilute solutions is somewhat unexpected. The dimerization is known in principle for olefins, and for stilbene in particular, but it is normally efficient at rather high olefin concentrations, about  $10^{-2}$  M [18]. In our case dimerization took place in dilute solutions ( $10^{-4}$  -  $10^{-5}$  M) when unimolecular processes such as *trans*  $\rightleftharpoons$  *cis* isomerization and photocyclization should have occurred. However, the reactions do take place within a wide range of concentrations ( $10^{-5}$  -  $10^{-2}$  M) and both in the presence and in the absence of dissolved oxygen. The pyrenylethylenes studied appeared to display no photocyclization at all under the experimental conditions employed; the photocyclization products were found only when iodide was introduced into the solution. The reason for this particular behaviour is not yet understood. We speculate that, before photodimerization, the pyrenylethylenes form some sandwich-like structure which prepares the two molecules for the photochemical reaction. Of particular interest is the question of which configurational and conformational isomers are the precursors of the photodimers formed in dilute solutions.

In conclusion, the diarylethylenes with 3-pyrenyl substituents displayed luminescent and photochemical properties which are both well known and widely accepted, and in addition some features which are peculiar to these particular compounds. These features are not yet understood and therefore should stimulate further interest in these compounds.

TABLE 1

Fluorescent and photochemical properties of diarylethylenes with 3-pyrenyl substituents

Compound	Solvent	$\phi_{fl}(\text{trans})^a$	$\tau_{fl}(\text{ns})$		$\phi(\text{trans} \rightarrow \text{cis}) + \phi(\text{trans} \rightarrow \text{dimer})^d$	$\phi(\text{cis} \rightarrow \text{trans})^d$	$\phi(\text{dimer} \rightarrow \text{trans})^d$	
			trans	cis				dimer
1-phenyl-2-(3-pyrenyl)ethylene	n-hexane	0.70 <sup>b</sup>	4 <sup>b</sup>	3 <sup>e</sup>	224 <sup>e</sup>	0.04	0.70	0.80
		1.0 <sup>c</sup>	6 <sup>c</sup>					
1-(1-naphthyl)-2-(3-pyrenyl)ethylene	n-hexane	0.70 <sup>b</sup>	3 <sup>b</sup>	4 <sup>e</sup>	217 <sup>e</sup>	0.05	0.60	0.80
		1.00 <sup>c</sup>	5 <sup>c</sup>					

<sup>a</sup>Experimental accuracy,  $\pm 10\%$ ;  $\lambda_{ex}$ , 313, 334 and 366 nm.<sup>b</sup>In the presence of dissolved oxygen and at 300 K.<sup>c</sup>In argon-flushed solutions and at 300 K.<sup>d</sup>Experimental accuracy,  $\pm 30\%$ .<sup>e</sup>Experimental accuracy,  $\pm 0.5$  ns [14].

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