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SOME PECULIARITIES OF DIARYLETHYLENES WITH 3-PYRENYL FRAGMENTS*

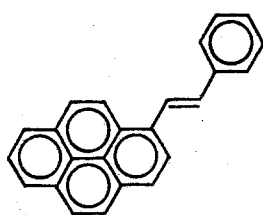
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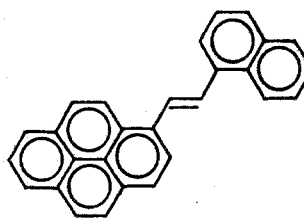
The fluorescence and photochemical properties of diarylethylenes have been investigated chiefly for stilbene and its derivatives [1-3], while among the higher analogs of stilbene, only naphthylethylenes have been studied in detail [4-10].

In this work we investigated the spectral-fluorescent properties and direct photoisomerization of diarylethylenes with 3-pyrenyl fragments.

The compounds in the trans-form used in the work were synthesized by the method of Horner [11] from 3-pyrenyl aldehyde and the corresponding phosphonate. Purification was performed by recrystallization from benzene, n-hexane, and chromatography of hexane solutions on Al₂O₃. Thus, we obtained trans-1-phenyl-2-(3-pyrenyl)ethylene, mp = 156°C (cf. [12]) and trans-1-(1-naphthyl)-2-(3-pyrenyl)ethylene, mp = 182-183°C (cf. [12]), arbitrarily denoted for brevity as trans-I and trans-II, respectively:



trans-I



trans-II

The cis-isomers, just as before [8], were produced in two steps: photolysis of dilute solutions ($C = 10^{-4}$ - 10^{-5} M) of the trans-isomers to the photostationary state (Fig. 1a), and chromatography on Al₂O₃, permitting separation of the starting materials and final product. The composition of the solution was monitored according to the absorption spectra, both in photolysis and in chromatography.

The solvents used for the spectral investigations were CP grade n-hexane, subjected to redistillation, CP toluene, and methanol-ether (2:1).

The molecular weights of the trans-isomers, as well as the photolysis products, were determined by an ebullioscopic method with external heating of the solution according to Beckman.

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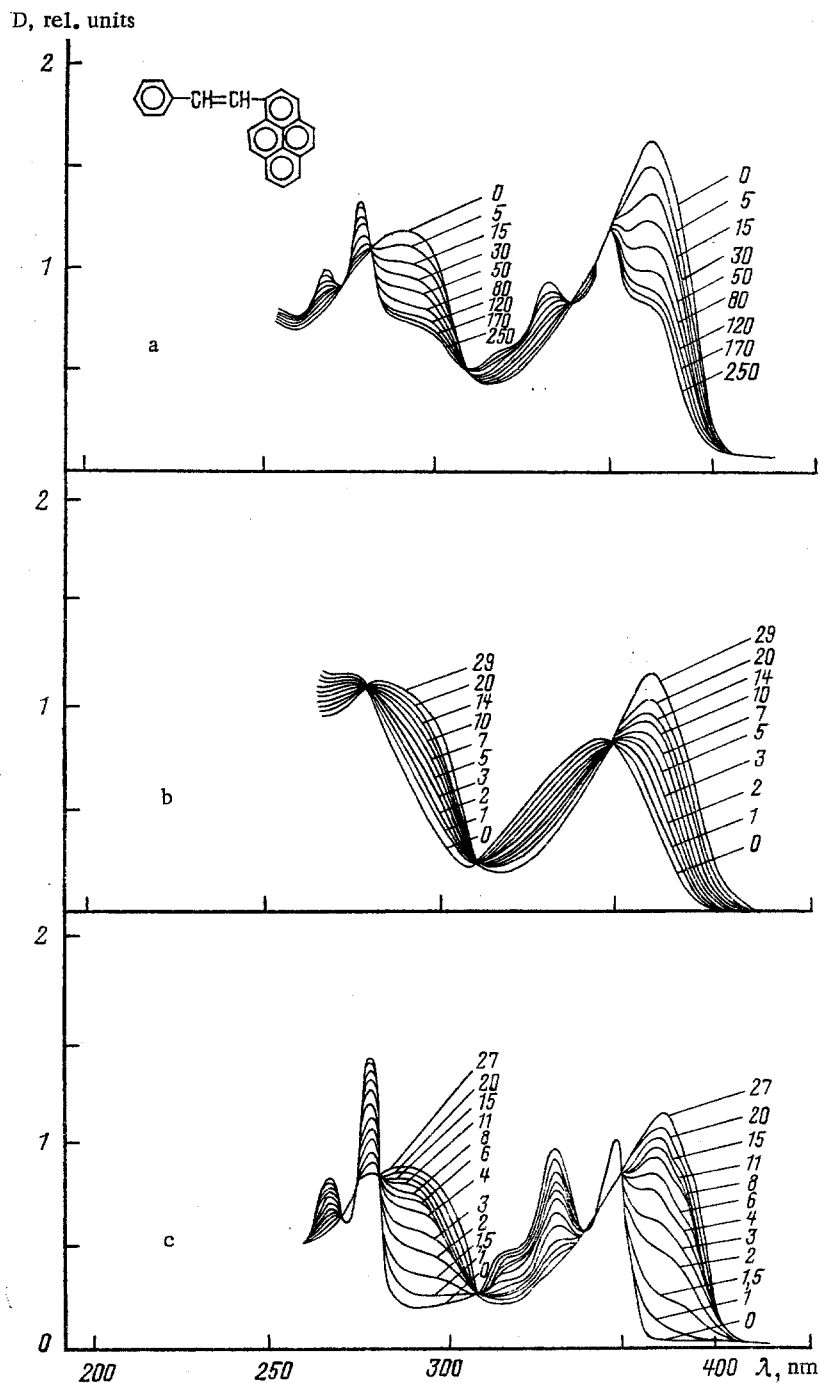


Fig. 1. Photoconversion of 1-phenyl-2-(3-pyrenyl)ethylene: trans $\xrightarrow{\lambda 405 \text{ nm}}$ cis-isomer + cyclodimer (a), cis $\xrightarrow{\lambda 366 \text{ nm}}$ trans-isomer (b), and cyclodimer $\xrightarrow{\lambda 366 \text{ nm}}$ trans-isomer (c). Solvent n-hexane, $T = 25^\circ\text{C}$, $C = (3-5) \cdot 10^{-5} \text{ M}$, solutions purged with argon. The numbers next to the curves represent the time of irradiation in minutes.

The absorption spectra were recorded on a Unicam SP-800 spectrophotometer. The fluorescence spectra were recorded on a standard SDL-1 spectrofluorometer with double grid monochromator with excitation at an angle of 90° . The excitation of the investigated solutions was performed with monochromatic radiation of a DRSh-250 mercury lamp, stabilized in intensity. Individual groups of lines were isolated with a monochromator and light filters.

Measurements of the quantum yields of fluorescences of the trans-isomers were performed at room temperature by comparison with a standard. Anthracene, for which $\Phi_{f1} = 0.29$ in n-hexane [13, p. 251], was taken as the fluorescence standard.

Measurement of the lifetime of fluorescence (τ_{f1}) was performed in hexane solutions at 300°K and 77°K in the presence of atmospheric oxygen and in argon-purged samples with the aid of the fluorometric setup described in [14].

The quantum yields of cis \rightleftharpoons trans-photoisomerization were determined spectrophotometrically [8]. The intensity of the incident light was measured with a ferrioxalate actinometer [13, p. 200]; the light intensity at $\lambda = 313, 334, 366,$ and 405 nm was $6.6 \cdot 10^{14}, 3.4 \cdot 10^{14}, 4.0 \cdot 10^{15},$ and $4.3 \cdot 10^{15}$ photons \cdot cm $^{-2} \cdot$ sec $^{-1}$, respectively. Monitoring of the lamp system ensured constancy of these values with an accuracy of $\pm 15\%$ throughout the entire period of work.

Figure 2 presents the electronic absorption and fluorescence spectra of the pyrenylethylenes trans-I and II, obtained in this work. The absorption spectra of these compounds consist of three structureless bands, which practically coincide in position of the maxima for both compounds. From a comparison of the absorption spectra of transpyrenylethylenes with stilbene and naphthylethylenes, a substantial shift of the first absorption band in pyrenylethylenes by 50-70 nm into the red region and negligible shifts of the second and third bands can be noted, while the nature of the absorption bands of transpyrenylethylenes does not differ from that of previously investigated diarylethylenes [1-9]. The values of the coefficients of extinction for pyrenylethylenes are close to the values of the coefficients of extinction of the trans-isomers of stilbene and other diarylethylenes.

The fluorescence spectra of the compounds trans-I and II have a pronounced vibrational structure with three maxima and are also analogous in nature of the fluorescence spectra of stilbene and naphthylethylenes. Thus, the absorption and fluorescence spectra of the trans-forms of other previously investigated diarylethylenes [1-10].

The cis-isomers of compounds I and II, produced photochemically, are characterized (Fig. 2) by the absence of a vibrational structure in the absorption and fluorescence spectra, a long-wave shift of the absorption spectra, and a substantial long-wave shift of the fluorescence spectra in comparison with those of the trans-isomers, an increase in the Stokes shift in comparison with the trans-isomers, the absence of fluorescence in solutions at room temperature, and photoconversion of the cis-form to the trans-form (Fig. 1b). Analogous properties are possessed by the cis-isomers of stilbene and its previously studied analogs [2-9].

In the chromatographic separation of products of the photochemical conversion of the compounds trans-I (or II), together with the cis-isomers, still another product could be isolated, and moreover, predominantly (70-75% of the original amount of the initial trans-isomer). These compounds, obtained from trans-I and II, are close in spectral-fluorescent properties and differ substantially from the initial trans-isomers and the corresponding cis-isomers (Fig. 2). In their absorption and fluorescence spectra, a pronounced vibrational structure is detected; the absorption spectrum has an appreciable similarity to the absorption spectrum of pyrene; All the vibrational frequencies of pyrene appear, with a small bathochromic shift, while the fluorescence spectrum is similar to the fluorescence spectrum of 3-ethylpyrene [13, pp. 364, 366]. Fluorescence is observed in solutions only at low temperatures. At room temperature these products do not fluoresce. It is interesting to note that photoexcitation of solutions of these compounds leads to a quantitative conversion of these compounds to the initial trans-isomers (Fig. 1c).

To identify the compounds obtained, in addition to spectral fluorescent measurements, we measured their molecular weights, which were 590 and 675 for products I and II, respectively, which is equal to twice the value of the molecular weights of the initial compound. This suggests that the unknown products are dimers of pyrenylethylenes of the cyclobutane type. Some confirmation of this may be provided by their comparatively low thermal stability and the similarity of the spectral fluorescent and photochemical properties of the compounds obtained and pyrene (Fig. 2, Table 1). In tetraarylcyclobutanes, in contrast to diarylethylene molecules, the chain of conjugation between the aryl fragments is interrupted, as a result of which, individual aryl fragments should appear in the absorption and fluorescence spectra, which we also observed in our case.

Measurements of the lifetime of the fluorescent state showed that τ_{f1} at 77°K for trans-I and II, as well as their cis-isomers, just as in previously investigated diaryl ethylenes [14], are several nanoseconds, whereas τ_{f1} of cyclobutane dimers of compounds I and II are close to those of pyrene and are 224 and 217 nsec, respectively (Table 1). The quantum yields of the fluorescence of the trans-isomers of compounds I and II in solutions at room temperature are rather high: 0.6-0.7 in the presence of atmospheric oxygen and close to one in argon-purged samples.

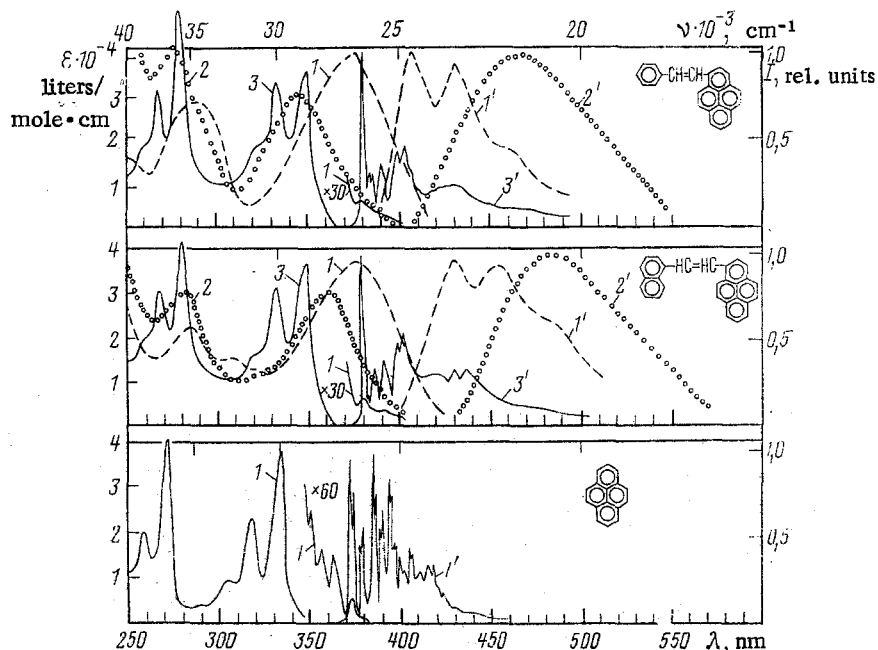


Fig. 2. Absorption (1-3) and fluorescence spectra (1'-3') of trans- (1, 1') and cis-isomers (2, 2') and cyclodimers (3, 3') of 1-phenyl-2-(3-pyrenyl)- and 1-(1-naphthyl)-2-(3-pyrenyl)ethylenes, as well as the absorption (1) and fluorescence (1') spectra of pyrene. All the absorption spectra were recorded at 300°K; the fluorescence spectra of the cis-isomers, cyclodimers, and pyrene were recorded at 77°K, and those of the trans-isomers at 300°K. The solvent was n-hexane, $C = (3-5) \cdot 10^{-5}$ M. The coefficients of extinction of the cis- and trans-isomers correspond to Fig. 2; the coefficient of extinction of the dimer is halved.

TABLE 1. Fluorescent and Photochemical Characteristics of Diaryl Ethylenes with 3-Pyrenyl Fragments

Compound	τ_{fl} , nsec			ϕ cis \rightarrow trans
	trans	cis	dimer	
1-Phenyl-2-(3-pyrenyl)-ethylene	4a 6b	3*	224*	0,7
1-(1-Naphthyl)-2-(3-pyrenyl)-ethylene	3a 5b	4*	217*	0,6

* τ_{fl} of the cis-isomers and dimers were measured at 77°K.

Notes. The solvent was n-hexane, $\phi_{fl}^{trans} = 0.7$ was determined in the presence of atmospheric oxygen and in argon-purged samples, in which the values of ϕ_{fl} were close to one; λ_{excit} 313, 334, and 366 nm. The accuracy of the determination of ϕ_{fl} was $\pm 10\%$, the quantum yields of the photochemical reactions $\pm 30\%$. τ_{fl} of the trans-isomers were determined at 300°K in the presence of atmospheric oxygen (a) and in argon-purged samples (b). The accuracy of the measurement of τ_{fl} was 0.5 nsec. The source of excitation of the fluorescence in the measurement of τ_{fl} was a nitrogen laser with wavelength of radiation $\lambda = 337$ nm and duration of pulse 10 nsec,

ϕ trans \rightarrow cis + dimer = 0.01 ± 0.003 ; ϕ dimer \rightarrow trans = 0.8.

Let us note that the process of photoconversion of the trans-isomers of compounds I and II to the corresponding cis-isomers and cyclodimers is reversible. The photolysis of preliminarily irradiated ($\lambda = 405$ nm) solutions of the trans-isomers, as well as the cis-isomers and dimers isolated chromatographically, by light with $\lambda = 366, 334,$ and 313 nm leads to a complete restoration of the initial trans-isomers (Fig. 1). The values of the summary quantum yields of the photoconversion of the trans-isomers I and II to the cis-isomers and cyclodimers, which we took as tetraarylcyclobutanes, are $0.01-0.007$; those of the cis-isomers and tetraarylcyclobutanes to the trans-isomers are an order of magnitude higher: $0.5-0.8$ (Table 1).

It should be emphasized that the formation of dimers in dilute solutions of diarylethylenes is somewhat unexpected and is an interesting peculiarity of the investigated compounds. In principle, the dimerization reaction is possible for olefins, and in particular, for stilbene, but it requires rather high olefin concentrations ($C = 10^{-2}$ M) [15, 16]. Photolysis of compounds of trans-3-pyrenyl ethylenes, however, was performed in dilute solutions ($C = 10^{-3}-10^{-5}$ M), when monomolecular processes characteristic of diarylethylenes should primarily have occurred, such as, e.g., the reactions of trans-cis-photoisomerization and photocyclization with the formation of condensed hydrocarbons. Actually, photoirradiation of pyrenylethylenes trans-I and II in the presence of atmospheric oxygen and in argon-purged samples in a broad range of concentrations ($C = 10^{-5}-10^{-2}$ M) leads to the production of two products: the traditional cis-isomer and the product of dimerization of pyrenylethylenes. The reaction of photocyclization was not observed under the conditions of our experiments, and only in the presence of iodine were products of photocyclization of the investigated pyrenylethylenes detected.

The results cited above are an example of the influence of aromatic substituents on the properties of diarylethylenes. Diarylethylenes with 3-pyrenyl fragments exhibited both common features characteristic of the class of diarylethylenes and certain peculiarities, the cause of the appearance of which is of interest for further investigations.

In conclusion, the authors would like to express their gratitude to V. F. Razumov for aid in measuring the lifetime of the fluorescence and Yu. B. Shekk for discussion of the results of the work.

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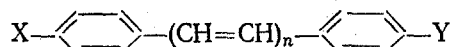
SPECTROSCOPIC INVESTIGATION OF THE ASSOCIATION OF MOLECULES WITH AN ARYLETHYLENE GROUP IN SOLUTIONS*

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and L. Ya. Malkes

UDC 535.37

The investigation of molecules with an arylethylene group is due to their wide use in various fields of science and technology. The available studies have been devoted to the influence of solvents [1, 2], temperature, viscosity [3], and other factors on the spectral properties and photochemical reactions of arylethylene (AE) molecules existing in a monomer state.

At present there are no investigations devoted to processes of association of AE molecules; moreover, it is noted in [4] that these molecules have a low ability to form associated molecules, both in the ground state and in the excited state. In this work we undertook to disclose the conditions under which associated AE molecules are formed, to investigate their spectral characteristics, and to study the influence of the nature of the solvents, concentration, and temperature of the solution, as well as the influence of the structure of dissolved molecules on processes of association of AE. The following AE and arylbutadienes (AB) with a regularly varying structure:



where $n = 1-3$; X, Y (in various combinations) = H, OH, CN, OCH₃, NH₂, NH-COCH₃, NO₂, N(CH₃)₂, Cl, were selected as objects of investigation.

First of all, we studied the concentration dependence ($4 \cdot 10^{-6}$ - 10^{-3} M) of the electronic spectra of the selected compounds in solvents of various kinds: in chloroform, cyclohexane, dimethyl sulfoxide (DMSO), and dioxane (D-n). Our experiments showed that the absorption and fluorescence spectra of all the investigated solutions remained constant within a broad range of concentrations and belong to molecules in a monomer state. Then we studied the absorption and fluorescence spectra of AE in a binary mixture (dioxane + water). As an example, Fig. 1a presents the changes in the absorption spectra of stilbene ($C = 4 \cdot 10^{-4}$ M, X = Y = H) in the transition from dioxane solution to aqueous dioxane solution. It can be seen that with increasing fraction of water in the binary mixture, a drop in the integral absorption capacity is observed in the absorption spectrum, and the vibrational structure disappears simultaneously; when the fraction of water is further increased, the spectrum becomes structureless. In the selected binary solvents, analogous spectral changes are observed for stilbene derivatives (X = H, Y = OH, CN, Cl; X = NH₂, Y = OCH₃, and X = N(CH₃)₂, Y = NHCOCH₃).

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