

Brief Communications

One-quantum process of formation of *trans*-1,2-di(2-naphthyl)ethylene under photolysis of 4a,4b-dihydrodibenzphenanthrene

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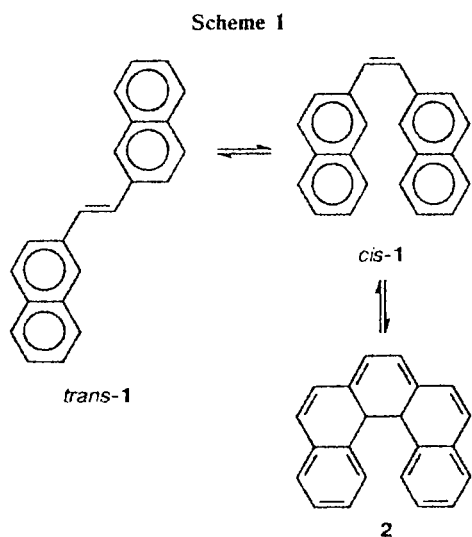
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The *trans*-isomer of 1,2-di(2-naphthyl)ethylene is formed along with the *cis*-isomer in the one-quantum process under irradiation at the wavelength corresponding to the long-wave absorption band of 4a,4b-dihydrodibenzphenanthrene. The quantum yields of the photoinitiated processes were measured. The adiabatic mechanism was suggested for the photoinitiated ring opening in 4a,4b-dihydrodibenzphenanthrene.

Key words: photochemistry, diarylethylenes, 1,2-di(2-naphthyl)ethylene, photoisomerization, photocyclization, adiabatic mechanism of reaction.

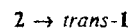
Two reversible photochemical reactions occur in dilute solutions of diarylethylenes: photoisomerization and

photocyclization.^{1,2} The commonly accepted scheme of transformations of diarylethylenes (using 1,2-di(naphth-2-yl)ethylene (**1**) as an example) is the following (Scheme 1).



Up until now, it was considered that for stilbene and naphthylethylenes, the transition from the *trans*-isomer to the cyclic product requires successive absorption of two photons. However, it has been found recently that the product of intramolecular cyclization (dihydronicene) can be obtained in the one-quantum process by the excitation of *trans*-1,2-di-(naphth-1-yl)ethylene.³

In the present work, we consider the possibility of the direct one-quantum transformation of 4a,4b-dihydrodibenzphenanthrene (**2**) into *trans*-isomer (**1**) under irradiation at the long-wave absorption band.



This does not contradict the law of energy conservation, since it is known^{1,2,4} that the chemical energy ($\sim 40\text{--}50\text{ kJ mol}^{-1}$ for **2** in the ground state) is accumulated during photocyclization of *cis*-1.

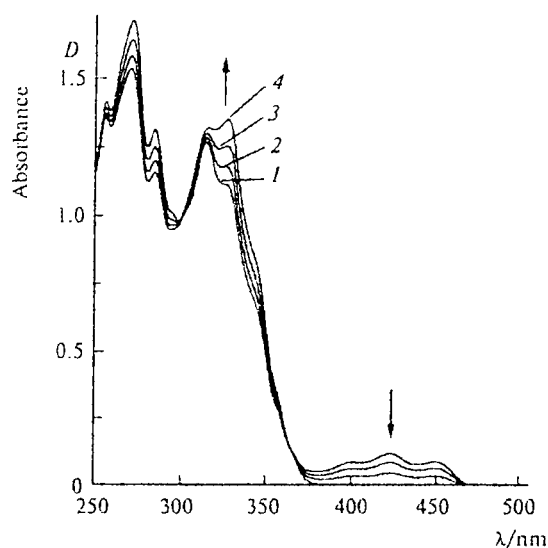


Fig. 1. Series of absorption spectra of the photostationary mixture of *cis*-1, *trans*-1, and 2 under successive irradiation with a mercury lamp at $\lambda = 436$ nm; τ /min: 0 (1), 2 (2), 6 (3), and 30 (4).

A solution of *cis*-1 (concentration $5.7 \cdot 10^{-5}$ mol L $^{-1}$) in *n*-heptane was irradiated with a mercury lamp at 366 nm to achieve the photostationary equilibrium between the starting *cis*-isomer 1 and compounds *trans*-1 and 2 that formed. Then the solution was irradiated at the wavelength of 436 nm corresponding to the absorption of 2 only.

The corresponding series of absorption spectra is presented in Fig. 1. It is well seen that the long-wave absorption of 2 disappears with a simultaneous increase in the optical density at $\lambda \leq 400$ nm. The distinct isobestic point at $\lambda = 367$ nm can indicate that the concentrations of only two substances (in the given case, 2 and *cis*-1) change during the reaction, whereas the concentration of *trans*-1 remains unchanged.

However, the deconvolution of the spectra into basis spectra^{4,5} shows (Fig. 2) that the relative concentration of *trans*-1 increases from 20% to 30% along with an increase in the concentration of *cis*-1. The result obtained contradicts the commonly accepted mechanism of photoinitiated opening of cycle 2 resulting in the formation of the *cis*-isomer only.¹ If it is assumed that the fraction of *trans*-1 during photolysis of 2 remains unchanged and equal to the fraction of *trans*-1 in the end of photolysis (*i.e.*, 30%), the apparent change in the concentration of *trans*-1 can be explained by an inaccuracy in determination of the absorption spectrum of 2. In particular, it can be assumed that the absorption spectrum of 2 used in the work is a linear combination of the true spectrum of 2 and the spectrum of *trans*-1.

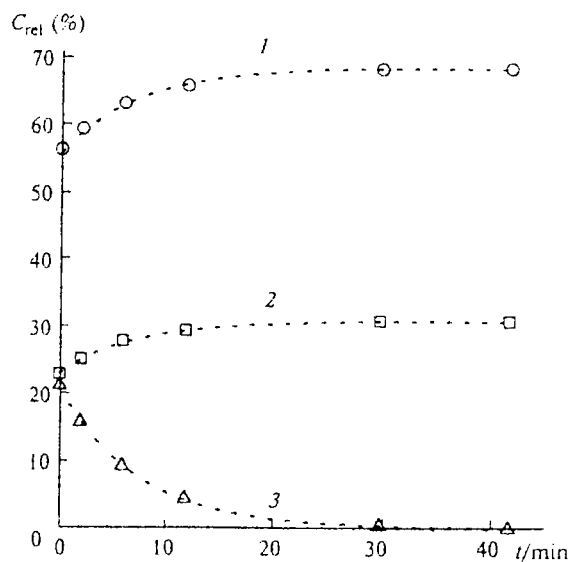


Fig. 2. Kinetic dependences of the relative concentrations (C_{rel} (%)) of components under successive irradiation of the photostationary mixture of *cis*-1 (1), *trans*-1 (2), and 2 (3) with a mercury lamp at $\lambda = 436$ nm.

For example, it is known¹ that the extinction coefficient of the long-wave band of 2 ($\lambda_{max} = 425$ nm) in a mixture of methylcyclohexane and 2-methylpentane is the following: $\epsilon_{max} = 12000$ L mol $^{-1}$ cm $^{-1} \pm 10\%$. Since only 2 absorbs at 425 nm, its relative concentration in the photostationary mixture can be calculated: $[2] = 17 \pm 2\%$. Then accepting that $[trans-1] = 30\%$, we find

$$[cis-1] = 100\% - [trans-1] - [2] = 53 \pm 3\%.$$

If the fractions of absorption of *trans*-1 and *cis*-1 corresponding to their relative concentrations assumed (30% and 53%, respectively) are subtracted from the experimental spectrum (Fig. 3, curve 2), the true absorption spectrum of 2 should be obtained.

The result of this subtraction is shown in Fig. 3 (curve 4). It is seen that the resulting spectrum of 2 has the region of negative absorption ($D_{min} = 0.1$), which shifts substantially from the limits of experimental error ($\delta_D < 0.01$). This indicates that before irradiation at $\lambda = 436$ nm, the concentration of *trans*-1 was considerably lower than that after the complete disappearance of 2.

Thus, it can be concluded that we observe the one-quantum process of photoinitiated transformation of 2 into *trans*-1, which suggests the adiabatic mechanism of photodecyclization of 2. In this case, the isobestic point is explained by the fact that *cis*-1 and *trans*-1 are formed in a constant ratio during photolysis of 2. In fact, the ratio of concentrations of *cis*-1 and *trans*-1 formed during irradiation of 2 at $\lambda = 436$ nm is unchanged and equal to 1.5, *i.e.*, compound 2 gives 60% *cis*-isomer, and

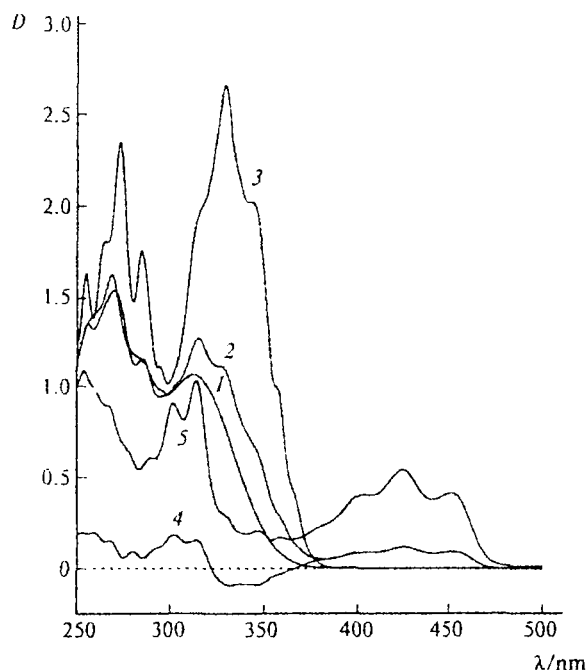


Fig. 3. Absorption spectra: 1, starting solution of *cis*-1 in *n*-heptane; 2, photostationary mixture of *cis*-1, *trans*-1, and 2 after irradiation of the starting solution of *cis*-1 at $\lambda = 366$ nm; 3, solution of *trans*-1 in *n*-heptane; 4, compound 2. Absorption spectrum obtained by subtraction of spectra 1 and 3 multiplied by coefficients 0.53 and 0.3, respectively, from spectrum 2 (5). All spectra (except for 5) are presented for a concentration of $5.7 \cdot 10^{-5}$ mol L $^{-1}$.

the rest 40% molecules of 2 are directly transformed into the *trans*-isomer. The measured quantum yields of

ring opening $\phi_2 \rightarrow \textit{cis}$ -1 and $\phi_2 \rightarrow \textit{trans}$ -1 are equal to $1.2 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$, respectively.

Experimental

All experiments were carried out with dilute solutions of 1,2-di-(2-naphthyl)ethylene in *n*-heptane in sealed quartz spectrophotometric cells from which air was removed by three freezing-thawing cycles at the temperature of liquid nitrogen followed by evacuation to 0.015 Torr. Solutions were irradiated at 20 °C with a DRSh-250 mercury lamp. Lines at 366 and 436 nm were isolated by standard glass light filters. A PP-1 bolometer was used for the determination of light intensity.

Absorption spectra of solutions were measured on an automated Specord M40 spectrometer during irradiation at certain time intervals. Concentrations of 2, *cis*-1, and *trans*-1 were calculated by subsequent mathematical processing.⁴ The absorption spectrum of 2 was determined by the procedure described previously.

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