Photochromic properties of phenanthroline-annulated spirooxazine in the solid state

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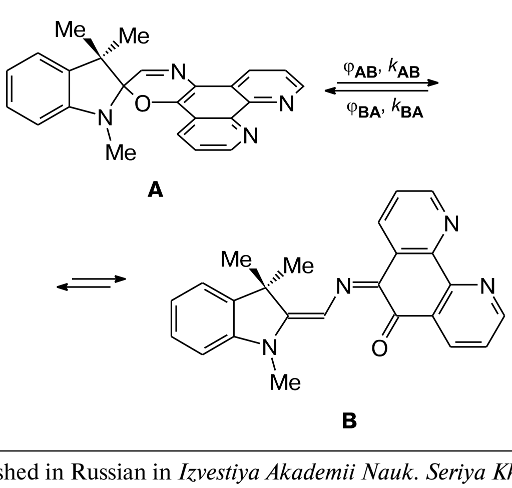
Photochromic transformations of phenanthroline-annulated spirooxazine were observed in polycrystalline powders and solid-phase films obtained from solutions by solvent evaporation. The spectral and kinetic properties of the solid-phase films were studied by stationary absorption spectroscopy and laser flash photolysis. The mechanism of photoinitiated reactions of solid-phase samples of phenanthroline-annulated spirooxazine includes mutual transformations of different transoid isomers of the merocyanine form.

Key words: photochemistry, photochromism, laser flash photolysis, spectrophotometry.

Organic photochromic compounds can be used in the development of various photosensitive systems, such as optical media with nonlinear absorption, systems of optical information recording, and optical switchers. Compounds retaining ability to photochromic transformations in solid films or in the crystalline state are of special interest. Such compounds are actively used during the recent decade (see reviews[1,2] and references therein). Photochromic transformations were observed in both polycrystalline films and single crystals of diarylethenes[3,4] and derivatives of salicylaldehyde,[1,5] arylhydrazides,[6] fulgides,[7] and chromenes.[8]

Scheme 1



Spiropyrans and spirooxazines (Scheme 1) refer to the most widely studied classes of photochromic compounds. In this case, photochromic transformations are due to transitions between the closed spiro form **A** and open merocyanine form **B**. As a rule, spiropyrans and spirooxazines are not photochemically active in microcrystalline powders and single crystals.[9] This is explained by the fact that the phototransformations caused by bond cleavage between the spiro-carbon atom and oxygen atom followed by isomerization of the molecule require large free volume.

However, several examples for the manifestation of the ability of spiropyrans and spirooxazines to photochromic transformations in the poly- and monocrystalline states are described in the literature. These properties are characteristic of crystals of spiropyran[9—11] and spirooxazine[12] salts including pyridinium moiety. In this case, the possibility of photoisomerization is determined, most likely, by the specific feature of the structures of these compounds in the solid state. The crystal structure formed by cationic layers separated by particular iodide ions provides a sufficient volume for phototransformations. Several examples are known for the non-salt spiro compounds exhibiting photochromic transformations. The photochromic properties of single crystals of *N*-(*n*-propyl)nitrospiropyran were observed.[13] The photochromic transformations of spirooxazine containing the azahomoadamantyl group were reported.[14] The free volume necessary for photoisomerization is provided by either cavities in the crystal packing[13] or a large size of one of the functional groups.[14]

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 119—126, January, 2011.

Photochromism of two spirooxazines and two naphthopyrans of rather complicated structure in the polycrystalline state was found recently.[15] An interesting effect is the formation of the short-lived (characteristic lifetime about several nanoseconds) isomers of the nonplanar photocolored form upon irradiation with femtosecond laser pulses of microcrystalline powders of the spiro compounds that exhibit no photochromic properties under the conditions of steady-state irradiation.[16—19]

In this work, the photochromic transformations of phenanthroline-annulated 3,3-trimethylspiro[indoline-2,2´-bipyrido-[3,2-*f*][2,3-*h*][1,4]benzoxazine] (SPO1)[20] in the polycrystalline state (see Scheme 1) were found and studied.

Experimental

Spirooxazine SPO1 was synthesized according to the procedure described earlier.[21] Spirooxazines synthesized by the standard method were polycrystalline powders.[20,21] Samples of three types were used. Samples of the first type are powders of SPO1 placed between two polished quartz plates. The existence of microcrystals results in light scattering and an increase in the background absorbance of the sample, which increases substantially in the UV spectral region. Samples of the second type are powders of SPO1 molded in a KBr pellet 8 mm in diameter and 1 mm thick. The optical quality of the pellets was also low (the absorbance caused by light scattering was ~1).

More high-grade samples of the third type were prepared as films from solutions of SPO1. Propan-2-ol (Aldrich) was used as a solvent. Films on quartz supports were prepared by solvent evaporation in air at room temperature. Then the samples were placed in a desiccator and stored for 3—5 h under a pressure of ~0.1 Torr to remove residues of the solvent and water. The film thickness (calculated from the known amount of spirooxazine and the surface area of the film) was ~100 nm. The relative heterogeneity of the absorbance along the film with a surface area of ~3 cm^2 did not exceed 30%, and the background light scattering was considerably less than that in the samples of the first and second types. The phase composition of the films was not determined, and they could be either polycrystalline or amorphous. A possible variant is the presence of both polycrystalline and amorphous phases in such samples.

The samples were irradiated with light from a DRSh-500 high-pressure mercury lamp with a set of glass filters for picking out radiation with the needed wavelength. Quantum yields of photolysis were estimated for the samples of the third type assuming homogeneity of the thickness of the film obtained by solvent evaporation using the formula

$$\varphi_{\text{solid}} = [(\mathrm{d}D/\mathrm{d}t)_{\text{solid}} S N_{\text{A}}]/[I_0 \varepsilon_{\text{solid}}(1 - 10^{-D_{\text{ex}}})], \qquad (1)$$

where $(\mathrm{d}D/\mathrm{d}t)_{\text{solid}}$ is the rate of changing the absorbance of the film sample at small conversions, S is the surface area of the film, D_{ex} is the absorbance of the sample at the excitation wavelength, $\varepsilon_{\text{solid}}$ is the molar absorption coefficient of SPO1 at the detection wavelength (at the maximum of the absorption band of the **B** form), I_0 is the number of excitation quanta per time unit, and N_{A} is Avogardo´s number. It was assumed in the calculations that the molar absorption coefficient of the **B** form in the film coincides with its value in the nonpolar solvent (toluene, $\varepsilon_{\mathbf{B}} = 5.2 \cdot 10^4$ L mol^{-1} cm^{-1} (see Ref. 20)). Note that the values of molar absorption coefficients of the **B** form of SPO1 in various solvents (polar and nonpolar) differ by less than 10% (see Ref. 20). Solutions of spirooxazines in alcohols with the known values of quantum yields were used to measure the incident light intensity.[20] In addition, the light intensity was monitored by the Gentec-EO system (Canada) with a SOLO-2 monitor and a PH100-SiUV photodiode detector. The radiation power of the mercury line at 365 nm ranged from 10 to 30 mW cm^{-2} ((1.8—5.5) $\cdot$ 10^{16} quantum cm^{-2} s^{-1}). The measurement accuracy of quantum yields for the film samples was estimated by the data scatter for a series of five samples.

Optical spectra of the film samples were recorded on an Agilent 8453 spectrophotometer (Agilent Technologies). The diode array of this spectrophotometer makes it possible to record spectra in a region of 190—1100 nm for several seconds, which is substantial for studying fast photochromic transformations. A Specord UV-Vis spectrophotometer (Carl Zeiss) with a narrow probing light beam (width ~0.8 mm) was used for monitoring homogeneity of the film samples. A USB 4000 spectrophotometer (Ocean Optics) was used for recording dispersed powdered samples of the first type. A small diameter of the probing light beam (~3 mm) of this instrument and the possibility to accumulate up to 100 spectral curves made it possible to record spectra of powdered samples of the first type with satisfactory quality.

Laser flash photolysis of solutions was carried out on the technique with excitation with a neodymium laser (third harmonic 355 nm, pulse duration 7 ns, energy 0.3—1.5 J cm^{-2}).[22] The exciting and probing light beams fell on the sample at a small angle (~2°). Kinetic curves were detected at various probing wavelengths. A QE25SP-H-MB pyroelectric detector (Gentec-EO) was used for measurements of the laser pulse energy.

In flash photolysis experiments, each laser pulse should fall on the non-irradiated region of the sample, because the content of the **A** form of spirooxazine decreases substantially within one pulse. To improve the signal-to-noise ratio, kinetic curves were accumulated after 5—10 laser pulses on various regions of the film. Heterogeneity of the thickness and initial absorbance of the film at the laser radiation wavelength (355 nm) results in the variation of the value of the intermediate absorption signal. To take into account this heterogeneity, the signals were renormalized by an internal standard, which was the absorption in a range of 40—50 μs. The absorbance does not change after this time, and the spectrum corresponds to the spectrum of the **B** form appeared upon steady-state irradiation. This spectrum was used for renormalization of the signals and determination of the spectrum at short times, for example, immediately after a laser pulse.

Results and Discussion

1. Steady-state photolysis of SPO1 in the solid phase.

At room temperature spirooxazine SPO1 is a mixture of isomers of the closed and open forms (see Scheme 1). The **B** form has an intense absorption in the visible spectral region. The both forms have intense absorption bands in the UV spectra region. For solutions of SPO1 in methanol and ethanol, the equilibrium content of the **B** form was determined,[20] being ~7% at 300 K. On going from solutions to solid films, the shape of the electronic absorption spectrum does not substantially change. This suggests that the percent content of the **B** form in the starting film samples is close to its percent content in solutions (~7%). Transitions between the **A** and **B** forms of spirooxazines in both directions can occur both thermally and under irradiation. The spectral parameters and rate constants of photochromic transformations of SPO1 in methanol are presented in Table 1. The corresponding values for solutions of SPO1 in methanol and propan-2-ol are similar. The absorption spectra of the **B** form of SPO1 in propan-2-ol and in the film (sample of the third type) are shown in Fig. 1 (curves *1* and *2*). Specific features of the spectrum of the **B** form of spirooxazine in the film are the shift of the long-wavelength absorption band maximum from 595 to 605 nm, an increase in the relative intensity of the shoulder at 570 nm, and band broadening.

Irradiation of the SPO1 films in the UV region at the initial stage of the process initiates mainly transition **A** → **B** due to the high content of the **A** form. Figure 2, *a* presents the change in the optical spectra upon irradiation of the film with the wavelength 365 nm. The absorbance of the **B** form at 605 nm increases from the value of 0.2 corresponding to the initial equilibrium content of this form (7%) to 0.83 upon prolonged irradiation. Thus, the maximum content of the **B** form at the used radiation intensity can be brought to ~30%, which corresponds to a new photostationary state. It is determined by the competition of the photochemical and dark processes in the both directions (**A** → **B** and **B** → **A**).

The content of the **B** form can be not only increased (by the UV irradiation of the film, see Fig. 2, *a*) but also decreased (by the irradiation of the film in visible spectral region). Figure 2, *b* shows a decrease in the absorption band intensity of the **B** form upon the irradiation of the sample with the light of the mercury lamp lines with the wavelengths 546 and 578 nm. In this case, irradiation makes it possible to decrease the content

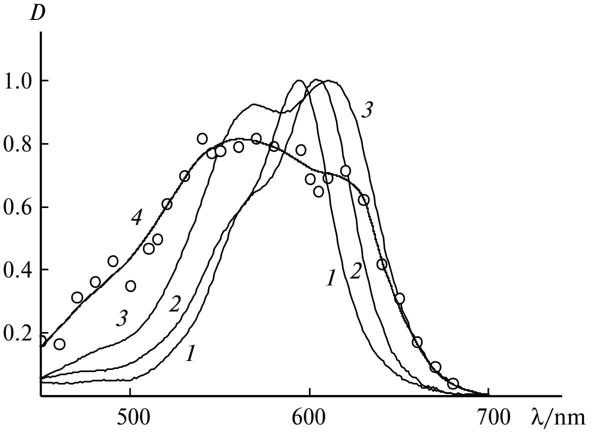


Fig. 1. Shape of the long-wavelength band of the **B** form of SPO1: *1*, propan-2-ol; *2*, film (sample of the third type); *3*, film after UV irradiation; and *4*, spectrum appeared after a laser pulse (50 ns).

Table 1. Content of the **B** form, the position of the maximum (λ_{max}), the molar absorption coefficient (ε_B) of the long-wavelength absorption band of the **B** form of SPO1, the quantum yields (φ) of photolysis of the **A** and **B** forms (irradiation at 365 and 546 nm, respectively), and the kinetic parameters of the dark isomerization reactions of spirooxazine SPO1 in a methanol solution of 298 K (see Refs 18 and 20)

Parameter	Value	Parameter	Value
B form (%)	7.0	$k_{\mathbf{AB}}$/s^{-1}	0.011
λ_{max}/nm	595	$k_{\mathbf{BA}}$/s^{-1}	0.15
ε_B^{max}/L mol^{-1} cm^{-1}	57700	$E_{\mathbf{AB}}$/kJ mol^{-1}	85.7
$\varphi_{\mathbf{AB}}$	0.24	$E_{\mathbf{BA}}$/kJ mol^{-1}	77.5
$\varphi_{\mathbf{BA}}$	0.022		

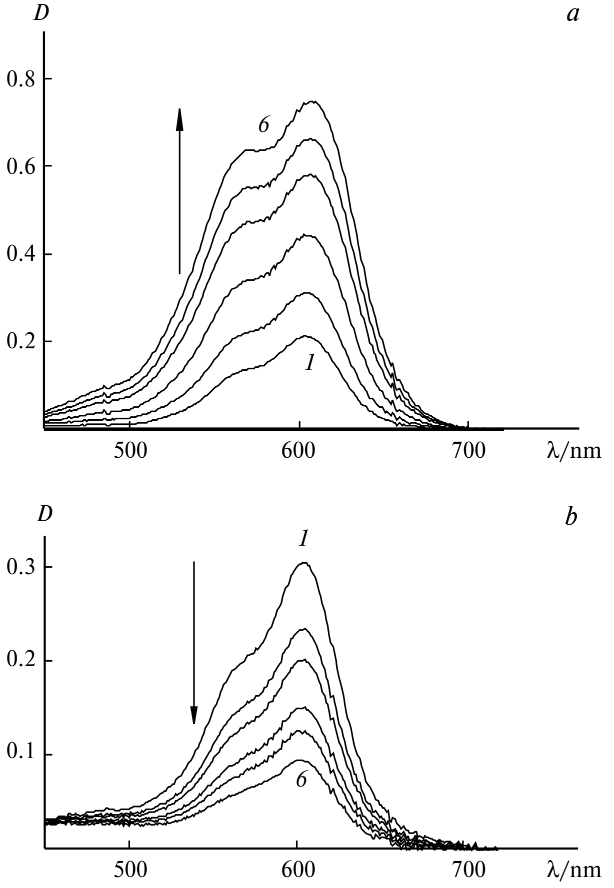


Fig. 2. Change in the absorption spectrum of the film of SPO1 (sample of the third type upon irradiation: *a*, phototransformation **A** → **B** in the film ~100 nm thick, photolysis at the wavelength 365 nm for 0 (*1*), 30 (*2*), 70 (*3*), 130 (*4*), 200 (*5*), and 300 s (*6*); *b*, phototransformation **B** → **A** (film thickness ~150 nm); photolysis at the wavelengths 546 and 578 nm for 0 (*1*), 30 (*2*), 60 (*3*), 150 (*4*), 300 (*5*), and 600 s (*6*).

of the **B** form in the photostationary state from the initial 7 to ~2.5% .

The changes in the optical absorption spectra upon photochromic transformations for the powder samples of this first type are shown in Fig. 3. As in the case of the films, the reactions of photoisomerization of SPO1 are observed in the both directions (**A** → **B** and **B** → **A**). For the powders in the photostationary state, the content of the **B** form also increases to the value >20%. The initial quantum yields of phototransformations for the both types are similar. For the film samples (see Fig. 2) it could be assumed that the molecules in the amorphous phase only undergo photochromic transformations, whereas the experiment with the powder samples proves the possibility of phototransformations of SPO1 in the polycrystalline state. For SPO1 in a KBr pellet, the photochromic reactions in both directions proceed with rates and conversions close to the values for the film and powder samples.

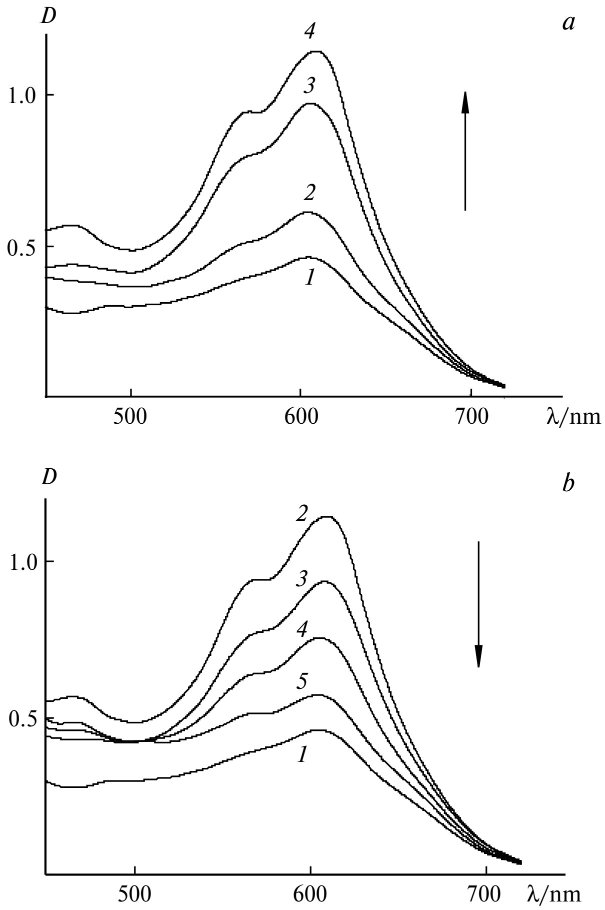


Fig. 3. Change in the absorption spectrum of the polycrystalline powdered sample of SPO1 (sample of the first type) upon irradiation: *a*, phototransformation **A** → **B**, photolysis at the wavelength 365 nm for 0 (*1*), 30 (*2*), 600 (*3*), and 1500 s (*4*); *b*, phototransformation **B** → **A**, photolysis at the wavelength 365 nm for 0 (*1*) and 1500 s (*2*); photolysis at the wavelengths 546 and 578 nm for 10 (*3*), 80 (*4*), and 360 s (*5*).

2. Quantum yield of photochromic transformations of SPO1 in the solid phase. Good optical homogeneity and the absence of considerable light scattering of the film samples made it possible to carry out quantitative measurements of parameters of the photochromic processes for SPO1 in the solid state. The quantum yields of the direct (**A** → **B**) and backward (**B** → **A**) reactions were measured. The rate constants at various temperatures were determined, and the activation energy of the thermal reaction **B** → **A** was estimated.

The quantum yield of the direct reaction for the film samples of SPO1 upon irradiation with light of the wavelength 365 nm turned out to be $(1.5\pm0.3)\cdot10^{-3}$ (298 K), which is two orders of magnitude lower than that in alcohol solutions (see Table 1). The quantum yield of the backward reaction upon irradiation of the **B** form at 546 nm is $(2.5\pm0.7)\cdot10^{-5}$, which is three orders of magnitude lower than that in alcohol solutions. These quantum yields were measured from the initial slopes of the kinetic curves of accumulation or disappearance of absorption of the **B** form and concern the molecules with the maximum ability to photochromic transformations. It is most likely that there is a broad distribution of quantum yields and a considerable portion of the solid-phase molecules is not involved in these transformations. Photolysis of SPO1 in the powder samples and in KBr showed that the quantum yields of the reactions in both directions are close to those for the dried films.

3. Kinetics of thermal relaxation of the B form. The characteristic lifetimes of the **B** form in the polycrystalline state substantially exceed the corresponding values for solutions. The non-exponential kinetic curves corresponding to the thermal backward reaction **B** → **A** at various temperatures are given in Fig. 4 (the initial amplitudes were normalized to unity). The delayed kinetics of the reactions in the solid phase is related to the heterogeneous character of the local environment of the reactants.

There are different approaches to the kinetics of chemical transformations in the solid phase. One of these approaches is the use of the Kohlrausch—Williams—Watts (KWW) empirical equation,[23] determining the change in the reactant concentration by the expression

$$c(t) = c_0e^{-(t/\tau)^\beta}, \tag{2}$$

where τ is the averaged characteristic time of the process, and parameter β ranges from 0 to 1 (see Ref. 24). The experimental kinetic curves (see Fig. 4) can satisfactorily be described by the KWW equation with parameter $\beta \approx 0.5$.

Another method for processing of experimental kinetic data is also used: presentation of the overall kinetics by a set of exponential curves with different times and amplitudes. Two or three exponentials can be used in the simplest variant. In this case, the times obtained determine the range of changing the characteristic times in different local environments. The kinetics of the dark process **B** → **A** for SPO1 in the film was processed by the equation

$$c(t) = c_1e^{-(t/\tau_1)} + c_2e^{-(t/\tau_2)} + c_0, \quad (3)$$

where c_0 is the term corresponding in fact to the third exponential with infinite time and concerns molecules that are not involved in transformations. This equation also describes well the experimental kinetic curves (see solid curves in Fig. 4) with the parameters presented in Table 2. This processing shows that there are molecules of the **B** form, which are transformed into the **A** form in the solid film during times about 150 s; however, the number of these molecules at room temperature is ~5%. Approximately 25% molecules undergo the transformation during ~3000 s, and the most part (~70%) cannot transform into the **A** form during the detection time. The temperature rise does not strongly change the characteristic times of the exponentials (see Table 2), but results in a substantial shift of the number of molecules to the region with shorter transformation times. For example, the temperature increase by 18° more than threefold increases the number of molecules with the transformation time 100—150 s (up to 17%). Approximately 42% are transformed into the **A** form within ~2000 s, and the number of inactive molecules decreases almost two times (down to 41%). Thus, the spectrum of the characteristic transformation times **B** → **A** for SPO1 in the film lies in the range 10^2—10^5 s. Such a transformation for the **B** form of SPO1 in solutions takes a time shorter than 10 s (see Table 1).

Table 2. Results of processing of the normalized kinetic curves of the reaction **B** → **A** for SPO1 at different temperatures (see Fig. 3) using the equation $D(t) = D_0 + D_1e^{(t/\tau 1)} + D_2e^{(t/\tau 2)}$

T/K	D_0	D_1	τ_1/s	D_2	τ_2/s
297.9	0.682	0.052	156	0.266	2800
303.8	0.596	0.096	162	0.308	2810
308.8	0.534	0.108	119	0.358	1700
315.7	0.410	0.166	139	0.424	1750

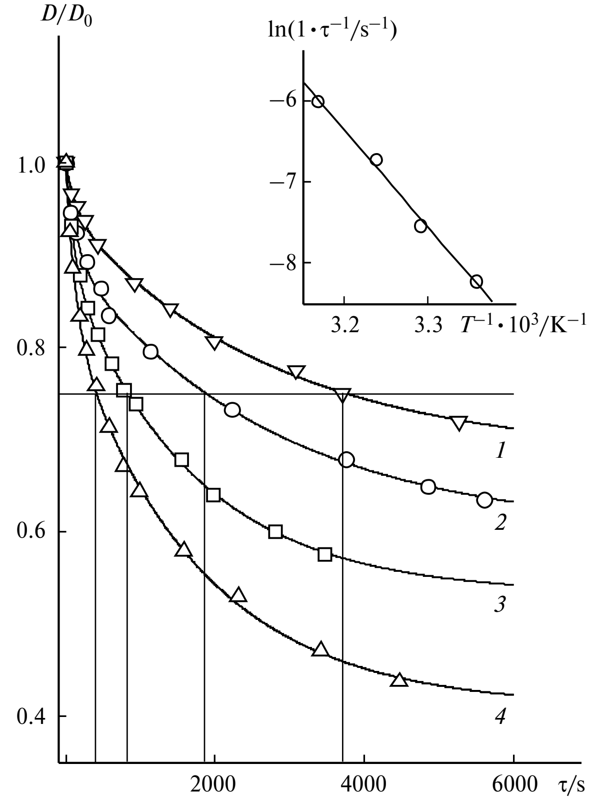


Fig. 4. Kinetic curves (605 nm) for the backward thermal reaction **B** → **A** in the films of SPO-1 (thickness ~100 nm) at 298 (*1*), 304 (*2*), 309 (*3*), and 316 K (*4*). Solid curves are processing by formula (3) with the parameters presented in Table 2. The curves are normalized to D_0 (the increase in the absorbance after irradiation). The plot of the logarithm of (1/τ) *vs* inverse temperature, where τ is the time of the decrease in the ratio $D_0/D(t)$ by 25% (horizontal line in the main figure), is presented in inset.

The durations of the reaction proceeding to a certain depth were compared to evaluate the temperature effect on the rate of thermal reaction **B** → **A**. The result is shown in Fig. 4 (see inset), where 1/τ is the inverse time of 25% decrease of the absorption band of the **B** form (605 nm). Thus estimated activation energy of isomerization **B** → **A** for the film samples is 98±6 kJ mol^{-1}, which exceeds the characteristic values for liquid solutions (77.5 kJ mol^{-1}, see Table 1).

The times of thermal transformations **B** → **A** for the powdered samples of SPO1 in KBr pellets are comparable with the times for the film samples. These results and closeness of the quantum yields of photochromic transformations for all types of the samples indicate that the films obtained by drying of the solution are most likely polycrystalline.

4. Laser flash photolysis of SPO1 in the solid phase. Earlier experiments on nanosecond laser flash photolysis (308 nm) of SPO1 in a liquid solution (methanol) showed that the open form was originated within the action of a laser pulse (15 ns).[22] Slight (about several percents) changes in the absorption band of the **B** form in a time interval of several tens of microseconds were explained by the establishment of equilibrium between isomers of the **B** form. Similar small spectral changes in the microsecond time range were also observed for photolysis of other spirooxazines in liquid solutions.[25,26]

Laser flash photolysis (355 nm) of the film samples showed that the absorption of the **B** form also appeared within the laser pulse action (~7 ns). The band shape changes in the time interval shorter than 20 μs. The examples of the kinetic curves are presented in Fig. 5. The transient absorption spectra are shown in Fig. 1. Curve *4* is the transient spectrum appeared immediately after the laser pulse. Twenty μs after the pulse, the absorbance stops changing and the spectrum gains the shape coinciding with the stationary spectrum of the **B** form in the film (Fig. 1, curve *3*).

In the spectrum appeared immediately after a laser pulse, the intensity of absorption at 470—530 nm is higher, whereas that in the region of 570—630 nm has a lower intensity compared to the stationary spectrum. Figure 1 also presents the absorption spectra of the **B** form of SPO1 in a propan-2-ol solution (curve *1*) and in the film without irradiation (curve *2*). It is seen that the spectrum of the **B** form appeared due to photolysis (curves *3* and *4*) is substantially broader than the stationary spectrum (curve *2*), and the maximum width and distortion of the shape are achieved immediately after a laser pulse. The intensity of nonequilibrium absorption detected in pulse experiments at 470—530 nm decreases within 2—5 μs, while the absorption at 560—640 nm increases during the same time (Fig. 5).

The kinetics of additional absorption at 600—610 nm is nonexponential; however, it can be approximated using two exponentials with the characteristic times 0.5—1 and 5—7 μs. Thus, there is rather broad molecular distributions over times of formation of the stationary spectrum of the **B** form. In the range from 470 to 520 nm, where the absorbance decreases with time, the signal is considerably weaker and, therefore, noises make it possible only to evaluate the characteristic times (in the one-exponential approximation) lying in the same range of 2—5 μs (see Fig. 5).

The observed kinetic curves of intermediate absorption in the solid-phase samples can be determined by different factors. We will discuss the influence of three possible factors, namely,

— establishment of equilibrium between various isomers of the **B** form;

— aggregation processes of different types between molecules of the **B** form and **A** form of SPO1;

— heat removal from the region of the film locally heated with a laser pulse.

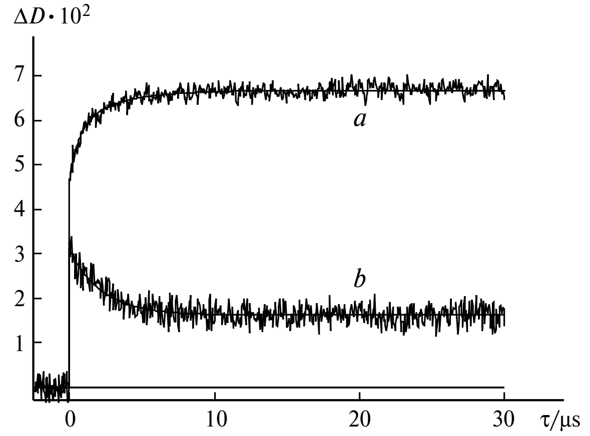
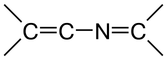
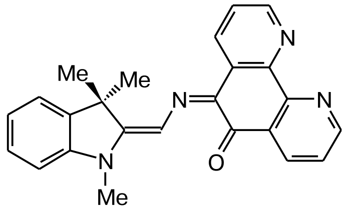


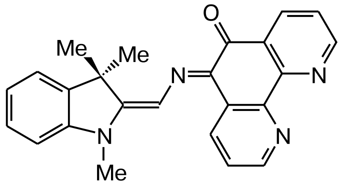
Fig. 5. Kinetic curves of the appearance of absorption of the **B** form at 610 (*a*) and 510 nm (*b*) upon laser flash photolysis (355 nm) of the film of SPO1 (thickness ~100 nm). Solid curves are the approximation by the equation $\Delta D(t) = \Delta D_0 + A_1(1 - e^{-(t/\tau1)}) + A_2(1 - e^{-(t/\tau2)})$ for the kinetics (*a*) with the parameters $\Delta D_0 = 0.0473$, $A_1 = 0.016$, $A_2 = 0.00383$, $\tau_1 = 1.05$, $\tau_1 = 6.7$ μs; (*b*) approximation by the equation $\Delta D(t) = \Delta D_\infty + A_1 e^{-(t/\tau1)}$ for the kinetics with the parameters ΔD_∞ = 0,0162, A_1 = 0.0147, τ_1 = 2.3 μs.

We consider the process of equilibrium establishment between the isomers of the open form as the most probable explanation of specific features of photolysis of SPO1 in the solid-phase film manifested in both steady-state and pulse experiments.

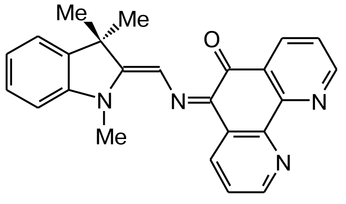
cis—trans-Isomerization relative to three bond  linking two fragments of the merocyanine form allows eight isomers of the open form to exist.[27] Of them transoid structures are most thermodynamically stable.[28] Under normal conditions in solutions, the merocyanine isomers of spirooxazines exist, as a rule, in the most stable **TTC** form.[28] However, other transoid isomers, for instance, **CTC** configurations, are possible along with **TTC** due to the stabilizing effect of the solvate environment at low temperature or the crystal lattice.[27] The cisoid (nonplanar) isomers of the open form are thermally unstable. In the literature they are usually associated with Fischer´s



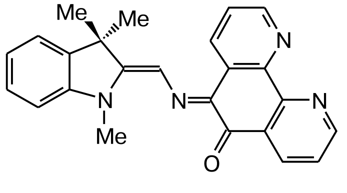
TTC



TTT



CTC



CTT

X-isomers,[29,30] which are intermediate photolysis products of the spiro compounds formed due to the spiro bond cleavage.

The width of the absorption band of the **B** form appeared upon UV irradiation of the SPO1 film (see Fig. 2, *a*) increases compared to the initial width (in the film before irradiation) due to the shift of the maximum from 605 to 610 nm and an increase in the relative intensity of the shoulder by 575 nm. An analysis of the literature data shows that in all cases, when the spiro compounds in the crystalline state exhibit photochromic activity, the long-wavelength absorption band of the photoinduced **B** form is considerably broadened and distorted compared to the spectrum in solution.[10—12,14] These spectral changes can be attributed to the redistribution of the relative contribution of various isomers of the **B** form or to a change in the geometry of the isomers upon stabilization in the solid phase. The distribution over isomers of the open form appeared due to photolysis can substantially differ from the equilibrium one.

In liquid solutions, the absorption of the **B** form of spirooxazines and spiropyrans is manifested, as a rule, within the time of 1—10 ps.[17,27,31—36] It is usually assumed that this process is followed within 10—1000 ps by the establishment of equilibrium between different isomers of the **B** form.[23,32] The probability of formation of various isomers of the **B** form of BIPS (1´,3´,3´-trimethylspiro-[2*H*-1-benzopyran-2,2´-indoline]) was analyzed and the internal temperature of the molecule upon UV excitation was estimated.[37] The value obtained (~900 K) made it possible to suggest the random appearance (roulette model) of any of eight isomers of the **B** form.[37] The characteristic lifetime of the nonplanar cisoid isomers formed upon the photoexcitation of spiropyrans and spirooxazines is several nanoseconds in the polycrystalline state.[16—18]

The broad distribution of molecules of the **B** form over planar transoid isomeric forms appears as a result of local melting of a microcrystal of SPO1 under the action of a laser pulse. The effect of nonequilibrium distribution over isomeric forms is manifested in the transient absorption spectra and kinetics of formation of the absorption of the **B** form in experiments on laser flash photolysis (see Figs 1 and 5). Indeed, the shape of the absorption band appeared immediately after a laser pulse (see Fig. 1, spectrum *4*) differs from that detected upon stationary UV irradiation (see Fig. 1, spectrum *3*). Note that the spectral changes observed in experiments on laser flash photolysis cannot be ascribed to the formation of cisoid isomers of the open form (X-isomers). According to the published data,[16—18] the lifetime of the X-isomers in spirooxazine polycrystals is several nanoseconds, and there is no basis to assume that this time is shifted to the microsecond range in our case.

An alternative explanation of peculiarities of photolysis in the solid-phase films can be as follows. The observed spectral changes are determined, to this or another extent, by aggregation processes of different types between molecules of the merocyanine form or between molecules of the spiro form and merocyanine form. This possibility seems rather improbable for the following reasons.

First, it is known that the processes of photoinduced aggregation (including formation of J-aggregates and H-aggregates) are characteristic of nitro-substituted spiro compounds.[38,39] This is probably due to the participation of the triplet state of the closed form in aggregation processes.[39] Just for nitro-substituted spiropyrans the quantum yield of intersystem crossing is rather high, whereas for the most part of other spiro compounds no excitation to triplet is experimentally observed as well as no aggregation occurs. In the case of spironaphthooxazines, no indications to the formation of triplets of the closed form were detected in experiments on laser flash photolysis in liquid solutions and in frozen matrices.[22]

Second, the experimental data on steady-state photolysis of SPO1 in various solvents, including nonpolar (hexane, toluene) are presented.[20] The results indicate that spectral changes, which could be ascribed to the formation of associates, do not occur with an increase in the concentration of the open form during photolysis.

Third, it could be expected that the formation of associates is favored by elevated temperatures of experiments. However, an increase in the temperature of photolysis to 50 °C only accelerates the backward reaction (see Fig. 4).

The relaxation of local warming is an additional process that can affect the behavior of the solid-phase film after a laser pulse. According to the published data,[16—18] the duration of this relaxation lies in the microsecond range. Therefore, we cannot exclude the possibility that the kinetic curves presented in Fig. 5 are determined not only by the rate of intramolecular transitions but also by the heat removal from the locally warmed region.

Thus, we found the photochromic activity of phenanthroline-annulated spirooxazine SPO1 in the polycrystalline state. It can be assumed that the free volume necessary for photoisomerization is provided due to rather large size of the oxazine fragment of an SPO1 molecule. This situation is analogous to the earlier described[14] photochromic reaction of spirooxazine containing the azahomoadamantyl group. The results of this work along with other data[15] suggest that photochromism of spirooxazines in the crystalline state is not so rare phenomenon as it was believed earlier. Search for compounds of this class, in single crystals of which the molecules would retain the ability to photochromic transformations, is of special interest.

The authors are sincerely grateful to reviewers of the "*Russian Chemical Bulletin, International Edition*" journal.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 08-03-00313, 09-03-00283, and 07-02-91016-AF).

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Received February 9, 2010;
in revised form October 11, 2010