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Photochromism of 6'-Cyanosubstituted Spirooxazines in Frozen Alcohol Matrices[1]

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Abstract—For three 6'-cyanosubstituted spironaphthooxazines, spectral characteristics of an open form and quantum yields of photoisomerization were determined both at room temperature and in frozen alcohol matrices. Spironaphthooxazines have demonstrated fairly high (0.01–0.02) quantum yields of open form appearance at 77 K. The observed peculiarities of the open form UV spectra were explained by the temperature dependence of the open form isomers distribution. Partial stabilization of the nonequilibrium isomers of an open form in the low-temperature matrices was revealed.

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Spirooxazines correspond one of the most important family of organic photochromic compounds [1, 2]. The interest to spirooxazines is stipulated by two factors. First, they demonstrate high intensity of the open form color (in English literature the term "colorability" is used, which means the product of the quantum yield of an open form appearance and its absorption coefficient, $\phi_{col}\varepsilon_B$ [3]). Second, spirooxazines are more resistant to photochemical degradation in comparison with structurally close spiropyrans [2].

Photochromic properties of spirooxazines are determined by mutual transitions between colorless spiro-form (or closed form, or A-form) and colored open form (or merocyanine form, or B-form, Scheme 1). In the closed form the indoline and oxazine moieties of the molecule are perpendicular to each other and do not form conjugated bonds. In an open form the molecule has the almost flat geometry and the common conjugated π-electronic system. In accord with the structure, the closed form has an absorption only in the UV spectral region whereas the open form demonstrates a very intensive absorption in the visible spectral region (absorption coefficient typically exceeds 50000 M^{-1} cm^{-1}).

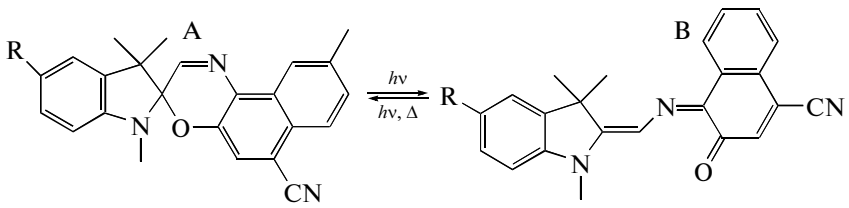
Typically, irradiation of spirooxazines in the UV spectral region results in blue coloration of the samples due to the photochemical reaction A ⟶ B. The backward reaction B ⟶ A occurs both thermally and photochemically.

[1] The article was translated by the authors.

The mechanism of photochromic transformations in spirooxazines was studied in liquid solutions by means of stationary photolysis [4–6] and laser flash photolysis with nano- [7–9], pico- [10–12], and femtosecond [13–15] time resolution. It is considered that the absorption of light quantum by the A-form of spirooxazione (or spiropyran) leads to the cleavage of the bond between spiro-atom of carbon and atom of oxygen [16]. This results in the formation of an intermediate which is called by Fisher et al. [17, 18] "X-isomer." In the X-isomer, the spiro-bond C–O is broken, but the planes of the two moieties of the molecule remain perpendicular to each other. After the rotation of indoline and oxazine moieties relative to each other, the plane structure of the open form is formed. Typically, intermediate absorption in the region of 400–500 nm forming when A-form of spiropyrans [19] and spirooxazines [20] is photochemically excited, is attributed to the X-isomer. The characteristic lifetime of this intermediate in a low-viscous solvent at room temperature is about 1–30 ps, which coincides with the characteristic time of the B-form occurrence.

Experiments on the femtosecond laser photolysis show that the reaction mechanism depends on the structure of the compounds. Besides the formation of the open form via X-isomer (A ⟶ X ⟶ B), another reaction pathways are discussed in the literature:

(1) A ⟶ X* ⟶ B, in which X-isomer exists only in excited state X* [13];



Scheme 1. Closed form (spiro-form, A-form) and open form (merocyanine form, B-form) of 6'-cyanosubstituted spironaphthooxazines.

(2) $A(S_0) \longrightarrow A(S_1) \longrightarrow B$, when the B-form isomers are formed directly from the singlet excited state of the-A-form escaping the stage of X-isomer [21];

(3) different mechanisms involving the triplet excited state of the A-form [16, 22–24].

In addition to time-resolved experiments the information on the mechanism of photochromic transformations in spirocompounds could be obtained from the experiments performed at low temperatures, because in this case one could expect an increase in the lifetimes of the intermediates. The experiments were performed both in frozen matrices [17, 18, 25–27] and polymeric films [28, 29]. In [27], the photochemistry of phenanthroline-containing spirooxazines in methanol glasses was studied using laser flash photolysis. The formation of an intermediate was registered, which transformed to the open form in several microseconds at 77 K. This intermediate was interpreted as X-isomer. For one of the studied spirooxazines, a suggestion about partial stabilization of X-isomers at 77 K was made.

In this work the photochemistry of previously synthesized [30, 31] 6'-cyanosubstituted spironaphthooxazines is studied in ethanol matrices at 77 K. The goal of the research is to obtain quantitative information about absorption spectra and quantum yields of photolysis in low-temperature glasses.

EXPERIMENTAL

Photochemistry of three 6'-cyanosubstituted spironaphthooxazines (SNO1, SNO2, and SNO3, Scheme 2) with the substituents of different length in 5-position of the indoline moiety was studied. The synthesis of SNO was described in [30].

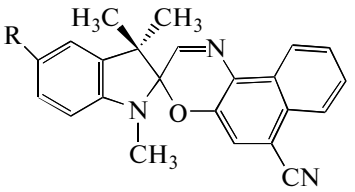
Fractionally distilled ethanol was used for the preparation of solvents and frozen matrices. Stationary photolysis was performed by a high pressure mercury lamp with a set of glass filters for discrimination of necessary wavelength of irradiation. UV absorption spectra were recorded using the Agilent 8453 spectrophotometer (Agilent Technologies).

Low-temperature photochemical experiments were performed using procedure described in detail in [32]. The solutions were frozen in quartz optical cells 1–2 mm thick. Coefficient of volume compression of ethanol due to freezing (0.82) was taken into account when calculating SNO concentrations in solid phase. Experiments on thermal annealing of the samples at $T = 100$–130 K were performed in the stream of gaseous nitrogen. The accuracy of setting and stabilization of temperature was ±1 K. During the annealing experiments the sample was photolysed at 77 K, then annealed at the target temperature. After annealing the sample was cooled to 77 K again, and its UV spectrum was recorded. Potassium ferrioxalate actinometer [33] was used to measure light intensity when determining quantum yields.

RESULTS AND DISCUSSION

Photochromic Properties of SNO Solutions at 300 K

Typically, spirooxazines exist in solutions as equilibrium mixture of closed and open forms. For the case of SNO, the part of the open form does not exceed 0.3%, which is supported by practical absence of absorption in the visible spectral region (curve *1* in Fig. 1). Irradiation of SNO1, SNO2, and SNO3 by the UV light at room temperature results in initiation of both forward ($A \longrightarrow B$) and backward ($B \longrightarrow A$) photochemical reactions. Figure 1 shows changes in the UV spectrum of SNO1 ethanol solution in the course of irradiation (365 nm) at 300 K. An intensive increase of absorption in the range of 500–700 nm is characteristic for the B-form appearance [1]. Prolonged irradiation leads to the establishing of a photostationary state. When irradiation is stopped, the thermal equilibrium between A- and B-forms is recovered for about several tens of minutes. Kinetic curves of thermal decoloration of the merocyanine form are satisfactorily fitted by a monoexponential dependence.



SNO1 R = H_7C_3O
SNO2 R = $H_{19}C_9O$
SNO3 R = $H_{33}C_{16}O$

Scheme 2. Studied spirooxazines (A-form).

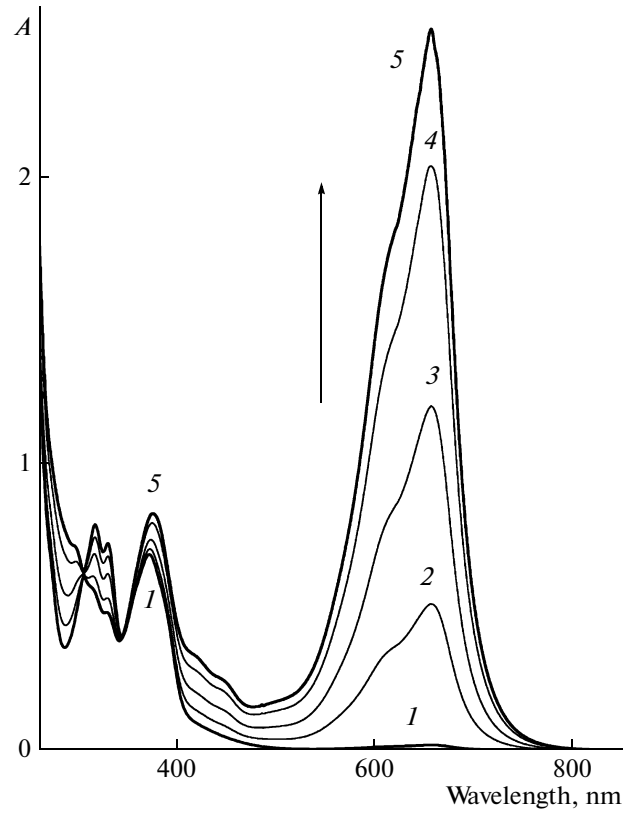


Fig. 1. Changes in the electronic absorption spectra caused by the photolysis (366 nm) of SNO1 in ethanol solution (1.08×10^{-4} M in a 1 cm cell). Temperature 300 K. Spectra *1–5* correspond to 0, 5, 15, 66, and 110 s of irradiation.

Spectral, photochemical, and kinetic parameters of SNO at room temperature are listed in Table 1. It is evident that the size of an aliphatic substituent in the indoline moiety of the closed form of SNO does not effect on the spectra of both closed and open forms and on the efficiency of either photochemical or thermal processes.

Temperature Dependence of the SNO Electronic Absorption Spectra

For understanding of the results on the photochemistry of SNO in frozen matrices one needs to discuss the temperature dependencies of the UV spectra of closed and open forms. When ethanol solutions of the closed form of SNO were frozen to 77 K, only small changes in the UV spectra were observed. The slight narrowing of the absorption bands occurs, and their intensity increases at 15–20% in comparison with liquid solutions. The values of the absorption bands maxima and absorption coefficients are shown in Table 2.

It is known that the UV absorption spectra of spirocompounds could demonstrate strong temperature dependence [17]. Such dependencies were observed for SNO solutions. Figure 2a shows the results of SNO1 B-form cooling in the ethanol solution. The open form was obtained by the photolysis of the closed form at 270 K. Then the solution was cooled to a desired temperature in a cryostat by a thermally stabilized stream of gaseous nitrogen, and the UV spectrum was recorded. As low temperature as 116 K (glass transition temperature for ethanol [34]) was achieved. It is shown in Fig. 2a that the maximum of the B-form absorption band is shifted to the blue spectral region at the value of 33 nm (from 657 to 624 nm) with the conservation of an isosbestic point at 641 nm. The existence of an isosbestic point testifies that the spectral changes are conditioned by transitions between two forms of the spirooxazine.

The changes in the UV absorption spectra of SNO in nonpolar solutions are even more dramatic. Figure 2b demonstrates the spectral changes of SNO1 in 3-methylpenthane solution. In this case, a 75 K decrease in temperature leads to the transition of the absorption band with a maximum at 643 nm and a shoulder at 602 nm to the band with the maximum at 542 nm. An isosbestic point at 577 nm is conserved.

Table 1. Spectral (positions of maxima and absorption coefficients of closed and open forms absorption bands), kinetic (rate constant of B $\longrightarrow$ A reaction) and photochemical (quantum yield of A $\xrightarrow{h\nu}$ B reaction) characteristics of SNO in ethanol at 300 K

Compound	λ^{A}_{max}, nm	$\varepsilon^{A}_{max} \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$	λ^{B}_{max}, nm	$^{*}\varepsilon^{B}_{max} \times 10^{-4}$, $l\,mol^{-1}\,cm^{-1}$	$k_{BA} \times 10^{4}$, s^{-1}	φ_{AB}
SNO1	316	7.0	656	6.3	5.1	0.053 ± 0.003
	327	6.6				
	370	6.3				
SNO2	316	7.7	656	6.3	4.9	0.056 ± 0.003
	327	7.2				
	370	6.9				
SNO3	316	8.1	656	6.1	5.6	0.043 ± 0.002
	329	7.4				
	370	7.1				

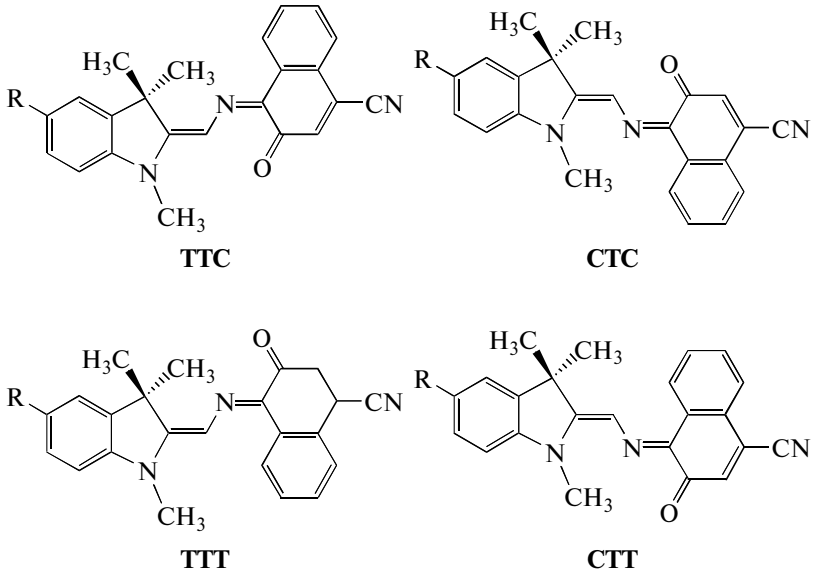
* Measured in [31].

Table 2. Spectral and kinetic properties of SNO in frozen ethanol matrices (77 K)

Compound	λ^{A}_{max}, nm	$\varepsilon^{A}_{max} \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$	λ^{B}_{max}, nm	$\varepsilon^{B}_{max} \times 10^{-4}$, $l\,mol^{-1}\,cm^{-1}$	φ_{AB}
SNO1	316	8.8	622	4.8	0.017 ± 0.004
	327	7.2			
	370	9.7			
SNO2	316	8.5	622	5.6	0.019 ± 0.005
	327	7.4			
	370	8.7			
SNO3	316	8.8	622	6.0	0.011 ± 0.003
	329	7.9			
	370	8.0			

Temperature behavior of the absorption spectra of SNO B-form could be explained by changes in the open form isomers distribution. Cis–trans isomerization relative to three bonds linking the two moieties of the molecule leads to the possible existence of eight isomers of the open form [12]. Designations indicating the position of the bond starting with the indoline part of the molecule are typically used for the classification of these isomers. Among 8 possible configurations, cis isomers relative to the central bond (TCT, TCC, CCT, and CCC) are unstable due to the repulsion of two parts of the molecule [12]. Trans isomers relative to the central C–N bond (Scheme 3) are more or less stable. In equilibrium achieved at room temperature the open form of spirooxazines is typically a mixture of the most stable TTC isomer and close in energy CTC isomer [35, 36]. Quantum chemical calculations [36, 37] have shown that for different spirooxazines the difference in standard enthalpies of formation between TTC and CTC isomers is about 1.5–2 kcal/mol. Standard enthalpies of formation for CTT and TTT isomers are ca. 8 kcal/mol higher than for TTC isomer; therefore their equilibrium concentrations at room temperature are negligible [36, 37].

The most intense band in the visible absorption spectrum of the spirooxazines open form corresponds to the $S_0 \longrightarrow S_2$ electronic transition [38]. The S_2 excited state is highly polar, which leads to its sufficient stabilization in polar solvents. This fact explains large bathochromic shifts of the main absorption band of the open form caused by transitions from gas phase to polar solvent or from nonpolar solvent to polar solvent [38]. A striking example of this shift is demonstrated by UV absorption spectra of SNO1 in 3-methylpenthane (Fig. 2b) and in ethanol (Fig. 2a).



Scheme 3. Trans isomers of the open form of SNO.

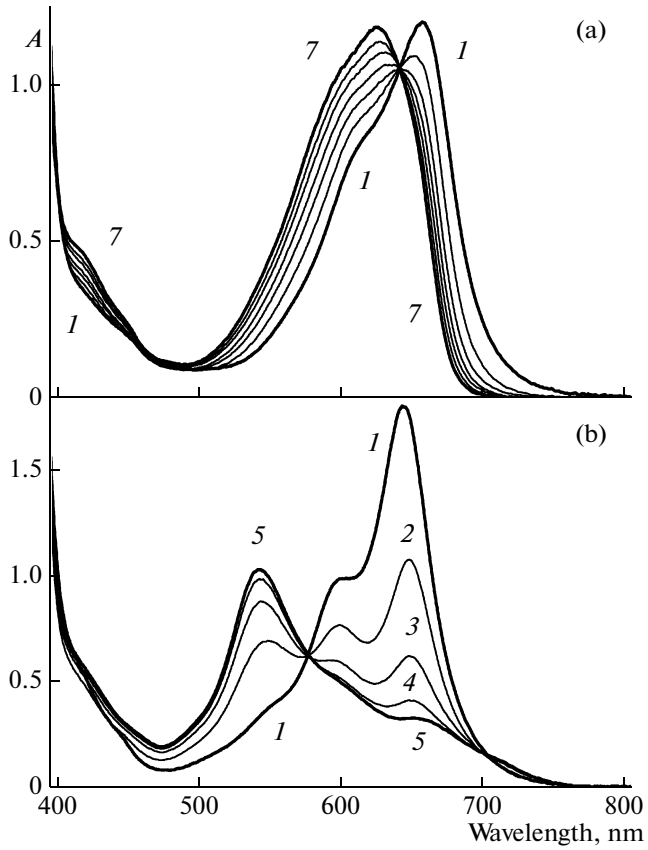


Fig. 2. Changes in the electronic absorption spectra of the B-form of SNO1 in ethanol and 3-methylpenthane. Photolysis of the closed form at 270 K followed by cooling. (a) Ethanol solution (SNO concentration 2.1×10^{-3} M in a 1.15 mm cell). Spectra *1*–*7* correspond to temperatures 270, 220, 190, 160, 140, 120, and 115 K. (b) 3-methylpenthane solution (SNO concentration 2.3×10^{-4} M in a 1 cm cell). Spectra *1*–*5* correspond to temperatures 270, 240, 210, 205, and 195 K.

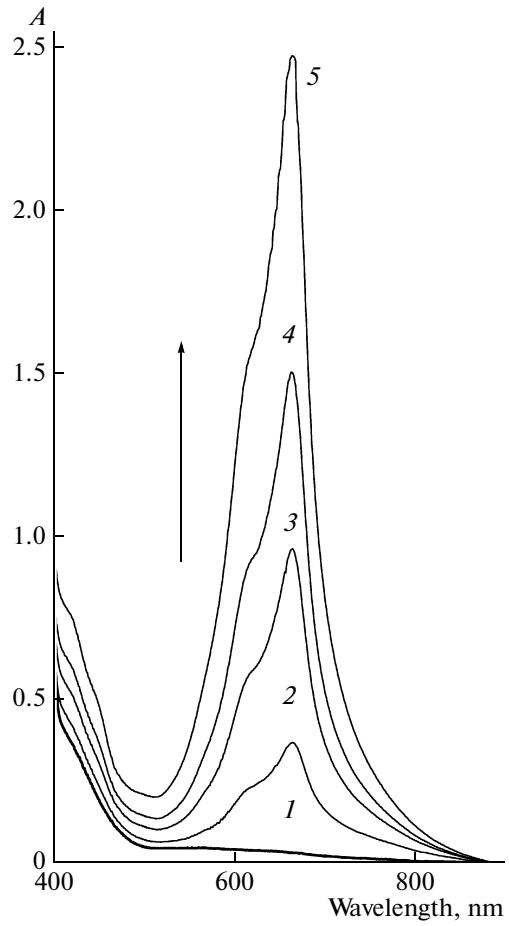


Fig. 3. Changes in the electronic absorption spectra caused by the photolysis (366 nm) of SNO1 (2.4×10^{-3} M in a 1 mm cell) in frozen ethanol matrix (77 K). Spectra *1*–*5* correspond to 0, 5, 20, 40, and 110 s of irradiation.

The temperature changes in the UV spectra of the open form (Fig. 2) could be explained by transitions between TTC and CTC isomers. At lowest temperatures the almost pure TTC state with a small addition of CTC state is observed. In fact, the distribution of isomers at 77 K seems to correspond to the equilibrium distribution at the glass transition temperature of ethanol. When temperature is close to 300 K, the part of CTC state is not less than 50%. Estimation made using the ratio of the band intensities at different temperatures indicates that the difference of standard enthalpies of TTC and CTC formation should be less than 0.5 kcal/mol. This value is appreciably different of the value 1.5–2 kcal/mol obtained from quantum chemical calculations of spirooxazines [36, 37].

Photochemistry of SNO at 77 K

Spectral changes caused by the photolysis of SNO1 in ethanol matrix (77 K) are shown in Fig. 3. The similar spectral changes corresponding to the open form appearance were observed for another SNO.

It is interesting to compare the spectra of B-form obtained by the photolysis of SNO in solution at room temperature and in ethanol matrix at 77 K (see spectra *1* and *2* in Fig. 4 correspondingly. The maximal absorption of spectrum *2* is normalized on the maximal absorption of spectrum *1*). Spectra of B-form obtained by photolysis in liquid solutions and in frozen matrices have close positions of band maxima (the difference is 7 nm). The main feature of the B-form spectrum in a frozen matrix is a long-wavelength wing in the region of 750–850 nm.

At the same time, spectrum *2* (Fig. 4) demonstrates a considerable difference with the equilibrium spectrum of the B-form in a frozen matrix (spectrum *3* in Fig. 4). As already mentioned (see Fig. 2a), in the process of freezing the maximum of the B-form absorption band is shifted at more than 30 nm to the blue spectral region. Thermal annealing of the sample irradiated at 77 K (see Fig. 5) results in the progressive

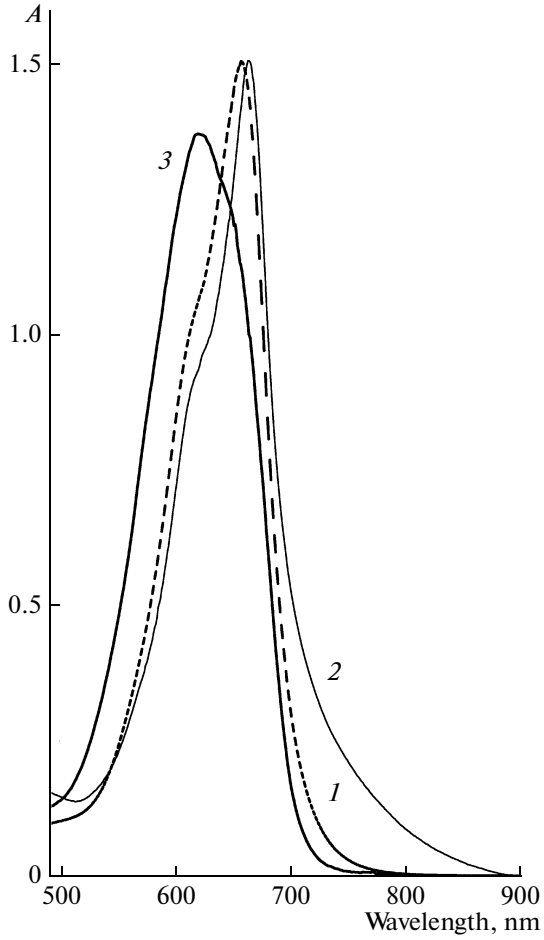


Fig. 4. Electronic absorption spectra of the SNO1 B-form in ethanol (initial B-form concentration 2.4×10^{-4} M in a 1 mm cell). (*1*) Spectrum at 300 K, (*2*) spectrum of the sample irradiated at 77 K, (*3*) spectrum of the sample irradiated at 300 K and rapidly frozen.

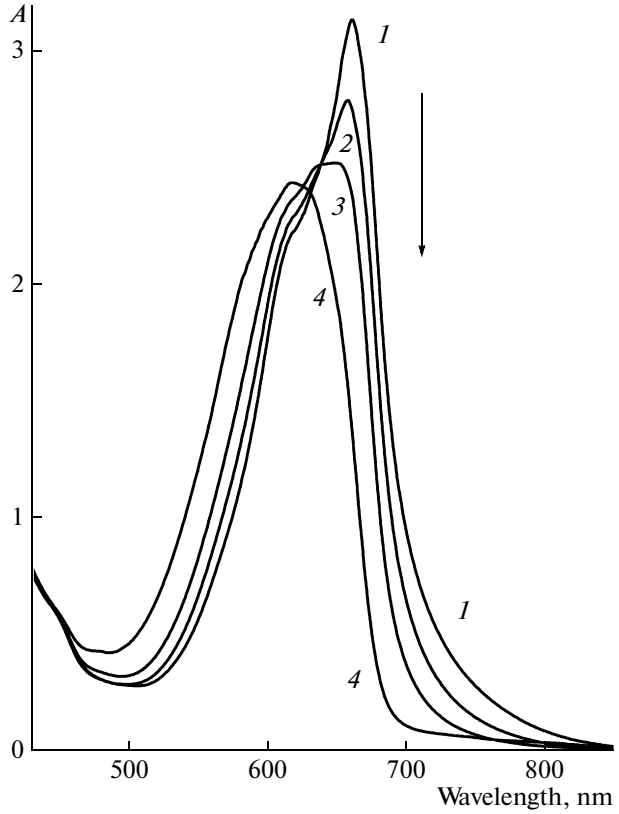


Fig. 5. Changes in the electronic absorption spectra of the SNO1 B-form obtained by the photolysis in ethanol matrix (77 K) in the course of annealing. (*1*) Spectrum after photolysis at 77 K; (*2–4*) spectra after annealing at 99 K (3 and 30 min) and 118 K (5 min), respectively. The spectra were recorded at 77 K.

transformation of the initial asymmetric spectrum with a maximum at 650 nm to a more symmetric spectrum with $\lambda_{max} = 620$ nm, corresponding to equilibrium spectrum for the glass transition temperature of ethanol (T_g). Changes in the B-form spectrum in a course of annealing (up to T_g) demonstrate a quite precise conservation of the isosbestic point at 640 nm.

Proximity of the distributions of the open form isomers obtained at 77 and 300 K could be determined by a local heating of the matrix near the excited molecules. The internal temperature of excited spiropyran in the course of photolysis was estimated as ca. 900 K [21]. The local heating provides the possibility of the rotation of indoline and oxazine moieties of the SNO molecule relative to each other. As a result of local heating, the conditions of the B-form occurrence at 300 and 77 K appears to be close enough. Because of fast cooling of vibrationally excited B-form molecules, the distribution of TTC and CTC isomers close to stationary at room temperature (spectra *1* and *2* in Fig. 4) appears in the matrix. This distribution does not coincide with the equilibrium distribution at the glass transition temperature of ethanol, which is observed at 77 K. The annealing of the samples containing B-form obtained at 77 K gives rise to the distribution close to equilibrium at the glass transition temperature (Fig. 5). In this case, the TTC isomer is dominant.

An alternative mechanism of a photochemical reaction in a frozen matrix does not require local heating. The reaction could occur from the highly excited ("hot") vibrational states without vibrational energy transfer to the molecules of the solvent. For example, in [38] it was shown that the isomerization of nitrenes occurred by the photolysis of phenylazide and its derivatives to azepines occurred in a time of vibrational relaxation (ca. 10 ps). In [39], the mechanism of singlet nitrenes isomerization to ketenimines in the argon matrix at 12 K was considered. The reaction was shown to occur only from the "hot" state.

In our case, the reaction of a cisoid SNO isomer transition to a transoid one needs free volume. This free volume could be provided by the structure defects in the frozen matrix. Therefore, the both mechanisms (the local heating and the "hot" states reaction) could

in principle allow the occurrence of photoisomerization A ⟶ B in a low temperature matrix.

To explain the nature of a long-wave wing of the absorption band of open form obtained by the low temperature photolysis (spectrum *2* in Fig. 4), we now direct our attention to the theoretical study of the spirooxazine photochromism performed in [40]. The absorption of a light quantum by a spirocompound is followed by the rupture of the spiro-bond with the formation of unstable cisoid isomers—CCC and TCC. Fisher's X-isomer [17, 18] is in fact the cisoid isomer of the open form. The geometry of cisoid isomers is similar to that of the closed form, i.e. the angle ϕ between the planes of indoline and oxazine fragments of the molecule is about 90°. The quantum chemical calculations for 1,3,3-trimethylspiro[indolin-2,3'-naphtho[2,1-b][1,4]oxazine, performed in [40], have shown that the electronic absorption spectra of cisoid isomers have intense bands in the region of 400–500 nm and less intense bands in the region of 700–850 nm. During the process of isomerization the ϕ angle is changed from 90° to 180°, causing the formation of transoid isomers. Calculations performed in [40] have shown that the isomerization is accompanied by the evolution of the electronic absorption spectrum. Increase in the ϕ angle results in the red-side shift of the absorption band, increase of its intensity and narrowing. The characteristic feature of the spectrum at $90° < \phi < 180°$ is a long-wave wing, which almost completely disappears at $\phi = 180°$, i.e. when the trans-isomer state is achieved. At room temperature the characteristic time of cis–trans isomerization is several picoseconds. The changes in the absorption spectra observed in the works on picosecond photolysis of spirooxazines [12, 20] usually correspond to the described theoretical picture.

When spirooxazines are photolysed in a low-temperature matrix, the time of cisoid isomers transition to transoid isomers (X ⟶ B) greatly increases in comparison with the case of liquid solutions. In [27] the photolysis of spirooxazines SPO1 (3,3-dimethyl-1-methyl-2,2'-[2H]bipyrido-[3,2-f][2,3-h][1,4]benzoxazin) and SPO2 (3,3-dimethyl-1-hexadecylspiro[indolin-2,2'-[2H]bipyrido-[3,2-f][2,3-h][1,4]benzoxazin) was studied in frozen alcohol matrices. It was shown that because of steric hindrances in glassy matrix at 77 K the characteristic times of X ⟶ B reaction are distributed of the time scale from nanoseconds to milliseconds [27]. Prolonged photolysis of SPO2 (having a long substituent in the indoline moiety) was found to result in formation of a new absorption band in the region of 400–520 nm. This band was not associated with the photodegradation of the initial compound. It was proposed that this band belongs to cisoid isomers (X-isomers), the part of which could be stabilized in a low-temperature matrix [27].

In the current study the formation of a similar absorption band was not observed in the case of photolysis of SNO at 77 K. However, the part of the molecules of the SNO open form could not reach the state of a transoid isomer because of steric hindrances. These molecules could be frozen in the state with $\phi < 180°$. It is precisely these isomers that could (according to quantum chemical calculations [40]) provide the existence of a long-wavelength wing of the open form absorption band. In the course of annealing of the irradiated samples (Fig. 5) the rotational mobility is unfrozen, and almost all the nonequilibrium isomers transit to TTC state.

Conservation of isosbestic point in the process of annealing of samples containing the B-form of SNO (Fig. 5) allows one to estimate the absorption coefficients of the open form, which gives a possibility to determine the quantum yields of photolysis in a frozen matrix. The results are listed in Table 2.

Comparison of Tables 1 and 2 shows that transition from liquid ethanol solution to the frozen matrix leads to the decrease of quantum yields of SNO photolysis in a factor of 3 approximately. It allows one to estimate the effective activation energy of the photochemical reaction of the open form occurrence. This value is ca. 0.3 kcal/mol. Note that the length of alkyl substituent in the 5-position of the indoline ring does not sufficiently affect the values of quantum yields at 300 and 77 K, in spite of much higher viscosity of the matrix in comparison with liquid solutions.

CONCLUSIONS

The work demonstrates that the studied spirooxazines conserve their photochromic properties in a frozen matrix. The quantum yield of photolysis at 77 K drops only in a factor of 3 comparing with the room temperature. One of the goals of the study was to examine the possibility that the intermediates of SNO photolysis (X-isomers) could be stabilized at the temperature of liquid nitrogen. Earlier, such stabilization was reported in [17, 18, 27]. For the case of SNO, the formation of absorption in the region of 400–500 nm corresponding to the X-isomer stabilization was not observed. It is possible that partial stabilization of nonequilibrium isomers of the open form (with the angle between planes of indoline and oxazine moieties $\phi < 180°$) occurs in the matrix.

The prolonged irradiation of the spirooxazine SPO3 was found to result in a specific reaction of the open form with the solvent molecules. A separate communication will be devoted to this reaction.

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