Photo- and thermochromic properties of 1´,3´,3´-trimethyl-6-nitro-8-pyridiniomethylspiro[2H-[1]benzopyran-2,2´-indoline] chloride in the crystalline state

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1´,3´,3´-Trimethyl-6-nitro-8-pyridiniomethylspiro[2H-[1]benzopyran-2,2´-indoline] chloride (1) was synthesized. Single crystals (crystal hydrates) of the open merocyanine form of compound 1 were obtained under the dark conditions, and their crystal structure was studied. On irradiation with visible light compound 1 crystallizes from propan-2-ol in the polycrystalline closed form. The spectral and photochemical properties of compound 1 in the polycrystalline state and the kinetic characteristics on thermal transformation of the closed form to the open form were studied.

Key words: spiropyran salts, crystal structure, photochromism, thermochromism.

Hybrid polyfunctional compounds of a principally new class have recently been synthesized.[1,2] They combine two sublattices in one crystal structure: the photochromic cationic sublattice of spiropyrans and magnetic anionic sublattice, for instance, of bimetallic oxalate $[Cr^{III}Mn^{II}(ox)_3]^-$. Spiropyran (SP) acts as a photochemical molecular switcher perturbing the magnetic sublattice. The main problem of design of these polyfunctional compounds is to collect different functional "building" blocks in one crystal structure retaining specific features of the crystal structures of the blocks, which determine their properties in individual compounds. The design of hybrid materials is also impeded by the fact that the photochromic transformations of SP require a considerable free volume and, hence, they are hindered in the crystalline state. It has recently been shown[3,4] that the structure of the magnetic anionic sublattice of bimetallic oxalates $[M^{III}M^{II}(ox)_3]^-$ allows cation size variation to perform in a wide range, and the crystal structure of the spiropyran cation in salts with chloride and iodide anions is found to be favorable for reversible photochromic transformations of spiropyrans.[5,6] These features of the structures of the cationic and anionic sublattices allowed crystal chemical modeling of photochromic ferromagnets to be performed.[1,2] In this case, it was important that the SP⁺ cation was involved in the reaction in the closed form. Therefore, the equilibrium "closed form of the spiropyran cation SP⁺ ⇌ open cationic merocyanine form MC⁺" in solution was shifted to the closed SP form using irradiation with the visible light. No hybrid structure can be obtained from the merocyanine form.

In the present work, we repeated the synthesis of photochromic 1´,3´,3´-trimethyl-6-nitro-8-pyridiniomethylspiro[2H-[1]benzopyran-2,2´-indoline] chloride (1) containing the pyridinium fragment in the lateral aliphatic chain and prepared two forms: closed SP form (1a) (polycrystals) and open MC form (1b) (single crystals) as shown

Scheme 1

1a

1b
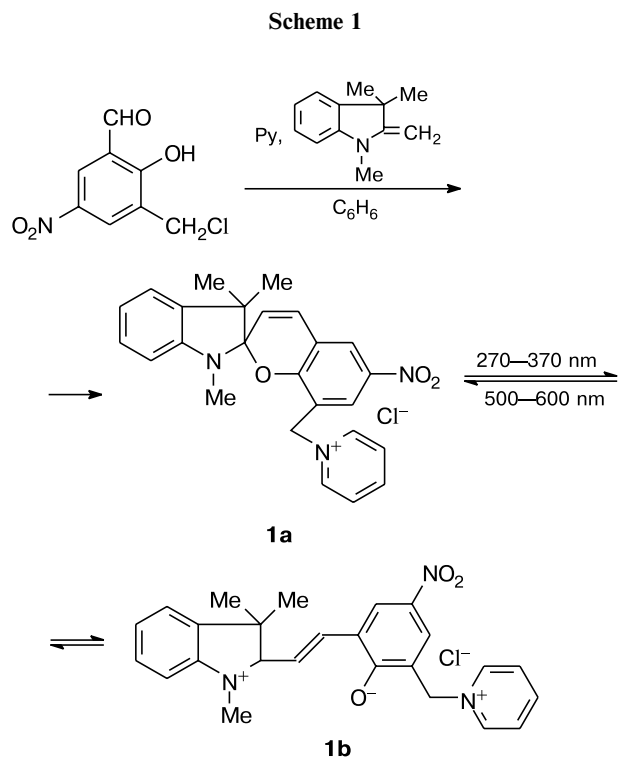
in Scheme 1. The crystal structure of compound **1b** and photochromic properties of compound **1a** were studied, as well as the kinetic characteristics for the thermal transformation of the closed form to the open form in the polycrystalline state.

Experimental

1´,3´,3´-Trimethyl-6-nitro-8-pyridiniomethylspiro[2*H*-[1]benzopyran-2,2´-indoline] chloride (1) was synthesized according to the earlier described procedure[2,7] with some modifications, in particular, intermediate 8-chloromethyl-1´,3´,3´-trimethyl-6-nitro[spiro[1-2*H*]benzopyran-2,2´-indoline] chloride was not isolated. 2,3-Dihydro-1,3,3-trimethyl-2-methylene-indole (0.346 g, 2.0 mmol) was added with stirring in an inert atmosphere to a boiling solution of 3-chloromethy-2-hydroxy-5-nitrobenzaldehyde (0.431 g, 2.0 mmol) in benzene. The mixture was refluxed for 1 h, then pyridine (0.237 g, 3 mmol) was added, and the reaction was continued for 3 h. Then the precipitate that formed was filtered off and washed with benzene, and the residue was recrystallized from propan-2-ol. The yield was 0.719 g (80%), m.p. 178 °C. Found (%): C, 66.8; N, 9.31; Cl, 7.93; H, 5.49. $C_{25}H_{24}ClN_3O_3$. Calculated (%): C, 65.88; N, 9.36; Cl, 7.91; H, 5.13.

^{1}H NMR spectra (300 MHz) were recorded on a Varian Unity-300 spectrometer at 20 °C; the δ values were measured with an accuracy to 0.01 ppm, and the spin-spin coupling constants were determined with an accuracy to 0.1 Hz. ^{1}H NMR of compound **1** (DMSO-d$_6$), δ: 0.99 (s, 3 H, C(3´)H$_3$); 1.13 (s, 3 H, C(3´)H$_3$); 2.49 (s, 3 H, C(1´)H$_3$); 5.83 (d, 1 H, H(3), *J* = 10.5 Hz); 5.91, 6.20 (both d, 1 H each, C(8)H$_2$Py, *J* = 14.0 Hz); 6.53 (d, 1 H, H(7´), *J* = 7.7 Hz); 6.93 (d, 1 H, H(4), *J* = 10.5 Hz); 6.98 (td, 1 H, H(5´), *J* = 7.4, 0.9 Hz); 7.02 (dd, 1 H, H(4´), *J* = 7.3, 1.2 Hz); 7.28—7.34 (td, 1 H, H(6´), *J* = 7.6, 1.3 Hz); 7.70 (m, 2 H, H(3), H(5)(Py)); 8.03 (d, 1 H, H(5), *J* = 2.6 Hz); 8.38 (t, 1 H, H(4)(Py), *J* = 7.7 Hz); 8.71 (d, 2 H, H(2), H(6)(Py), *J* = 5.9 Hz); 8.93 (d, 1 H, H(7), *J* = 2.6 Hz).

Spectral properties of solutions and polycrystals (layer thickness 0.1—0.5 mm) were studied on a Specord M-40 spectrophotometer. Samples were irradiated with a DRSh-1000 mercury lamps with a set of light filters. The density of the irradiation power in the UV range (270—370 nm) was ~0.01 W cm^{-2}, and that in the visible range (500—600 nm) was ~0.1 W cm^{-2}. A sample was successively irradiated at 270—370 nm (20 min) and 500—600 nm (20 min). Luminescence spectra were recorded on a Perkin Elmer LS-55 spectrophotometer, the width of the exciting light gap being 10 nm.

Diffraction experiment was carried out on an KM4 diffractometer (Kuma Diffraction, Poland) at 300 K, λ(Mo-Kα) = 0.71073 Å, and ω/2θ scan mode. The structure was determined by a direct method. Positions and temperature parameters of non-hydrogen atoms were refined in the isotropic and then anisotropic approximation using the full-matrix least squares method. Positions of hydrogen atoms were revealed from difference syntheses. No hydrogen atoms were included in the refinement. The main refinement parameters: *R* = 0.0660, R_w = 0.2339, GOOF = 0.996. All calculations were performed using the SHELXL-97 program package. The selected interatomic distances (*d*) and bond angles (ω) in structure **1b**·3H$_2$O are presented in Tables 1 and 2, respectively.

Table 1. Selected interatomic distances (*d*) in crystal **1b**·3H$_2$O

Distance	*d*/Å	Distance	*d*/Å
O(1´)—C(8A´)	1.267(5)	O(2)—N(2)	1.243(4)
O(3)—N(2)	1.227(4)	N(1)—C(2´2)	1.305(5)
N(1)—C(3A)	1.414(5)	N(1)—C(1)	1.464(5)
N(2)—C(6´)	1.409(5)	N(3)—C(11)	1.343(5)
N(3)—C(15)	1.338(5)	N(3)—C(10)	1.497(5)
C(3)—C(4A)	1.509(5)	C(3)—C(2´2)	1.528(5)
C(3)—C(8)	1.528(5)	C(3)—C(9)	1.521(6)
C(4)—C(4A)	1.405(5)	C(4)—C(5)	1.380(6)
C(5)—C(6)	1.391(7)	C(6)—C(7)	1.378(6)
C(7)—C(3A)	1.376(6)	C(10)—C(8´)	1.482(5)
C(11)—C(12)	1.380(6)	C(12)—C(13)	1.346(7)
C(13)—C(14)	1.398(7)	C(14)—C(15)	1.356(6)
C(2´2)—C(3´)	1.417(5)	C(3´)—C(4´)	1.349(5)
C(4´)—C(4A´)	1.439(5)	C(5´)—C(6´)	1.377(5)
C(5´)—C(4A´)	1.386(5)	C(6´)—C(7´)	1.414(5)
C(7´)—C(8´)	1.357(5)	C(8´)—C(8A´)	1.444(5)
C(3A)—C(4A)	1.386(6)	C(4A´)—C(8A´)	1.464(5)

Compound **1** crystallizes in the triclinic system with the main cell parameters: *a* = 7.032(1) Å, *b* = 9.698(2) Å, *c* = 18.952(4) Å, α = 94.32(3)°, β = 92.39(3)°, γ = 99.52(3)°, *V* = 1269.1(4) Å^3, *Z* = 2, space group $P\bar{1}$, ρ$_{calc}$ = 1.287 g cm^{-3}, μ = 0.193 mm^{-1}. Diffraction experiment was carried out in the angle range θ$_{min}$—θ$_{max}$ = 1.08—26.09°, and the total number of reflections was 5030 of which 2027 reflections had the intensity higher than 2σ(*I*).

Results and Discussion

The synthesized product was recrystallized from propan-2-ol. Irradiation with the visible light (500—600 nm) results in the precipitation from the solution of a yellow polycrystalline compound: spiropyran **1** in the closed form (**1a**), which is related to different solubilities in alcohols of the more polar open form and less polar closed form. Single crystals of compound **1** in the open merocyanine form, which are crystal hydrates **1b**·3H$_2$O, were obtained from the less polar solvent butan-2-ol under dark conditions.

Structure of crystal hydrates 1b·3H$_2$O. X-ray diffraction studies of the structure of crystal hydrate **1b**·3H$_2$O were carried out for a bright red irregular crystal ~0.35 mm in size at 300 K. The structure of molecule **1b** and its projection to the unit cell plane *bc* are shown in Figs 1 and 2, respectively. The independent part of the crystal structure consists of the organic cation, chloride anion, and three water molecules (see Fig. 1), and the cation is virtually planar; torsion angles of turn about the C(22´)—C(3´), C(3´)=C(4´), and C(4´)—C(4a´) bonds are 1.5°, 6.5°, and 0.7°, respectively. The nitro group is turned about the N(2)—C(6´) bond by 4.8°. The phenolate oxygen atom O(1) does not shift from the ring plane (deviation from the mean plane is 0.0039 Å) and is situated at a distance of 2.131 Å from the HC(3´) atoms to
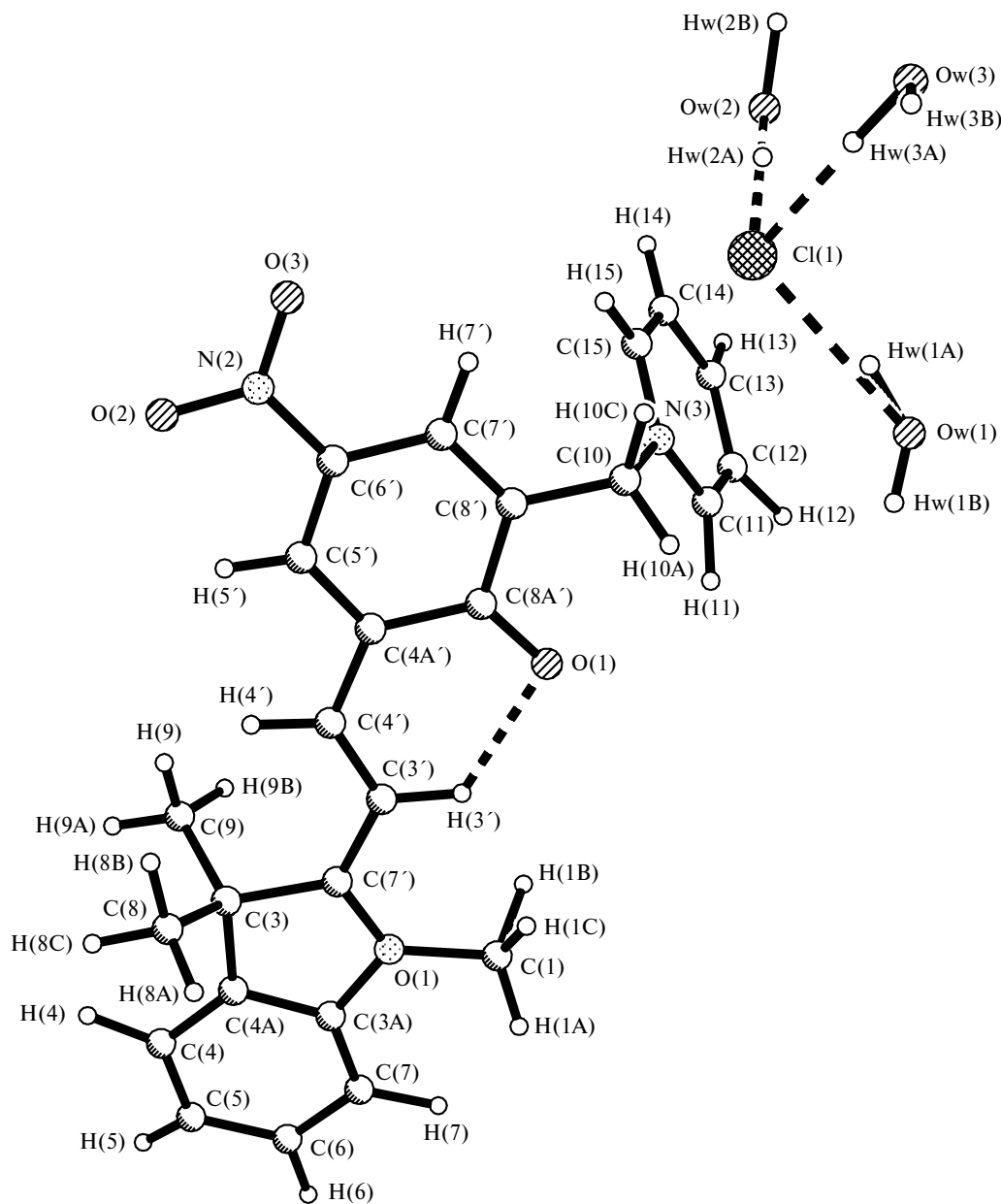
Fig. 1. Structure of the MC form of molecule **1b**; dashed lines show hydrogen bonds.

form an intramolecular hydrogen bond (see Fig. 1). The plane of the pyridine ring is turned about the C(8´)—C(10) (torsion angle C(7´)C(8´)C(10)N(3)) and C(10)—N(3) bonds (torsion angle C(8´)C(10)N(3)C(11)) by 99.2° and 77.1°, respectively, and forms with the plane of the central part of the molecule an angle of 66.8°.

The bond length distribution in the central part of cation **1b** is close to that in the earlier studied open MC forms of neutral spiropyrans[7] and indicates a strong delocalization of the electron density in the planar part of the molecule. Nevertheless, the short N(1)—C(2´2) bond (1.305 Å) and the elongated bond with the phenolate oxygen atom O(1)—C(8a´) (1.267 Å) indicate the pre-

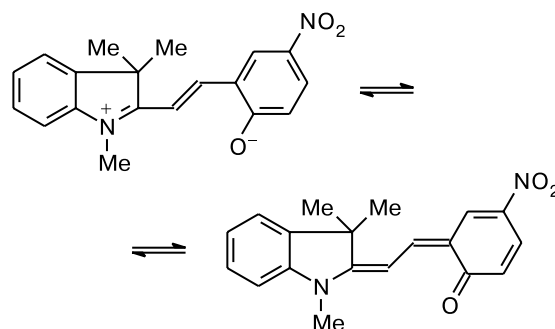dominantly bipolar rather than quinoid structure of the molecule.

Table 2. Selected bond angles (ω) in structure **1b**·$3H_2O$

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(2´2)—N(1)—C(3A)	112.8(3)	C(8´)—C(7´)—C(6´)	119.9(3)	N(3)—C(10)—C(8´)	112.6(3)
C(3A)—N(1)—C(1)	121.1(3)	C(7´)—C(8´)—C(10)	120.7(3)	C(13)—C(12)—C(11)	120.6(4)
O(2)—N(2)—C(6´)	119.3(3)	C(7)—C(3A)—C(4A)	123.8(4)	C(15)—C(14)—C(13)	118.7(4)
C(11)—N(3)—C(15)	121.6(4)	C(4A)—C(3A)—N(1)	107.3(3)	N(1)—C(2´2)—C(3´)	122.6(4)
C(15)—N(3)—C(10)	119.7(3)	C(4)—C(4A)—C(3)	131.0(4)	C(3´)—C(2´2)—C(3)	127.7(3)
C(4A)—C(3)—C(8)	109.5(3)	C(5´)—C(4A´)—C(4´)	118.0(3)	C(3´)—C(4´)—C(4A´)	128.1(4)
C(4A)—C(3)—C(9)	109.9(3)	C(4´)—C(4A´)—C(8A´)	123.1(3)	C(5´)—C(6´)—N(2)	120.5(3)
C(8)—C(3)—C(9)	112.6(3)	O(1´)—C(8A´)—C(4A´)	122.8(3)	N(2)—C(6´)—C(7´)	119.1(3)
C(6)—C(5)—C(4)	121.5(4)	C(2´2)—N(1)—C(1)	126.1(3)	C(7´)—C(8´)—C(8A´)	122.0(3)
C(3A)—C(7)—C(6)	116.3(4)	O(2)—N(2)—O(3)	121.1(3)	C(8A)—C(8´)—C(10)	117.2(3)
N(3)—C(11)—C(12)	118.8(4)	O(3)—N(2)—C(6´)	119.6(3)	C(7)—C(3A)—N(1)	128.9(4)
C(12)—C(13)—C(14)	119.4(4)	C(11)—N(3)—C(10)	118.6(3)	C(4)—C(4A)—C(3A)	119.1(4)
N(3)—C(15)—C(14)	120.8(4)	C(4A)—C(3)—C(2´2)	100.5(3)	C(3A)—C(4A)—C(3)	109.8(3)
N(1)—C(2´2)—C(3)	109.6(3)	C(2´2)—C(3)—C(8)	111.8(3)	C(5´)—C(4A´)—C(8A´)	118.9(3)
C(4´)—C(3´)—C(2´2)	125.1(4)	C(2´2)—C(3)—C(9)	111.9(3)	O(1´)—C(8A´)—C(8´)	120.4(3)
C(6´)—C(5´)—C(4A´)	122.1(3)	C(4A)—C(4)—C(5)	117.6(4)	C(8´)—C(8A´)—C(4A´)	116.8(3)
C(5´)—C(6´)—C(7´)	120.3(3)	C(5)—C(6)—C(7)	121.7(4)		
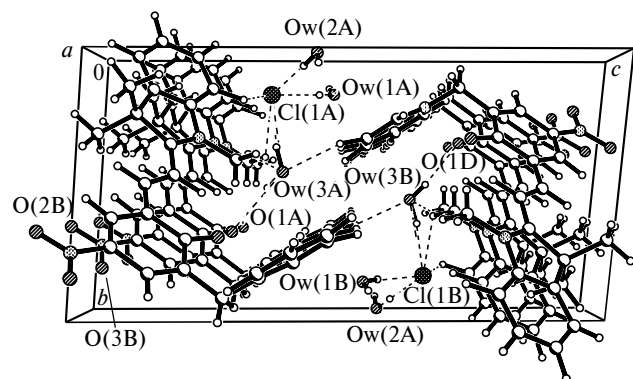
Fig. 2. Projection of the fragment of crystal structure **1b**·$3H_2O$ on the unit cell plane *bc*; dashed lines show hydrogen bonds.

The negatively charged phenolate atom O(1) is situated at 3.293 Å from the positively charged pyridinic N(3) atom. The Cl⁻ anion lies at 3.872 Å from the N(3) atom.

The projection of the fragment of crystal structure **1b**·$3H_2O$ on the unit cell plane *bc* is shown in Fig. 2. Two organic cations, two chloride anions, and six water molecules fall on one unit cell in the crystal structure. All the three water molecules are involved in hydrogen bonds with the choride anion (see Figs 1 and 2), the Cl(1)...Ow(1), Cl(1)...Ow(2), and Cl(1)...Ow(3) distances being 3.16, 3.19, and 3.17 Å, respectively, and Cl(1)...H(1A), Cl(1)...H(2A), and Cl(1)...H(3A) are 2.18, 2.18, and 2.13 Å. The organic cations are packed above one another to form translational stacks along the *a* axis. The Cl⁻ anions are arranged in the space between the stacks. The water molecule designated in Fig. 1 as Ow(1) is involved in two hydrogen bonds with two water molecules

designated as Ow(2) (2.82 Å). The Ow(3) water molecule is involved in the hydrogen bond with the phenolate oxygen atom (O(1)...Ow(3) 2.82 Å, O(1)...H(3) 2.02 Å). Thus, crystal structure **1b**⁺Cl⁻ forms a dense stack packing additionally stabilized by electrostatic interactions and intermolecular hydrogen bonds. Such a structure should prevent the isomerization of MC forms of the molecules and formation of closed SP forms in crystals, as observed for spiropyrans in the non-salt form,[7] unlike the salt forms.[5,6]

Spectral and photochemical properties. It has been shown that compound **1** synthesized previously[2] exhibits photochromic properties in solutions.

Spectral properties of crystal hydrate 1b·$3H_2O$. The study of the photochromic properties of crystal hydrate **1b**·$3H_2O$ showed that the irradiation with both visible and UV light did not noticeably change the absorbance of the crystal. This can be due to the above mentioned dense packing of merocyanine molecules in crystal of the salt.

Merocyanine form **1b** exhibits luminescence properties in both solutions and crystalline state. The luminescence spectrum of crystal hydrates **1b**·$3H_2O$ at room temperature is shown in Fig. 3. This spectrum is bell-shaped, and its position is virtually independent of the excitation wavelength. The luminescence maximum is insignificantly shifted to the short-wavelength region upon excitation with a longer-wavelength light (see Fig. 3, curve *2*). This can be related to the fact that during excitation of a shorter-wavelength light a portion of energy is consumed to vibrational relaxation ("heating" of a molecule) leading to conformational molecular changes and, as a result, the long-wavelength luminescence maximum shift is observed.
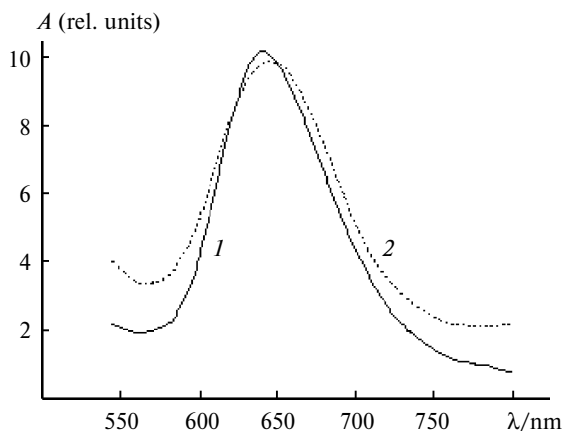
Fig. 3. Luminescence spectra of crystal hydrate $1b \cdot 3H_2O$ upon photoexcitation at the wavelength 440 (curve *1*) and 470 nm (curve *2*) at room temperature.

Spectral properties of polycrystalline 1a. Under the dark conditions at room temperature, decolorized polycrystals **1a** prepared by crystallization from propan-2-ol are transformed into a more stable (lifetime $\tau_{1/2} = 5.4 \cdot 10^5$ s) MC form with the rate constant $k \approx 2 \cdot 10^{-6}$ s^{-1}, while the kinetic curve differs substantially from exponent. Under irradiation photochromic transformations presented in Fig. 4 are observed. Compound **1** prepared in the closed SP form upon UV irradiation (270—370 nm) is transformed into the open MC form (see Fig. 4, curves *1—5*), while irradiation with the visible light (500—600 nm) results in the disappearance of the crystal color (see Fig. 4, curve *6*). When the colored sample is irradiated with the visible light at 500—600 nm, the long-wavelength shoulder first disappears in the absorption spectrum (see Fig. 4, curve *6*), and the short-
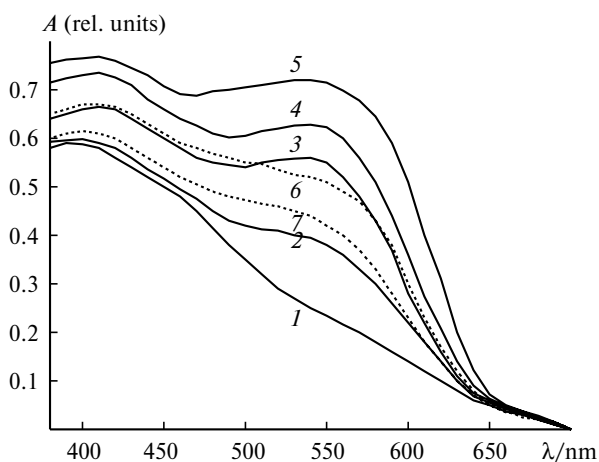
wavelength of the spectrum decays upon the subsequent irradiation at 420—550 nm (see Fig. 4, curve *7*). It is most likely that the sample contains several conformers of the open MC form. They are formed from the closed SP form upon irradiation and are consecutively transformed into each other.

Different conformers of the MC form of neutral spiropyrans were studied in Ref. 8, where the authors showed that in viscous solutions several MC forms can exist and transform into each other upon photoexcitation or thermal treatment. In our case, the conformers are most characteristic in the luminescence spectra upon photoexcitation at different wavelengths (Fig. 5) for polycrystalline sample **1a** after prolong storage at room temperature. As follows from the data in Fig. 5, different luminescence spectra range from 550 to 700 nm, which confirms that the sample contains numerous configuration of open MC form **1b**.

Note that irradiation of the polycrystalline SP form results in the formation of MC conformers luminescing in a longer-wavelength region than the region of luminescence of the MC form in single crystals. It is most likely that in these conformers the pyridine ring is coplanar to the plane of the spiropyran molecule and π-conjugation increases, which results in the long-wavelength shift in the luminescence spectra. In single crystal $1b \cdot 3H_2O$ the pyridine ring is perpendicular to the plane of the spiropyran molecule, and the π-conjugation is thus restricted only by the spiropyran part of the molecule.

It can be assumed that aggregation and deaggregation of the molecules can occur in the sample in addition to conformational transformations upon irradiation of the SP form. For example, it was found[9] that in nonpolar solvents the nitrogen-containing non-salt SP in the open form (upon UV irradiation of the solution) can form spontaneous aggregates and J-aggregates, which are observed in the absorption and luminescence spectra.
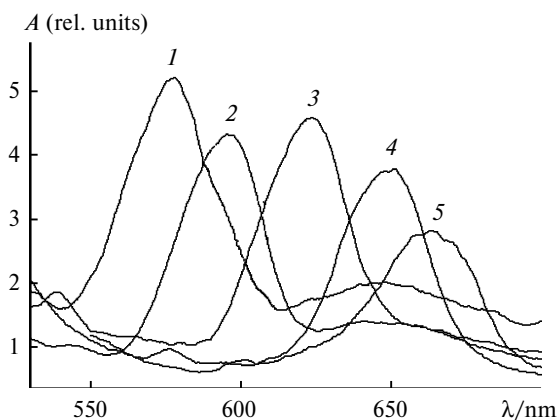

Fig. 4. Absorption spectra of compound **1a** in the polycrystalline state: initial state (*1*); absorption spectra after consecutive UV irradiation (270—370 nm) for 2 (*2*), 5 (*3*), 10 (*4*), and 20 min (*5*); absorption spectra after irradiation with the visible light at the wavelength 500—600 (*6*) and 420—550 nm (*7*) for 20 min.

Fig. 5. Luminescence spectra of polycrystalline MC form **1b** upon photoexcitation at the wavelength 400 (*1*), 420 (*2*), 450 (*3*), 480 (*4*), and 500 nm (*5*) at room temperature.
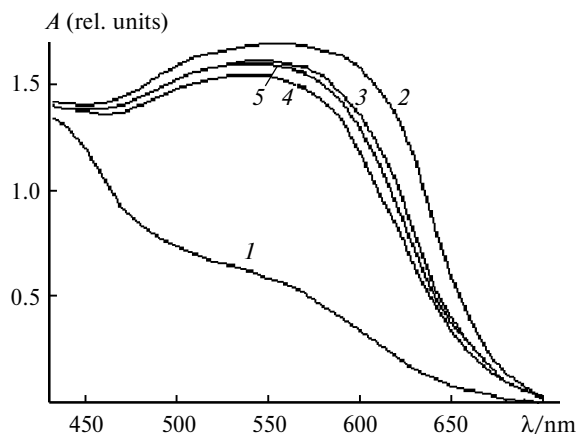
Fig. 6. Absorption spectra of polycrystal **1a**: initial sample (*1*), after heating for 1 h at 100 °C (*2*), storage at room temperature for 1 h (*3*), cooling at 0 °C for 5 h (*4*), and storage after cooling to 0 °C at room temperature for 1 h (*5*).

Fig. 7. Polychronic kinetics of transformations of the SP form of the spiropyran salt into the MC form upon consecutive storage of the samples at temperatures 20 (initial sample) (*1*), 50 (*2*), 60 (*3*), 70 (*4*), and 80 °C (*5*). Absorption at 560 nm.

We studied the behavior of the absorption spectra of a polycrystalline sample of **1a** with the temperature increase. Upon the thermal transformation of the SP form into the MC form, the absorption first increases uniformly over the whole spectrum and is shifted to the red region with the further temperature increase. The absorption spectrum of the sample recorded immediately after heating the sample at 100 °C (curve *2*), stored at room temperature for 1 h (curve *3*), cooled at 0 °C for 5 h (curve *4*), and then stored at room temperature for 1 h (curve *5*) is presented in Fig. 6. As follows from the data in Fig. 6, the reversible thermochromic effect is observed in the absorption spectra. It can be assumed that aggregation and deaggregation of the formed MC forms **1c** occur along with isomerization in the polycrystalline state, which explains the temperature shift of the absorption spectra. For some organic compounds, reversible thermochromism is manifested as luminescence of single crystals, which is related[10] to the appearance of intermolecular interactions: dimeric (excimeric), interdimeric, and stacking interactions.

The kinetics of thermal coloring of polycrystalline samples **1a** was studied. The non-exponential polychronic kinetics of the transformation of the SP form into the MC form is observed on heating the initial samples by successive temperature increasing and is presented in Fig. 7. The sample was heated in an oven followed by cooling to room temperature at which the absorption spectrum was recorded. The complete transformation into the open MC form occurs on heating the initial colorless sample for 1 h at 100 °C. This polychromic kinetics of coloring can be explained by the fact that molecules of MC form **1b** that formed exist under different conditions in polycrystals or aggregates: from the surface layer to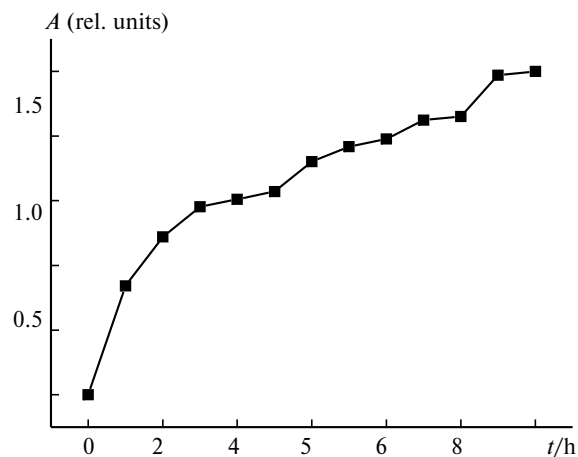 volume bulk. A molecule in the MC form can have at least four different planar conformations caused by the turn of the relatively central double C=C bond (configurational isomerism) and conformational rotation of the indoline and phenolate parts by 180°. The presence of the pyridinium substituent in the molecule increases substantially the number of isomeric forms and impedes their mutual transformation into each other due to steric factors.

On repeating the photochromic transformation of polycrystalline samples **1a** the maximum absorption of the open form during 10 cycles decreases by 10 times, and the absorption at 400 nm increases. However, on storage of this sample for 7 days and more under the dark conditions, the intensity of absorption of the MC form at 500 nm increases to a half of the initial intensity, and the absorption band at 400 nm is retained.

The studies showed that the synthesized crystal structure of the open MC form of the spiropyran salt containing the positively charged pyridinium fragment has a dense stack packing of planar molecule. This packing is unfavorable for photochromic transformations and unpromising as a building block for the creation of hybrid polyfunctional materials. However, polycrystals of this SP obtained in the closed form are reversibly photochromic. In this case, the open MC form obtained by UV irradiation of SP polycrystals represents a series of different conformers and associates characterized by different spectral and luminescence properties. The thermal transformation of the SP polycrystals into the MC form is characterized by a polychronic kinetics.

Thus, the crystal structure of the closed form of salt **1a** is favorable for reversible photochromic transformations and design of hybrid photochromic materials.

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