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Structure and photochromic properties of a single-crystalline spiro[indolinepyranopyridinium] salt

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The molecular and crystal structure of single crystalline 5´-hydroxymethyl-1,3,3,7´,8´-pentamethylspiro[indoline-2,2´-[2*H*]-pyrano[3,4-*b*]pyridinium] iodide (**1**) was studied. The crystal structure is composed of cation layers separated by iodide ions and provides a sufficient volume for the phototransformation of compound **1**. The spectroscopic and photochromic properties of this compound in the crystalline state were investigated. Upon irradiation with light at 270—370 nm, up to 600 layers of single crystals are subjected to photochromic transformations. The quantum yield of formation of the open form is ~0.1, and the quantum yield of decoloration is 0.04. After ten reversible photocyclizations, the absorption of the colored form was decreased by 10%. The photochromic properties were related to the single-crystal structure.

Key words: spiropyran salt, spiro[indolinepyranopyridinium] iodide, single crystal, photochromic properties.

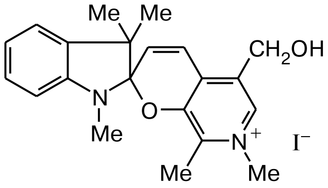
In recent years, solid-state photochromic transformations of spiropyrans have attracted considerable interest not only from the viewpoint of the design of new materials for optical information storage and processing[1,2] but also for the preparation of new polyfunctional materials combining different properties in a crystal lattice.[3,4] In these crystals, photoinduced transformations can give rise to new functions (for example, photoswitching of nonlinear optical properties[5]). However, photochromic transformations in crystals of spiropyrans and spirooxazines are rather hindered due to the close packing of the molecules in the crystal lattice and also because these phototransformations, which are associated with the C_{spiro}—O bond cleavage followed by isomerization of the molecule, require a large free volume. As a rule, spiropyrans and spirooxazines in microcrystalline powders do not exhibit the photochromic properties under conditions of stationary irradiation. However, the use of intense femtosecond laser irradiation leads to the formation of a short-lived photocolored form in microcrystals, whose absorption spectrum is identical to the spectra of the photo forms of spiropyran and spirooxazine in solutions.[6]

Recently, pyridinium-containing salts of spiropyrans and spirooxazines, which possess the photochromic properties in the crystalline state, have been synthesized.[3,7,8] Study of ultrathin pressed microcrystalline samples demonstrated that they become colored under continuous UV irradiation. The constant of thermal decoloration of the resulting photo form (k) is 10^{-4}—10^{-8} s^{-1}. The unusual behavior of the crystals of spiropyrans and spirooxazines was attributed to the electron-withdrawing effect of the positively charged *N*-methylpyridinium ring and/or the characteristic features of the crystal packing of salts of spiropyran and spirooxazine. To correctly interpret the properties of these compounds, it is necessary to study the structures of their single crystals and photochromic transformations occurring in the crystals.

In the present study, we synthesized cationic spiropyran containing the quaternized nitrogen atom at position 7´ with respect to the pyran oxygen atom. The photochromic properties and the single-crystal structure of this spiropyran, *viz.*, 5´-hydroxymethyl-1,3,3,7´,8´-pentamethylspiro[indoline-2,2´-[2*H*]-pyrano[3,4-*b*]pyridinium] iodide (**1**), were studied for the first time.

Experimental

Salt **1** was synthesized according to a known procedure.[7] Single crystals were grown by slow crystallization from an ethanolic solution.



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The absorption spectra of single crystals were studied on an apparatus developed earlier.[9] Samples were irradiated using DRSh-1000 mercury lamps equipped with a kit of glass light filters.

X-ray diffraction data were collected on a KM-4 KUMA DIFFRACTION diffractometer (Poland) equipped with a graphite monochromator (λ(Mo-Kα) = 0.71073 Å) at 298 K using the $\omega/2\theta$ scanning technique. Principal crystallographic data are as follows: salt **1** crystallizes in the monoclinic system, space group $P2_1/n$; the unit cell parameters: a = 12.789(3) Å, b = 10.807(2) Å, c = 15.612(3) Å, β = 108.09(3)°, V = 2050.8(7) Å^3, Z = 4, d_{calc} = 1.578 g cm^{-3}, μ = 15.8 cm^{-1}. The scan range was $0° < \theta < 25°$, the total number of reflections was 3631 (R_{int} = 0.1513), of which 2003 reflections were with $I \geq \sigma(I)$; the number of parameters in the refinement was 244; $R_1(I \geq \sigma(I))$ = 0.0841, wR_2 = 0.2390, GOOF = 0.887.

The structure was solved by direct methods. The positional and thermal parameters of the nonhydrogen atoms were refined first isotropically and then anisotropically by the full-matrix least-squares. In the cation, the OH group is disordered over two positions with equal occupancies. The positions of all hydrogen atoms were derived from difference Fourier maps, except for the hydrogen atom at the C(11) atom, which is, apparently, disordered due to disorder of the hydroxy group. The hydrogen atoms were not included in the refinement. All calculations were carried out with the use of the SHELXL-97 program package.[10] The interatomic distances and bond angles in the cationic moiety of the molecule are given in Table 1.

Results and Discussion

Crystal structure. In the cation of salt **1** (Fig. 1), the indoline group is orthogonal to the pyranopyridinium fragment. Both these fragments are nonplanar. The pyranopyridinium fragment is folded along the lines passing through the C(3´) and O(1´) atoms and the C(4´) and O(1´) atoms; the folding angles α = 20.0° and β = 12.9°, respectively. The indoline fragment is folded along the line passing through the N(1) and C(3) atoms with φ = 35.3° (the angle between the planes passing through the N(1), C(2´2), and C(3) atoms and the N(1), C(3a), C(4a), and C(3) atoms). The N(1) and C(3) atoms are in the plane of the benzene ring of the indoline fragment. The deviation of the N(1) atom from the plane passing through the C(3a), C(1), and C(2´2) atoms bound to this nitrogen atom is 0.35 Å, and the sum of the bond angles at N(1) is 345.3°, which is indicative of the pyramidal con-

Table 1. Bond lengths (d) and bond angles (ω) in molecule **1**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
C(4)—C(4A)	1.385(12)	C(4A)—C(4)—C(5)	118.7(10)	C(6)—C(5)—C(4)	116.4(10)
C(4)—C(5)	1.404(14)	C(5)—C(6)—C(7)	127.1(10)	C(3A)—C(7)—C(6)	114.9(10)
C(5)—C(6)	1.416(17)	N(1)—C(3A)—C(7)	128.4(9)	N(1)—C(3A)—C(4A)	109.0(6)
C(6)—C(7)	1.342(16)	C(7)—C(3A)—C(4A)	122.6(9)	C(4)—C(4A)—C(3A)	120.1(8)
C(7)—C(3A)	1.367(11)	C(4)—C(4A)—C(3)	131.8(8)	C(3A)—C(4A)—C(3)	108.1(7)
C(3A)—C(4A)	1.430(12)	N(1)—C(2´2)—C(3´)	114.4(7)	N(1)—C(2´2)—O(1´)	105.9(5)
C(4A)—C(3)	1.484(10)	C(3´)—C(2´2)—O(1´)	109.3(6)	N(1)—C(2´2)—C(3)	102.7(6)
C(2´2)—C(3´)	1.505(10)	C(3´)—C(2´2)—C(3)	117.0(6)	O(1´)—C(2´2)—C(3)	106.5(6)
C(3A)—N(1)	1.349(11)	C(9)—C(3)—C(4A)	116.5(7)	C(9)—C(3)—C(2´2)	115.1(6)
C(2´2)—N(1)	1.437(9)	C(4A)—C(3)—C(2´2)	99.5(6)	C(9)—C(3)—C(10)	108.3(6)
C(2´2)—O(1´)	1.485(9)	C(4A)—C(3)—C(10)	107.6(6)	C(2´2)—C(3)—C(10)	109.4(6)
C(2´2)—C(3)	1.548(10)	C(4´)—C(3´)—C(2´2)	123.2(7)	C(3´)—C(4´)—C(4A´)	120.6(7)
C(3)—C(9)	1.466(11)	C(8A)—C(4A´)—C(5´)	117.1(7)	C(8A)—C(4A´)—C(4´)	117.7(7)
C(3)—C(10)	1.573(11)	C(5´)—C(4A´)—C(4´)	125.2(7)	O(1´)—C(8A)—C(4A´)	121.7(6)
C(11)—O(2´)	1.229(17)	O(1´)—C(8A)—C(8´)	115.8(5)	C(4A´)—C(8A)—C(8´)	122.4(6)
C(1)—N(1)	1.478(12)	N(7´)—C(8´)—C(8A)	117.3(5)	N(7´)—C(8´)—C(12)	120.9(6)
C(3´)—C(4´)	1.334(12)	C(8A)—C(8´)—C(12)	121.8(5)	C(5´)—C(6´)—N(7´)	122.9(7)
C(4´)—C(4A´)	1.442(12)	C(8A)—O(1´)—C(2´2)	122.2(5)	C(3A)—N(1)—C(2´2)	107.6(6)
C(4A´)—C(8A)	1.402(9)	C(3A)—N(1)—C(1)	121.1(7)	C(2´2)—N(1)—C(1)	116.6(8)
C(4A´)—C(5´)	1.389(11)	C(8´)—N(7´)—C(6´)	120.0(7)	C(6´)—N(7´)—C(13)	119.6(7)
C(8A)—O(1´)	1.331(8)	C(6´)—C(5´)—C(4A´)	120.3(7)	C(6´)—C(5´)—C(11)	119.0(8)
C(8A)—C(8´)	1.389(9)	C(4A´)—C(5´)—C(11)	120.7(9)	O(2´)—C(11)—O(2)	73.1(11)
C(8´)—N(7´)	1.359(8)	O(2´)—C(11)—C(5´)	115.5(12)	O(2)—C(11)—C(5´)	106.8(8)
C(8´)—C(12)	1.480(9)	C(11)—O(2)—O(2´)	51.6(9)	C(11)—O(2´)—O(2)	55.3(10)
C(6´)—C(5´)	1.309(13)				
C(6´)—N(7´)	1.389(9)				
N(7´)—C(13)	1.389(12)				
C(5´)—C(11)	1.523(10)				
C(11)—O(2)	1.289(16)				
O(2)—O(2´)	1.50(2)				

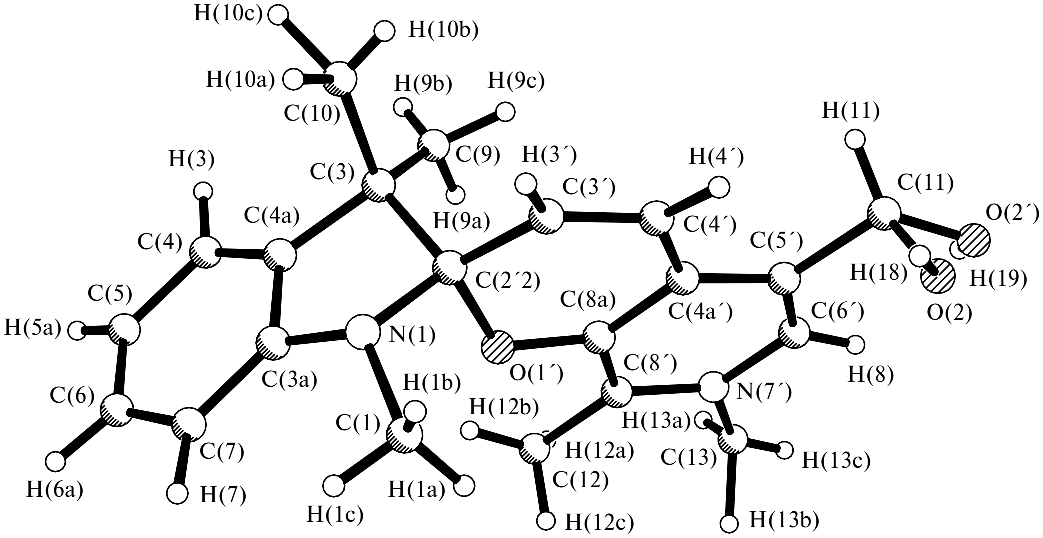


Fig. 1. Structure of cation **1**$^+$.

figuration of the nitrogen atom and the pronounced sp^3 character of the lone pair of N(1). The orientation of the valence bonds at the N(1) atom corresponds to the *trans* position of the lone pair of the nitrogen atom with respect to the C(2´2)—O(1´) bond. The angle between the C(2´2)—O(1´) bond vector and the plane passing through the atoms, which form the base of the pyramid with the N(1) vertex, is 174.5°. This orientation is favorable for orbital interactions between the n lone pair of the N(1) atom and the antibonding σ^* orbital of the C(2´2)—O(1´) bond.

This interaction should lead to strengthening of the C(2´2)—N(1) bond and weakening of the C(2´2)—O(1´) bond. In fact, the C(2´2)—O(1´) bond is elongated to 1.485(9) Å, whereas the C(2´2)—N(1) bond (1.437(9) Å) is shortened compared to the typical bonds in such heterocycles. The C$_{\text{spiro}}$—O bond in cation **1**$^+$ is even more elongated than the analogous bond in 1´,3´,3´-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2´-indoline],[11] although the n—σ^* interaction in spiropyran molecules is known to be efficiently strengthened in the presence of electron-withdrawing substituents in the benzopyran fragment. In salt **1**, the quaternized nitrogen atom of the pyridine ring serves as a strong electron-withdrawing center. The elongated C(2´2)—O(1´) bonds provide evidence that the efficient bond cleavage should occur in the photoexcited state of salt **1**. However, the efficiency of the phototransformation in the crystalline state depends also on the crystal structure, which substantially limits flexibility of the molecules.

The crystal structure of salt **1** can be represented by layers formed by cations **1**$^+$, which are parallel to the OXY crystallographic plane and are separated by the I$^-$ anions (Fig. 2). The organic cations in these layers are linked to each other by van der Waals contacts (C(7)...C(9), 3.46 Å; C(7)...C(11), 3.50 Å; C(1)...O(2´), 3.19 Å; and C(13)...O(2), 3.04 Å). A fragment of the organic layer is shown in Fig. 3. The cavities between the

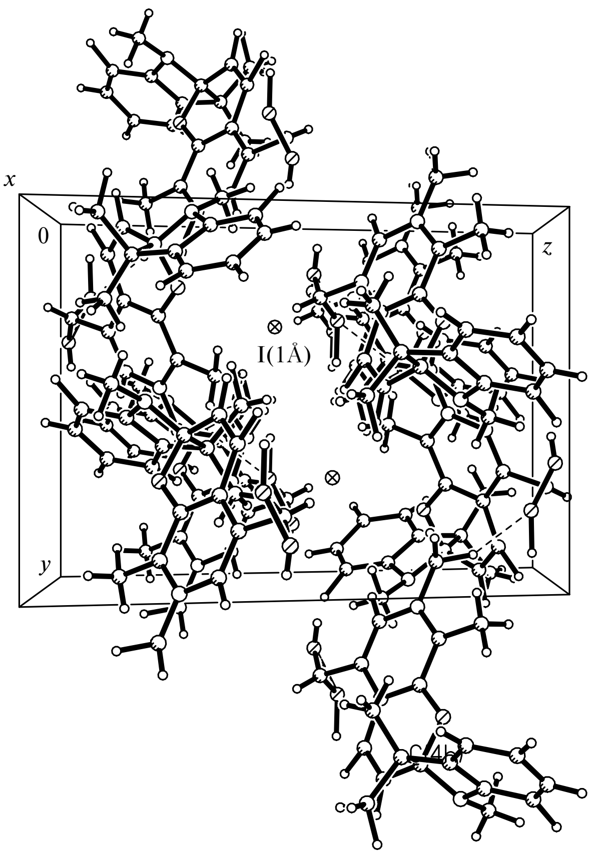


Fig. 2. Crystal packing of salt **1**.

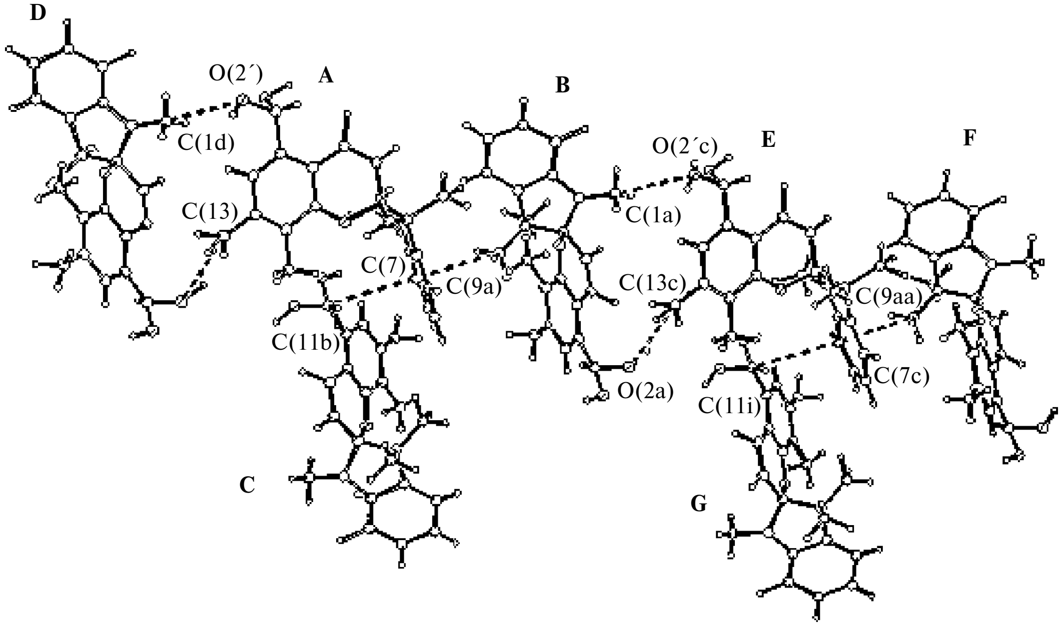


Fig. 3. Fragment of the cation layer of salt **1**; intermolecular contacts are shown by dashed lines.

layers are occupied by the I$^-$ anions, through which the layers are linked to each other to form a three-dimensional structure (I...O(2), O(2′), 3.43 Å; and I...C(8′), 3.84 Å).

In the crystal structure, the iodine atom is closer to the hydroxymethyl group than to the quaternary N(7′) atom (I...O(2), O(2′), 3.43 Å; and N(7′)...I, 4.10 Å). This arrangement of the I$^-$ ions in the crystal structure is, apparently, associated with the formation of an intermolecular I$^-$...HO hydrogen bond. The total energy of the cation sublattice (the energy of interactions with the iodide ions was ignored) is 25.40 kcal mol^{-1}. The energies of interactions between the molecules presented in Fig. 3 are as follows: –6.77 (**A—B**), –6.03 (**A—C**), –2.38 (**A—D**), –4.21 (**B—E**), and –5.79 kcal mol^{-1} (**E—G**). The energy of intermolecular interactions was calculated with the use of the 6-exp program.[12] The calculated energies are indicative of the close packing of the molecules in the layer.

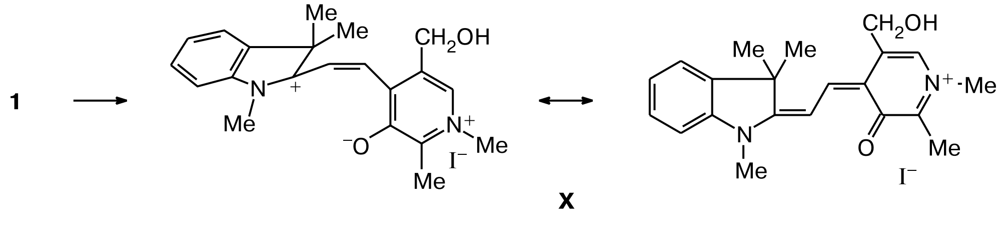
The free volume per molecule (199 Å^3) in the crystal structure under study differs only slightly from the analogous values in the crystals of neutral spiropyrans (186 Å^3). The free unit-cell volume per molecule was calculated according to the equation

$$V_{p/z} = (V_{\text{cell}} - ZV_{\text{mol}})/Z,$$

where V_{cell} and V_{mol} are the volumes of the unit cell and the molecule, respectively, and Z is the number of molecules in the unit cell. The molecular volume was calculated from the average-statistical van der Waals radii.[13] However, the formation of cation layers separated by I$^-$ ions can provide a sufficient volume for the phototransformation of **1**, because the distance between the cation layers, according to our estimates, is ~6 Å.

The pyran-ring opening in molecule **1**, which has absorbed a light quantum, gives rise to an unstable bipolar structure of the isomer **X** (Scheme 1). In cation **1**$^+$, the ring opening will substantially compensate the positive charge in the pyridinium ring through the negative charge transfer from the oxygen atom. As a result, the positive charge of the cation will be localized on the indoline fragment rather than on the pyranopyridinium moiety (see Scheme 1).

Scheme 1



This "recharge" of the cation stabilizing the structure of the isomer **X** will lead to violation of the balance of electrostatic interactions in the crystal, and can cause the displacement of the I^- anion from the pyranopyridinium moiety to the indoline fragment providing isomerization of the molecule in the crystal lattice to give a planar photoproduct.

Spectroscopic and photochemical properties of spiropyrans. For neutral spiropyran in the polycrystalline state irradiated with UV light, no increase in the absorbance in the 500—600 nm region is observed. On the contrary, the crystalline salt of spiropyran **1** exhibits the photochromic properties. The absorption spectra of a single crystal of **1** before irradiation (curve *1*) and after irradiation with UV light at 270—370 nm (curve *2*) are presented in Fig. 4. The absorption spectrum shows a new band (see Fig. 4, curves *2* and *4*) characteristic of absorption of the open form of spiropyran, which has been studied earlier in solutions and polycrystalline samples.[7] After irradiation of this sample with visible light at 500—600 nm, the long-wavelength absorption band disappears and the absorption spectrum returns to the initial spectral pattern (see Fig. 4, curve *3*). These photochromic transitions were observed in a single crystal upon ten-times reversible sample irradiation without its decomposition, the absorption of the open form being decreased by 10%. A slight increase in absorption was observed during irradiation at short-wavelengths (400—450 nm). This may be associated with surface effects, which is indicative of partial photodestruction of the compound. In single crystals, the color remains visually unchanged at room temperature for 1 month. To estimate the quantum yield of the transition from the closed to open form, we assumed that the extinction coefficient of the open form of spiropyran in the crystalline state at 522 nm is equal to the extinction coefficient of this form in water. Salt **1** dissolved in water is completely transformed into the open form. In this case, the extinction coefficient of the open form ε_{max} (492 nm) is *ca.* 3500 L mol^{-1} cm^{-1}, and the quantum yield in a single crystal, φ_1 (270—370 nm), is ~0.1 for the transition from the closed to open form and φ_2 (500—600 nm) is ~0.04 for the back transition.

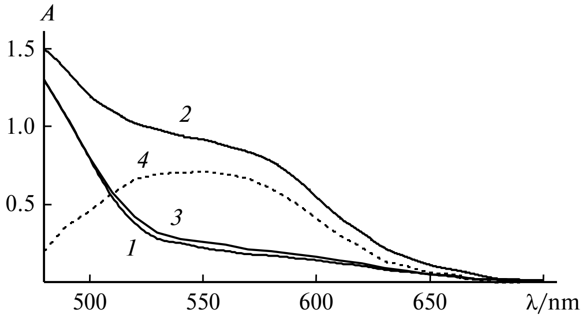


Fig. 4. Absorption spectra of a single crystal of salt **1** before irradiation (*1*), after irradiation with UV light at 270—370 nm (*2*), after irradiation with visible light at 500—600 nm (*3*), and the difference spectrum (*4*) between the absorption spectra of the irradiated sample (*2*) and the starting sample (*1*).

Table 2. Spectroscopic properties of the open form of compound **1** in different solvents and in a single crystal

Solvent	λ_{max}/nm	ε^a	n^b
Water	486	80.0	1.3332
Ethanol	522	25.2	1.3614
Chloroform	572	4.72	1.4464
Without a solvent^c	545	—	1.3925^d

[a] The dielectric constant of the solvent.
[b] The refractive indices of the solvent and the single crystal.
[c] The single crystal.
[d] Calculated by Eq. (1).

Let us consider the spectroscopic parameters of molecule **1** in a single crystal as compared to the absorption maxima of the open form of **1** in various solvents (Table 2, since the absorption spectra of the open form have a dome shape, only the maxima of transitions are given). The single crystal can be represented, in a first approximation, as a uniform isotropic dielectric, and the molecule can be represented as a rigid dipole. In the latter case, the dipole moment of the molecule depends only slightly on the dielectric properties of the solvent, whereas the electronic transitions depend on the solvation energy of the dipole (molecule) both in the ground and excited states. In absorption spectra, the dipole polarization of the solvent with dielectric constant ε is of little importance but the electronic polarizability of the solvent has a certain effect, *i.e.*, the transition energy should depend on the refractive index of the medium *n*. For a model of a rigid point dipole with the dipole moment μ in a sphere of an isotropic dielectric with a radius *r*, the transition frequency can be described, in a first approximation, by the equation[14]

$$h\nu = h\nu_0 + \mu^2 f'/r^3, \qquad (1)$$

where $f' = (n^2 - 1)/(2n^2 + 1)$, and $h\nu_0$ is the transition energy in the gas phase.

In fact, in the case under consideration, the transition maxima in various solvents satisfy the above dependence. If a single crystal is represented as a uniform dielectric and its refractive index is estimated by Eq. (1), the refractive index $n = 1.3925$ corresponds to the transition at 545 nm.

This dependence of λ_{max} of the open form of compound **1** in solutions on the refractive index of the medium shows that the dipole moment of salt **1** in the excited state is higher than that in the ground state.

No substantial changes in the crystal structure after irradiation with UV light were revealed by single-crystal X-ray diffraction study. Apparently, the photochromic transformations occur in a thin near-surface layer. The thickness of the layer involved in photochromic transformations can be estimated as follows. The maximum absorbance in the visible region is 0.8, and, consequently, the concentration of the colored form calculated for the solution is $2.3 \cdot 10^{-4}$ mol L $^{-1}$ or $1.37 \cdot 10^{17}$ molecules cm^{-3}. If the volume of one molecule is 275.4 Å^3, the thickness of the colored layer is ~3770 Å, and the number of monolayers is 580. It means that a considerable portion of a single crystal, rather than a thin near-surface layer, undergoes photochromic transformations. However, this is not detected by X-ray diffraction. These efficient photochromic transformations in single crystals of the salt compared to neutral spiropyran are, presumably, associated with both the looser structure of the salt containing iodide ions (see Fig. 2) and the above-discussed "recharge" in the isomer **X** of the salt (see Scheme 1).

Several types of organic compounds were documented, in which reversible photochromic transformations in single crystals occur: aryl hydrazides,**[9]** diarylethenes,**[15]** and derivatives of salicylaldehydes.**[16]** We demonstrated that photochromic transformations in single crystals of spiropyran salts can occur in the crystal bulk without degradation of the crystal structure.

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