

PHOTO- AND THERMOCHROMIC SPIRANES. 29*. NEW PHOTOCHROMIC INDOLINOSPIROPYRANS CONTAINING A QUINOLINE FRAGMENT

V. V. Tkachev¹, S. M. Aldoshin¹, N. A. Sanina¹, B. S. Lukyanov², V. I. Minkin²,
A. N. Utenyshev¹, K. N. Khalanskiy², and Yu. S. Alekseenko²

A new photochromic spiroopyran of the indoline series, containing a quinoline fragment, has been synthesized. The photochromic properties of the spiroopyran and its iodomethylate have been studied. Features of the molecular structure of the compounds were determined by X-ray structural investigations. It was established that the pyridopyran fragments of the cations in the crystal of the iodomethylate salt, unlike those in the crystal of the neutral spiroopyran, emerge from 2₁-stacks, disposed jointly with I⁻ ions, which causes their higher mobility and aids the course of reversible photoconversions on UV irradiation in solution.

Keywords: indolinospiroopyran, quinoline fragment, X-ray structural analysis, photochromism.

The synthesis of spiroopyran salts (SP^{+X⁻}), the investigation of their molecular, crystal structure, and photochromic conversions in the solid phase has caused immense interest [2-7] in the design of new polyfunctional materials based on them, combining in one crystal lattice several beneficial properties (photoswitching nonlinear optical properties [8] or photomagnetism [9]) and raising the prospect of using crystalline hybrids in miniature electronic instruments.

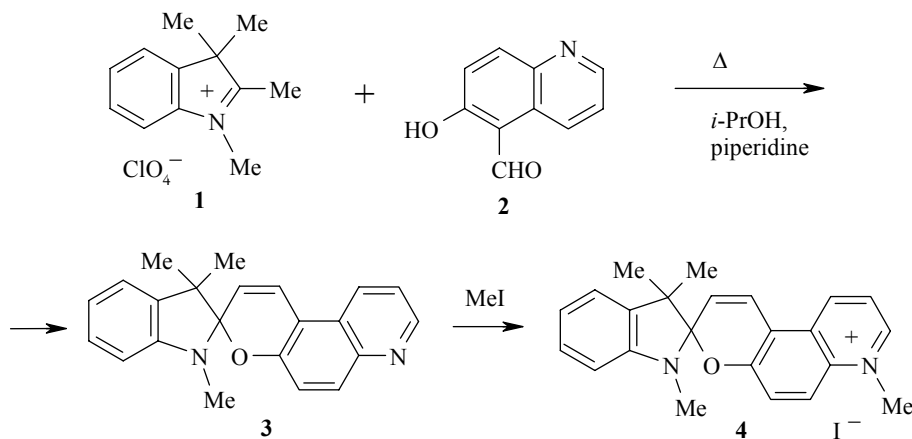
Photochromic conversions of neutral spiroopyrans, linked with cleavage of the C_{spiro}-O bond and subsequent isomerization of the molecule, require a large open space and consequently is extremely hindered in crystals by the total packing in the lattice. As a rule the neutral spiroopyrans in monocrystals and microcrystalline powders under stationary radiation conditions do not display photocoloration caused by the formation of open photomerocyanine structures [10], as was observed in solution or in the amorphous state.

Investigation of ultrathin pressed microcrystalline samples of salts of spiroopyrans and spiroxazines with N-methylated pyranopyridine rings [6, 11, 12] showed that at constant UV irradiation (365 nm) they are colored reversibly with the development of a broad absorption band between 500 and 650 nm, as was also observed in solution. The photochromic conversions are reversible and monocrystals survive some tens of cycles before structural and spectral changes. To establish the features of the molecular and crystal structure which provide reversible photochromic conversions of salts of spiroopyrans under crystal packing conditions we carried out the synthesis and systemic investigation of the structure of new salts of various classes of spiroopyrans [5, 6, 12, 13].

* For Part 28 see [1].

¹Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Moscow region; e-mail: sma@icp.ac.ru. ²Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don 344090, Russia; e-mail: minkin@ipoc.rsu.ru. Translated from Khimiya Geterotsiklicheskih Soedinenii, No. 5, pp. 690-702, May, 2007. Original article submitted November 25, 2006.

The spiro(1,3,3-trimethylindolino-2,3'-3H-pyrano[3,2-*f*]quinoline) (**3**) studied in the present work and its derivative spiro(1,3,3-7'-tetramethylindolino-2,3'-3H-pyrano[3,2-*f*]quinolinium iodide) (**4**), containing a quaternized nitrogen atom, were synthesized according to the following scheme:



In the IR spectra of compounds **3** and **4** there were $\nu_{C=C}$ absorption bands for the 2H-chromene fragment at 1593-1673 and 1527-1600 cm^{-1} (for compounds **3** and **4** respectively). In the ^1H NMR spectra of the obtained spiropyrans the signals of the H-1' and H-2' protons were an AB system (compound **3** at 5.97 (H-1') and 7.50 (H-2'), $J_{1,2'} = 10.4$ and compound **4** at 6.10 (H-1') and 7.72 ppm (H-2'), $J_{1,2'} = 10.6$ Hz). The signals of the methyl group at the nitrogen atom (N-CH₃) in position 3 of the indoline fragment were displayed as a singlet three-proton signal at 2.73 and 2.74 ppm, but in compound **4** a three-proton singlet signal was noted at 4.83 ppm for the methyl group at the quaternary nitrogen atom. The *gem*-dimethyl groups at position 3 of the indoline fragment are a convenient diastereotopic label reflecting the spiropyran structure of the compounds. The presence in the ^1H NMR spectra of two singlet signals of the *gem*-dimethyl groups (*gem*-(CH₃)₂) at 1.20, 1.32 and 1.23 and 1.32 ppm for compounds **3** and **4** respectively are caused by the presence of the asymmetric carbon atom in the molecule, confirming the spirocyclic structure of the compounds.

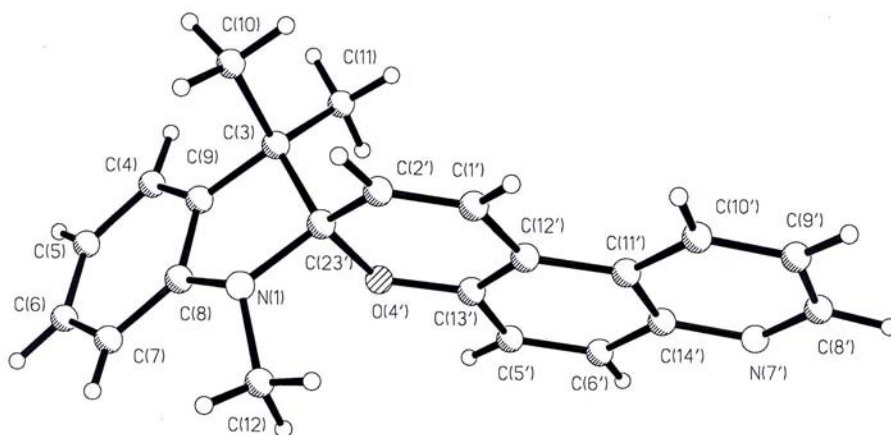


Fig. 1. General shape of compound **3** according to X-ray structural data.

Monocrystals were grown and an X-ray structural investigation was carried out for a more detailed study of the structure of the synthesized spiropyrans by the experimental selection of solvents (EtOH for compound **3** and a MeOH-H₂O, 5 : 1 mixture, for compound **4**) (Tables 1-4).

Table 2. Bond Lengths (*l*) in the Spiropyrans **3** and **4** Molecules

Bond	<i>l</i> , Å		Bond	<i>l</i> , Å	
	3	4		3	4
O ₍₄₎ -C ₍₁₃₎	1.361(2)	1.359(6)	C ₍₁₄₎ -C ₍₆₎	1.420(3)	1.404(7)
O ₍₄₎ -C _(23')	1.474(2)	1.467(6)	C ₍₆₎ -C ₍₅₎	1.357(3)	1.342(7)
N ₍₁₎ -C ₍₈₎	1.404(3)	1.398(7)	C ₍₅₎ -C ₍₁₃₎	1.410(2)	1.416(7)
N ₍₁₎ -C ₍₂₃₎	1.446(3)	1.446(7)	C ₍₁₀₎ -C ₍₉₎	1.366(3)	1.343(8)
N ₍₁₎ -C ₍₁₂₎	1.454(3)	1.447(10)	C ₍₉₎ -C ₍₈₎	1.392(3)	1.367(9)
N ₍₇₎ -C ₍₈₎	1.318(3)	1.330(7)	C ₍₃₎ -C ₍₉₎	1.508(3)	1.500(8)
N ₍₇₎ -C ₍₁₄₎	1.369(2)	1.369(6)	C ₍₃₎ -C ₍₁₁₎	1.511(3)	1.531(9)
C ₍₂₃₎ -C ₍₂₎	1.489(3)	1.519(7)	C ₍₃₎ -C ₍₁₀₎	1.551(3)	1.538(9)
C ₍₂₃₎ -C ₍₃₎	1.562(3)	1.553(8)	C ₍₉₎ -C ₍₄₎	1.383(3)	1.363(8)
C ₍₂₎ -C ₍₁₎	1.317(3)	1.301(7)	C ₍₉₎ -C ₍₈₎	1.385(3)	1.389(8)
C ₍₁₎ -C ₍₁₂₎	1.460(3)	1.476(7)	C ₍₄₎ -C ₍₅₎	1.393(3)	1.394(10)
C ₍₁₂₎ -C ₍₁₃₎	1.367(2)	1.348(7)	C ₍₅₎ -C ₍₆₎	1.364(4)	1.392(11)
C ₍₁₂₎ -C ₍₁₁₎	1.426(2)	1.410(7)	C ₍₆₎ -C ₍₇₎	1.378(4)	1.359(10)
C ₍₁₁₎ -C ₍₁₀₎	1.412(3)	1.409(7)	C ₍₇₎ -C ₍₈₎	1.383(3)	1.390(8)
C ₍₁₁₎ -C ₍₁₄₎	1.416(3)	1.415(6)	N ₍₇₎ -C ₍₁₅₎		1.492(8)

TABLE 3. Valence Angles (ω) in the Compounds **3** and **4** Molecules

Angle	ω , deg		Angle	ω , deg	
	3	4		3	4
C ₍₁₃₎ -O ₍₄₎ -C ₍₂₃₎	122.53(13)	120.2(4)	O ₍₄₎ -C ₍₁₃₎ -C ₍₁₂₎	123.51(16)	123.8(4)
C ₍₈₎ -N ₍₁₎ -C ₍₂₃₎	107.01(15)	107.5(5)	O ₍₄₎ -C ₍₁₃₎ -C ₍₅₎	114.60(15)	115.2(4)
C ₍₈₎ -N ₍₁₎ -C ₍₁₂₎	118.9(2)	122.4(5)	C ₍₁₂₎ -C ₍₁₃₎ -C ₍₅₎	121.89(17)	121.0(5)
C ₍₂₃₎ -N ₍₁₎ -C ₍₁₂₎	117.8(2)	120.6(5)	C ₍₉₎ -C ₍₁₀₎ -C ₍₁₁₎	119.50(19)	121.0(5)
C ₍₈₎ -N ₍₇₎ -C ₍₁₄₎	117.06(18)	121.7(5)	C ₍₁₀₎ -C ₍₉₎ -C ₍₈₎	119.2(2)	120.7(5)
N ₍₁₎ -C ₍₂₃₎ -O ₍₄₎	106.62(14)	105.5(4)	N ₍₇₎ -C ₍₈₎ -C ₍₉₎	124.3(2)	120.3(5)
N ₍₁₎ -C ₍₂₃₎ -C ₍₂₎	112.16(17)	112.1(5)	C ₍₉₎ -C ₍₃₎ -C ₍₁₁₎	115.42(16)	112.8(5)
O ₍₄₎ -C ₍₂₃₎ -C ₍₂₎	111.29(16)	109.3(4)	C ₍₉₎ -C ₍₃₎ -C ₍₁₀₎	108.55(16)	109.5(5)
N ₍₁₎ -C ₍₂₃₎ -C ₍₃₎	103.11(15)	103.4(4)	C ₍₁₁₎ -C ₍₃₎ -C ₍₁₀₎	108.93(18)	108.6(5)
O ₍₄₎ -C ₍₂₃₎ -C ₍₃₎	106.36(14)	108.7(4)	C ₍₉₎ -C ₍₃₎ -C ₍₂₃₎	99.75(14)	101.5(4)
C ₍₂₎ -C ₍₂₃₎ -C ₍₃₎	116.53(16)	117.1(5)	C ₍₁₁₎ -C ₍₃₎ -C ₍₂₃₎	113.56(17)	113.0(5)
C ₍₁₎ -C ₍₂₎ -C ₍₂₃₎	124.33(18)	123.3(5)	C ₍₁₀₎ -C ₍₃₎ -C ₍₂₃₎	110.28(16)	111.3(5)
C ₍₂₎ -C ₍₁₎ -C ₍₁₂₎	121.08(18)	120.2(5)	C ₍₄₎ -C ₍₉₎ -C ₍₈₎	119.55(19)	120.1(6)
C ₍₁₃₎ -C ₍₁₂₎ -C ₍₁₁₎	118.90(16)	119.5(4)	C ₍₄₎ -C ₍₉₎ -C ₍₃₎	131.56(19)	131.4(6)
C ₍₁₃₎ -C ₍₁₂₎ -C ₍₁₎	116.89(17)	116.8(4)	C ₍₈₎ -C ₍₉₎ -C ₍₃₎	108.88(16)	108.4(5)
C ₍₁₁₎ -C ₍₁₂₎ -C ₍₁₎	124.20(16)	123.7(4)	C ₍₉₎ -C ₍₄₎ -C ₍₅₎	118.8(2)	119.4(7)
C ₍₁₀₎ -C ₍₁₁₎ -C ₍₁₄₎	116.86(17)	116.8(5)	C ₍₆₎ -C ₍₅₎ -C ₍₄₎	120.7(2)	119.5(6)
C ₍₁₀₎ -C ₍₁₁₎ -C ₍₁₂₎	123.65(17)	123.7(4)	C ₍₅₎ -C ₍₆₎ -C ₍₇₎	121.4(2)	121.7(6)
C ₍₁₄₎ -C ₍₁₁₎ -C ₍₁₂₎	119.48(16)	119.5(4)	C ₍₆₎ -C ₍₇₎ -C ₍₈₎	117.9(2)	118.1(7)
N ₍₇₎ -C ₍₁₄₎ -C ₍₁₁₎	123.03(17)	119.5(4)	C ₍₇₎ -C ₍₈₎ -C ₍₉₎	121.7(2)	121.2(6)
N ₍₇₎ -C ₍₁₄₎ -C ₍₆₎	117.81(17)	121.4(4)	C ₍₇₎ -C ₍₈₎ -N ₍₁₎	128.3(2)	128.3(6)
C ₍₁₁₎ -C ₍₁₄₎ -C ₍₆₎	119.16(17)	119.1(5)	C ₍₉₎ -C ₍₈₎ -N ₍₁₎	110.03(16)	110.4(5)
C ₍₅₎ -C ₍₆₎ -C ₍₁₄₎	120.58(18)	120.3(4)	C ₍₈₎ -N ₍₇₎ -C ₍₁₅₎		118.6(5)
C ₍₆₎ -C ₍₅₎ -C ₍₁₃₎	119.97(17)	120.6(5)	C ₍₁₄₎ -N ₍₇₎ -C ₍₁₅₎		119.7(4)

The pyranopyridine fragment in compound **3** is almost planar but in compound **4** is not planar. The bend at the line C₍₂₎-O₍₄₎ and C₍₁₎-O₍₄₎ $\alpha = 4.30$, $\beta = 3.5^\circ$ in **3** and $\alpha = 18.90$, $\beta = 14.6^\circ$ in **4** respectively. Probably this is the reason that the molecule of compound **3** and the molecular cation of **4** are significantly different from

one another on joining them in the plane of the indoline fragment (Fig. 3). The maximum deviation between the $C_{(8)}$ atoms in compounds **3** and **4** is 3.4 Å. The $C_{(23)}-O_{(4)}$ bond length in compound **3** is 1.474(2), in **4** it is 1.467(6) Å, which is greater than the usual values of 1.41-1.43(1) Å [14]. The emergence of the $N_{(1)}$ atom from the plane through the $C_{(23)}$, $C_{(8)}$, and $C_{(12)}$ atoms linked with it is 0.33 in **3** and 0.26 Å in **4**, but the sum of the valence angles at $N_{(1)}$ is 343.7 in **3** and 350.5° in **4**, which indicates a pyramidal configuration for the nitrogen atom and significant sp^3 -character for the unshared electron pair of the $N_{(1)}$ atom. The orientation of the valence bonds at the $N_{(1)}$ atom in compounds **3** and **4** corresponds to a *trans* disposition of the unshared electron pair of the nitrogen atom to the $C_{(23)}-O_{(4)}$ bond. The angle between the $C_{(23)}-O_{(4)}$ bond vector and the plane formed through the atoms which form the base of the pyramid with apex $N_{(1)}$ is 170.8 and 169.2° for compounds **3** and **4** respectively. A similar orientation makes possible an orbital interaction of the unshared electron pair of the $N_{(1)}$ atom with the antibonding $C_{(23)}-O_{(4)}$ σ^* -orbital. This interaction leads to weakening of the $C_{(23)}-O_{(4)}$ bond and its lengthening which makes possible efficient rupture of this bond in the photoactivated state.

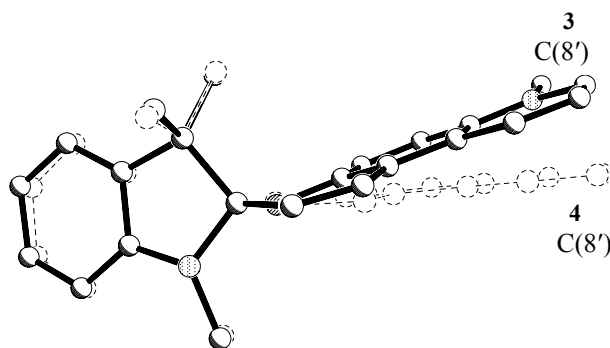


Fig. 3. The superposed molecule **3** and molecular cation **4**.

Analogously to the previously studied compounds of this class [5] monocrystals of neutral spiropyran **3** and its salt derivative **4** have space groups $P2(1)/c$, $Z = 4$, and $P2(1)/n$, $Z = 4$, respectively with densities 1.263 and 1.517 g/cm³.

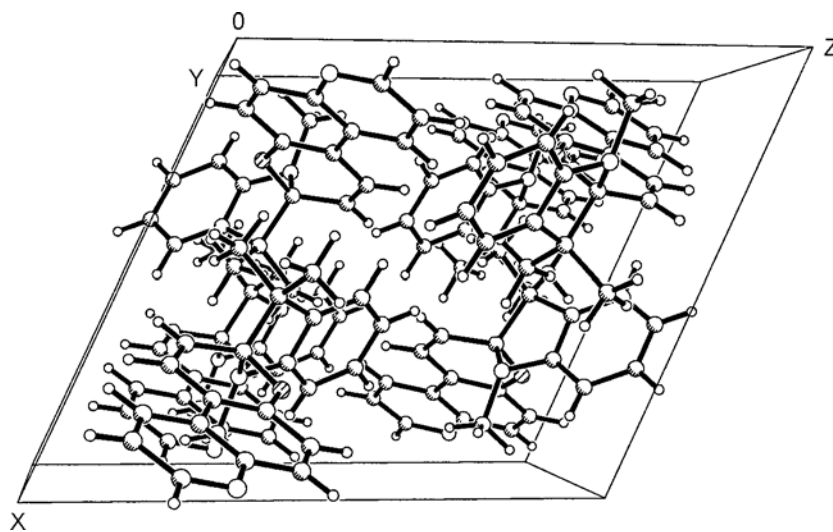


Fig. 4. Fragment of the crystal structure of compound **3**.

The crystal structure of compound **3** is represented in Fig. 4. The total energy of the crystal lattice is -31.4 kcal/mol. A main contribution to the total energy is made by the energy of intermolecular pair interactions between the molecules, linked by a second order screw axis, equal to -8.6 kcal/mol. Between the molecules linked with the center of symmetry weak intramolecular bonds arise of the C–H···N type (Fig. 5) with

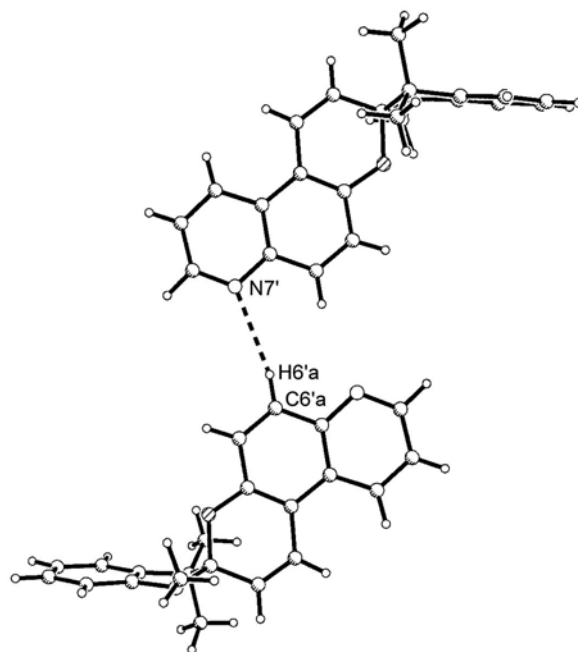


Fig. 5. Molecules of compound **3** linked by intermolecular hydrogen bonds.

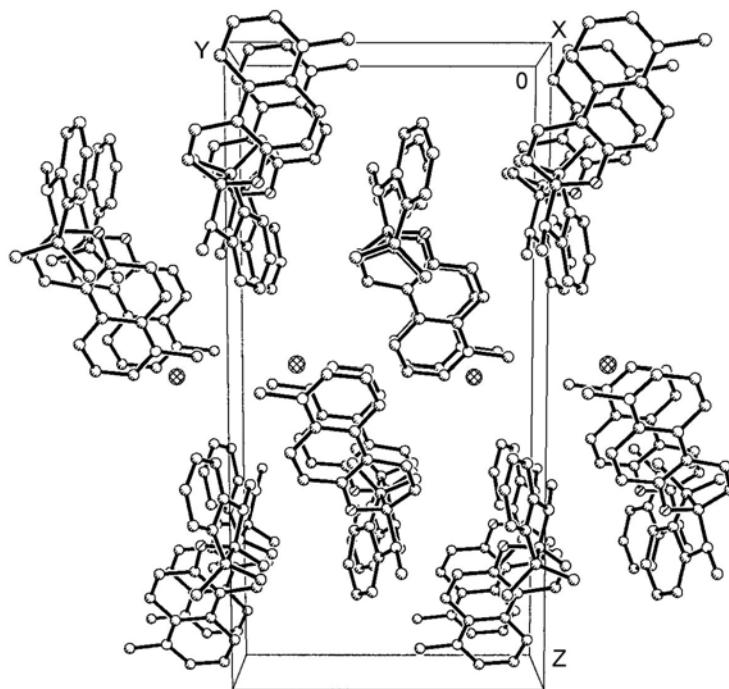


Fig. 6. Fragment of the crystal structure of compound **4** along the *x*-axis.

parameters $N_{(7)}\cdots H-6'a$ 2.70, $N_{(7)}\cdots C_{(6a)}$ 3.637, $N_{(7)}-H-6a'-C_{(6a)}$ 167.7°. The $N_{(7)}$ atom has an intermolecular contact of 2.92 Å with a hydrogen atom of the $C_{(12)}$ methyl group of the molecule, which is linked by a second order screw axis with translations 0-10.

The crystal structure of salt **4** is represented in Figs. 6-8. The cations of compound **4** form block packing. Along the axis of crystallographic direction x the organic cations are linked in relays (Fig. 6) and form channels in which the iodine anions are localized.

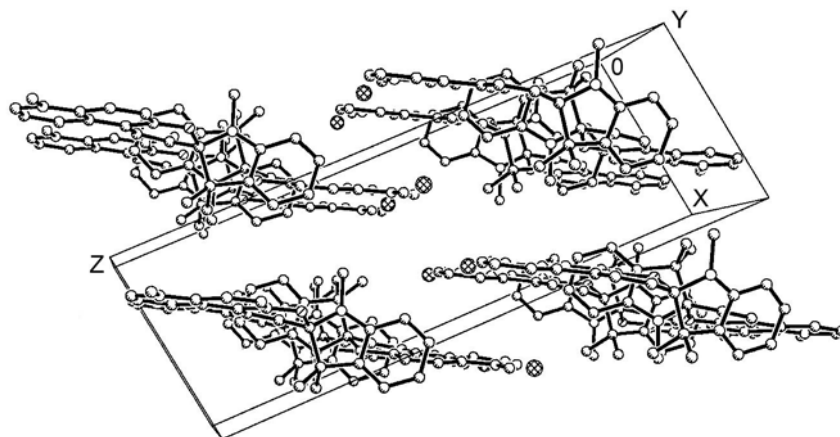


Fig. 7. Fragment of the crystal structure of compound **4** along the y -axis.

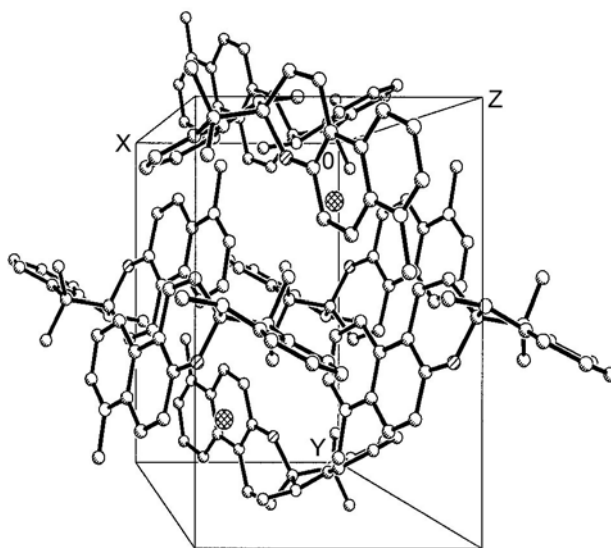


Fig. 8. Fragment of the crystal structure of compound **4** along the z -axis.

The I^- anions are approximately equally removed from the positively charged nitrogen atoms of the pyranopyridine fragments of the cations linked in relays at distances of 4.04 and 4.19 Å for the $I_{(16)}\cdots N_{(7)}$ bond in compounds **3** and **4** respectively (Fig. 9). These distances are greater than the analogous distances for one salt and correspond to another (in [5] 3.75 and 4.10 Å respectively). The shortest distance formed by the iodine anion and effected between the $I_{(16)}$ anion and the $C_{(10)}$ atom is equal to 3.762 Å. Along the y -axis it is possible

to isolate stacks formed by the organic cations (Fig. 7). In the stacks the cations are linked by the second order screw axes (Fig. 10). In the 2_1 -stacks the cations are packed with the indoline fragments, but the pyridopyrans emerge from the stacks at different sides (Fig. 10). In this way the indoline fragments are disposed one above the other. The angle between the mean planes of the indoline fragments of neighboring molecules in the 2_1 -stacks is 47.9° , and between this plane and the 2_1 -axis it is 156.0° . The planes of the pyridopyran fragments are at an angle of 96.9° from the 2_1 -axis. In the previously studied crystals of salts [5] the 2_1 -stack was also packed along the y -axis.

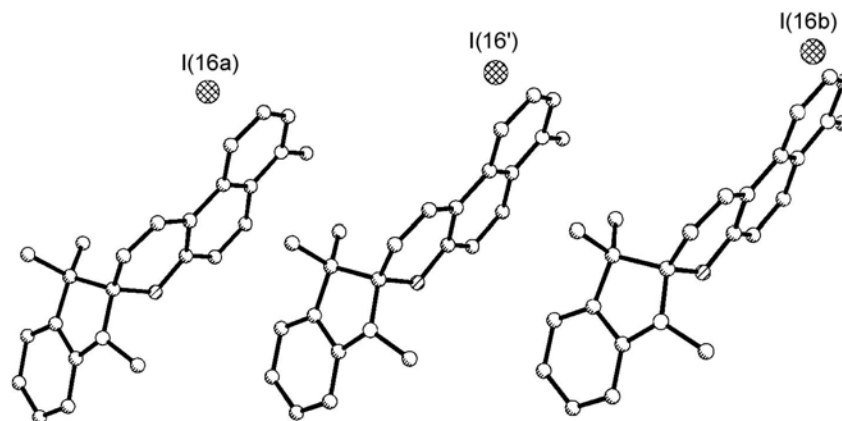


Fig. 9. Disposition of the compound 4 molecules repeatedly linked in the direction of the x -axis.

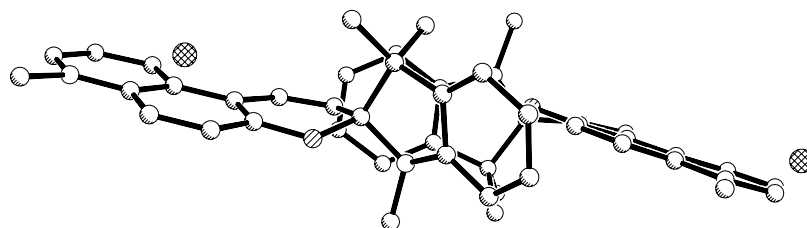


Fig. 10. Disposition of the molecules of compound 4 in the 2_1 -stacks along the direction of the y -axis.

The 2_1 -stacks in the crystal of compound 4, unlike the stack in the crystal of compound 3, are therefore arranged such that the pyridopyran fragments of the cations emerge from the 2_1 -stack, disposed jointly with $I_{(16)}$ ions, and may possess a fairly high mobility. Considering that cleavage of the $C_{\text{spiro}}\text{-O}$ bond and subsequent isomerization occurs in the pyridopyran fragment of the spirocyclic compound, it might be expected that in monocrystals of the salts the crystal structure will be capable of photoconversion under UV irradiation.

In reality, an equilibrium was observed for compound 3 (Fig. 11) in ethanol with a small content of the merocyanine form, which gives a solution of a light-lilac color. On selective activation of the open form the reverse photoreaction was not observed, evidently due to competition with the far more efficient thermal processes. On irradiation of the solution with $365/\Sigma$ light a small increase is observed in the content of the colored form in comparison with equilibrium. The reversibility is caused by thermal relaxation to the state of

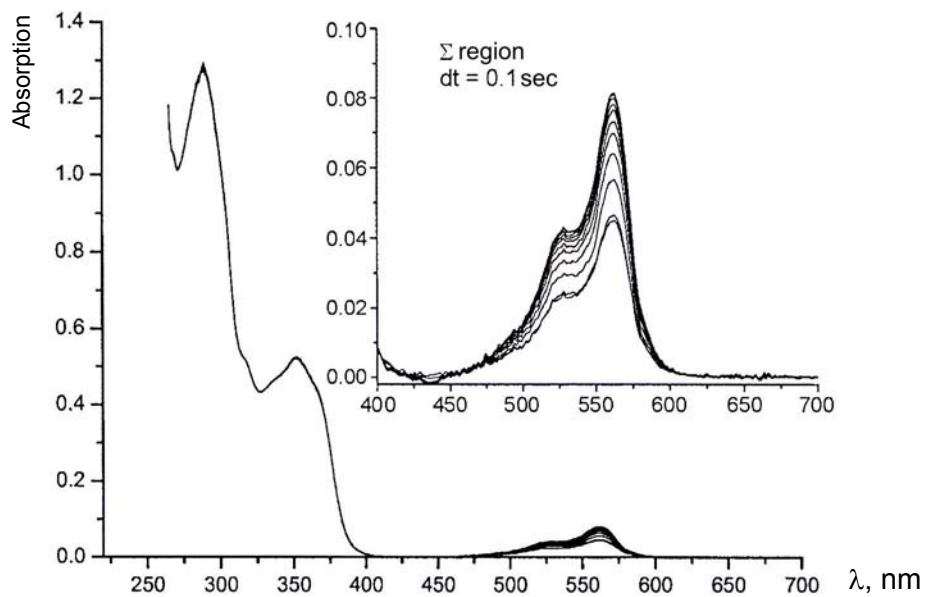


Fig. 11. Photoinduced spectral changes of a solution of compound **3** in ethanol on UV irradiation.

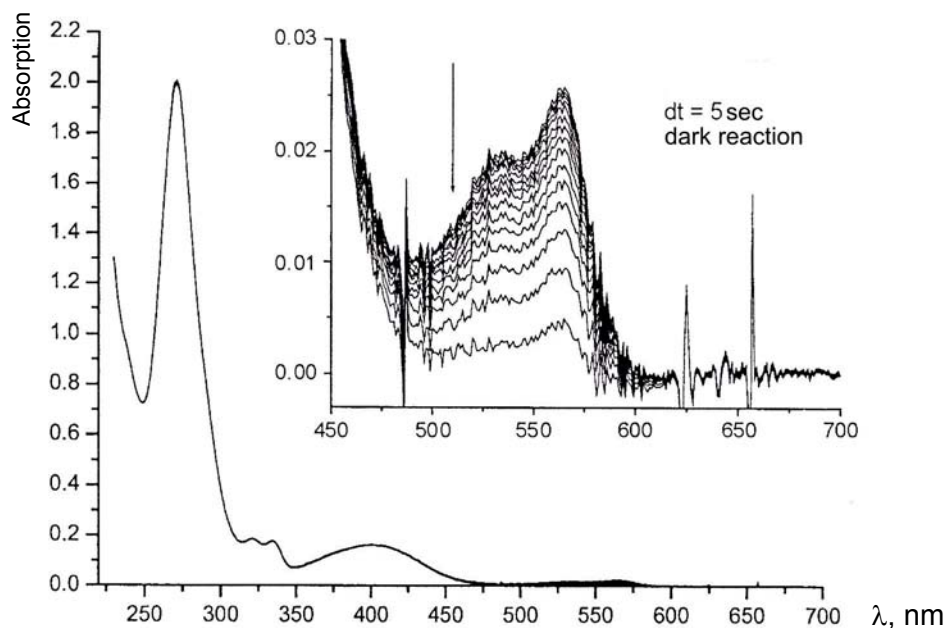


Fig. 12. Thermal relaxation of system **4** in ethanol to thermodynamic equilibrium after UV irradiation (λ_{\max} 546 nm).

thermodynamic equilibrium. The extinction coefficients of form A (Table 4) were calculated from the assumptions that the content of the merocyanine form is negligibly small and $[C_0] = [A_0]$. In compound **4** (Fig. 12), unlike compound **3**, both direct and reverse photoreactions occur together with the thermal processes. This makes it possible to calculate the extinction coefficients of form A without additional assumptions (see Table 4).

TABLE 4. Spectral and Kinetic Characteristics of Compounds **3** and **4** (A) and Their Photoinduced Forms (B) in Ethanol at 24°C

Compound	λ_{\max}^A , nm	$\varepsilon(\lambda_{\max}^A)$, $M^{-1}\cdot cm^{-1}$	λ_{\max}^B , nm	τ_{24}^B , sec
3	247	48390	527 (sh) 562	0.43
	289	11060		
	317 (sh)	4450		
	336 (sh)	4000		
	352	4440		
	367 (sh)	3660		
4	271	42090	534 564	26.0
	321	4090		
	334	3870		
	399	3490		

EXPERIMENTAL

The IR spectra were recorded on a Specord IR 71 prism double beam spectrometer. Calibration of the sample was carried out with polystyrene. The electronic spectra of the investigated compounds were obtained on a Carey Varian spectrophotometer. A DRSh-250 mercury lamp with light filters isolating light with λ_{\max} 313 and 365 nm was used as activating source. The 1H NMR spectra were recorded on a Varian Unity 300 spectrometer (300 MHz) in $CDCl_3$, assignment of signals was carried out relative to the residual protons of the deuterated solvent $CDCl_3$ signal (δ 7.26 ppm).

Spiro(1,3,3-trimethylindolino-2,3'-3H-pyrano[3,2-f]quinoline) (3). Piperidine (1.073 g, ~1.1 ml, 13 mmol) was added dropwise to a boiling mixture of 1,2,3,3-tetramethylindolinium perchlorate (2.74 g, 10 mmol) and 6-hydroxyquinoline-5-carbaldehyde **2** [15] (1.90 g, 11 mmol) in 2-propanol (15 ml). The reaction mixture was boiled for 15 min and left overnight at room temperature. The precipitated crystals were filtered off, and recrystallized from hexane. Mp 162°C; yield 65%. Found, %: C 80.32; H 6.23; N 8.47. $C_{22}H_{20}N_2O$. Calculated, %: C 80.46; H 6.14; N 8.53.

Spiro(1,3,3,7'-tetramethylindolino-2,3'-3H-pyrano[3,2-f]quinolinium) Iodide (4). A mixture of compound **3** (0.328 g, 1 mmol) and MeI (0.213 g, ~0.09 ml, 1.5 mmol) in absolute acetone (15 ml) was boiled for 3 h, left for 2 days, the precipitated solid was filtered off, and washed with absolute acetone. Mp >250°C (acetone); yield 80%. IR spectrum (thin film), ν , cm^{-1} : compound **3**, 1673, 1633, 1593 (C=C); compound **4**, 1600, 1580, 1533 (C=C). 1H NMR spectrum, δ , ppm (J , Hz): compound **3**, 1.20 (3H, s, *gem* (CH₃)₂); 1.32 (3H, s, *gem* (CH₃)₂); 2.73 (3H, s, N-CH₃); 5.83 (1H, d, $J = 10.4$, H-2'); 6.53 (1H, d, $J = 8.1$, H-6'); 6.85 (1H, t, $J = 7.3$, H-5); 7.09 (1H, d, $J = 6.1$, H-7); 7.16-7.22 (2H, m, H-6,4); 7.39 (1H, q, $J = 8.5$, H-9'); 7.50 (1H, d, $J = 10.4$, H-1'); 7.86 (1H, d, $J = 9.3$, H-10'); 8.34 (1H, d, $J = 8.1$, H-5'); 8.74 (1H, d, $J = 4.2$, H-8'); compound **4**, 1.23 (3H, s, *gem* (CH₃)₂); 1.32 (3H, s, *gem* (CH₃)₂); 2.74 (3H, s, N₍₁₎-CH₃); 4.83 (3H, s, N_(7')-CH₃); 6.10 (1H, d, $J = 10.6$, H-2'); 6.57 (1H, d, $J = 7.8$, H-7); 6.91 (1H, t, $J = 7.4$, H-5); 7.12-7.22 (2H, m, H-6,4); 7.61 (1H, d, $J = 9.6$, H-6'); 7.72 (1H, d, $J = 10.6$, H-1'); 8.12 (1H, d, $J = 9.6$, H-5'); 8.17 (1H, m, $J = 8.8$, H-9'); 9.35 (1H, d, $J = 8.8$, H-10'); 10.08 (1H, d, $J = 5.6$, H-8'). Found, %: C 58.61; H 5.05; N 6.03. $C_{23}H_{23}IN_2O$. Calculated, %: C 58.73; H 4.93; N 5.96.

X-ray Structural Investigation of Spiropyran 3 and Its Salt 4 was carried out on monocrystals of light-pink or brown color respectively of arbitrary shape, sizes 0.5 x 0.4 x 0.45 (**3**) and 0.2×0.2×0.2 mm (**4**) at 293K on a KUMA Diffraction KM4 diffractometer ($\lambda MoK\alpha$) = 0.71073 Å, $\omega/2\theta$ -scanning). The crystallographic data and the main parameters of the refinement are given in Table 1. Structures were solved by the direct method [16]. The positions and the temperature parameters of the non-hydrogen atoms were refined in

an anisotropic approximation by the full matrix least squares method [17]. The positions of the hydrogen atoms emerged from difference syntheses and were subsequently refined with superposition according to the *rider* model [17] allowing for the randomization of the hydrogen atoms at the C₍₁₂₎ methyl atom in two positions located equivalently relative to the plane of the ring. All the calculations were carried out using the SHELXL97 set of programs [16].

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