

## New Salt Spiropyran of Indoline Series with Fluorine Substituent

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**Abstract**—Synthesis, study of structure and photochromic properties of new salt spiropyran of indoline series containing a fluorine substituent in the 6'-position of the 2*H*-chromene moiety have been described in the work. The structure of the compound has been confirmed by <sup>1</sup>H NMR spectroscopy and X-ray diffraction analysis. Comparison of the structure of the compound with the previously studied analogue containing a methyl group instead of a fluorine atom in the 6'-position of the [2*H*]-chromene moiety has been made. This compound has been found to be photochromic, long-wavelength absorption maximum of its open form shows a bathochromic shift, and lifetime is increased three times as compared with the methyl analogue.

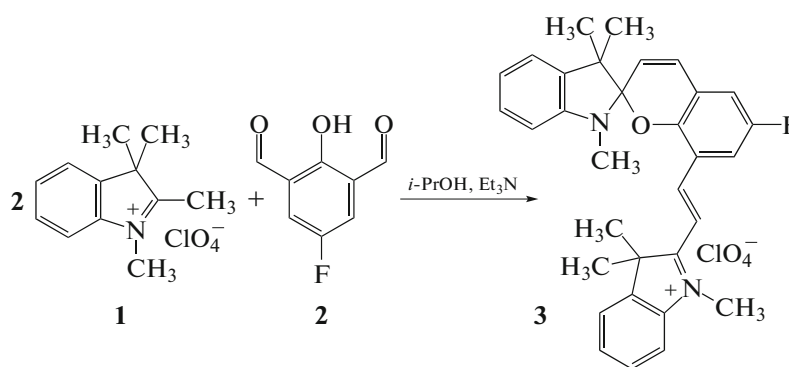
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Spiropyrans are a promising class of organic photochromes due to the relatively easy modification of their structure, which provides a possibility to control photodynamic characteristics, and due to a considerable difference in the physicochemical properties between the initial and photoinduced forms [1, 2]. Owing to these properties, dynamic systems and hybrid materials based on spiropyrans find applications in different knowledge-intensive technologies such as molecular electronics and photonics [3, 4], biology [5], and medicine [6].

It was previously shown that a loose packing of the crystal lattice in salt spiropyran systems incorporating

an organic ion produces no steric hindrances for photoisomerization of the closed form of spiropyran to the corresponding merocyanine isomers. The use of a complex counterion provides an opportunity to obtain a system with photocontrolled magnetic properties [7]. In a similar system, a spiro compound behaves as a photochemical molecular switch perturbing the magnetic sublattice.

In this work, we synthesized 1,3,3-trimethyl-6'-fluoro-8'-[(*E*)-2-(1',3',3'-trimethylindol-1'-ium-2'-yl)vinyl]spiro[indoline-2,2'-2*H*-chromene] perchlorate **3**:



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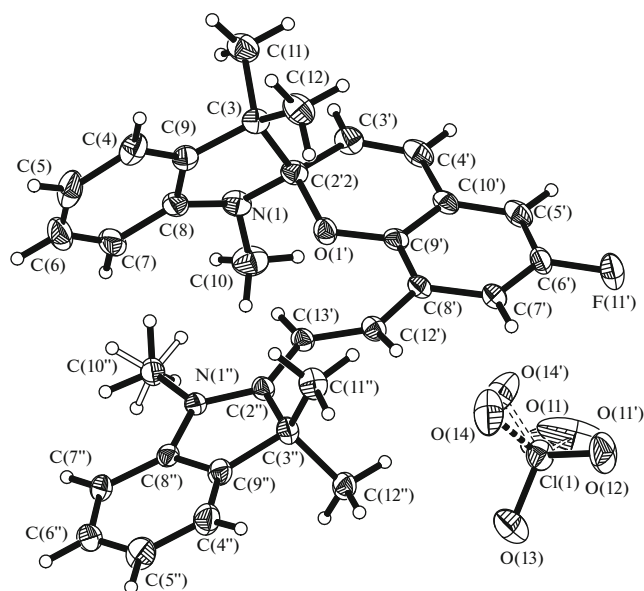
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The structure of compound **3** was confirmed by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy.

The IR spectrum of salt spiropyran **3** displays characteristic absorption bands corresponding to the stretching vibrations of C<sub>spiro</sub>–O bond (929 cm<sup>-1</sup>),



**Fig. 1.** Molecular structure of compound **3** according to X-ray diffraction study.

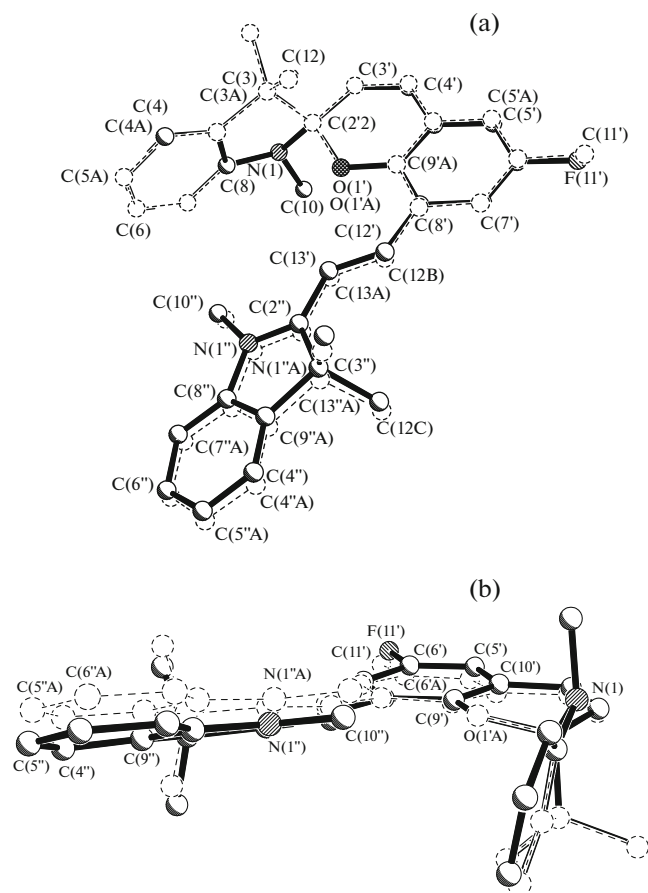
$\text{ClO}_4^-$  group ( $1094\text{ cm}^{-1}$ ), and  $\text{C}(3')=\text{C}(4')$  bond of  $2H$ -pyran ring ( $1610\text{ cm}^{-1}$ ).

The  $^1\text{H}$  NMR spectrum of *gem*-dimethyl groups of the cationic moiety shows a six-proton singlet at 1.27 ppm, which indicates their magnetic equivalence, while *gem*-dimethyl groups of the neutral moiety exhibit two three-proton singlets at 1.18 and 1.31 ppm. The characteristic signal of proton in the  $3'$ -position is observed at 6.12 ppm as a doublet with a spin–spin coupling constant of 10.37 Hz, which indicates the *cis* configuration of the vinyl moiety  $\text{C}(3')=\text{C}(4')$ . Proton signals of  $\text{N}-\text{CH}_3$  groups appear as three-proton singlets at 2.68 and 3.75 ppm for the neutral and salt moieties, respectively. The effect of fluorine atom on the conjugated system of the molecule is expressed in the splitting of signals of aromatic protons in the  $^1\text{H}$  NMR spectrum.

To investigate the molecular structure of compound **3** in detail, we obtained its single crystals and studied its molecular structure by X-ray diffraction analysis.

Figure 1 shows the molecular structure for salt spiropyran **3** according to X-ray diffraction data.

Like in the previously studied compound **4** [8] containing methyl group instead fluorine atom (Fig. 2a), the salt indoline moiety in compound **3** has a flat structure (the sum of angles at  $\text{N}(1'')$  is  $360^\circ$ ) and  $\text{N}(1'')-\text{C}(2'')$  double bond is  $1.324(4)$  ( $1.321(2)$ ) Å long. Hereinafter, for comparison of structural details for two these structures, a similar value for the previously studied structure is given in parentheses and coincides with analogous structure in 1,2,3,3-tetramethyl- $3H$ -indolium iodide [9] except for the



**Fig. 2.** (a) Molecular structure of spiropyran **4** containing methyl substituent in the  $6'$ -position of the benzene ring of the  $2H$ -chromene moiety, (b) superposition of the molecular structures of compounds **3** and **4**.

orientation of  $\text{CH}_3$  group at the nitrogen atom where hydrogen atoms are disposed in two alternative positions in ratio close to 0.6 : 0.4, combining both modes of hydrogen atoms orientation [8, 9].

Figure 2b displays both molecules superposed at the indoline fragment.

Like in **4**, there is a weak intramolecular hydrogen bond in molecule **3**:  $\text{O}(1')\cdots\text{H}(13') = 2.198$  ( $2.205$ ) Å,  $\text{O}(1')\cdots(\text{C}13') = 2.832$  ( $2.843$ ) Å and  $\text{O}(1')-(13')-(\text{C}13')$  angle is  $124.6^\circ$  ( $125.0^\circ$ ). The six-membered ring of the benzopyran moiety is bent along the  $\text{O}(1')\cdots\text{C}(3')$  line (the bend angle is  $13.1^\circ$  ( $15.6^\circ$ )). The indoline moiety is also nonplanar with a bend along the  $\text{N}(1)\cdots\text{C}(3)$  line (the bend angle is  $29.0^\circ$  ( $30.7^\circ$ )), the sum of angles at the  $\text{N}(1)$  nitrogen atom is  $348.3^\circ$  ( $346.7^\circ$ ). Two oxygen atoms in the perchlorate anion are distributed over two positions with site occupancy factors 0.75 : 0.25 each, while the two others oxygen atoms are reliably localized in their positions being involved in weak contacts ( $2.50$ – $2.62$  Å) between the pairs of oxygen atoms ( $\text{O}(12)$ ,  $\text{O}(13)$ ) and the pairs of

hydrogen atoms of the methyl group at the nitrogen atoms in the indoline moieties.

Analysis of mutual arrangement of superposed molecules in projection onto the plane of the  $\pi$ -conjugated bonds of the vinyl moiety shows that the “right” moiety in molecule **3** is more planar, while the divergence between the C(6'') and C(5') atoms and their analogs in **4** is 0.62 and 0.28 Å in the opposite directions, with the C(6')–F(11') distance being shortened to 1.391 Å as compared with C(6')–C(11') = 1.507 Å in **4**, which indicates better conjugation of the  $\pi$  orbitals of the right moiety of the studied spiropyran containing fluorine and therefore the flattening of the moiety.

The positive charge in compound **3** is localized on N(1''), while perchlorate anion carries the negative charge.

Compound **3** is photochromic (Fig. 3). As compared with previously prepared compound **4**, spectrum shows a bathochromic shift of the absorption maximum from 728 to 738 nm and a considerable increase in the lifetime for the open form from 8.4 to 27.8 s (Table 1) due to the replacement of the donor methyl substituent in compound **4** by acceptor fluorine in compound **3**.

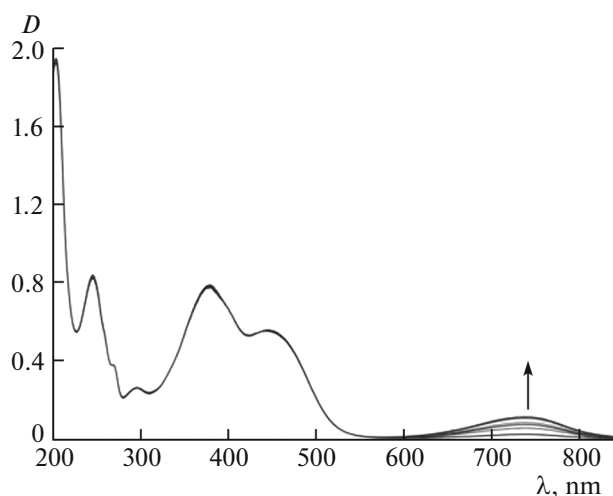


Fig. 3. Electronic absorption spectrum of compound **3** on exposure to light with a wavelength of 365 nm in acetonitrile ( $T = 293$  K, 10 s).

## EXPERIMENTAL

$^1\text{H}$  NMR spectrum in DMSO was recorded in a pulsed Fourier transform mode on a Bruker DPX-250 spectrometer (250 MHz) at the Scientific and

Table 1. Spectral and kinetic characteristics of salt spirocyclic compounds **3** and **4** (acetonitrile, 293 K)

Compound no.	Structure		$\lambda_{\text{max}}$ , nm ( $\epsilon \times 10^{-4}$ , $\text{M}^{-1} \text{cm}^{-1}$ )	$\tau_{1/2}$ , s
<b>3</b>		A	204 (4.96), 246 (2.12), 270 sh (0.96), 296 (0.66), 379 (2.01), 445 (1.47)	27.8
		B	738	
<b>4</b>		A	246 (2.64), 273 sh (1.22), 289 sh (0.81), 388 (2.56), 451 (1.57)	8.4
		B	728	

sh, shoulder.

Educational Laboratory of Resonance Spectroscopy, Department of Natural and High Molecular Compounds Chemistry of Southern Federal University. Chemical shifts are reported on the delta  $\delta$  scale, signal assignment was made relative to the residual proton signals of the deuterated solvent  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm). The IR spectra were recorded on a Varian Excalibur 3100 FT-I spectrophotometer by the attenuated total reflection method. The electronic absorption spectra before and after irradiation in acetonitrile solutions were recorded on an Agilent 8453 spectrophotometer equipped with a temperature-control unit. Solution photolysis was performed with the use of a Newport system equipped with a 200 W mercury lamp with a set of interference light filters.

Elemental analysis was carried out by the classical microanalysis method [10]. Melting points were determined on a Fisher Scientific Fisher-Johns Melting Point Apparatus.

**X-ray diffraction analysis.** The unit cell parameters of a crystal and a 3D set of intensities were obtained at 150 K on an Xcalibur, Eos automated diffractometer ( $\text{MoK}_\alpha$  radiation, graphite monochromator). Red single crystals of  $\text{C}_{32}\text{H}_{32}\text{FN}_2\text{O} \cdot \text{ClO}_4$  are monoclinic:  $a = 12.3538(15)$  Å,  $b = 13.857(2)$  Å,  $c = 16.867(2)$  Å,  $\beta = 96.193(11)^\circ$ ,  $V = 2870.6(7)$  Å<sup>3</sup>,  $M = 579.05$ ,  $Z = 4$ ,  $\rho(\text{calcd.}) = 1.340$  g/cm<sup>3</sup>,  $\mu(\text{MoK}_\alpha) = 0.184$  mm<sup>-1</sup>, space group  $P2_1/n$ . The intensities of 12 693 reflections were measured in the range ( $2\theta \leq 52.06^\circ$ ) by  $\omega$  scanning from a single crystal with dimensions  $0.38 \times 0.22 \times 0.17$  mm. An empirical absorption correction was applied by using the Multiscan procedure. After exclusion of systematic absences and averaging of equivalent reflection intensities, the working array of measured  $F^2(hkl)$  and  $\sigma(F^2)$  included 5604 independent reflections, 3175 of which were with  $F^2 > 2\sigma(F^2)$ . The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL software in anisotropic approximation for non-hydrogen atoms; the majority of the H atoms in the crystal structure were located from a difference Fourier synthesis, then, the coordinates and isotropic thermal parameters of all hydrogen atoms were refined by the least squares procedure with an idealized riding model [11], the absolute shifts of all 390 variables in the last cycle of full-matrix refinement were less than  $0.001\sigma$ , final  $R_1$  value is 0.080.

**1,3,3-Trimethyl-6'-fluoro-8'-[(E)-2-(1'',3'',3''-trimethylindolium-2''-yl)vinyl]spiro[indoline-2,2'-2H-chromen] perchlorate (3).** 2-Hydroxy-3-formyl-5-fluorobenzaldehyde **2** (0.375 g, 2 mmol) was dissolved on heating in 15 mL of isopropyl alcohol. Next, a solution of 1.094 (4 mmol) of 1,2,3,3-tetramethyl-3H-indolium perchlorate **1** was added and 0.28 mL of (one

molar equivalent) of triethylamine was added dropwise with stirring. The mixture was refluxed with stirring for about 30 min. The resultant precipitate was separated by filtration and recrystallized from acetonitrile. The precipitate (orange crystals) was separated by filtration and washed with cold acetonitrile. Mp 249°C (from acetonitrile). Yield 56.2%. <sup>1</sup>H NMR ( $\delta$ , ppm,  $J$ , Hz): 1.18 (s, 3H,  $-\text{CH}_3$ ), 1.27 (s, 6H,  $-\text{CH}_3$ ), 1.31 (s, 3H,  $-\text{CH}_3$ ), 2.68 (s, 3H,  $\text{N}-\text{CH}_3$ ), 3.75 (s, 3H,  $\text{N}^+-\text{CH}_3$ ), 6.12 (d, 1H,  $J = 10.4$  Hz, H-3'), 6.69 (d, 1H,  $J = 7.6$  Hz, H-7), 6.93 (t, 1H,  $J = 7.4$  Hz, H-5), 7.27–7.08 (m, 3H, arom. protons), 7.65–7.42 (m, 4H, arom. protons), 7.77–7.70 (m, 1H, arom. proton), 7.88–7.81 (m, 1H, arom. proton), 8.04–7.91 (m, 2H, arom. proton).

## ACKNOWLEDGMENTS

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