

Studies of structure and photochromic properties of spiropyrans based on 4,6-diformyl-2-methylresorcinol*

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Indoline-derived spiropyrans, the precursors of nonsymmetric bis-spiropyrans, which are the promising prototypes of multistate molecular switches, were synthesized based on 4,6-diformyl-2-methylresorcinol. Molecular structure of one of these compounds was studied by X-ray diffraction analysis. Photochemical studies showed the presence of photochromic properties in the obtained spiropyrans at room temperature.

Key words: spiropyran, bis-spiropyran, photochromism, molecular switch, X-ray diffraction analysis.

Spiropyrans (SP) are one of the most studied classes of organic photochromic compounds, which are of special interest due to a possibility of the photoinduced switching between two isomeric forms, the colorless spirocyclic and brightly colored merocyanine ones.^{1–3}

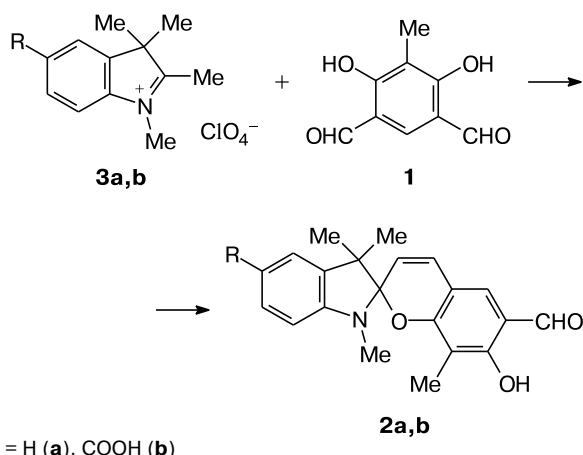
Indoline spiropyrans (ISP) obtained based on 2,4-dihydroxyisophthalic aldehyde and containing *ortho*-arranged hydroxy and formyl groups at positions 5' and 6' of the [2H]-chromene fragment, respectively, were described earlier.⁴ The presence of this functional fragment in the molecule makes these compounds to be the precursors of bis-spiropyrans (BSP), containing in the structure two photoactive centers and, therefore, having a potential possibility of switching between three and more isomeric forms, that allows one to consider them as the prototypes of multistate molecular switches.⁵

4,6-Diformyl-2-methylresorcinol **1** is the primary precursor of bis-spirocyclic compounds. There are known examples of the synthesis of symmetric indoline BSP based on **1**, however, the photochemical studies showed that the irradiation of their solutions with UV light causes the photoinduced opening of only one of the pyran rings.⁶ The use of nonsymmetric BSP can solve this problem, that has been shown in our preceding works.^{7,8} Thus, the purpose of the present work is the synthesis and studies of the ISP based on 4,6-diformyl-2-methylresorcinol **1** containing

the *ortho*-arranged hydroxy and aldehyde groups at positions 7' and 6' of the [2H]-chromene fragment — precursors of nonsymmetric BSP.

The target SP **2a,b** were obtained by the condensation of the equimolar amounts of 4,6-diformyl-2-methylresorcinol **1** with the corresponding indoleninium perchlorates **3a,b** in the presence of piperidine upon reflux in isopropyl alcohol (Scheme 1). The carboxy group at position 5 of compound **2b** was introduced not only as an acceptor substituent, but also as an additional functional group for its further binding. The presence of the carboxy group increases the solubility of the spiropyran in water, that

Scheme 1



* Dedicated to Academician of the Russian Academy of Sciences V. I. Minkin on the occasion of his 80th birthday.

undoubtedly is an advantage when these compounds are used in biological studies or as chemosensors for metal ions.

The structure of obtained SP **2a,b** was confirmed by elemental analysis, ^1H NMR spectroscopy, IR spectroscopy, and mass spectrometry.

The ^1H NMR spectra of SP **2a,b** exhibit signals for all the proton-containing groups, whose chemical shifts and spin-spin coupling constants completely confirm the structure of compounds obtained. The protons of the *gem*-dimethyl groups resonate as two singlets because of the acoplanarity of structures **2a,b**. The characteristic signals for the protons at positions 3' and 4' are observed as two doublets with the spin-spin coupling constants of 10.3 Hz, that indicates the *cis*-configuration of the corresponding CH=CH fragment and, therefore, the cyclic structure of the spirocompound molecules. The signals for the aromatic protons in **2a** were unambiguously assigned using 2D NMR experiments, namely, ^1H - ^1H COSY and ^1H - ^1H NOESY. The ^1H NMR spectrum of compound **2b** was assigned by analogy.

Molecular structure of SP **2a** was found by X-ray diffraction analysis (Fig. 1).

Principal bond distances and bond angles of SP **2a** are given in Tables 1 and 2, respectively.

It should be noted that the earlier studied spiro[1,3,3-trimethylindoline-2,3'-3*H*-pyrano[3,2-*f*]quinoline] (**4**) has a similar structure.⁹ The molecules of **2a** and **4** superimposed at the plane of atoms N(1)—C(2',2)—C(3) are shown in Fig. 2. In such an orientation when the indoline fragments of the molecules completely coincide, a slight deviation of the chromene (**2a**) and the quinoline (**4**) fragments is noticeable: both fragments bend to the same side along the line of atoms O(1')—C(3) of the [2*H*]-pyran fragments. This bend is equal to 11.6° and 22.8° in molecules **2a** and **4**, respectively.

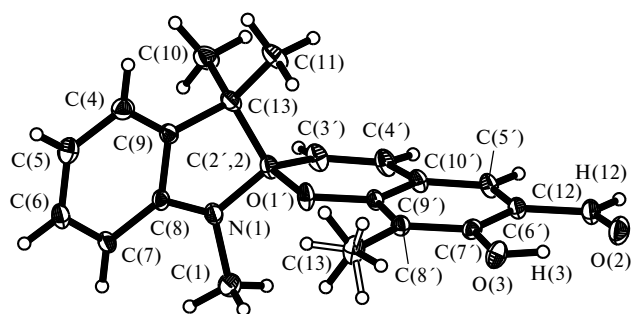
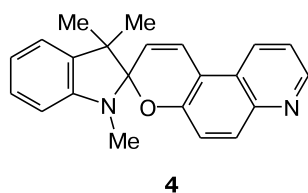


Fig. 1. General view of the molecule of compound **2a**.

Table 1. Principal bond distances (*d*) in SP **2a**

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
O(1')—C(9')	1.347(1)	O(1')—C(2',2)	1.485(1)
O(3)—C(7')	1.351(2)	O(3)—H(3)	0.91(2)
N(1)—C(8)	1.408(2)	N(1)—C(2',2)	1.442(1)
N(1)—C(1)	1.455(2)	C(3)—C(9)	1.5156(2)
C(3)—C(11)	1.522(2)	C(3)—C(10)	1.550(2)
C(3)—C(2')	1.567(2)	C(4)—C(9)	1.373(2)
C(2',2)—C(3')	1.498(2)	C(3')—C(4')	1.335(2)
C(4')—C(10')	1.454(2)		

The indoline and the [2*H*]-chromene/pyranopyridine fragments in molecules of spiropyrans **2a** and **4** are arranged almost orthogonal to each other (the angle is 89.4° and 89.2° in compounds **2a** and **4**, respectively). The indoline fragment is folded along the line N(1)—C(3): the angles between the planes N(1)—C(2',2)—C(3) and N(1)—C(3)—C(8)—C(9) are 33.0° in compound **2a** and 32.8° in compound **4**. The atoms N(1) and C(3) lie in the plane of the benzene ring of the indoline fragment. The bond length C(2',2)—O(1') ($C_{\text{spiro}}-\text{O}$) in compound **2a** is 1.485(1) Å, that is slightly longer than in compound **4** (1.474(2) Å), but is still within the range of common values for ISP (1.485–1.492 Å). The deviation of atom N(1) from the plane passing through the C(2',2)—C(8)—C(1) atoms is 0.318 Å, whereas the sum of the bond angles at N(1) is equal to 345.6°. This indicates a pyramidal configuration of the nitrogen atom and a noticeable sp^3 -character of the lone electron pair (LEP) on atom N(1). The orientation of the valent bonds at atom N(1) corresponds to the *trans*-arrangement of the LEP on the nitrogen atom relative to the $C_{\text{spiro}}-\text{O}$ bond. Such an orientation makes possible the orbital interaction of the LEP on atom N(1) with the anti-bonding σ^* -orbital of this bond. This interaction leads to the weakening of the $C_{\text{spiro}}-\text{O}$ bond and its elongation, that facilitates an efficient cleavage of this bond in the photoexcited state.

The hydrogen atoms of the methyl group at atom C(13) are disordered over two positions in the ratio 4 : 1. It should be noted that the molecule **2a** is characterized by an in-

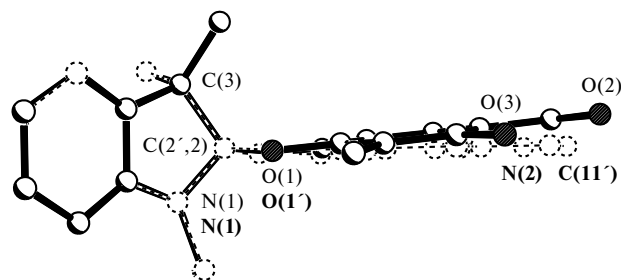


Fig. 2. Superimposition of structures **2a** and **4**. Structure **4** is shown in dashed line, numbers of atoms in structure **4** are given in bold.

Table 2. Principal bond angles (ω) in SP **2a**

Angle	ω/deg
C(9')—O(1')—C(2',2)	124.2(1)
C(8)—N(1)—C(2',2)	107.0(1)
C(2')—N(1)—C(1)	118.9(1)
C(9)—C(3)—C(10)	108.6(1)
C(9)—C(3)—C(2',2)	100.2(1)
C(10)—C(3)—C(2',2)	109.6(1)
C(7)—C(8)—N(1)	128.6(1)
C(4)—C(9)—C(8)	120.3(1)
C(8)—C(9)—C(3)	108.1(1)
N(1)—C(2',2)—O(1')	105.8(1)
N(1)—C(2',2)—C(3)	102.9(1)
C(3')—C(2',2)—C(3)	116.4(1)
C(3')—C(4')—C(10')	121.8(1)

Angle	ω/deg
C(7')—(3)—H(3)	103.1(1)
C(8)—N(1)—C(1)	119.6(1)
C(9)—C(3)—C(11)	114.9(1)
C(11)—C(3)—C(10)	109.9(1)
C(11)—C(3)—C(2',2)	113.1(1)
C(7)—C(8)—C(9)	121.2(1)
C(9)—C(8)—N(1)	110.1(1)
C(4)—C(9)—C(3)	131.6(1)
O(2)—C(12)—C(6')	124.6(1)
N(1)—C(2',2)—C(3')	112.8(1)
O(1')—C(2',2)—C(3)	106.7(1)
C(4')—C(3')—C(2',2)	122.8(1)

tramolecular hydrogen bond O(2)...H(3)—O(3) with the following parameters: the distances H(3)—O(3) 0.91 Å, O(2)—H(3) 1.754 Å, O(2)...O(3) 2.608 Å, the angle O(2)—H(3)—O(3) 154.8°.

The photochemical studies of SP **2a,b** showed the presence of the photochromic properties. Under the normal conditions, these compounds exist predominantly in the closed spirocyclic form, however, irradiation of their solutions in acetonitrile with nonfiltered light led to the formation of long-wavelength absorption maxima at 545 (**2a**) and 560 nm (**2b**), which corresponded to the open merocyanine forms of the compounds (Fig. 3).

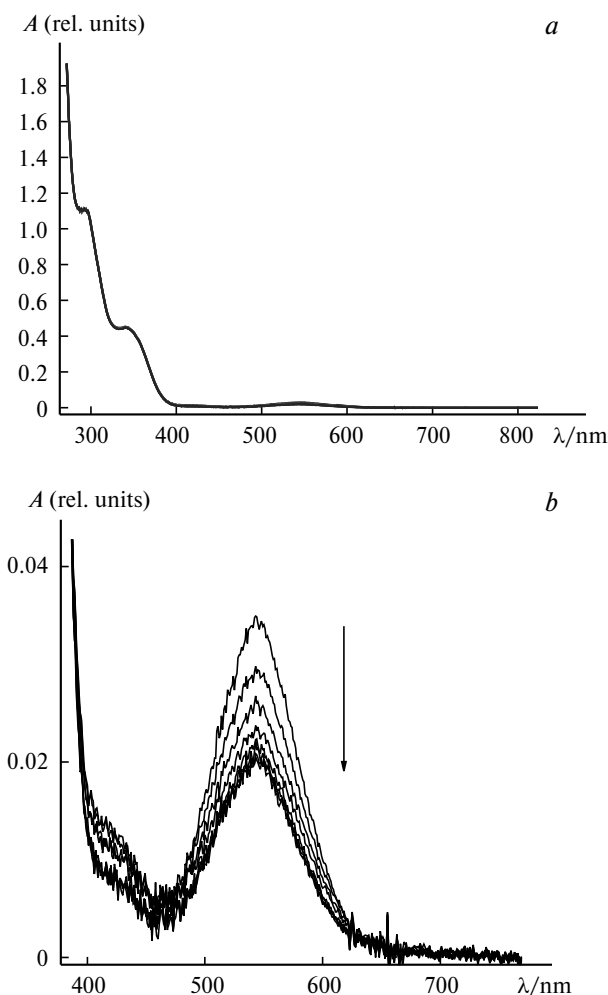
The spectral and kinetic properties of the synthesized SP are given in Table 3. From the obtained data, it follows that the introduction of the electron-withdrawing carboxy group at position 5 of the indoline fragment leads not only to a bathochromic shift of the absorption maximum of the open form, but also to the 1.5 times increase in the lifetime (τ) of the merocyanine.

In conclusion, we synthesized two new indoline-derived photochromic spiropyran containing hydroxy and aldehyde groups at positions 7' and 6' of the [2H]-chromene fragment, respectively. According to

Table 3. Spectral and kinetic properties of compounds **2a,b** in acetonitrile at 20 °C

Compound	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ($\epsilon \cdot 10^{-3}/\text{L mol}^{-1} \text{cm}^{-1}$)		τ/s
	SP	MC	
2a	202 (25.3), 292 (9.3), 340 (3.75)	543	19.3
2b	234 (19.5), 300 (26.6), 259 (35.4), 345 (4.85)	560	29.3

Note: SP is the spiropyran form, MC is the merocyanine form.

**Fig. 3.** Electron absorption spectra of SP **2a** in MeCN after the exposure to the white non-filtered light at 20 °C (*a*) and a decrease in the absorption intensity in the long-wavelength maximum in the course of thermal photobleaching reaction (magnified) (*b*).

the X-ray diffraction data, the molecular structure of SP **2a** is similar to the structure of ISP studied earlier. The photochemical studies showed the presence of the photochromic properties in the obtained SP in solutions in acetonitrile at room temperature. An increase in the lifetime of the open form of SP upon the introduction of the electron-withdrawing carboxy substituent into the indoline moiety of the molecule requires further studies.

Experimental

¹H NMR spectra were recorded on a Bruker 250 spectrometer (250 MHz) in the pulse Fourier-mode in CDCl₃, chemical shifts of signals for compounds under study were determined in the δ scale. The signals were assigned relative to signals of residual protons of the deuterated solvent (CDCl₃, δ 7.26). IR spectra of compounds were recorded on a Varian Excalibur 3100 FT-IR using a partial internal reflection method. Electron absorption spectra were recorded on a Cary 100 Scan Varian spectrophotometer in solutions in acetonitrile. A DRSh-250 mercury lamp with a standard kit of filters was used as a source of radiation. Mass spectrum was recorded on a Shimadzu GCMS-QP2010SE spectrometer. Elemental analysis was carried out by a conventional method.¹⁰ Melting points were determined on a Fisher—Jones apparatus (Fisher Scientific).

4,6-Diformyl-2-methylresorcinol (**1**) was obtained according to the known procedure.¹¹

6-Formyl-7-hydroxy-1',3',3',8-tetramethylspiro[[2H]-chromene-2,2'-indoline] (2a). Piperidine (0.1 mL) was added dropwise to a solution of 1,2,3,3-tetramethylindoleninium perchlorate (274 mg, 1 mmol) and 4,6-diformyl-2-methylresorcinol (**1**) (190 mg, 1.05 mmol) in isopropyl alcohol (5 mL) with heating and the reaction mixture was refluxed for 10 min. The solvent was evaporated, the residue was purified by column chromatography on silica gel (eluent chloroform). The product was recrystallized from hexane. The yield was 68%, m.p. 82 °C. IR, ν/cm^{-1} : 2965 (OH); 1634 (C=O); 1608 (C=C); 1101, 925 (C_{spiro}—O). ¹H NMR (CDCl₃), δ : 1.16 (s, 3 H, C(3')CH₃); 1.24 (s, 3 H, C(3'')CH₃); 1.82 (s, 3 H, C(8)CH₃); 2.69 (s, 3 H, NCH₃); 5.65 (d, 1 H, C(3)H, $J = 10.3$ Hz); 6.52 (d, 1 H, C(7')H, $J = 7.7$ Hz); 6.78–6.88 (m, 2 H, C(4)H and C(5')H); 7.02–7.10 (m, 2 H, C(5)H and C(4'')H); 7.16 (td, 1 H, C(6'')H, $J = 7.6$ Hz, $J = 1.2$ Hz); 9.64 (s, 1 H, CHO); 11.64 (s, 1 H, OH). MS (EI, 70 eV), m/z ($I_{\text{rel}}(\%)$): 335 (72.4) [M⁺]; 320 (39.8); 159 (100.0); 158 (52.3); 144 (36.0). Found (%): C, 75.23; H, 6.25; N, 4.21. C₂₁H₂₁NO₃. Calculated (%): C, 75.20; H, 6.31; N, 4.18.

6-Formyl-5'-carboxy-7-hydroxy-1',3',3',8-tetramethylspiro[[2H]-chromene-2,2'-indoline] (2b) was synthesized according to the procedure described above for compound **2a**. The yield was 62%, m.p. 276 °C. IR, ν/cm^{-1} : 2965 (OH); 1664, 1643 (C=O); 1609 (C=C); 1100, 926 (C_{spiro}—O). ¹H NMR (CDCl₃), δ : 1.18 (s, 3 H, C(3')CH₃); 1.29 (s, 3 H, C(3'')CH₃); 1.84 (s, 3 H, C(8)CH₃); 2.78 (s, 3 H, NCH₃); 5.63 (d, 1 H, C(3)H, $J = 10.3$ Hz); 6.54 (d, 1 H, C(7')H, $J = 8.3$ Hz); 6.85 (d, 1 H, C(4)H, $J = 10.3$ Hz); 7.10 (s, 1 H, C(5)H); 7.78 (s, 1 H, C(4'')H); 8.01 (d, 1 H, C(6'')H, $J = 9.1$ Hz); 9.66 (s, 1 H, CHO); 11.65 (s, 1 H, OH). Found (%):

C, 69.60; H, 5.60; N, 3.64. C₂₂H₂₁NO₅. Calculated (%): C, 69.65; H, 5.58; N, 3.69.

X-ray diffraction studies. Parameters of the crystal unit cell and a three-dimensional set of intensities were obtained on a Xcalibur Eos automated diffractometer (MoK α radiation, graphite monochromator, ω -scan technique). Yellow crystals of **2a** are monoclinic, C₂₁H₂₁NO₃, $M = 335.39$; $a = 14.4241(4)$, $b = 7.4276(2)$, $c = 16.2844(5)$ Å, $\beta = 98.786(3)^\circ$, $V = 1724.16(9)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.292$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.086$ mm⁻¹, space group $P2_1/a$. Intensities of 11141 reflections were measured in the range of angles ($2\theta \leq 58.14$) at 150 K from a 0.50×0.47×0.43-mm single crystal. After elimination of the systematically canceled reflections and averaging intensities of equivalent reflections, the working body of measured F^2_{hkl} and $\sigma(F^2)$ was 4583 independent reflections, from which 3591 were with $F^2 > 4\sigma(F^2)$. The structure was solved by direct method and refined by the full-matrix least squares method relative to F^2 using the SHELXTL program in anisotropic approximation for nonhydrogen atoms. In the crystal structure of **2a**, all the H atoms were localized in the Fourier synthesis of difference electron density. Then, the coordinates and the isotropic thermal parameters for all the H atoms were refined by the least squares method using a riding model.¹² In the last cycle of the full-matrix refinement, the absolute shifts of all 222 varied parameters of structure **2a** were less than 0.001 σ . The final refinement parameters: $R_1 = 0.049$, $wR_1 = 0.13$; GOF = 1.032. After the refinement was complete, the maximum and minimum values of difference electron density were 0.332 and -0.189 e Å⁻³. The full information about the structure under study was deposited with the Cambridge Crystallographic Data Center (CCDC 1044953) and is available free of charge upon request at www.ccdc.cam.ac.uk/data_request/cif.

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