New photochromic 1,1,3-trimethylspiro[benzo[*e*]indoline-2,3′-[3*H*]-pyrano[3,2-*f*]quinoline]

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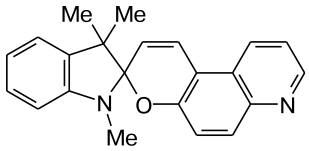
A new photochromic spiropyran of the benzoindoline series containing the quinoline moiety was synthesized. Its structure was determined by IR and ^{1}H NMR spectroscopy. The crystal structure of the new compound was established by X-ray diffraction. The photochromic properties of the synthesized spiropyran were investigated.

Key words: benzannulated indoline spiropyran, quinoline moiety, photochromism, X-ray diffraction study.

The photochromic properties of spiropyrans are determined by the effect of various substituents in the hetarene and [2*H*]-chromene moieties of the molecule on the structure of these compounds.[1] Of particular interest are spirocyclic salt-like compounds containing complex anions, such as spiro[1,3,3,7′-tetramethylindoline-2,3′-3*H*-pyrano[3,2-*f*]quinolinium] tris(oxalato)chromate(III) positioned as a photocontrolled magnetic material.[2]

In continuation of investigations on the structures and photochemical properties of spirocyclic compounds **1** of the indoline series containing the quinoline moiety[3] suitable for the preparation of cationic forms of spiropyrans, we synthesized new photochromic spiropyran **2** containing the benzannulated moiety in the indoline part of the molecule (Scheme 1).



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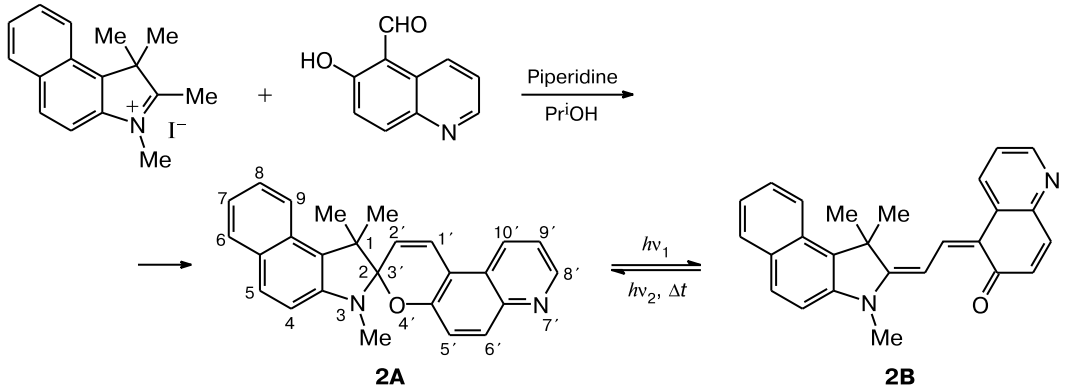
Scheme 1



2A **2B**

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The structure of spiropyran **2** was determined by elemental analysis and by IR and ^{1}H NMR spectroscopy.

The IR spectrum of spiropyran **2** shows absorption bands corresponding to C=C stretching vibrations of the pyran ring (1624 cm^{-1}) and C_{spiro}—O stretching vibrations (at 984 and 969—975 cm^{-1}).

In the ^{1}H NMR spectrum of spiropyran **2**, the signals for the H(1′) and H(2′) protons of the [2*H*]-chromene ring appear as one-proton doublets that form an AB system at δ 7.57 and 5.92, respectively, with the spin-spin coupling constant J = 10.3 Hz. This confirms the *cis* configuration of the C(1′)=C(2′) double bonds of the vinyl group. The three-proton singlet of the N—Me group appears at δ 2.83. The signals for the protons of the *gem*-dimethyl groups of the indoline moiety are observed individually at δ 1.39 and 1.68. This confirms the presence of the asymmetric carbon atom, which is, in turn, indicative of the spirocyclic structure of compound **2**.

The electronic absorption spectrum of the cyclic isomer **A** of spiropyran **2** in acetonitrile is characterized by long-wavelength absorption bands with maxima at 349 and 291 nm (Table 1) corresponding to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions, respectively. Compared to compound **1** studied earlier,[3] the positions and shapes of the absorption bands in the spectrum of spiropyran **2** containing the benzannulated indoline moiety do not change significantly. This is, in turn, consistent with the assumption of the additivity of the absorption spectra for the noncoplanar moieties of spiropyrans[4] and with the assumption that the longest-wavelength electron transition is localized on the pyran moiety of the molecule. However, the benzannulation can lead to the intramolecular energy transfer from the pyran ring to the indoline moiety, which accounts for a decrease in the efficiency of photocoloration of spiropyran **2** compared with its non-annulated analog **1**.[3] The long-wavelength absorption maximum of the acyclic merocyanine isomer **2B** is observed at 576 nm typical of the absorption of merocyanine isomers of spiropyrans.[5,6] A comparison of the absorption maxima of the colored isomers of spiropyrans **1** and **2** revealed a bathochromic shift in the spectrum of compound **2** due to a larger π-conjugation system in the benzannulated compound. In the starting (before irradiation) solution, compound **2** exists almost completely in the spirocyclic form **A**. A weak absorption with a maximum at 576 nm is indicative of the presence of an insignificant amount of the colored form **B** in the equilibrium. Upon UV irradiation, a solution of spiropyran **2** in acetonitrile turned colored (Fig. 1), which is associated with the C_{spiro}—O bond cleavage followed by *cis—trans* isomerizations to form the colored metastable form **B**. After the cessation of the UV irradiation, the molecular system is rapidly decolorized and returns to the thermodynamic equilibrium.

Table 1. Spectral characteristics of spiropyran **2**, such as the absorption maxima (λ_{max}) and the corresponding molar extinction coefficients ($\varepsilon(\lambda_{max})$), of the spirocyclic isomer **2A** and the colored merocyanine isomer **2B**

Isomer **2A**		Isomer **2B**, λ_{max}/nm
λ_{max} /nm	$\varepsilon(\lambda_{max})$ /L mol^{-1} cm^{-1}	
291	17220	576
301	14480	
349	8610	
363 sh	7580	

Note. Due to the very fast thermal reverse reaction **2B** → **2A**, it is difficult to reliably determine the lifetime of the open form because of instrumental limitations; τ < 0.1 s.

The results of the single-crystal X-ray diffraction study of compound **2** are presented in Fig. 2. A comparison of the structures of two independent molecules upon their superimposition using the 1,1,3-trimethylbenzo[*e*]indoline moieties (Fig. 3) shows that two independent molecules differ in that they are bent along the O(1′)—C(3′) and O(21′)—C(23′) lines of the [2*H*]-pyran moieties by 22.8° and 23.6°, respectively, in the opposite directions. The geometric parameters of two independent molecules are approximately equal. The N(1) atom deviates from the C(2′2)—C(13)—C(16) plane in the direction opposite to the O(1′) atom (see Fig. 2) by 0.266 Å. The sum of the angles at the N(1) atom is 349.8°.

Apparently, this combination of two independent molecules in the asymmetric unit is attributed to the crystal lattice effect on the geometry of the benzopyran moieties.

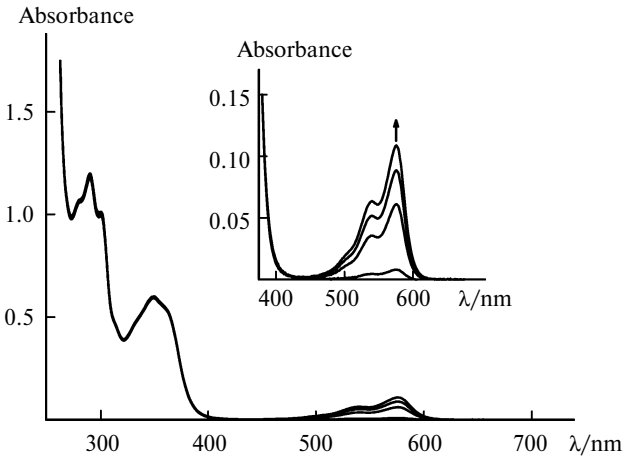

Fig. 1. Electronic absorption spectra of spiropyran **2** ($7.0 \cdot 10^{-5}$ mol L^{-1}, MeCN, 293 K) in the course of the photochemical coloration reaction under irradiation with polychromatic light from a mercury lamp (λ_{irr} < 400 nm, Δt = 0.1 s). The inset shows an increase in the long-wavelength absorption band of the merocyanine isomer **2B** on an enlarged scale.

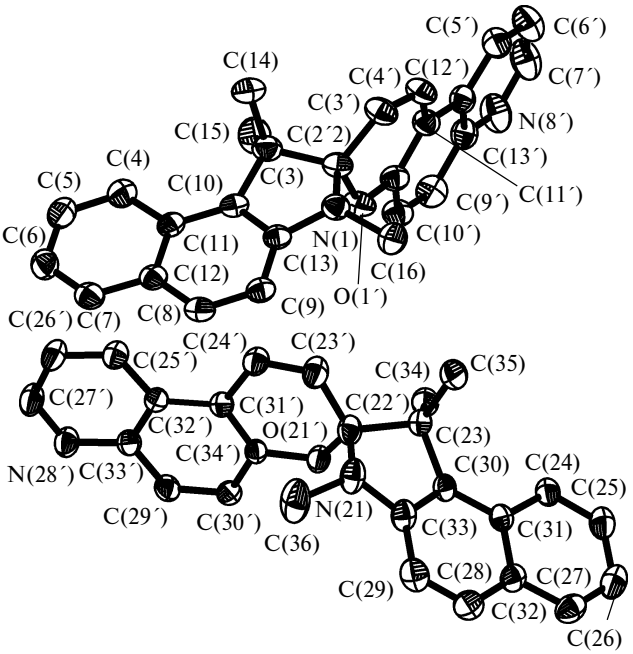

Fig. 2. Structures of two independent molecules of compound **2** with displacement ellipsoids drawn at the 30% probability level. Here and in Fig. 3, the atoms in the second molecule are labeled by adding 20 to the identification numbers of the corresponding atoms in the first molecule.

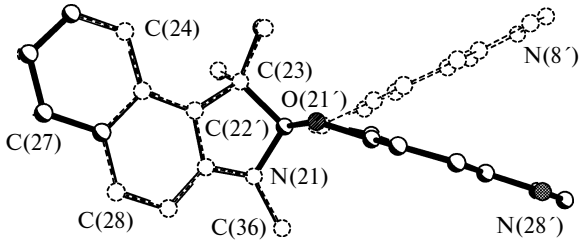

Fig. 3. Superimposition of two independent molecules of compound **2** based on the 1,1,3-trimethylbenzo[*e*]indoline moieties.

A comparison of the corresponding geometric parameters of spiropyran **2** and compound **1** studied earlier reveals the redistribution of the bond lengths. Thus, there are the following bond lengths in molecule **2**: C(10)—C(11), 1.408(3) Å; C(12)—C(11), 1.420(3) Å; C(8)—C(12), 1.414(3) Å; C(8)—C(9), 1.360(3) Å; C(9)—C(13), 1.395(3) Å. The corresponding bond lengths in molecule **1** are 1.383(3), 1.393(3), 1.364(4), 1.378(4), and 1.383(3) Å, which is typical of naphthalene-like moieties.

Experimental

The IR spectrum was recorded on a Varian Excalibur 3100 FT-IR instrument using the attenuated total internal reflection technique. The ^{1}H NMR spectrum was measured on a Bruker 250 radio-frequency spectrometer (250 MHz) in $CDCl_3$ with respect to the signals of residual protons of deuteriochloroform. The electronic absorption spectra were recorded on an Agilent 8453 spectrophotometer (USA) equipped with a temperature-control accessory. The photolysis of solutions was performed by irradiation with a mercury lamp (200 W, Newport) equipped with an UFS-1 light filter ($\lambda_{irr} < 400$ nm).

1,1,3-Trimethylspiro[benzo[*e*]indoline-2,3′-[3*H*]-pyrano-[3,2-*f*]quinoline] (2). Piperidine (0.085 mL, 0.854 mmol) was added dropwsie to a boiling mixture of 1,1,2,3-tetramethylbenzo[*e*]indolinium iodide (0.3 g, 0.854 mmol) and 6-hydroxyquinoline-5-aldehyde (0.148 g, 0.854 mmol) in propan-2-ol (15 mL). The reaction mixture was refluxed for 15 min and kept overnight at ~20 °C. The precipitate that formed was filtered off, washed with water, and dried. Then the precipitate was successively recrystallized from ethyl acetate and aqueous ethanol. The yield was 107 mg (33 %), m.p. 198—199 °C. Found (%): C, 82.46; H, 5.86; N, 7.34. $C_{26}H_{22}N_2O$. Calculated (%): C, 82.51; H, 5.86; N, 7.40. UV (MeCN, 20 °C), λ_{max}(**2A**)/nm (log ε): 291 (4.24), 301 (4.16), 349 (3.94); λ_{max}(**2B**)/nm: 576. The lifetime of the open form of spiropyran $\tau < 0.1$ s. IR, ν/cm^{-1}: 969, 984 (C—O); 1624 (C=C). ^{1}H NMR ($CDCl_3$), δ: 1.39 (s, 3 H, *gem*-Me); 1.68 (s, 3 H, *gem*-Me); 2.83 (s, 3 H, N—Me); 5.92 (d, 1 H, H(2′), J = 10.3 Hz); 6.98 (d, 1 H, H(6), J = 8.4 Hz); 7.15 (d, 1 H, H(4), J = 9.1 Hz); 7.25 (d, 1 H, H(6′), J = 6.5 Hz); 7.40 (d, 1 H, H(5′), J = 6.5 Hz); 7.42 (t, 1 H, H(9′), $J_{H(9'),H(8')}$ = 4.2 Hz, $J_{H(9'),H(10')}$ = 8.6 Hz); 7.57 (d, 1 H, H(1′), J = 10.3 Hz); 7.74—7.96 (m, 4 H, H(5), H(7), H(8), H(9)); 8.37 (d, 1 H, H(10′), J = 8.4 Hz); 8.76 (d, 1 H, H(8′), J = 4.2 Hz).

X-ray diffraction study. The unit cell parameters were determined and a three-dimensional set of intensities was measured on a KUMA automated diffractometer (Mo-Kα radiation, graphite monochromator). Colorless transparent crystals of **2** are monoclinic, $C_{26}H_{22}N_2O$, M = 378.45; a = 21.906(4) Å, b = 8.343(2) Å, c = 21.898(4) Å, β = 93.22(3)°, V = 3995.8(2) Å^3, Z = 8, d_{calc} = = 1.258 g cm^{-3}, μ(Mo-Kα) = 0.77 mm^{-1}, space group $P2_1/c$. The intensities of 8051 reflections were measured within a quadrant of reciprocal space ($2\theta \le 50°$) with the use of the ω/2θ-scanning technique from a single crystal of dimensions 0.40×0.37×0.34 mm. After rejection of the systematic absences and merging of equivalent reflections, the X-ray data set contained 7828 independent reflections ($F^2(hkl)$ and $\sigma(F^2)$), of which 3474 reflections were with $F^2 > 4\sigma(F^2)$. The structure was solved by direct methods with the use of the SHELXTL program package[7] and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms against F^2 using the SHELXL program package.[7] In the crystal structure of **2**, all H atoms were located in difference Fourier maps, and then the coordinates and isotropic thermal parameters of all H atoms were refined by the least-squares method using a riding model.[7] In the last cycle of the full-matrix refinement, the absolute shifts of all 529 variable parameters of the structure **2** were smaller than 0.001σ. The final refinement parameters were R_1 = 0.042, wR_1 = 0.10 based on 3474 observed reflections with $I \ge 2\sigma(I)$; GOF = 0.868. After the refinement, the maximum and minimum difference electron densities were 0.152 and 0.156 e A^{-3}, respectively.

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