

New indoline spiropyrans containing azomethine fragment

O. A. Komissarova,^{a*} B. S. Lukyanov,^{a,b} M. B. Lukyanova,^a I. V. Ozhogin,^a E. L. Mukhanov,^a
M. S. Korobov,^a I. A. Rostovtseva,^a and V. I. Minkin^a

^aInstitute of Physical and Organic Chemistry at Southern Federal University,
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.

Fax: +7 (863) 243 4177. E-mail: lab811@ipoc.sfedu.ru

^bDon State Technical University,

1 pl. Gagarin, 344000 Rostov-on-Don, Russian Federation

The new spiropyran systems with an azomethine bridge were synthesized from a spiropyran containing aminogroup at 6' position of the benzopyran fragment and substituted aromatic aldehydes. The chemical structure of compounds is confirmed by elemental analysis data, NMR (¹H and ¹³C) and IR spectroscopy. Photochemical studies revealed the presence of photochromic properties at room temperature for one of the obtained spiropyrans.

Key words: spiropyran, photochromism, molecular switch, azomethine, Schiff base.

Spiropyrans and their derivatives are one of the most interesting classes of organic photochromes.^{1–5} Their photochromic properties are based on a photoinduced cleavage of the C_{spiro}–O bond with following isomerization leading to the "open" merocyanine form.⁶ These properties make it possible to use spiropyrans in many cutting edge areas: molecular electronics and photonics, chemosensorics, biomedicine, etc.^{7–9}

An increase in the conjugation system during photo-initiated opening of the pyran fragment may lead to a significant bathochromic shift of the maximum in an electronic absorption spectrum, making such materials promising for the creation of information recording systems based on near-IR lasers.¹⁰

Compounds having the photochromic spiropyran bound by a common conjugation system with a spatially enlarged substituent are characterized by the fact that an electronical interaction is possible between the fragments of their molecules, resulting in the ability of a substituent to have a significant effect on the spectral and photokinetic characteristics of such structures.¹¹

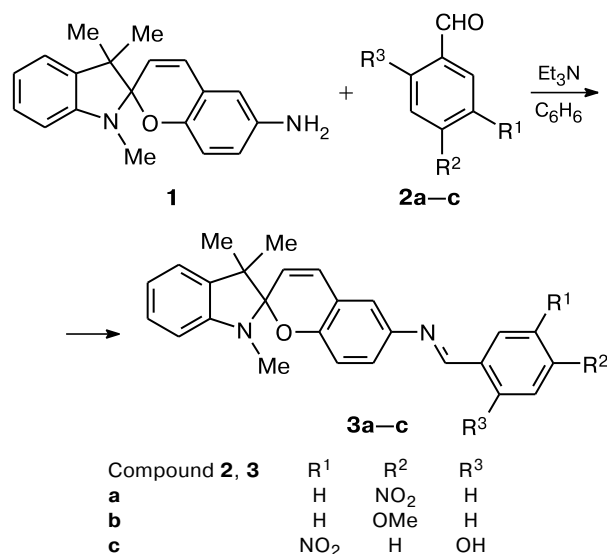
This work is aimed at the synthesis and study of new spiropyran systems based on spiropyran **1**, containing aminogroup at 6' position of the benzopyran fragment, and various aromatic aldehydes. In the obtained spiro compounds the spatially enlarged substituent is bound to 2*H*-chromene fragment of spiropyran molecule *via* a conjugated π-acceptor C=N bond, which distinguishes these systems from previously studied ones.^{12,13}

Results and Discussion

The desired spiropyrans were obtained by condensation between equimolar amounts of spiropyran **1** and ap-

propriate aromatic aldehydes **2** in the presence of triethylamine in boiling benzene (Scheme 1).

Scheme 1



The chemical structures of spiropyrans **3** were confirmed by elemental analysis data, NMR and IR spectroscopy.

¹H NMR spectra of the spiropyrans show signals from all the proton-containing groups, while values of the chemical shifts and *J*-coupling constants confirm completely the structure of the obtained compounds.

The signals of the *gem*-dimethyl groups at position 3 appear as two three-proton singlet signals at 1.17 and 1.31 ppm, the singlet signals of methyl protons at posi-

tion 1 (N—CH₃) are located at 2.74 ppm and practically do not depend on the variation of substituents.

The position of the signals from the protons of the azomethine group depends on properties of the substituents in the aldehyde fragment. The most "upfield shifted" signal at 8.38 ppm belongs to compound **3b** with an electron-donating methoxy group at *para* position, while the "downfield shifted" signal at 8.65 ppm (characteristic of compound **3c**) appears due to the strong intramolecular hydrogen bond of the six-membered cycle ($\delta_{\text{OH}} = 14.62$ ppm). The dependence on substituents for the chemical shifts characteristic of the signals from 3'- and 4'-protons of the spiropyrans is similar to the dependence for the signals from protons of the imine fragment, while *J* constant remains the same and equal to 10.2 Hz, which confirms the cyclic structure of the 2*H*-pyran fragment of molecules.

The photochemical studies of the obtained spiropyrans revealed the absence of photochromic properties for compounds **3a** and **3b**, and their presence for spiropyran **3c**.

Under normal conditions compound **3c** exists predominantly in a closed spirocyclic form, but an exposure of its acetonitrile solution to UV light with $\lambda = 365$ nm leads to emergence and growth of a long-wave absorption band with a maximum at 619 nm (Fig. 1), which indicates the formation of an open merocyanine form of compound MC (Scheme 2).

It should be noticed that this absorption band of spiropyran **3c** has a bathochromic shift in comparison with the band at 600 nm, observed upon exposure of the acetonitrile solution of spiropyran **1** to irradiation under similar conditions.

The spectral and kinetic properties of synthesized spiropyrans are summarized in Table 1.

As it was reported earlier,¹⁵ the condensation of a formyl-containing indoline spiropyran with amines leads toward formation of azomethine derivatives, which do not demonstrate photochromic properties in solutions under steady-state exposure to UV light. This has an obvious reason since the azomethine substituent has electron-donating properties due to the presence of an electron pair at the nitrogen atom. As it is known,¹¹ the presence of electron-donating substituents in the benzene ring

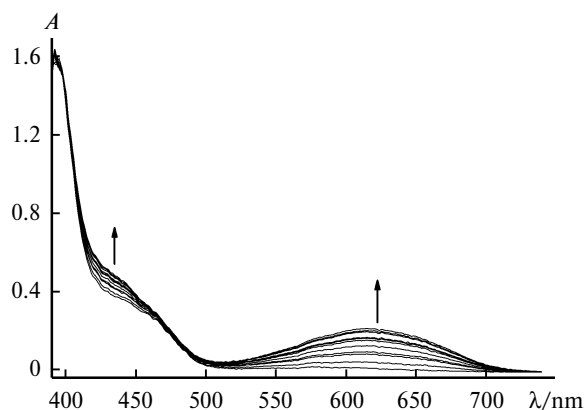
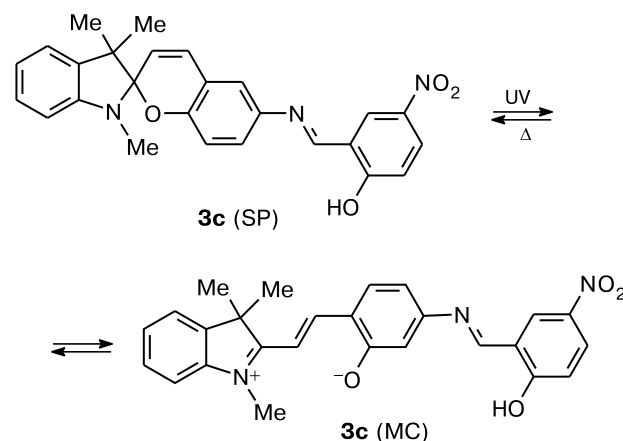


Fig. 1. Changes in the absorption spectra of acetonitrile solution of compound **3c** under exposure to UV light ($\lambda_{\text{exp}} = 365$ nm, irradiation time interval = 5 s, $T = 293$ K).

Scheme 2



of 2*H*-chromene fragment of spiropyrans leads to a decreased probability or blocking of the pyran ring opening, *i.e.* towards the disappearance of photochromic properties, while the presence of acceptor substituents enhances the photochromic properties. This factor may explain the absence of photochromic properties for compounds **3a** and **3b**. The oxygen atom in the hydroxy group of spiropyran **3c**, located at the *ortho* position with respect to the

Table 1. The spectral and kinetic properties of compounds **1**, **3a–c** in acetonitrile at 20 °C*

Compound	$\lambda_{\text{max}}^{\text{abs}}$ (SP)/nm ($\epsilon \cdot 10^{-3}/\text{mol}^{-1} \text{L cm}^{-1}$)	$\lambda_{\text{max}}^{\text{abs}}$ (MC)/nm	τ/s
1	206 (34.3), 243 (27.5), 352 (2.5),	605	1.05
3a	204 (42.8), 245 (30.2), 279 (24.0), 388 (15.9)	—	—
3b	205 (42.9), 222 (31.1), 235 (31.6), 278 (31.3), 334 (22.8)	—	—
3c	205 (48.1), 243 (38.7), 268 (33.0), 311sh (23.5), 349 (26.0), 362 sh (25.1), 443 sh (1.6)	619	30.7

* Legend: $\lambda_{\text{max}}^{\text{abs}}$ is the wavelength of the maximum in the absorption band of the spirocyclic (SP) and merocyanine (MC) isomers respectively; τ is lifetime of the open form; sh is shoulder.

azomethine group, withdraws an electron pair from the azomethine nitrogen atom, which reduces the electron-donating properties of the azomethine substituent, resulting in exhibition of photochromic properties by spiro-pyran **3c**. To provide a more detailed explanation for the photochromic behavior of the obtained spiro compounds, some further high-level quantum chemical calculations are scheduled.

In conclusion, the three new spiro-pyrans were synthesized, which contain the conjugated π -acceptor C=N bond. The photochemical studies revealed photochromic activity for spiro-pyran **3c** at room temperature in its acetonitrile solution. An interesting observation requiring further studies was an increased lifetime for the open form of spiro-pyran **3c** upon introduction of the spatially enlarged substituent containing hydroxy and nitro groups located at the *para* position.

Experimental

¹H NMR spectra were recorded in a pulsed Fourier mode on a Bruker 250 spectrometer in CDCl₃ using solvent residual signals as the internal standard (CDCl₃, 7.26 ppm). IR spectra of the compounds were recorded on a Varian Excalibur 3100 FT-IR instrument using the incomplete internal reflection method. Electronic absorption spectra were obtained for acetonitrile solutions on an Agilent 8453 spectrophotometer with a thermostating attachment for the samples. Photolysis of the solutions was carried out using the Newport system equipped with a 200 W mercury lamp and a set of interference filters.

1,3,3-Trimethylspiro-[indoline-2,2'-chromene]-6'-amine (1) was prepared according to previously reported procedure.¹⁴

1'-(4'-Nitrophenyl)-N-(1,3,3-trimethylspiro-[indoline-2,2'-chromene]-6'-yl)-methanimine (3a). A few drops of triethylamine were added to a heated solution of amine **1** (300 mg, 1.03 mmol) and *para*-nitrobenzaldehyde **2a** (155 mg, 1.03 mmol) in benzene (20 mL), and the reaction mixture was refluxed for 3 hrs. Then the solvent was evaporated, the residue was dried. The obtained product was recrystallized from alcohol. The yield was 63%. M.p. 180–183 °C. ¹H NMR, δ : 1.17 (s, 3 H, *gem*-C(CH₃)₂); 1.31 (s, 3 H, *gem*-C(CH₃)₂); 2.74 (s, 3 H, NCH₃); 5.75 (d, 1 H, C(3'), *J* = 10.2 Hz); 6.53 (d, 1 H, C(7), *J* = 7.7 Hz); 6.75 (d, 1 H, C(8'), *J* = 8.4 Hz); 6.84 (t, 1 H, C(5), *J* = 7.6 Hz); 6.88 (d, 1 H, C(4'), *J* = 10.2 Hz); 7.16–7.03 (m, 3 H, ArH); 7.19 (t.d, 1 H, C(6), *J* = 7.7 Hz, *J* = 1.2 Hz); 8.02 (d, 2 H C(2'', 6''), *J* = 8.8 Hz); 8.29 (d, 2 H, C(3'', 5''), *J* = 8.8 Hz); 8.55 (s, 1 H, N=CH). ¹³C NMR, δ : 20.2 (CH₃); 25.9 (CH₃); 29.0 (NCH₃); 51.9 (C(3)); 104.8 (C(2)); 106.9 (C(7)); 115.8 (C(3')); 119.3 (C(8')); 119.5 (C(5'a)); 120.0 (C(5)); 120.5 (C(5'')); 121.6 (C(4)); 122.6 (C(7'')); 124.0 (C(3''), C(5'')); 127.7 (C(6)); 129.1 (C(2''), C(6'')); 129.1 (C(4'')); 136.7 (C(4a)); 142.0 (C(1'')); 143.0 (C(6'')); 148.1 (C(4'')); 149.0 (C(7a)); 154.3 (C(8'a)); 154.4 (CH=N). Found (%): C, 73.43; H, 5.41; N, 9.91. C₂₆H₂₃N₃O₃. Calculated (%): C, 73.40; H, 5.45; N, 9.88.

1'-(4'-Methoxyphenyl)-N-(1,3,3-trimethylspiro-[indoline-2,2'-chromene]-6'-yl)-methanimine (3b) was prepared according to the similar procedure for compound **3a**. The yield was 47%. M.p. 197–200 °C. ¹H NMR, δ : 1.16 (s, 3 H,

gem-C(CH₃)₂); 1.31 (s, 3 H, *gem*-C(CH₃)₂); 2.73 (s, 3 H, NCH₃); 3.85 (s, 3 H, OCH₃); 5.71 (d, 1 H, C(3'), *J* = 10.2 Hz); 6.52 (d, 1 H, C(7), *J* = 7.6 Hz); 6.71 (d, 1 H, C(8'), *J* = 8.4 Hz); 6.83 (t, 1 H, C(5), *J* = 7.4 Hz); 6.86 (d, 1 H, C(4'), *J* = 10.2 Hz); 6.90–7.11 (m, 5 H, ArH); 7.17 (t, 1 H, C(6), *J* = 7.6 Hz); 7.80 (d, 2 H, C(3''), C(5''), *J* = 8.7 Hz); 8.38 (s, 1 H, CH=N). ¹³C NMR, δ : 20.2 (CH₃); 25.9 (CH₃); 29.0 (NCH₃); 51.6 (3); 55.4 (OCH₃); 104.4 (C(2)); 106.9 (C(7)); 114.2 (C(3''), C(5'')); 115.5 (C(3'')); 119.1 (C(5'a)); 119.2 (C(5'')); 119.3 (C(8'')); 120.1 (C(5)); 121.6 (C(4)); 122.2 (C(7'')); 127.6 (C(6)); 129.4 (C(4'')); 129.5 (C(1'')); 130.3 (C(2''), C(6'')); 136.8 (C(4a)); 144.7 (C(7a)); 148.2 (C(6'')); 153.0 (C(8'a)); 157.6 (CH=N); 162.0 (C(4'')). Found (%): C, 79.03; H, 6.30; N, 6.86. C₂₇H₂₆N₂O₂. Calculated (%): C, 79.00; H, 6.38; N, 6.82.

1'-(2'-Hydroxy-5'-nitrophenyl)-N-(1,3,3-trimethylspiro-[indoline-2,2'-chromene]-6'-yl)-methanimine (3c) was prepared according to the similar procedure for compound **3a**. The yield was 60%. M.p. 195–198 °C. ¹H NMR, δ : 1.17 (s, 3 H, *gem*-C(CH₃)₂); 1.31 (s, 3 H, *gem*-C(CH₃)₂); 2.74 (s, 3 H, NCH₃); 5.78 (d, 1 H, C(3'), *J* = 10.2 Hz); 6.53 (d, 1 H, C(7), *J* = 7.7 Hz); 6.78 (d, 1 H, C(8'), *J* = 8.5 Hz); 6.85 (t, 1 H, C(6), *J* = 7.4 Hz); 6.89 (d, 1 H, C(4'), *J* = 10.2 Hz); 7.23–7.00 (m, 5 H, ArH); 8.22 (d.d, 1 H, C(4''), *J* = 9.1 Hz, *J* = 2.7 Hz); 8.36 (d, 1 H, C(6''), *J* = 2.7 Hz); 8.65 (s, 1 H, N=CH); 14.62 (s, 1 H, OH). ¹³C NMR, δ : 20.1 (CH₃), 25.9 (CH₃), 28.9 (NCH₃), 52.0 (C(3)), 104.9 (C(2)), 106.9 (C(7)), 116.1 (C(8'')), 118.2 (C(3'')), 118.3 (C(1'')), 119.4 (C(3'')), 119.4 (C(5'a)), 119.6 (C(5'')), 121.0 (C(5)), 121.5 (C(4)), 122.6 (C(7'')), 127.7 (C(6)), 128.8 (C(4'')), 128.0 (C(4'')), 136.5 (C(4a)), 138.7 (C(6'')), 139.8 (C(6'')), 143.9 (C(7a)), 148.0 (C(5'')), 154.8 (C(8'a)), 157.7 (CH=N), 166.9 (C(2'')). Found (%): C, 70.77; H, 5.20; N, 9.55. C₂₆H₂₃N₃O₄. Calculated (%): C, 70.74; H, 5.25; N, 9.52.

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