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Photo- and Ionochromic Indoline Spiropyrans Based on 7,8-Dihydroxy-4-methyl-2-oxo-2*H*-chromene-6-carbaldehyde

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Abstract—A number of indoline spiropyrans were synthesized from 7,8-dihydroxy-4-methyl-2-oxo-2*H*-chromene-6-carbaldehyde. The products were found to exhibit both photochromic and ionochromic properties. According to the UV, IR, and ^{1}H NMR spectral data, they exist in the spiro form. Irradiation at λ 365 nm in 2-methylbutane–propan-2-ol (4 : 1) at 203 K induces their isomerization into colored merocyanine structure. Addition of alkaline earth and transition metal salts to acetonitrile solutions of these compounds at room temperature changes the isomer ratio and leads to formation of merocyanine complexes characterized by different colors, so that visual detection of Zn^{2+}, Mg^{2+}, Hg^{2+}, and Pb^{2+} ions is possible.

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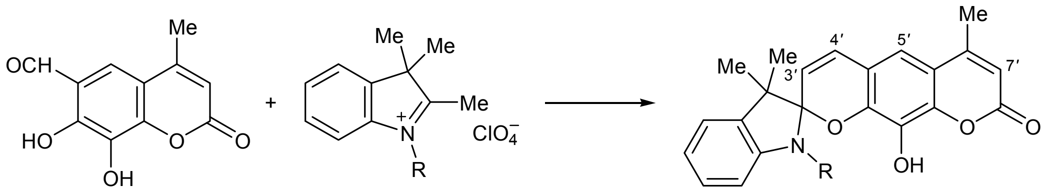
Photochromic spiropyrans exhibiting ionochromic properties attract interest from the viewpoint of their use as photodynamic chemosensors, photoswitches, and materials for data recording and storage [1–5]. We have continued studies on spiropyrans having a fused coumarin fragment as a part of the 2*H*-chromene moiety [6–9]. In the present article we describe the synthesis and properties of spiropyrans possessing an additional ligand center, hydroxy group in position *10* of the pyranochromene fragment.

7,8-Dihydroxy-4-methyl-2-oxo-2*H*-chromene-6-carbaldehyde (**I**) was synthesized according to the procedure reported in [10]. Condensation of aldehyde **I** with *N*-substituted 2,3,3-trimethyl-3*H*-indol-1-ium perchlorates in the presence of triethylamine gave the corresponding spiropyrans **IIa**–**IIe** (Scheme 1). The IR spectra of **IIa**–**IIe** contained absorption bands typical of C=C bond in the pyran ring (1600–1620 cm^{-1}), carbonyl group in the coumarin fragment (1690–1725 cm^{-1}), and hydroxy group (3320–3370 cm^{-1}). In the upfield region of the ^{1}H NMR spectra of **IIa**–**IIe** we observed two signals from magnetically nonequivalent methyl groups at δ 1.14–1.34 ppm. Signals from diastereotopic methylene protons in the *N*-benzyl substituent of compound **IIb** appeared as an *AB* quartet (two doublets at δ 4.25 and 4.58 ppm with a coupling constant ^2J of 16.50 Hz). Diastereotopic protons in the methyl groups of the *N*-isopropyl substituent of **IIc**

Scheme 1.



I

IIa–IIe

R = Me (**a**), $PhCH_2$ (**b**), *i*-Pr (**c**), C_6H_{13} (**d**), C_8H_{17} (**e**).

resonated as two doublets (*AB* quartet) at δ 1.33 and 1.39 ppm with a coupling constant ${}^3J$ of 6.95 Hz. These findings indicated cyclic structure of the condensation products. The 7-H proton resonated as a singlet at δ 6.12–6.13 ppm, protons in the 6-methyl group gave a singlet at δ 2.38–2.39 ppm, and signal from the 10-OH proton was located at δ 5.45–5.60 ppm.

Compounds **IIa**–**IIe** displayed in the electronic absorption spectra (2-methylbutane–propan-2-ol, 4:1, 203 K) a long-wave band at λ_{max} 332–340 nm with clearly defined vibrational structure, which is typical of cyclic isomers **IIA** (Scheme 2, Table 1) [1, 2, 11]. It is known that the long-wave maximum in electronic absorption spectra of spiropyrans corresponds to photochemically active coumarin fragment and that the maximum located at shorter wavelength corresponds to absorption of the indoline fragment [11].

Irradiation of solutions of compounds **II** at a wavelength corresponding to long-wave absorption of cyclic structure **A** leads to coloration due to appearance of two new structured bands in the visible region with their maxima at λ 445–460 (λ_1) and 580–652 nm (λ_2); these bands originate from the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, respectively, in open merocyanine isomer **B** (Scheme 2, Table 1) [2, 11].

Table 1. Electronic absorption spectra of spiropyrans **IIa**–**IIe** in 2-methylbutane–propan-2-ol (4:1) at 203 K

Comp. no.	Cyclic form **A**, λ_{max}, nm	Photoinduced form **B**, λ_{max}, nm
IIa	340	445, 580
IIb	335	460, 609
IIc	330	450, 590
IId	332	458, 603
IIe	335	455, 602

Addition of an equivalent amount of Zn^{2+}, Cd^{2+}, Ba^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, or Pb^{2+} acetate or Mg^{2+} or Ca^{2+} perchlorate to a solution of compound **II** in acetonitrile resulted in essential variation of the electronic absorption spectra due to formation of complex **C** with the merocyanine isomer. Complexes like **IIC** were reported by us previously [12]. The presence of OH group therein follows from insignificant change of the corresponding absorption band in the IR spectra. In the electronic absorption spectra we observed small in-

Table 2. Parameters of the electronic absorption spectra of spiropyrans **IIa**–**IIc** and **IIe** and their complexes with metal ions (M^{2+}) in acetonitrile at 293 K

Comp. no.	Metal	Absorption, λ_{max}, nm	Blue or red shift, $\Delta\lambda_{max}$, nm
IIa	–	467, 595	
	Zn	444, 540	–23, –55
	Mg	417, 524	–50, –71
	Cd	427	–40
	Ca	419, 538	–48, –57
	Ba	420	–40
	Pb	460, 566	–6, –29
IIb	–	449, 587	
	Zn	452, 562	+3, –25
	Mg	457, 561	+8, –26
	Ca	444, 560	–5, –27
	Co	475	+26
	Ni	487, 625	+38, +38
	Hg	470	+21
	Pb	470, 570	+21, –17
IIc	–	445, 588	
	Zn	442, 547	–3, –41
IIc	Mg	417, 529	–28, –59
	Cd	443, 576	–26, –12
	Ca	434, 520	–11, –68
	Co	455, 547	+10, –41
	Ni	467	+22
	Hg	468	+23
	Pb	460, 556	+15
IIe	–	442, 603	
	Zn	443, 551	+1, –52
	Mg	421, 524	–21, –79
	Ca	426, 542	–12, –61
	Ba	433, 577	–9, –26
	Co	466, 593	+16, –10
	Ni	471, 595	+29, –8
	Hg	470	+29
	Pb	459, 562	+17, –41

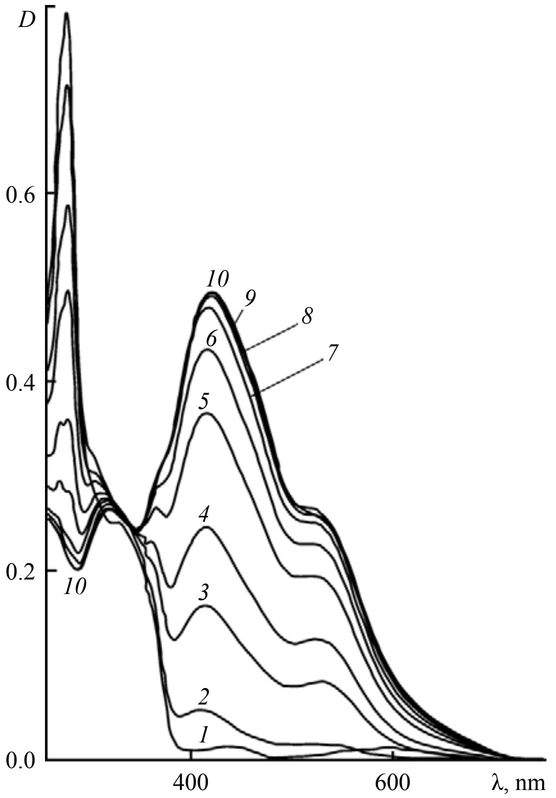


Fig. 1. Electronic absorption spectra of spiropyran **IIa** (*1*) before addition of $Mg(ClO_4)_2$ and in (*2*) 0, (*3*) 5, (*4*) 10, (*5*) 20, (*6*) 30, (*7*) 45, (*8*) 60, (*9*) 90, and (*10*) 120 min after addition of $Mg(ClO_4)_2$; $c_{\mathbf{IIa}} = 2.5 \times 10^{-5}$, $c_{Mg} = 5 \times 10^{-4}$ M; acetonitrile, 293 K.

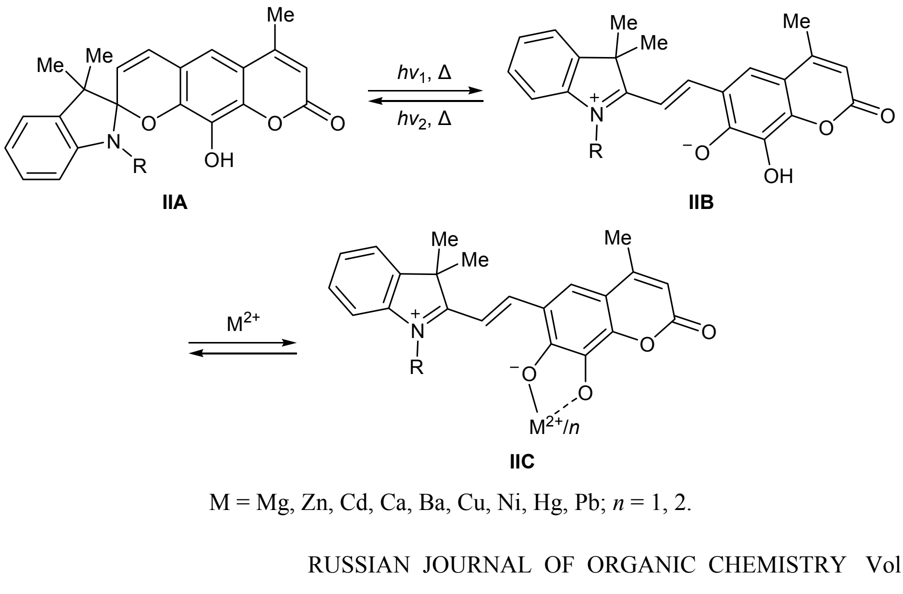
crease in the intensity of absorption maxima in the near-UV region, and new strong absorption bands appeared in the visible region due to complex formation; the position of the visible maxima depended on the nature of metal ion (Fig. 1, Table 2).

The reaction of spiropyrans **II** with metal ions is fairly specific. Solutions of **II** acquire different colors in the presence of different metal ions, so that this reaction may be used for qualitative detection of the latter. With a view to study the complex formation process with alkaline earths in more detail, 2 equiv of magnesium perchlorate was added to a solution of spiropyran **IIa** in acetonitrile-d_3 in the dark, and ^{1}H NMR spectra of the mixture were recorded in 10 min and 1 h after addition of the salt (Fig. 2).

The ^{1}H NMR spectrum of **IIa** contained signals typical of the spiro structure: two signals from magnetically nonequivalent geminal methyl groups at δ 1.71 and 1.83 ppm, a signal from the NCH_3 group at δ 3.30 ppm, a doublet from the 3-H proton at δ 6.40 ppm, and a singlet from 7-H at δ 6.62 ppm. No signals assignable to merocyanine isomer **B** were present (Fig. 2a). After addition of $Mg(ClO_4)_2$ in the dark, doublets belonging to the CH=CH protons in the merocyanine form appeared at δ 8.45 ppm. The intensity of signals belonging to spiro isomer **A** decreased approximately twofold. In addition, these signals were displaced upfield by about 0.50 ppm relative to the corresponding signals of **IIa** (Fig. 2b). These data suggest gradual displacement of the equilibrium toward merocyanine structure **IIB** as a result of formation of complex **IIC**. In 1 h after addition of magnesium perchlorate, signals from spirocyclic structure **IIA** disappeared completely (Fig. 2c).

To conclude, indoline spiropyrans **II** can be used as multifunctional signaling systems due to formation of differently colored solutions with alkaline earth and transition metal ions.

Scheme 2.



M = Mg, Zn, Cd, Ca, Ba, Cu, Ni, Hg, Pb; *n* = 1, 2.

EXPERIMENTAL

The electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer. Solutions of compounds **II** were irradiated with a DRSh-250 mercury lamp equipped with a set of light filters. The IR spectra were measured on a Varian Excalibur spectrometer with Fourier transform from samples dispersed in mineral oil. The ^{1}H NMR spectra were obtained on a Varian Unity-300 instrument (300 MHz) from solutions in CDCl$_3$ using the residual proton signal of the solvent as reference (CHCl$_3$, δ 7.25 ppm).

General procedure for the synthesis of indoline spiropyrans IIa–IIe. Triethylamine, 0.1 ml (0.7 mmol), was added to a hot solution of 2.42 g (1.1 mmol) of formylcoumarin **I** and 1 mmol of the corresponding 1-substituted 2,3,3-trimethyl-3*H*-indol-1-ium perchlorate in propan-2-ol. The mixture was heated for 5 h under reflux, cooled, poured into water, and extracted with several portions of chloroform. The extracts were combined, dried over CaCl$_2$, and evaporated to a volume of 10–15 ml. The residue was subjected to chromatography on silica gel using chloroform as eluent, and the product was additionally purified by recrystallization from benzene.

10′-Hydroxy-1,3,3,6′-tetramethyl-1,3-dihydro-8′*H*-spiro[indole-2,2′-pyrano[3,2-*g*]chromen]-8′-one (IIa). Yield 34%, mp 205–207°C. IR spectrum, ν, cm^{-1}: 3360, 1710, 1610, 920. ^{1}H NMR spectrum, δ, ppm: 1.19 s and 1.30 s (3H each, 3-CH$_3$), 2.39 s (3H, 6′-CH$_3$), 2.78 s (3H, NCH$_3$), 5.78 d (1H, 3′-H, J = 10.55 Hz), 5.60 br.s (1H, OH), 6.13 s (1H, 7′-H), 6.56 d (1H, 7-H, J = 7.62 Hz), 6.83–7.07 m (3H, 4′-H, 5-H, 5′-H), 7.09 d (1H, 4-H, J = 7.62 Hz), 7.20 t (1H, 6-H). Found, %: C 73.64; H 5.65; N 3.82. C$_{23}$H$_{21}$NO$_4$. Calculated, %: C 73.58; H 5.64; N 3.73.

1-Benzyl-10′-hydroxy-3,3,6′-trimethyl-1,3-dihydro-8′*H*-spiro[indole-2,2′-pyrano[3,2-*g*]chromen]-8′-one (IIb). Yield 45%, mp 215–217°C. IR spectrum, ν, cm^{-1}: 3370, 1720, 1620, 920. ^{1}H NMR spectrum, δ, ppm: 1.31 s and 1.34 s (3H each, 3-CH$_3$), 2.38 s (3H, 6′-CH$_3$), 4.25–4.58 q (2H, NCH$_2$, J = 16.50 Hz), 5.57 br.s (1H, OH), 5.82 d (1H, 3′-H, J = 10.30 Hz), 6.13 s (1H, 7′-H), 6.46 d (1H, 7-H, J = 7.62 Hz), 6.83–7.07 m (3H, 4′-H, 5-H, 5′-H), 7.05 d (1H, 4-H, J = 7.62 Hz), 7.10 t (1H, 6-H), 7.20–7.30 m (5H, H$_{\text{arom}}$). Found, %: C 77.5; H 5.52; N 3.19. C$_{29}$H$_{25}$NO$_4$. Calculated, %: C 77.17; H 5.58; N 3.10.

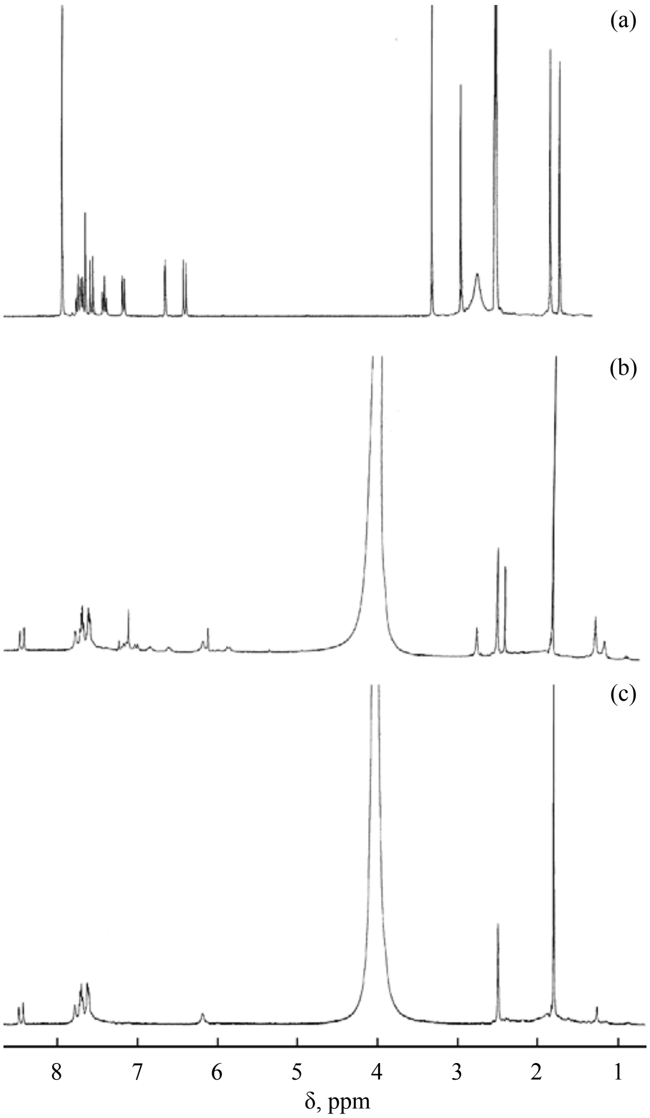


Fig. 2. ^{1}H NMR spectra of compound **IIa** in acetonitrile-d_3 (a) before addition and in (b) 10 min and (c) 1 h after addition of Mg(ClO$_4$)$_2$.

10′-Hydroxy-1-isopropyl-3,3,6′-trimethyl-1,3-dihydro-8′*H*-spiro[indole-2,2′-pyrano[3,2-*g*]chromen]-8′-one (IIc). Yield 48%, mp 268–269°C. IR spectrum, ν, cm^{-1}: 3350, 1720, 1620, 920. ^{1}H NMR spectrum, δ, ppm: 1.14 s and 1.27 s (3H each, 3-CH$_3$), 1.33–1.39 q (6H, CH$_3$, J = 6.95 Hz), 2.38 s (3H, 6′-CH$_3$), 3.82 m (1H, CH), 5.56 br.s (1H, OH), 5.57 d (1H, 3′-H, J = 10.30 Hz), 6.12 s (1H, 7′-H), 6.75–7.41 m (6H, 4-H, 4′-H, 5-H, 5′-H, 6-H, 7-H). Found, %: C 74.59; H 6.39; N 3.40. C$_{25}$H$_{25}$NO$_4$. Calculated, %: C 74.72; H 6.25; N 3.47.

1-Hexyl-10′-hydroxy-3,3,6′-trimethyl-1,3-dihydro-8′*H*-spiro[indole-2,2′-pyrano[3,2-*g*]chromen]-8′-one (IId). Yield 35%, mp 165–166°C. IR spectrum, ν, cm^{-1}: 3350, 1725, 1620, 940. ^{1}H NMR spectrum, δ, ppm: 1.18–1.28 m (21H, CH$_3$, CH$_2$), 2.38 s (3H, 6′-CH_3), 3.17 m (2H, NCH_2), 5.57 br.s (1H, OH), 5.74 d (1H, 3′-H, J = 10.30 Hz), 6.12 s (1H, 7′-H), 6.57 d (1H, 7-H, J = 7.62 Hz), 6.80–6.95 m (3H, 4′-H, 5-H, 5′-H), 7.08 d (1H, 4-H, J = 7.62 Hz), 7.10 t (1H, 6-H). Found, %: C 78.62; H 6.99; N 3.42. $C_{28}H_{31}NO_4$. Calculated, %: C 78.34; H 7.22; N 3.26.

10′-Hydroxy-3,3,6′-trimethyl-1-octyl-1,3-dihydro-8′*H*-spiro[indole-2,2′-pyrano[3,2-*g*]chromen]-8′-one (IIe). Yield 27%, mp 157–158°C. IR spectrum, ν, cm^{-1}: 3320, 1690, 1600, 930. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, CH_3), 1.19–1.29 m (14H, 3-CH_3, CH_2), 1.60 m (4H, CH_2), 2.38 s (3H, 6′-CH_3), 3.17 m (2H, NCH_2), 5.45 br.s (1H, OH), 5.86 d (1H, 3′-H, J = 10.50 Hz), 6.12 s (1H, 7′-H), 6.56–7.25 m (6H, 4-H, 4′-H, 5-H, 5′-H, 6-H, 7-H). Found, %: C 78.52; H 7.39; N 3.22. $C_{30}H_{35}NO_4$. Calculated, %: C 78.62; H 7.96; N 3.06.

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