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CHEMISTRY

Chromogenic Spiroindolinobenzopyrans of the Oxadiazole Series with Photodriven Ionochromic Properties

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Abstract—New photochromic 8-oxadiazolyl-substituted spirobenzopyran-indolines, which are able to undergo light-controllable cation-induced isomerizations, have been obtained.

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Design of functionalized photochromic molecular systems with photoswitchable chromogenic properties is an urgent task for contemporary chemistry [1]. Among the most promising photochromic molecules that can be used as a basis for synthesis of such polyfunctional structures are spiropyrans due to the relative ease of structural modification and the ability to change chromogenic properties under the action of different external factors [2, 3], including metal ions [4].

A key feature of ionochromic transformations of spiropyrans is the possibility to control complexation by light radiation, which is impossible for common ionochromes. Light radiation can produce coordinatively active form of compound or, on the contrary, cause decomplexation. This process is a rather promising approach to design molecular switches with photomodulaed complexing properties and photodriven sensors for metal ions with optical response [5–7].

In this context, the aim of this work is to obtain and study new 8-oxadiazolyl-substituted spirobenzopyran-indolines, whose merocyanine form contains bidentate chelating core that includes donor sites represented by the phenolate anion and the nitrogen atom of the oxadiazole ring.

Spiropyrans (SPs) **1a**–**1d** where prepared by the reaction of 3*H*-indolium salts **2a**–**2c** and hydroxyaldehydes **3a** and **3b** in the presence of triethylamine as a base (Scheme 1).

The structure of compounds **1a**–**1d** was established by ^{1}H and ^{13}C NMR spectroscopy and confirmed by elemental analysis data. ^{1}H NMR spectra of spiropyrans **1a**–**1d** show two signals of magnetically nonequivalent geminal methyl groups, a proton signal of the *N*-methyl substituents of the indoline and oxadiazole moieties in the upfield region, a formyl proton signal and several groups of coupled proton signals in the downfiled spectral region arising from the indoline, benzopyran, and oxadiazole moieties. The lack of proton signals of the indoline and benzopyran moieties in the spectral regions typical for the open merocyanine form [8–11] indicates that the obtained compounds in acetone-d_6 and $CDCl_3$ solutions are in the spirocyclic form. Spiropyran **1a** in acetone exists as cyclic form **A**; as a result, there is no marked absorption in the visible spectral region (Scheme 2).

In going from compound **1a** to **1b**, we observed a weak violet color of solution, which appeared as a slight absorption in the range 550–600 nm owing to the presence of merocyanine form **B**, involved in equilibrium with the spirocylic form. This may be caused by the stabilization of merocyanine **1b** as compared with **1a** due to the presence of the electron-withdrawing formyl group in the pyran moiety of molecule. The introduction of chlorine atom or trifluoromethyl group into the indoline moiety of the molecule, on the contrary, destabilizes the merocyanine form, which makes solutions of spiropyrans **1c** and **1d** to be colorless. Cyclic forms of spiropyrans **1a**–**1d** display bands with maxima at 334–352 nm with molar extinction coefficients of 4520–6870 L mol^{-1} cm^{-1} (Table 1).

When acetone solutions of spiropyrans **1a**–**1d** are exposed to UV light (λ = 365 nm) at T = 293 K, they become colored due to photochemical ring opening reaction and formation of merocyanine forms **B** (Fig. 1, Scheme 2) with absorption maxima in the range 574–608 nm (Table 1). The introduction of formyl group

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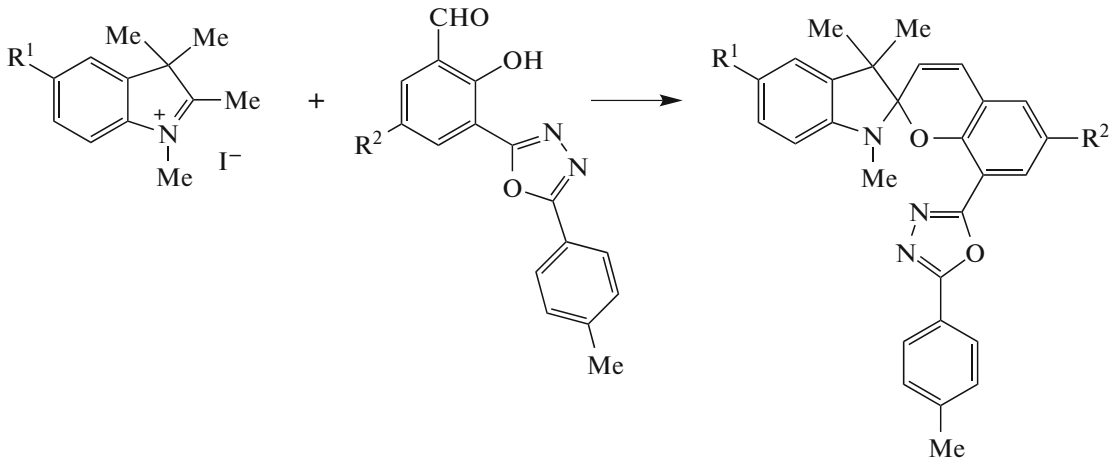
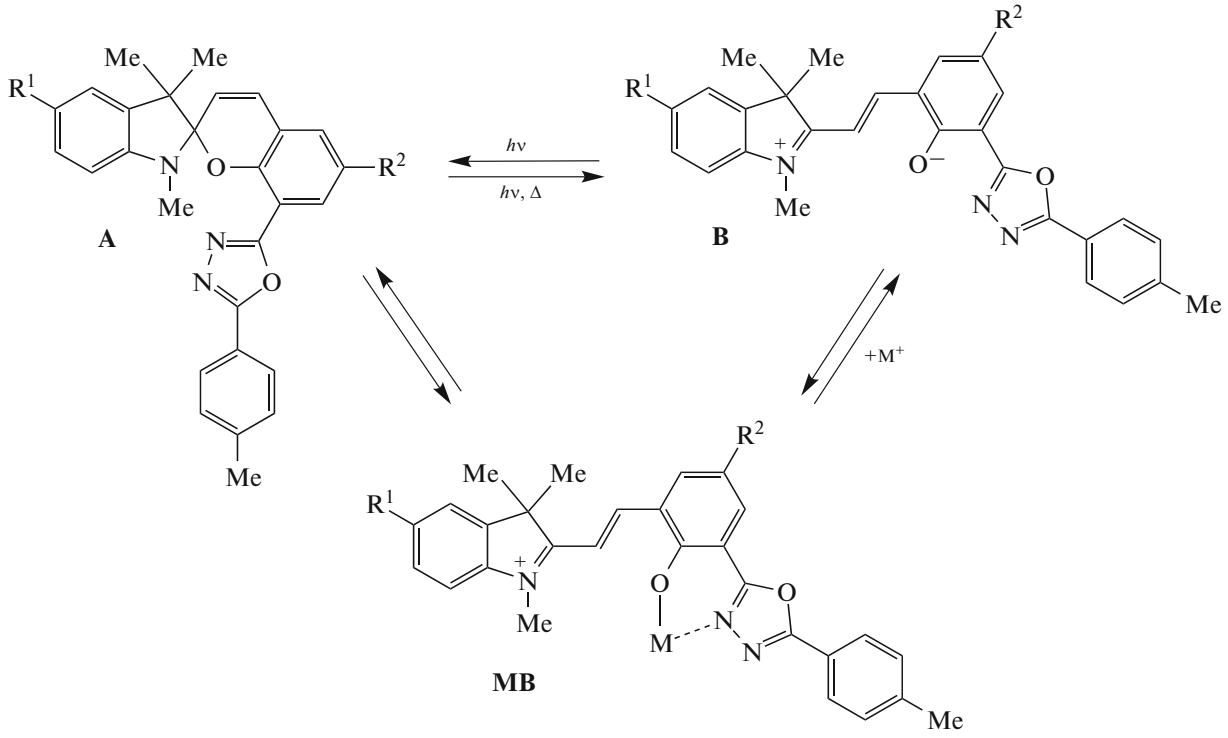


2a–2c **3a, 3b** **1a–1d**

1: (**a**) $R^1 = R^2 = H$; (**b**) $R^1 = H$, $R^2 = CHO$; (**c**) $R^1 = Cl$, $R^2 = CHO$; (**d**) $R^1 = CF_3$, $R^2 = CHO$; **2**: (**a**) $R^1 = H$; (**b**) $R^1 = Cl$; (**c**) $R^1 = CF_3$; **3**: (**a**) $R^2 = H$; (**b**) $R^2 = CHO$

Scheme 1.



Scheme 2.

into the pyran moiety of the molecule leads to a hypsochromic shift of the long-wavelength absorption band of merocyanines. The subsequent introduction of substituents into the indoline moiety, on the contrary, causes the bathochromic shift. The process of photoinduced coloration is reversible: after the irradiation was stopped, solution discoloration occurs because of the thermal recyclization reaction of form **B** to give the initial spirocyclic form. The kinetic curves of relaxation processes are satisfactorily

described by monoexponential function, which indicates the monomolecular character of the process. Characteristic relaxation times and activation barriers assessed from the Arrhenius equation are given in the table. On passing from compound **1a** to compound **1b**, the lifetime of colored form and activation barrier of thermal relaxation reaction increase, which is caused by the stabilization of the merocyanine form **B** due to the presence of electron-withdrawing formyl group in the pyran moiety of the molecule. On the contrary, the introduction of electron-withdrawing substituents in the indoline moiety of the molecule in going from compound **1b** to compounds **1c** and **1d** causes a decrease in the lifetime of merocyanine and in the activation energy.

The addition of Zn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+}, and Mn^{2+} salts to colorless or slightly colored solutions of spiropyrans **1a**–**1d** causes thermal accumulation of strongly colored products that have different position of absorption band maxima in the long-wavelength region depending on the metal ion (Fig. 2).

To assess structural changes caused by the reaction of the studied compounds with metal ions and resulting in coloration, we examined changes in ^{1}H NMR spectra. Addition of 1 equiv of $Zn(ClO_4)_2$ to a solution of spiropyran **1d** in acetone-d_6 led to changes in the ^{1}H NMR spectrum typical of the formation of merocyanine isomers. Geminal methyl groups appeared as a six-proton singlet and exhibited downfield shift. The signal of *N*-methyl group showed the largest downfield shift owing to the emergence of the positive charge on the nitrogen atom. The proton signals of the double bond of the pyran ring have constants typical for *trans* vinyl protons and also show downfield shift, which corresponds to the literature data for the merocyanine forms of spiropyrans [8–11]. Thus, the reaction of oxadiazolyl-substituted spiropyrans with metal ions led to formation of intensely colored complexes of merocyanine form **MB**.

We also found that complexes of spiropyrans **1a**–**1d** with cations Zn^{2+}, Cd^{2+}, and Mn^{2+} exhibit negative photochromism. When exposed to the visible light, they underwent reversible discoloration caused by the photodissociation of **MB** complex into free metal ion and the cyclic form of spiropyran.

Table 1. Spectral and kinetic characteristics of spiropyrans **1a**–**1d** in acetone

SP	λ_{max}(**A**), nm ($\varepsilon \times 10^{-3}$, L mol^{-1} cm^{-1})	λ_{max}(**B**), nm	τ_B^{293}, s	E_a, kJ/mol
1a	335 (6.87), 349 (5.11) sh	608	47.8	69.7
1b	335 (6.59), 352 (4.65)	574	405	101.7
1c	334 (6.29), 352 (4.52)	580	98.2	97.8
1d	334 (6.24), 351 (4.57)	583	27.7	74.3

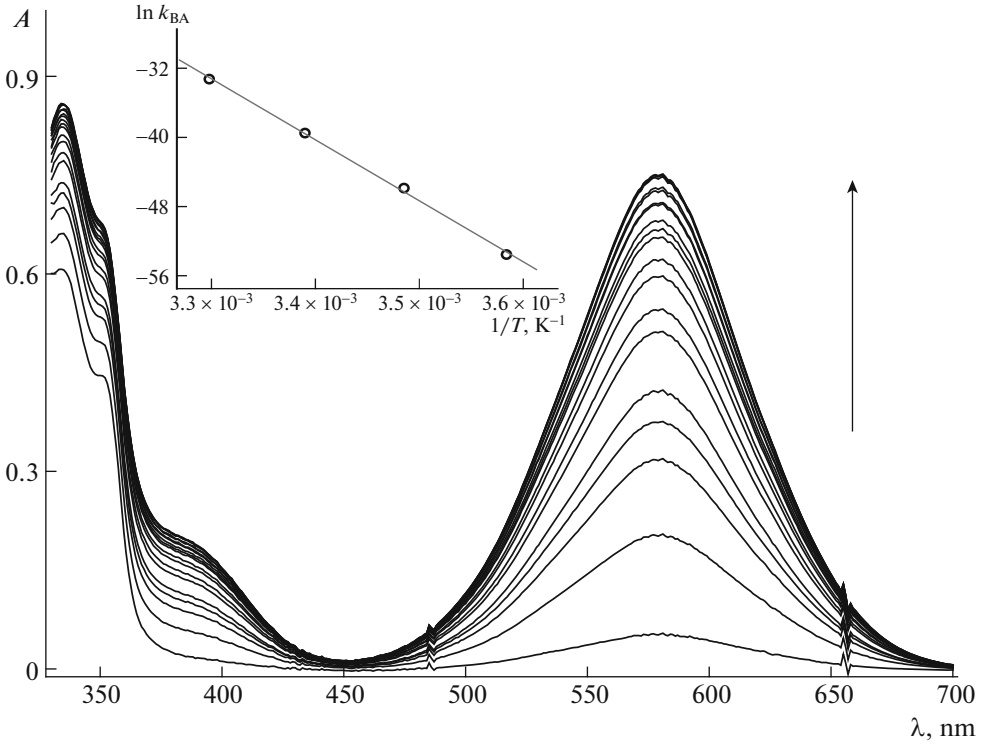


Fig. 1. Electronic absorption spectra for spiropyran **1a** solution when exposed to UV radiation (λ = 365 nm). Inset shows the plot of the natural logarithm of rate constant for reverse thermal reaction vs inverse temperature.

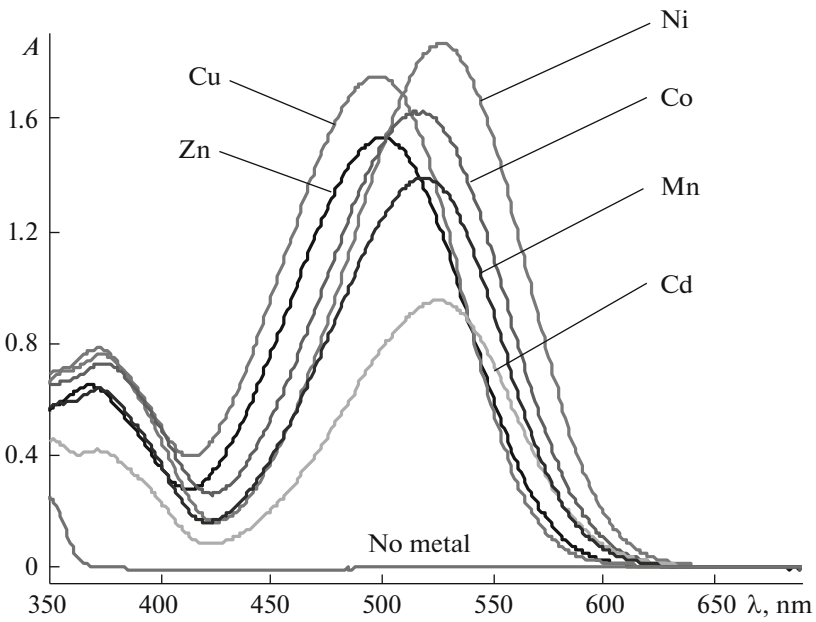


Fig. 2. Electronic absorption spectra for spiropyran **1a** solutions in acetone in the presence of metal cations at $T = 293$ K. c(**1a**) = 5.00×10^{-5} mol/L; c(M) = 1.00×10^{-4} (M = Zn^{2+}, Ni^{2+}, Cu^{2+},Co^{2+}), 5.00×10^{-4} mol/L (**M** = Cd^{2+}, Mn^{2+}).

Thus, we can affirm that 8-[5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl]-substituted spiropyrans **1a**–**1d** represent a photodynamic chromogenic system where complexation with metal ions can be controlled by light irradiation.

EXPERIMENTAL

Spectral studies were performed with the use of equipment of the Molecular Spectroscopy Shared Facility Center, Southern Federal University. ^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer operating at 300 MHz (^{1}H) in $CDCl_3$ and acetone-d_6 solutions at 20°C, chemical shifts were measured in the δ scale using residual signals of $CDCl_3$ (7.26 ppm) and acetone-d_6 (2.05 ppm) as a reference with accuracy up to 0.01 ppm for chemical shifts and 0.1 Hz for spin–spin coupling constants. Elemental analysis was performed on a Kovo CHN analyzer. Melting points were determined on a Boetius hot-stage apparatus.

Electronic absorption spectra and kinetic curves of thermal recyclization reactions of the studied compounds were recorded on an Agilent 8453 spectrophotometer with an accessory for sample temperature control. Solution photolysis was carried out with the use of a Newport system based on a 200-W mercury lamp with a set of interference light filters. Solutions were prepared using acetone of spectral purity grade (Sigma-Aldrich). Metal salts were introduced in solution as perchlorates (Sigma-Aldrich).

Visible light intensity was determined with a Newport 2935 light power meter, it was 2.2×10^{16} photon/s at a wavelength of 365 nm.

1',3',3'-Trimethyl-8-[5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl]spiro(2*H*-1-benzopyran-2,2'-indolines) 1a–1d (general procedure). A mixture of 1 mmol of 3*H*-indolium salt **2a**–**2c**, 1 mmol of aldehyde **3a** or **3b**, 1 mmol (0.14 mL) of triethylamine in a blend of 10 mL of toluene and 5 mL of 2-propanol was heated under reflux for 12 h, the solvent was evaporated, the residue was purified by column chromatography on Al_2O_3 (using benzene–acetone, 10 : 1, as an eluent), and crystalized from toluene–heptane (2 : 1) mixture.

1',3',3'-Trimethyl-8-[5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl]spiro(2*H*-1-benzopyran-2,2'-indoline) (1a). Yield 47%, mp 178–180°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J, Hz): 1.22 (s, 3H, 3'-Me), 1.37 (s, 3H, 3'-Me), 2.41 (s, 3H, Me–Ph), 2.79 (s, 3H, 1'-Me), 5.82 (d, 1H, J = 10.3, 3-H), 6.59 (d, 1H, J = 7.7, 7'-H), 6.94 (d, 1H, J = 10.3, 4-H), 6.96 (dt, 1H, J = 7.4, 1.0, 5'-H), 6.97 (dd, 1H, J = 8.0, 7.4, 6-H), 7.13–7.18 (m, 3H, 4'-H, Ph–H), 7.22–7.25 (m, 3H, 5-H, Ph–H), 7.27 (dt, 1H, J = 7.6, 1.2, 6'-H), 8.12 (dd, 1H, J = 8.0, 1.7, 7-H).

For $C_{28}H_{25}N_3O_2$ anal. calcd. (%): C, 77.22; H, 5.79; N, 9.65.

Found (%): C, 77.31; H, 5.64; N, 9.58.

1',3',3'-Trimethyl-8-[5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl]spiro(2*H*-1-benzopyran-2,2'-indoline)-6-carbaldehyde (1b). Yield 46%, mp 189–189.5°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J, Hz): 1.24 (s, 3H, 3'-Me), 1.37 (s, 3H, 3'-Me), 2.42 (s, 3H, Me–

Ph), 2.80 (s, 3H, 1'-Me), 5.94 (d, 1H, J = 10.4, 3-H), 6.62 (d, 1H, J = 7.8, 7'-H), 6.99 (dt, 1H, J = 7.4, 1.0, 5'-H), 7.03 (d, 1H, J = 10.4, 4-H), 7.15–7.18 (m, 3H, 4'-H, Ph–H), 7.24 (d, 2H, J = 8.3, Ph–H), 7.29 (dt, 1H, J = 7.6, 1.3, 6'-H), 7.82 (d, 1H, J = 2.1, 5-H), 8.64 (d, 1H, J = 2.1, 7-H), 9.94 (s, 1H, 6-CHO).

For $C_{29}H_{25}N_3O_3$. anal. calcd. (%): C, 75.14; H, 5.44; N, 9.07.

Found (%): C, 75.09; H, 5.50; N, 9.01.

1',3',3'-Trimethyl-8-[5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl]-5'-chlorospiro(2*H*-1-benzopyran-2,2'-indoline)-6-carbaldehyde (1c). Yield 42%, mp 240–241°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J, Hz): 1.25 (s, 3H, 3'-Me), 1.37 (s, 3H, 3'-Me), 2.44 (s, 3H, Me–Ph), 2.77 (s, 3H, 1'-Me), 5.91 (d, 1H, J = 10.4, 3-H), 6.51 (d, 1H, J = 8.2, 7'-H), 7.04 (d, 1H, J = 10.4, 4-H), 7.12 (d, 1H, J = 2.1, 4'-H), 7.22 (dd, 1H, J = 8.2, 2.1, 6'-H), 7.26–7.32 (m, 4H, Ph–H), 7.83 (d, 1H, J = 2.1, 5-H), 8.65 (d, 1H, J = 2.1, 7-H), 9.95 (s, 1H, 6-CHO).

For $C_{29}H_{24}ClN_3O_3$ anal. calcd. (%): C, 69.95; H, 4.86; N, 8.44.

Found (%): C, 69.88; H, 4.96; N, 8.49.

1',3',3'-Trimethyl-8-[5-(4-methylphenyl)-1,3,4-oxadiazol-2-yl]-5'-(trifluoromethyl)spiro(2*H*-1-benzopyran-2,2'-indoline)-6-carbaldehyde (1d). Yield 52%, mp 235–235.5°C. ^{1}H NMR ($CDCl_3$, δ, ppm, J, Hz): 1.25 (s, 3H, 3'-Me), 1.40 (s, 3H, 3'-Me), 2.39 (s, 3H, Me–Ph), 2.87 (s, 3H, 1'-Me), 5.92 (d, 1H, J = 10.4, 3-H), 6.64 (d, 1H, J = 8.1, 7'-H), 7.06 (d, 1H, J = 10.4, 4-H), 7.14 (d, 2H, J = 8.0, Ph–H), 7.30–7.33 (m, 3H, 4'-H, Ph–H), 7.55 (dd, 1H, J = 8.2, 1.7, 6'-H), 7.84 (d, 1H, J = 2.0, 5-H), 8.63 (d, 1H, J = 2.0, 7-H), 9.96 (s, 1H, 6-CHO).

For $C_{30}H_{24}F_3N_3O_3$ anal. calcd. (%): C, 67.79; H, 4.55; N, 7.91.

Found (%): C, 67.87; H, 4.41; N, 7.85.

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