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Research Article

Synthesis of Novel Iono- and Photochromic Spiropyrans Derived from 6,7-Dihydroxy-8-Formyl-4-Methyl-2H-Chromene-2-One

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Novel photochromic spiropyrans (SPPs) containing 6'-hydroxy group were synthesized and their spectral properties as well as abilities for complexation with metal ions studied. In solutions they exist as equilibrium mixture of spirocyclic (A) and merocyanine (B) isomers. The largest content of merocyanine form was found for the derivative with an electron-donating methyl group in position 5 of hetaryl fragment. The irradiation of SPPs in acetonitrile shifts the equilibrium to the B form. Similar effect causes the addition of metal cations due to formation of colored complexes with merocyanine isomers.

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1. Introduction

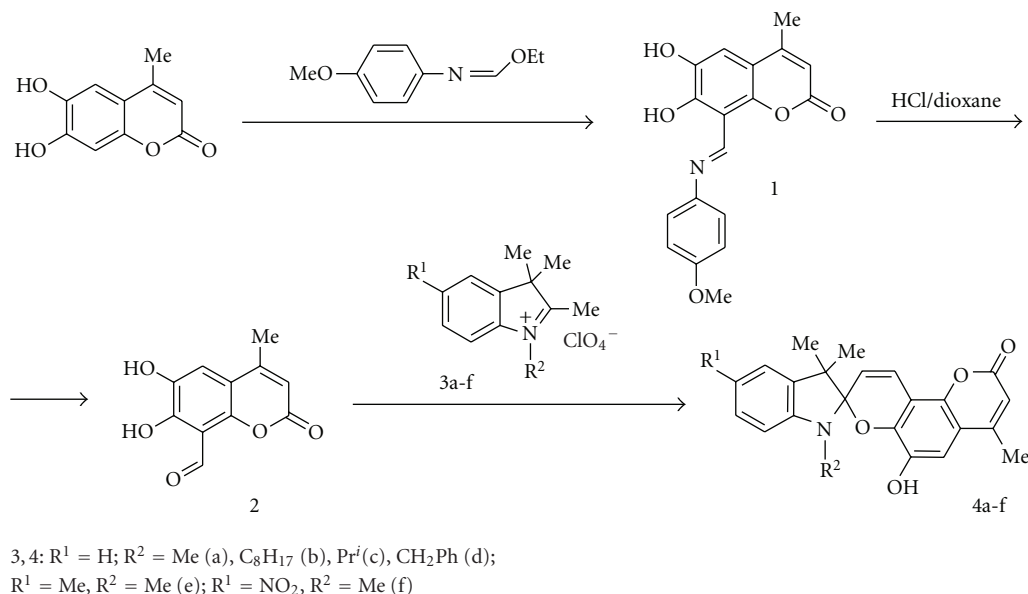
Design and synthesis of novel photochromic spiropyrans and spirooxazines (SPOs) displaying ionochromic properties are of significant interest due to their application as magnetic [1, 2], in devices of molecular electronics [3] and as effective photoswitchable chemosensors for metal cations [4–6]. The structure of the latter type compounds usually contains chelate [7–14], calixarene [15], or crown-ether ionophore groups [16, 17]. The coordination of metal cations occurring via interaction with ligating centers located in the chromene part of a spiropyran (or spirooxazine) can lead to thermally or photochemically driven cleavage of the C_{spiro}–O bond of the cyclic isomer followed by Z/E-isomerization to give the metastable colored merocyanine form. By contrast, the complexation with ionophore conjugated with the hetaryl fragment of a spiropyran (or spirooxazine) results in destabilization of the merocyanine form caused by electrostatic repulsion between a metal cation and the positively charged nitrogen atom in the hetaryl moiety [18, 19]. We synthesized a series of novel SPPs containing 6'-hydroxy group in order to study their structure in solutions, photochromic properties, and ionochromic ability towards the alkali-earth and d-metal cations.

2. Experimental

¹H NMR spectra were recorded on Bruker WM-250 (300 MHz) spectrometer using CDCl₃ as solvent. The ¹H chemical shifts were calibrated using the signals of solvent residual protons (δ 7.25 ppm). IR spectra were measured in Nujol using a Specord 75IR spectrometer. UV-Vis absorption spectra were obtained in acetonitrile with a Cary-100 spectrophotometer. Irradiation of solutions was carried out by filtered light of a high-pressure mercury lamp DRSh (250 W) supplied with glass filter ($\lambda_{irr} = 365$ nm).

3. Results and Discussion

3.1. Synthesis. The compound 6,7-Dihydroxy-8-formyl-4-methyl-2H-chromene-2-one (2) was prepared by coupling 6,7-dihydroxy-4-methyl-2H-chromene-2-one with ethyl N-p-methoxyphenylformimidate formed in situ from 4-methoxyphenylamine and triethyl orthoformate followed by the hydrolysis of Schiff base (1) with diluted hydrochloric acid (Scheme 1). The spiropyrans (4) were synthesized by condensation of aldehyde (2) with corresponding 3H-indolium perchlorates (3) in presence of triethylamine.



SCHEME 1

(i) *6,7-dihydroxy-8-[(4-methoxyphenylimino)methyl]-4-methylchromen-2-one (1)*. A mixture of 10 g (45 mmol) 6,7-dihydroxy-4-methyl-2H-chromene-2-one, 11 g (90 mmol) 4-methoxyphenylamine, and 14 mL triethyl orthoformate was kept for 5 hours at 170 °C. The precipitate obtained after cooling was filtered and washed with ethanol. The crude product was purified by recrystallization from DMFA. Yield 25%, mp 257–258 °C. ¹H NMR (CDCl₃): δ 2.35 (3H, s, CH₃), 3.88 (3H, s, OMe), 6.06–7.43 (7H, m, Ar-H + OH), 9.02 (1H, s, CH=), 15.70 (1H, s, OH). Anal. Calcd for C₁₈H₁₅NO₅: C, 66.46; H, 4.65; N, 4.31. Found: C, 66.36; H, 4.60; N, 4.41.

(ii) *6,7-dihydroxy-8-formyl-4-methyl-2H-chromene-2-one (2)*. 6,7-Dihydroxy-8-[(4-methoxyphenylimino)methyl]-4-methylchromen-2-one (1) (2.5 g, 7.7 mmol) was dissolved under heating in dioxane (300 mL) and 18% HCl (150 mL) was added. The solution obtained was allowed to stand 10–15 minutes at 60–70 °C and the reaction mixture was poured into the water (500 mL). The crude product was filtered, dried, and purified by recrystallization from 2-propanol. Yield 32%, mp 234–235 °C. ¹H NMR (CDCl₃): δ 2.40 (3H, s, CH₃), 5.64–7.35 (3H, m, Ar-H + OH), 10.59 (1H, s, CHO), 12.42 (1H, s, OH). Anal. Calcd for C₁₁H₈O₅: C, 60.01; H, 3.66. Found: C, 60.15; H, 3.58.

(iii) *spiropyrans (4a–f) (general procedure)*. A mixture of corresponding perchlorate (3) (1 mmol), aldehyde (2) (1.1 mmol) and 0.1 mL (0.7 mmol) triethylamine was refluxed in 2-propanol (20 mL) for 5 hours. The solvent was removed, the residue was purified by column chromatography on SiO₂ with chloroform as an eluent and recrystallized from 2-propanol.

(iv) *6'-hydroxy-1,3,3,4'-tetramethylspiro[indoline-2,8'-pyrano[2,3-f]benzopyran]-2'-(7'H)-one (4a)*. Yield 24%, mp 208–209 °C; IR (ν_{max}/cm⁻¹, nujol): 3120, 1685, 1580, 1560, 920. ¹H NMR (CDCl₃): δ isomer A 1.20, 1.30 (6H, s + s, 2 gem-(CH₃)₂), 2.34 (3H, s, CH₃), 2.77 (3H, s, NCH₃), 5.35

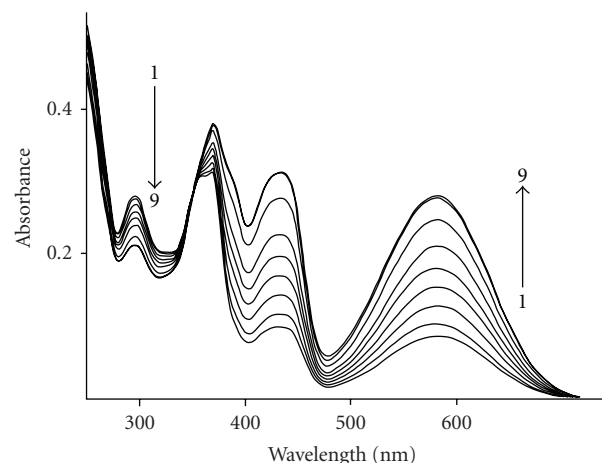
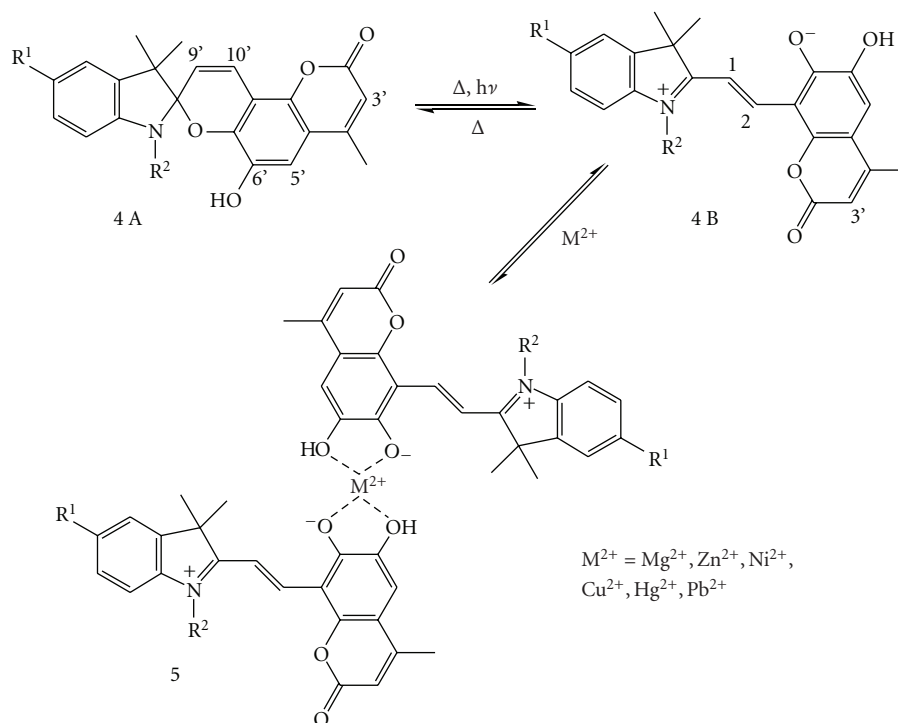


FIGURE 1: Absorption spectra of (4a) in acetonitrile solution before irradiation (1); after 15 seconds (2); 45 seconds (3); 90 seconds (4); 150 seconds (5); 180 seconds (6); 8 minutes (7); 16 minutes (8); 26 minutes (9) of irradiation ($\lambda_{\text{irr}} = 365 \text{ nm}$, $C = 2.5 \cdot 10^{-5} \text{ M}$).

(1H, br. s, OH), 5.84 (1H, d, H^{9'}, J 10.5), 6.16 (1H, s, H^{3'}), 6.58–7.22 (5H, m, Ar-H), 7.47 (1H, d, H^{10'}, J 10.5). Isomer B: 1.84 (6H, s, 2 gem-(CH₃)₂), 2.31 (3H, s, CH₃), 3.78 (3H, s, NCH₃), 5.98 (1H, s, H^{3'}), 6.16–7.22 (5H, m, Ar-H), 8.47 (1H, d, CH=, J 14.8), 8.92 (1H, d, CH=, J 14.8). Ratio of isomers A : B (see Table 1). Anal. Calcd for C₂₃H₂₁NO₄: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.41; H, 5.65; N, 3.82.

(v) *6'-hydroxy-1-octyl-3,3,4'-trimethylspiro[indoline-2,8'-pyrano[2,3-f]benzopyran]-2'-(7'H)-one (4b)*. Yield 27%, mp 145–146 °C; IR (ν_{max}/cm⁻¹, nujol): 3180, 1685, 1610, 1560, 920. ¹H NMR (CDCl₃): δ isomer A: 1.19–1.93 (21H, m, 3CH₃ + 6CH₂), 2.34 (3H, s, Me), 3.17 (2H, m, NCH₂), 5.30 (1H, br. s, OH), 5.81 (1H, d, H^{9'}, J 10.5), 6.17 (1H, s,



SCHEME 2

H^{3'}), 6.58–7.45 (6H, m, Ar-H + H^{10'}). Isomer B: 1.19–1.93 (21H, m, 3CH₃ + 6CH₂), 2.30 (3H, s, Me), 4.18 (2H, t, NCH₂), 5.96 (1H, s, H^{3'}), 6.58–7.45 (5H, m, Ar-H), 8.70 (1H, br. s, CH=), 8.92 (1H, d, CH=, *J* 15.3). Ratio of isomers A : B is (see Table 1). Anal. Calcd for C₃₀H₃₅NO₄: C, 76.08; H, 7.45; N, 2.96. Found: C, 76.18; H, 7.48; N, 2.87.

(vi) 6'-hydroxy-1-isopropyl-3,3,4'-trimethylspiro[indoline-2,8'-pyrano[2,3-f]benzopyran]-2' (7'H)-one (4c). Yield 68%, mp 214–215°C; IR ($\nu_{\max}/\text{cm}^{-1}$, nujol): 3160, 1685, 1660, 1615, 1580, 920. ¹H NMR (CDCl₃): δ isomer A: 1.18–1.83 (12H, m, 4Me), 2.34 (3H, s, CH₃), 3.84 (1H, m, CH), 5.42 (1H, br. s, OH), 5.81 (1H, d, H^{9'}, *J* 10.6), 6.16 (1H, s, H^{3'}), 6.77–7.41 (5H, m, Ar-H), 7.44 (1H, d, H^{10'}, *J* 10.6). Isomer B: 1.18–1.83 (12H, m, 4CH₃), 2.31 (3H, s, Me), 4.02 (1H, m, CH), 5.01 (1H, br. s, OH), 5.96 (1H, s, H^{3'}), 6.77–7.41 (5H, m, Ar-H), 8.80 (1H, br. s, CH=), 8.92 (1H, d, CH=, *J* 14.3). Ratio of isomers A : B (see Table 1). Anal. Calcd for C₂₅H₂₅NO₄: C, 74.42; H, 6.25; N, 3.47. Found: C, 74.35; H, 6.39; N, 3.40.

(vii) 6'-hydroxy-1-benzyl-3,3,4'-trimethylspiro[indoline-2,8'-pyrano[2,3-f]benzopyran]-2' (7'H)-one (4d). Yield 31%, mp 216–217°C; IR ($\nu_{\max}/\text{cm}^{-1}$, nujol): 3150, 1670, 1630, 1570, 928. ¹H NMR (CDCl₃): δ isomer A: 1.31, 1.34 (6H, s + s, 2 gem-(CH₃)₂), 2.35 (3H, s, CH₃), 4.21 (1H, d, CH₂, *J* 16.7), 4.63 (1H, d, CH₂, *J* 16.7), 5.40 (1H, br. s, OH), 5.89 (1H, d, H^{9'}, *J* 10.7), 6.16 (1H, s, H^{3'}), 6.37–7.55 (11H, m, Ar-H + H^{10'}). Isomer B: 1.25 (6H, s, 2 gem-(CH₃)₂), 1.89 (2H, s, NCH₂), 5.53 (1H, br. s, OH), 6.16 (1H, s, H^{3'}), 6.37–7.55 (10H, m, Ar-H), 8.49 (1H, br. s, CH=), 8.93 (1H, d, CH=, *J* 15.3). Ratio of isomers A : B (see Table 1). Anal. Calcd for C₂₉H₂₅NO₄: C, 77.14; H, 5.58; N, 3.10. Found: C, 77.07; H, 5.52; N, 3.19.

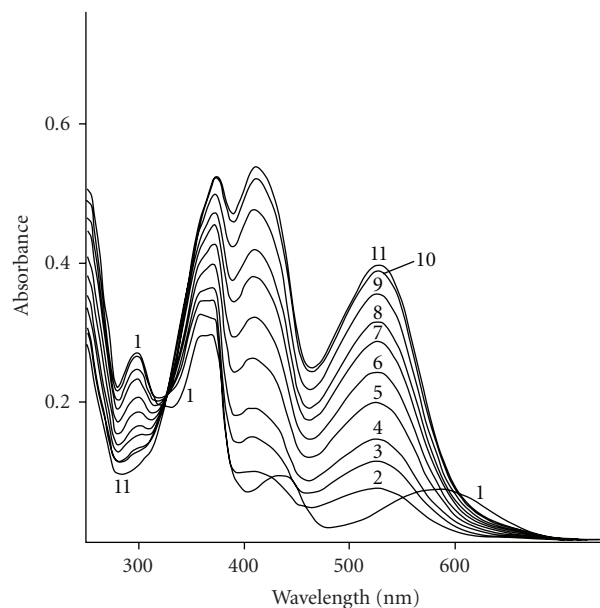


FIGURE 2: Absorption spectra of (4a) in dark conditions in acetonitrile solution before (1) and after addition of Mg(ClO₄)₂ (2); after 5 minutes (3); 10 minutes (4); 20 minutes (5); 30 minutes (6); 45 minutes (7); 60 minutes (8); 90 minutes (9); 120 minutes (10); 180 minutes (11) ([4a] = 2.5 × 10⁻⁵ M, [Mg²⁺] = 5 × 10⁻⁴ M).

(viii) 6'-hydroxy-1,3,3,5,4'-pentamethylspiro[indoline-2,8'-pyrano[2,3-f]benzopyran]-2' (7'H)-one (4e). Yield 29%, mp 276–277°C; IR ($\nu_{\max}/\text{cm}^{-1}$, nujol): 3170, 1685, 1610, 1570, 920. ¹H NMR (CDCl₃): δ isomer A: 1.20, 1.28 (6H,

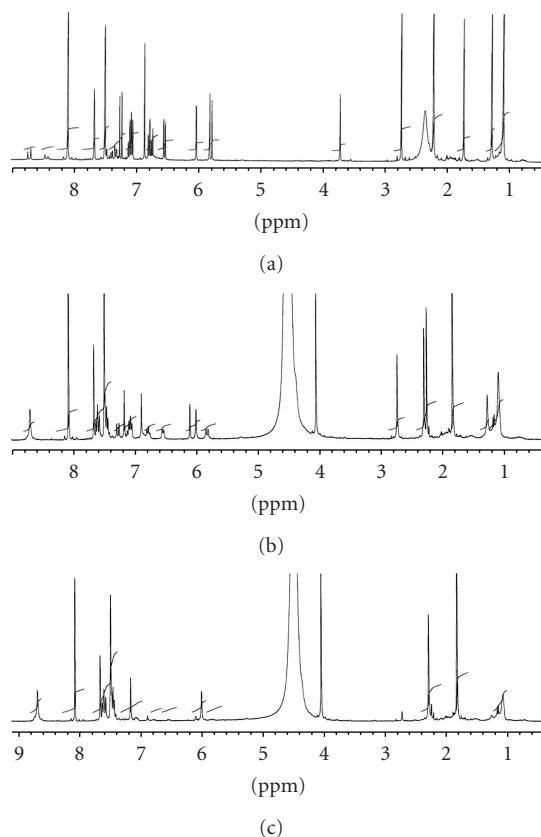


FIGURE 3: (a) ^1H NMR spectra of (4a) in dark conditions in CD_3CN -nitrobenzene- d_6 (1 : 1 v/v) and (b) in presence of $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ after 10 minutes; (c) 1 hour ($\nu_{\text{Mg}^{2+}}/\nu_{(4a)} = 5$).

s + s, 2 *gem*-(CH_3) $_2$), 2.35 (3H, s, CH_3), 2.48 (3H, s, CH_3), 2.73 (3H, s, NCH_3), 5.38 (1H, br. s, OH), 5.84 (1H, d, $\text{H}^{9'}$, J 10.7), 6.15 (1H, s, $\text{H}^{3'}$), 6.44–7.31 (4H, m, Ar-H), 7.46 (1H, d, $\text{H}^{10'}$, J 10.7). Isomer B: 1.25 (6H, s, 2 *gem* (CH_3) $_2$), 1.83 (6H, s, Me), 2.33 (3H, s, Me), 3.85 (3H, s, NMe), 5.99 (1H, s, $\text{H}^{3'}$), 6.44–7.31 (4H, m, Ar-H), 8.43 (1H, d, $\text{CH}=\text{C}$, J 15.1), 8.85 (1H, d, $\text{CH}=\text{C}$, J 15.1). Ratio of isomers A : B (see Table 1). Anal.Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4$: C, 74.02; H, 5.95; N, 3.60. Found: C, 74.19; H, 5.91; N, 3.55.

(ix) 6'-hydroxy-5-nitro-1,3,3,4'-tetramethylspiro[indoline-2,8'-pyrano[2,3-f]benzopyran]-2'-(7'H)-one (4f). Yield 25%, mp 281–282°C; IR ($\nu_{\text{max}}/\text{cm}^{-1}$, nujol): 3170, 1700, 1600, 1560, 970. ^1H NMR (CDCl_3): δ isomer A: 1.24, 1.37 (6H, s + s, 2 *gem*-(CH_3) $_2$), 2.36 (3H, s, CH_3), 2.90 (3H, s, NCH_3), 5.36 (1H, s, OH), 5.82 (1H, d, $\text{H}^{9'}$, J 10.5), 6.19 (1H, s, $\text{H}^{3'}$), 6.55–8.18 (6H, m, Ar-H + $\text{H}^{10'}$). Anal.Calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_6$: C, 65.71; H, 4.79; N, 6.66. Found: C, 65.70; H, 4.68; N, 6.78.

3.2. Spectral Properties and Complexation with Metal Ions.

Electronic absorption spectra of SPP (4f) in toluene, chloroform, and acetonitrile show broad absorption bands at 295 and 365 nm. For compounds (4a–e), the spectra contain also additional long-wavelength bands with maxima centered around 430 and 580 nm (Tables 1 and 2, Figure 1). For

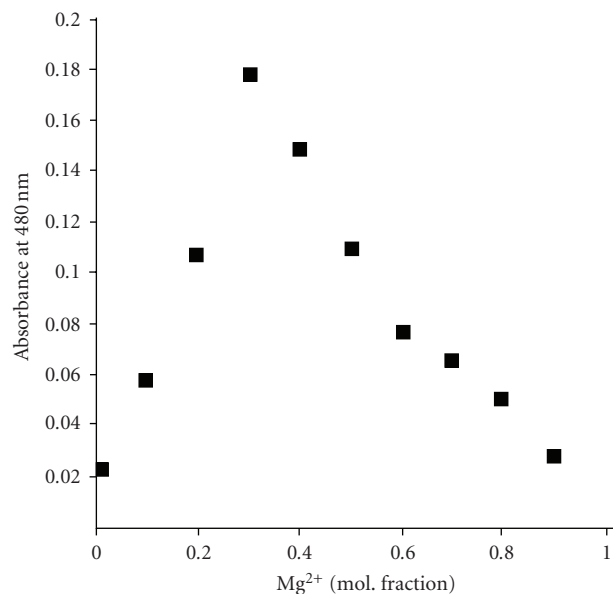


FIGURE 4: Continuous variation plot of the (4a)/ Mg^{2+} ($[\text{4a}] + [\text{Mg}^{2+}] = 5 \times 10^{-5}$ M) in acetonitrile.

SPPs (4a–e), the appearance of long-wavelength bands is accompanied by the additional proton signals of merocyanine isomers B in the ^1H NMR spectra. The long-wavelength bands in absorption spectra of cyclic ($\lambda_{\text{max}}^{\text{abs}} = 370\text{--}371$ nm) and merocyanine ($\lambda_{\text{max}}^{\text{abs}} = 580\text{--}650$ nm) forms correspond to $\text{S}_0 \rightarrow \text{S}_1$ transitions while the absorption bands of the cyclic form ($\lambda_{\text{max}}^{\text{abs}} = 294\text{--}299$ nm) and merocyanine form ($\lambda_{\text{max}}^{\text{abs}} = 456\text{--}471$ nm) correspond to $\text{S}_0 \rightarrow \text{S}_2$ transitions (Table 2). According to ^1H NMR and absorption spectroscopy data only SPP (4f) with an electron-withdrawing NO_2 -group exists in solution of chloroform entirely as the cyclic form A, while the solutions of (4a–e) contain both spirocyclic A and merocyanine B isomers (Scheme 2). The percentage of the merocyanine form in the equilibrium mixture was estimated using ^1H NMR data (Table 1). The largest content of form B is observed for the derivative (4e) with an electron-donating methyl group in position 5.

The irradiation of SPPs (4a–f) in acetonitrile ($\lambda_{\text{irr}} = 365$ nm) leads to increase in intensity of the long-wavelength absorption band in the regions of 430–471 and 580–653 nm due to the formation of merocyanine form which is thermally converted to the ring-closed isomer A (Figure 1).

Lifetimes of the photoinduced absorption bands of forms B allow to evaluate their thermal stability because content of merocyanine isomers in the equilibrium state in low-polarity solvent is substantially less than that of the cyclic isomers. Therefore, relaxation process rate constant is determined by the rate constant for the $\text{B} \rightarrow \text{A}$ reaction. The lowest lifetime of the photoinduced absorption was observed for compound (4f) with an electron-withdrawing group in 5th position and the highest lifetime for the compound (4e) with an electron donating group (Table 2). Analogous results were previously obtained for the spirooxazines [20].

TABLE 1: Long-wavelength maxima of (4) and parameters of (4A)-(4B) equilibrium in chloroform at 293 K.

Comp.	Absorption of (4), λ_{\max} , (nm), ($\epsilon \times 10^{-4}$, $1 \text{ mol}^{-1} \text{ cm}^{-1}$)	Content of form B, %	$K^{\circ} = [B]/[A]$
4a	448 (2.31), 595 (1.72)	28.6	0.401
4b	447 (2.35), 595 (1.78)	56.5	1.299
4c	447 (2.40), 596 (1.82)	23.5	0.307
4d	452 (3.07), 605 (2.04)	9.0	0.099
4e	448 (1.85), 593 (1.63)	63.0	1.702
4f	—	0	—

TABLE 2: Spectral characteristics of isomers A, B for (4a–f) and lifetimes for photoinduced absorption in toluene at 293 K.

Comp.	$^A \lambda_{\max}^{\text{abs}}$, (nm)	$^B \lambda_{\max}^{\text{abs}}$, (nm)	τ , s
4a	295, 354, 370	458, 614	161
4b	298, 355, 371	459, 617	205.7
4c	294, 354sh, 370	456, 619	170.9
4d	295, 354, 370	461, 617	44.1
4e	299, 356, 370	459, 614	257.7
4f	299, 355sh, 371	471, 653	6.5

Under dark conditions, addition of metal cations: Mg^{2+} (as perchlorate), Zn^{2+} , Ni^{2+} , Cu^{2+} , Hg^{2+} , Pd^{2+} (as acetates) shifts the equilibrium to the open form B with increase in the maximum of absorption band in the visible region due to the formation of complexes (5) (Figure 2). Position of the absorption maxima of these bands depends on the nature of the metal ion. For example, complex (4a) with Mg^{2+} is characterized by absorption bands at 369, 406, and 524 nm; with Zn^{2+} at 387, 440, and 550 nm; with Hg^{2+} at (372, 455, and 586 nm). The maxima of these absorption bands are hypsochromically shifted with respect to the free merocyanine absorption. The content of the complexes (5) is greatly raised under exposure of the solution to UV light ($\lambda_{\text{irr}} = 365 \text{ nm}$).

The structure of complexes (5) was estimated by IR spectroscopy. The IR-spectra of initial compounds contain broad absorption band of the hydroxyl group at $3100\text{--}3200 \text{ cm}^{-1}$ which slightly changes after complex formation, so the substitution of hydroxyl group protons was excluded.

^1H NMR, IR spectrometry and the spectrophotometric titration method were employed for the analysis of the complexation processes. The ^1H NMR spectral changes for (4a) upon the addition of Mg^{2+} ions in $\text{CD}_3\text{CN}/\text{nitrobenzene-}d_6$ (1 : 1 v/v) solution are shown in Figure 3.

In a metal-free solution, signals of both spiro- and merocyanine forms are present in the spectrum. This spectrum is characterized by a doublet centered at δ 5.80 ppm for the proton (4A)- $\text{H}^{9'}$, singlet at δ 6.1 ppm for the proton (4A)- $\text{H}^{3'}$ and two doublets at δ 8.4 ppm and 8.7 ppm for the protons (4B)- H^1 , (4B)- H^2 . The content of merocyanine isomer B was estimated as $\sim 16\%$. In the presence of metal salt chemical shifts of protons did not change significantly. After addition of $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ in darkness the appearance of a resonance signal at 6.00 ppm for the proton (4B)- $\text{H}^{3'}$ and substantial increase in the intensity of multiplet at δ 8.70 ppm for the protons (4B)- H^1 , (4B)- H^2

was observed (Figure 3). At the same time the intensity of the doublet at δ 5.80 ppm of the proton (4A)- $\text{H}^{9'}$ and singlet at δ 6.1 ppm for the proton (4A)- $\text{H}^{3'}$ was decreased. The data obtained indicate that the equilibrium is shifted to the merocyanine form due to the formation of complex (5) (Scheme 2). The content of the merocyanine form involved into the complexation with Mg^{2+} ion was estimated as $\sim 83\%$ (1 hour after salt addition).

The absorption at 480 nm (Figure 4) was chosen to determine the composition of the complex by the method of molar ratios [21]. The molar ratios plot shown in Figure 4 makes it evident that the composition of the (4a)- Mg^{2+} complex is 2 : 1.

4. Conclusions

Novel photochromic spiropyran containing 6'-hydroxy group in solutions exist as equilibrium mixture of spirocyclic and merocyanine isomers. The addition of metal salts leads to formation of complexes with merocyanine isomers and shifts the equilibrium to the ring-opened forms. The results obtained indicate that binding of cations is an important factor affecting position of the spiropyran-merocyanine equilibrium. These ionochromic compounds can be used as the basis for design of chemosensors for metal ions.

Acknowledgments

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