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Synthesis of New Spiropyranes and Study of the Effect of the Nature of Substituents on Their Photochromism and Complexation

L. D. Popov[a], A. O. Bulanov[a], E. A. Raspopova[a], A. N. Morozov[a], I. N. Scherbakov[a], O. I. Kobeleva[b], T. M. Valova[b], and V. A. Barachevskii[b]

[a] *Southern Federal University, ul. Zorge, 7, Rostov-on-Don, 344090 Russia*
e-mail: mrzv_61@mail.ru

[b] *Photochemistry Center, Russian Academy of Sciences, Moscow, Russia*

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Abstract—A series of new hydrazones based on 3,3-dimethyl-7-hydroxy-8-formyl-[2*H*]-1-benzopyran-2,1-[2]-oxaindane] with the substituents of different nature in the hydrazone moiety was synthesized. A comparative study of photochromism and complexation of the synthesized spiropyrans with a number of metal cations was carried out. Spectral and kinetic differences in photochromism and complexation of these compounds were revealed.

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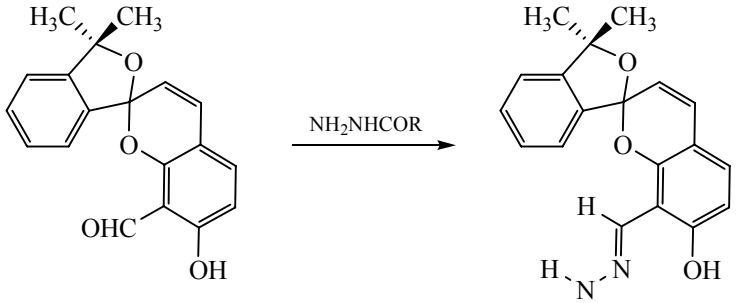
Spiropyrans comprise a large class of heterocyclic organic compounds capable of reversible structural transformation under the influence of light. Numerous spiropyran derivatives are described [1–4], including those containing azomethine and hydrazone groups [5–13]. A subclass of the least studied of these compounds are the derivatives of the spiropyrans of oxaindane series of type **I**. Previously, we obtained and explored some hydrazones based on 3,3-dimethyl-7-hydroxy-8-formyl-[2*H*]-1-benzopyran-2,1-[2]-oxaindane] [14]. This article is an extension of previous studies and is designed to continue the spectral-kinetic analysis of the effect of substituents nature on the photochromism and complexation of newly synthesized spiropyrans of this type.



I **IIa–IIc**

R = 4-MePh (**IIa**), 4-BrPh (**IIb**), ferrocenyl (**IIc**).

The synthesis of the compounds under study was carried out according to the scheme above.

The composition and structure of the compounds obtained were established on the basis of elemental analysis, IR, ^{1}H NMR, and electron spectroscopy.

The results of a comparative spectral-kinetic study of spiropyrans **IIa–IIc** are shown in the table and Figs. 1–4.

It is known that the spiropyrans of this type undergo photochromic transformations due to photo-

Spectral and kinetic characteristics of spiropyrans **IIa–IIc** and their complexes with metal ions in acetonitrile[a]

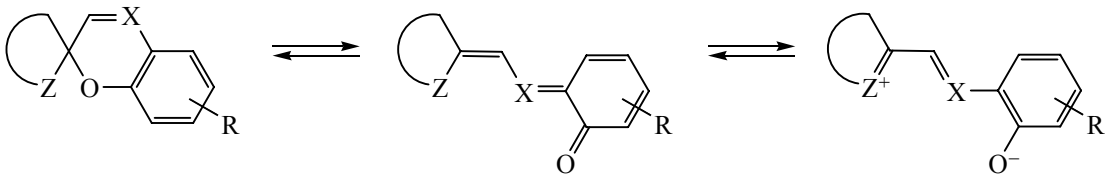
Comp. no.	Ion	[L]:[M]	λ_A^{max}, nm (D_A)	λ_B^{max}, nm (D_B)	ΔD_B^{phot}	k_{B-A}, s^{-1}
IIa	–		240 (0.8), 359 (0.8)	445	0.1	0.015
	Mg^{2+}	1:100	315 (1.4)	447 (1.4) 539 (2.1)	–	–
	Ca^{2+}	1:100	308 (1.4)	452 (1.2) 545 (1.2)	–	–
	Cu^{2+}	1:100	332 (1.2)	425 (0.6) 537 (2.2)	–	–
	Tb^{3+}	1:100	335 (1.1)	450 (1.2) 505 (2.1) 533 (2.5)	–	–
	Zn^{2+}	1:10	310 (1.2)	450 (0.9)	–	–
IIb	–		308 (1.2)	475	0.2	0.011
	Mg^{2+}	1:100	318 (1.1)	445 (1.0) 542 (1.7)	–	–
	Ca^{2+}	1:100	308 (1.1)	450 (0.9) 548 (1.0)	–	–
	Cu^{2+}	1:10	335 (1.0)	417 (0.6) 540 (1.9)	–	–
	Tb^{3+}	1:100	333 (0.9)	458 (1.2) 505 (1.9) 533 (2.1)	–	–
	Zn^{2+}	1:10	248 (0.8), 315 (0.9)	452 (0.8)	–	–
IIc	–		305 (1.1)	440	0.2	–
	Mg^{2+}	1:100	315 (1.0)	456 (1.0) 540 (1.4)	–	–
	Ca^{2+}	1:100	307 (1.0)	454 (0.9) 548 (0.8)	–	–
	Cu^{2+}	1:100	330 (0.7)	417 (0.5) 537 (1.7)	–	–
	Tb^{3+}	1:100	325 (0.8)	500 (2.1) 530 (1.7)	–	–
	Zn^{2+}	1:10	313 (0.8)	450 (0.9)	–	–

[a] λ_A^{max} and λ_B^{max} are the wavelengths of the absorption maxima of band of the initial and photoinduced (or complex) forms of spiropyrans, respectively; D_A and D_B are the optical densities at the maximum of the absorption band of the original form or the complex formed in the dark at introduction of metal ions in solution; ΔD_B^{phot} is the maximum of the optical density at the maximum of the absorption band of the photoinduced merocyanine form; k_{B-A}, s^{-1} is the rate constant of thermal relaxation in the dark; $\tau_{1/2}^{phd}$ is irreversible decrease of the ΔD_B value under the unfiltered radiation; L is photochromic ligand, Me is metal ion.

induced dissociation of C–O bond in the pyran heterocycle followed by reversible *cis-trans* isomerization [4].

Spiropyrans of oxaindane series differ from the well-known indoline series spiropyrans by higher resistance to the effects of radiation of different spectral composition, but they principally can be involved in thermo-, photo-, and solvatochromic transformations.

The absorption spectra of the initial cyclic and photoinduced forms of the spiropyran **IIb** (Fig. 1) differ from those of the spiropyran **IIa** by a red shift of 30 nm of the absorption band of merocyanine form and



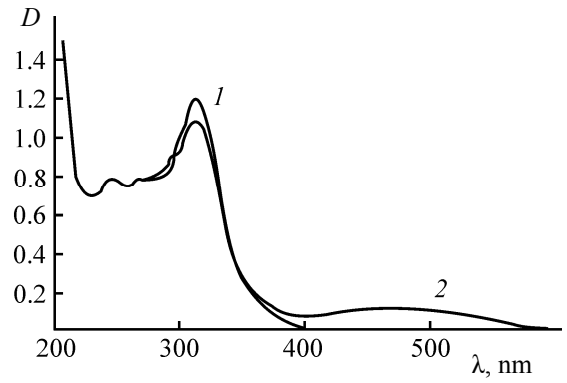


Fig. 1. The absorption spectra of solution of compound **IIb** in acetonitrile before (*1*) and after (*2*) irradiation with UV light through the filter UFS-1.

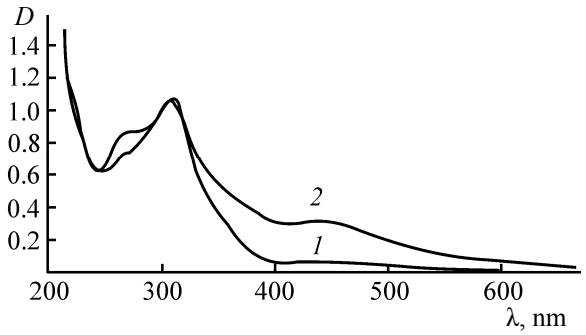


Fig. 2. Absorption spectra of solution of compound **IIc** in acetonitrile (*1*) before and (*2*) after irradiation with UV light through the filter UFS-1.

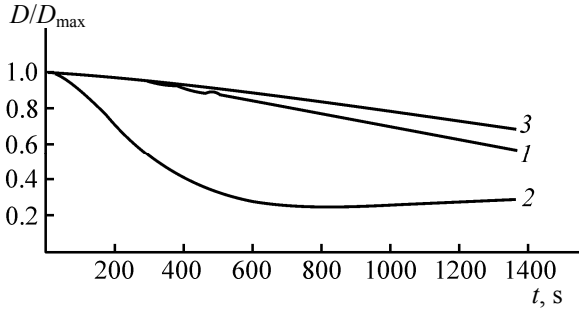


Fig. 3. Normalized kinetic curves of photodegradation of compounds (*1*) **IIa**, (*2*) **IIb**, and (*3*) **IIc**.

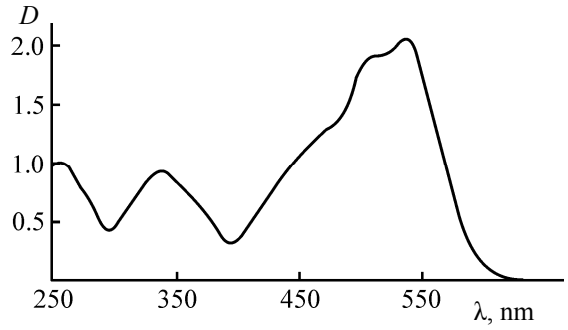


Fig. 4. Absorption spectra of compounds **IIb** in acetonitrile in the presence of cations Tb^{3+}.

a blue shift of the absorption band of the cyclic form. They are characterized by almost the same sensitivity estimated from the photo-induced optical density in a state of photo-equilibrium (ΔD_B^{phot}), and have comparable dark relaxation constants (see the table).

Spiropyran **IIc** with ferrocenyl substituent differs sharply from the above spiropyran **IIb** by a large blue shift of the absorption band of merocyanine form to 440 nm, which is almost identical to the corresponding absorption band of spiropyran **IIa** (Fig. 2). It should be noted that the original ferrocene also has absorption band in this area with λ_{max} = 440 nm. The above assumption is based on the fact that the intensity of this band (with respect to the band with λ_{max} = 310 nm) significantly increases after irradiation. Thus, we can assume that this band is a superposition of two bands due to *d–d* transition in the iron atom in ferrocene and related photochemical transformation.

Spiropyran **IIc** is more resistant to irreversible phototransformation compared to compounds **IIa** and **IIb** (Fig. 3).

A characteristic feature of the spiropyrans **IIa** and **IIb** is the formation of complexes with metal ions insensitive to light directly at the time of introduction the metals in the photochromic acetonitrile solution. The absorption spectra of the complexes of these compounds with the ions Mg^{2+}, Ca^{2+}, Cu^{2+}, Tb^{3+} shows two absorption bands, whose ratio of the intensity depends on the nature of the metal (see the table). Typical absorption spectra of these complexes are shown in Fig. 4 for compound **IIb** with Tb^{3+} ion.

According to the measured Jobs curve (Fig. 5), the composition of the complex formed by metal (Me) and ligand L (compound **IIb**) is 1:1

The same composition was found for the complexes of compound **IIb** with ions Cu^{2+} and Zn^{2+}. In the case of Zn^{2+} ions only one short-wavelength absorption band of the complex formed is spectrally manifested.

Spectral manifestations of the formation of light insensitive metal complexes was detected also at the dark complexation of **IIc** molecules with the ions Mg^{2+}, Ca^{2+}, Cu^{2+}, Tb^{3+}, and Zn^{2+}. However, unlike the

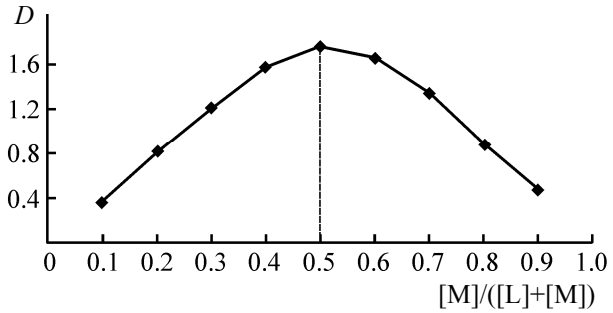


Fig. 5. The dependence of *D* on the [Me]/([L]+[Me]) ratio of compound **IIb** in the presence of Tb^{3+} in acetonitrile, measured at the maximum of the absorption band of the complex at 535 nm.

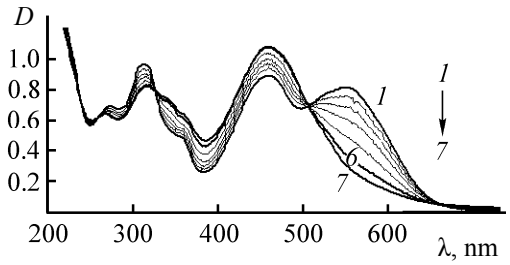


Fig. 6. The absorption spectra of compounds **IIc** in acetonitrile in the presence of Ca^{2+} cations (*1*) before, after irradiation with UV light through the filter (*2–6*) UFS-1 and (*7*) after the subsequent keeping in the dark.

compounds **IIa** and **IIb,** for molecules of spiropyran **IIc** pronounced photoinduced spectral changes in the presence of Mg^{2+}, Ca^{2+} ions were observed (Fig. 6).

Compound **IIc** forms the 1:1 complexes with all the metal ions except for Zn^{2+}. Based on the Jobs graph (Fig. 7), compound **IIc** forms MeL_2 complexes with Zn^{2+} ions.

We believe that the results of the spectral and kinetic studies indicate the formation of dark metal complexes whose structure, according to the spectral manifestation, depends on the nature of the ions, which interact with the molecules of photochromic compounds. For molecules of spiropyran **IIc** interacting with the ions Ca^{2+} and Mg^{2+} the exposure to light can lead to partial restructuring of the complexes.

Thus, in the study three new spiropyrans were synthesized. By spectral methods the formation in the dark of the light-insensitive complexes between the molecules of spiropyrans **IIa–IIc** and metal ions was established, therewith the structure of the complexes was determined by the nature of the ions. For spiropyran **IIc** and Ca^{2+} and Mg^{2+} irreversible photochemical rearrangement of the complexes was found. The identified spectral differences of the resulting complexes can be used to determine the content and concentration of these ions at the medical diagnostics.

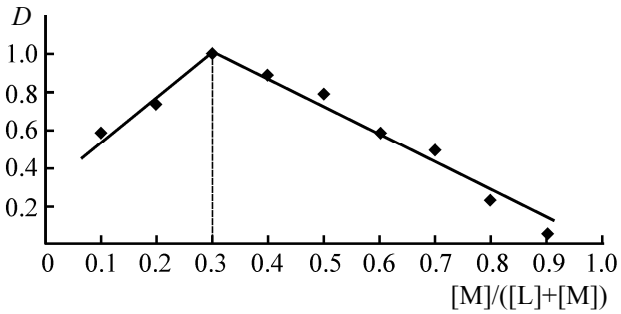


Fig. 7. The dependence of *D* on the [Me]/([L]+[Me]) ratio for compound **IIc** in the presence of Zn^{2+} ions in the mixed solvent acetonitrile–water, measured at the maximum of the absorption band of the complexes at 450 nm.

EXPERIMENTAL

IR spectra were recorded on a Varian Scimitar instrument in the range of 400–4000 cm^{-1}. The ^1H NMR spectra were taken in DMSO-d_6 on a Varian Unity 300 spectrometer (300 MHz).

The study of complex formation in solution was carried out in the presence of metal salts $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Cu(ClO_4)_2$, $Tb(NO_3)_3$, $ZnCl_2$, in the ratio of L:Me 1:100, 1:10, 1:1. The solvent was acetonitrile from Aldrich. The formation of complexes of the ligands with Zn^{+2} ions is slow, therefore the solutions of the ligands in the presence of metal ions were kept for a day, and then the spectroscopic measurements were performed. For other metals measurements were taken 15–20 min after mixing the solutions.

Spectrophotometric measurement (photostationary spectra) of the compounds in solution, kinetics of photocolorization, photodiscoloration, and photodegradation, as well as thermal discoloration of the photoinduced forms were carried out using a Cary 50 bio spectrophotometer. The maxima and bends (shoulders) of the absorption bands were determined directly from the absorption spectra. Their accuracy was limited by the spectrophotometer resolution 1.5 nm.

Working concentration of the solution was $c = 2\times10^{-4}$ M. For the measurements were used quartz cells of 0.2 cm thickness. The irradiation was carried

out with unfiltered and filtered light of a DRSh-250 and a Hamamatsu LC-4 lamps.

Ferrocenecarboxylic acid hydrazide [14]. 5 g of methyl ferrocenecarboxylate was mixed with an excess of hydrazine hydrate (1:100). The mixture first was heated until dissolution, and then for another 15 min, then cooled with water and ice. Brown precipitate was filtered off and recrystallized from ethanol. Yield 2.6 g (50%), mp 180°C.

3,3-Dimethyl-7-hydroxy-8-formyl[2*H*]-1-benzopyran-2,1-[2]-oxaindane] [15]. To a suspension of 2.6 g of 1-(2,4-dihydroxy-3-formyl)dimethyl-3*H*-isobenzofurylium perchlorate in diethyl ether was added 1.5 ml of triethylamine, and the mixture was left overnight. Ether was evaporated, yellow residue was recrystallized from alcohol. Yield 1.2 g (61%), mp 104°C. IR spectrum (mineral oil), ν, cm^{-1}: 3347 (OH), 1654 (C=O), 1605 (C–C) 1616, 1580 (C=C arom.), 982 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 1.45 s (3H, 3'-CH_3); 1.62 s (3H, 3'-CH_3); 5.62–7.55 m (8H, arom.) 10.09 s (1H, CHO); 11.32 s (1H, OH). Found, %: C 73.7, H 4.9. $C_{19}H_{16}O_4$. Calculated, %: C 74.0, H 5.2.

3,3-Dimethyl-7-hydroxy-8-formyl[2*H*]-1-benzopyran-2,1-[2]-oxaindane] ferrocenoylhydrazone (IIc). To a solution of 0.32 g of 3,3-dimethyl-7-hydroxy-8-formyl[2*H*]-1-benzopyran-2,1-[2]-oxaindane] [16] in 6 ml of ethanol was poured a hot solution of 0.24 g of ferrocenecarboxylic acid hydrazide in 6 ml of ethanol. The solution becomes brown. The mixture was boiled for 15 min, the precipitated brown crystalline substance was filtered off while hot, then washed twice with boiling ethanol, and recrystallized from acetonitrile. Yield 0.22 g (40%), mp 185–187°C. IR spectrum (mineral oil), ν, cm^{-1}: 3640 (O–H); 3220, 3402 (N–H), 1641 (C=O), 1612 (C=N). ^{1}H NMR spectrum, δ, ppm, *J*, Hz: 1.48 s (3H, 3'-CH_3), 1.65 s (3H, 3'-CH_3), 4.18 s (5H, C_5H_5), 4.45 s (2H, 2-H–C_5H_3), 4.86 s (2H, 3-H–C_5H_3), 5.76 d (1H, 3-H, *J* = 9.60), 6.59 d (1H, 6'-H, *J* = 8.42), 6.88 d (1H, 8-H, *J* = 9.60), 7.28 d (1H, 4'-H, *J* = 8.42), 7.42 m (4H, C_6H_4), 8.70 s (1H, 7-H), 11.59 s (1H, NH); 12.41 s (1H, OH), Found, %: C 67.8, H 4.7, N 10.3, Fe 10.4. $C_{30}H_{26}FeN_2O_4$. Calculated, %: C 67.4, H 4.8, N 10.5, Fe 10.5.

3,3-Dimethyl-7-hydroxy-8-formyl[2*H*]-1-benzopyran-2,1-[2]-oxaindane] *p*-methylbenzoylhydrazone (IIa) was synthesized according to [16]. Yield 49%, mp 163°C. IR spectrum, ν, cm^{-1}: 3391 (OH), 3247 (NH), 1651 (C=O), 1615 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.48 s (3H, 3'-CH_3), 1.64 s (3H, 3'-Me), 2.35 s (3H, Ph-CH_3) 5.74 d (1H, 3-ArH, $J_{3,4}$ = 9.60 Hz), 6.59 d (1H, 6-ArH, $J_{5,6}$ = 8.40 Hz), 6.89 d (1H, 4-ArH, $J_{3,4}$ = 9.60 Hz), 7.29 d (1H, 5-ArH, $J_{5,6}$ = 8.40 Hz), 7.31–7.50 m (4H, 4',5',6',7'-ArH), 7.78 d (2H, 2,6-ArH, $J_{2,3}$ = $J_{6,5}$ = 8.10), 8.77 s (1H, =CH), 12.18 s, 12.37 s (1H, 1H, NH, OH). Found, %: C 74.3, H 5.3, N 6.1, $C_{27}H_{24}N_2O_4$. Calculated, %: C 73.6, H 5.5, N 6.4.

3,3-Dimethyl-7-hydroxy-8-formyl[2*H*]-1-benzopyran-2,1-[2]-oxaindane] *p*-bromobenzoylhydrazone (IIb) was synthesized according to [16]. Yield 59%, mp 163°C. IR spectrum, ν, cm^{-1}: 3390 (OH), 3259 (NH), 1656 (C=O), 1617 (C=N). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.48 s (3H, 3'-CH_3), 1.64 s (3H, 3'-Me), 5.76 d (1H, 3-ArH, $J_{3,4}$ = 9.60 Hz), 6.60 d (1H, 6-ArH, $J_{5,6}$ = 8.40 Hz), 6.90 d (1H, 4-ArH, $J_{3,4}$ = 9.60 Hz), 7.30 d (1H, 5-ArH, $J_{5,6}$ = 8.40 Hz), 7.30–7.50 m (4H, 4',5',6',7'-ArH), 7.72 d (2H, 3,5-ArH); 7.83 d (2H, 2,6-ArH, $J_{2,3}$ = $J_{6,5}$ = 8.70), 8.77 s (1H, CH=), 12.27 br.s, 12.31 br.s (1H, 1H, NH, OH). Found, %: C 61.7, H 4.3, N 5.4. $C_{26}H_{21}BrN_2O_4$. Calculated, %: C 61.8, H 4.2, N 5.5.

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