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Preparation, Photochromism, and Complex Formation with Metal Ions of Pyrazolylazomethine Derivative of Spirooxazine

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Abstract—New hybrid spirooxazine has been prepared, based on amino-substituted spironaphthoxazine and pyrazolone. Photochromism and photoinduced complex formation with metal ions of the prepared compound has been studied. The effects of solvent polarity and the metal ion nature on the spirooxazine photochromism and the complex formation ability have been elucidated.

Keywords: spirooxazine, photochromism, complex formation, UV spectroscopy

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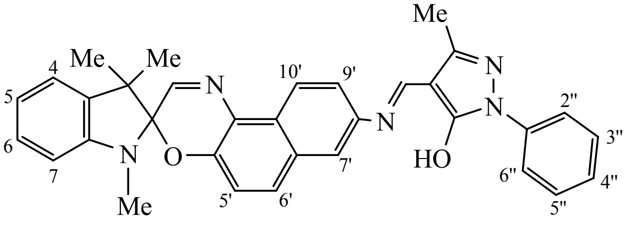
Requirements for new functional photochromic system determine the recently emerged interest to hybrid photochromic compounds [1–4]. Previously we reported on preparation and properties of spirooxazine derivatives containing salicylidenimine [5], 2-tosylaminobenzylidenimine [6], and azobenzenesalicylidenimine [7] fragments. We have demonstrated that complex formation of metal ions with the merocyanine form increases lifetime of the latter, and the complex formation efficiency is affected by electrostatic properties of the metal cation, in the cases of both the initial and the merocyanine form [5]. Extending these studies, herein we report on preparation and properties (photochromism and complex formation) of the pyrazolylmethine derivative of spirooxazine, prepared for the first time.

Compound **I** was prepared via condensation of 4-formyl-5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole with 8'-amino-1,3,3-trimethylspiro (2*H*-indole-2,3'-3*H*-naphtho[2,1-*b*][1,4]oxazine) [8] (Scheme 1).

Structure of compound **I** was elucidated from ^{1}H NMR data. Namely, molecules of **I** in $CDCl_3$ existed in the form of spirocyclic compound with hydroxyazomethine fragment in the enol form.

Photoinduced changes of absorption spectrum of compound **I** in the low-polar toluene are illustrated by Fig. 1 and described in Table 1.

Scheme 1.



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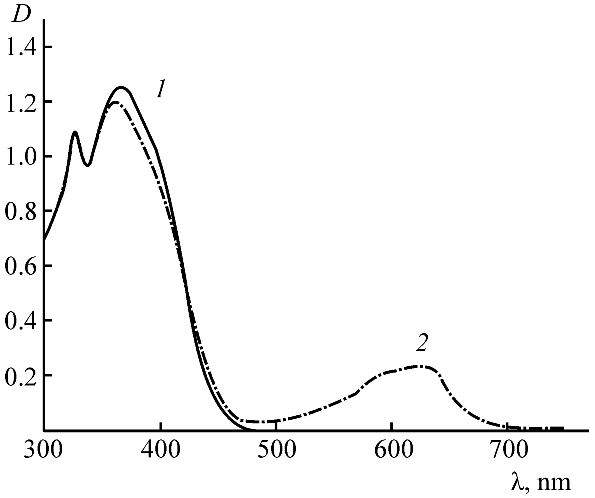


Fig. 1. Absorption spectra of solutions of compound **I** in toluene: initial state (*1*) under UV irradiation through the UFS-1 filter (*2*).

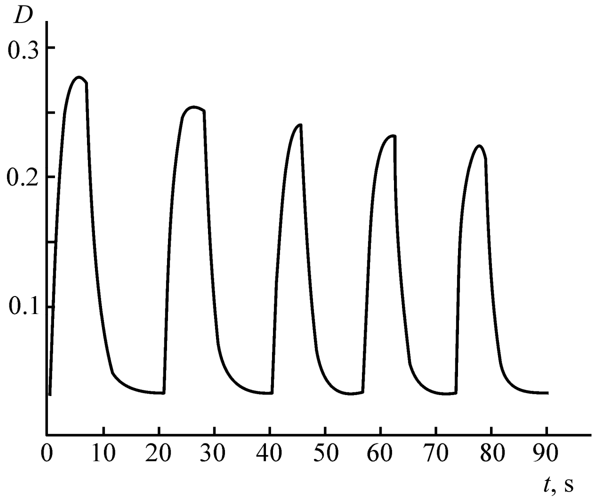


Fig. 2. Kinetic curves of coloration under UV irradiation through the UFS-1 filter and of spontaneous dark relaxation of compound **I** in toluene. Absorbance at 625 nm was monitored.

From the collected data it is to be seen that, similarly to the majority of spirooxazines, UV spectrum of compound **I** in toluene revealed absorption bands at 325 and 363 nm (Fig. 1, curve *1*). Upon UV irradiation, intensity of those bands went down, and a new absorption band appeared in the visible spectral range, at 625 nm (Fig. 1, curve *2*).

The compound **I** color change upon UV irradiation was reversible (Fig. 2). However, the repeated irradiation cycles led to decrease of the photoinduced absorption amplitude, thus pointing at steady degradation of the photochromic properties.

Such photochromism is typical of spirooxazines [5].

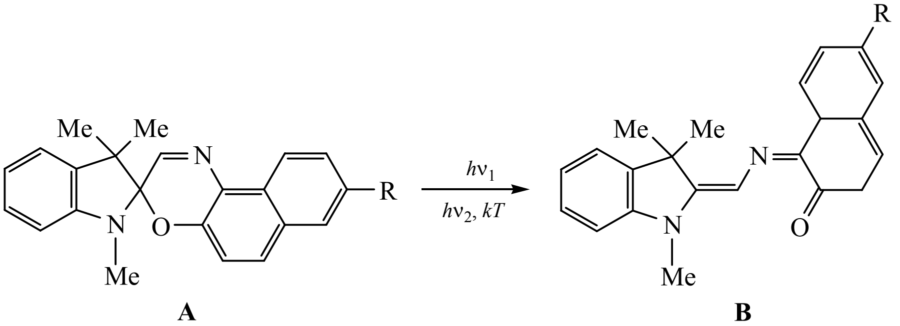
When the polar solvent (acetonitrile) was used instead of the low-polar toluene, no significant changes in the absorption spectra of the cyclic (**A**) and the merocyanine (**B**) forms of the compound **I** were revealed (Table 1); the sensitivity towards irradiation was the same as well (the irradiation sensitivity could be estimated, for instance, as ratio of the photoinduced absorbance change at the merocyanine absorption maximum to absorbance of the cyclic form at the long-wave maximum, ($\Delta D_B^{max}/D_A^{max}$). However, in the polar solvent, spontaneous discoloration of the merocyanine form was faster, and the stability of compound **I** with respect to the irreversible photoinduced transformation was enhanced (Scheme 2).

Table 1. Spectral and kinetic parameters of photochromic transformations of the hybrid spirooxazine **I**[a]

Растворитель	λ_A^{max}, nm	ε_A, L mol^{-1} cm^{-1}	λ_B^{max}, nm	$\Delta D_B^{max}/D_A^{max}$	k_{dd}, s^{-1}	$t_{0.5}$, s
Toluene	325	27000	625	0.2	0.58	25
	363	31250				
Acetonitrile	245	20200	625	0.2	1.16	59
	322	14000				
	363	16000				

[a] λ_A^{max} and λ_B^{max}, maximum of absorption bands of the initial cyclic form and of the photoinduced merocyanine form, respectively; ε, molar absorptivity of the initial cyclic isomer; D_A^{max} and ΔD_B^{max}, absorbance at the maximum of the absorption band of the initial cyclic form and the photoinduced change of absorbance at maximum of the absorption band of the merocyanine form, respectively; k_{dd}, rate constant of dark discoloration of the photoinduced merocyanine form at 25°C; $t_{0.5}$, time of two-fold irreversible decrease of D_B^{max} under irradiation with non-filtered light.

Scheme 2.



Kinetic study of the photoinduced complex formation of **I** with metal ions by means of spectrophotometry (Table 2 and Fig. 3) demonstrated that in the cases of some ions the complex formation was accompanied with red shift of absorption band of the photoinduced merocyanine form.

The almost equal rate constants of the dark discoloration and the close characteristic times of photodegradation of compound **I** in acetonitrile without any ions and in the presence of Sr^{2+} (Tables 1 and 2) demonstrated that Sr^{2+} did not form complex with compound **I**.

Addition of Mg^{2+} to the solution slowed down the dark discoloration, enhancing sensitivity of compound **I** to UV irradiation (Table 2), its stability with respect to irreversible photoinduced changes being enhanced as well. Hence, magnesium ions likely formed the complex with the merocyanine form of compound **I**.

Addition of Zn^{2+} to the solution slowed down the dark discoloration of the merocyanine form; at the same time, red shift of its absorption band (by 8 nm) was observed (Fig. 2 and Table 2). The more efficient complex formation led to the enhanced photoinduced degradation (Table 2).

The most efficient interaction was observed between compound **I** and Tb^{3+} ions, being reflected in the more significant red shift of the merocyanine form absorption (by 20 nm) as well as sharply slowing down

Table 2. Spectral and kinetic parameters of photochromic transformations of the hybrid spirooxazine **I** in acetonitrile in the presence of metal ions

Cation	λ_A^{max}, nm	λ_B^{max}, nm	$\Delta D_B^{max}/D_A^{max}$	k_{dd}, s^{-1}	$t_{0.5}$, s
Sr^{2+}	244	625	0.2	1.25	51
	322				
	364				
Mg^{2+}	242	625	0.6	0.22	73
	320				
	364				
Zn^{2+}	359	617	0.6	0.32	33
Tb^{3+}	320	605	0.6	0.04	1
	363				
Ni^{2+}	362	540			
		587			
		619	0.3	0.04	21
Cu^{2+}	326	~620	<0.005	–	68
	462				

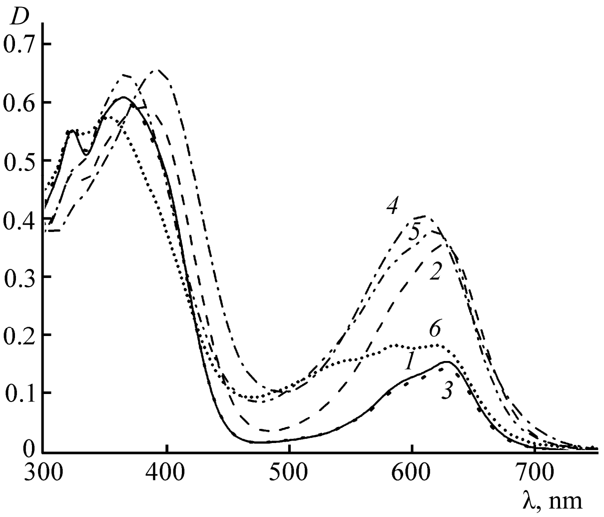


Fig. 3. Absorbance spectra of the solution of the photoinduced form of the hybrid spirooxazine **I** in toluene without metal ions (*1*) and in the presence of salt: magnesium perchlorate (*2*), strontium perchlorate (*3*), terbium nitrate (*4*), zinc chloride (*5*), and nickel perchlorate (*6*).

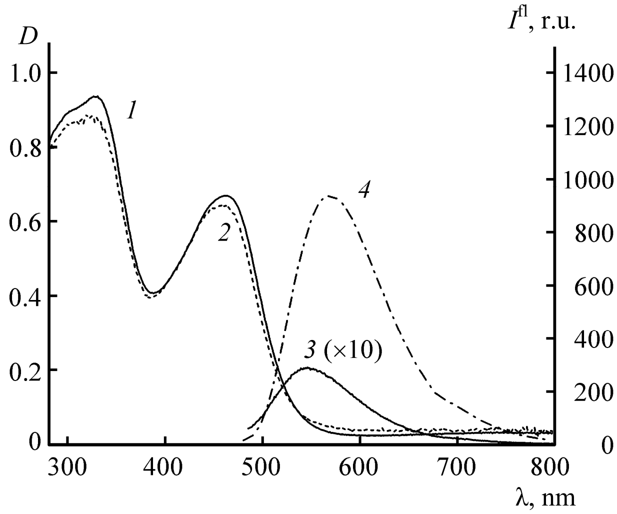


Fig. 4. Absorbance spectra (*1*, *2*) and fluorescence (excitation at 465 nm) spectra (*3*, *4*) of solutions of the hybrid spirooxazine I in acetonitrile in the presence of Cu^{2+} ions before (*1*, *3*) and after (*2*, *4*) UV irradiation.

of its dark discoloration (Table 2). Such a strong interaction accelerated the photoinduced degradation of compound **I** (Table 2).

Addition of Ni^{2+} to the solution led to red shift of the photoinduced form absorption, decrease of rate constant of its dark discoloration, and enhancement of the photoinduced degradation efficiency. On top of that, new bands appeared in the photoinduced absorption spectrum, at 587 and 540 nm.

In contrast to the above-discussed complexes revealing certain photochromism, the colored complexes with Cu^{2+} were formed immediately after the ions addition to the solution (Fig. 4); in particular, new absorption band appeared in the spectrum, at 465 nm. The photochromic transformation efficiency was simultaneously decreased. However, UV irradiation significantly enhanced the fluorescence excited by light with wavelength corresponding to the new complex absorption band.

Figure 5 displays the normalized kinetic curves of photoinduced degradation of compound **I** in its individual solutions and in the presence of metal ions.

From Fig. 5 and Table 1 it is to be seen that pure compound **I** in acetonitrile and its complex with Mg^{2+} were the most stable with respect to irreversible changes.

The observed difference in the spectral and kinetic properties of compound **I** and its complexes with various metal ions can be explained by the complex formation via the two complexing sites: phenolic oxygen of the photoinduced merocyanine form and pyrazolylazomethine fragment.

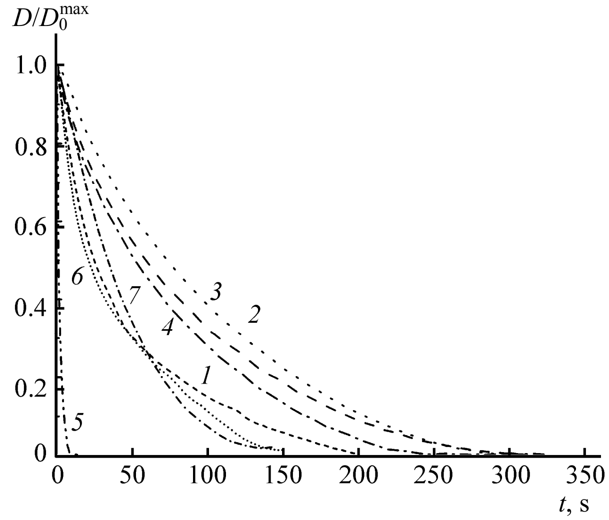


Fig. 5. Normalized kinetic curves of photoinduced degradation of spirooxazine **I** in toluene (*1*), in acetonitrile (*2*); in acetonitrile in the presence of salts: magnesium perchlorate (*3*), strontium perchlorate (*4*), terbium nitrate (*5*), nickel perchlorate (*6*), and zinc chloride (*7*) under irradiation with non-filtered light. The absorbance was followed at 605 nm (*5*), 620 nm (*6*), or in the absorption maximum of the merocyanine form (*1–4*, *7*).

To conclude, the prepared hybrid compound **I** revealed photochromic properties typical of spirooxazines. Its spectral and kinetic properties were sensitive to the solvent nature as well as to the introduced metal ions, making it promising for determination of metal ions in their solutions.

EXPERIMENTAL

Acetonitrile (99.9%) and toluene (99.8%) (Aldrich) were used as solvents. 1,3-Dihydro-8'-amino-1,3,3-trimethylspiro {2*H*-indlole-2,3'-(3*H*)-naphtho[2,1-*b*]-[1,4]oxazine} was prepared as described elsewhere [4].

The complex formation was studied in the presence of the following salts: $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, $Ni(ClO_4)_2$, and $Tb(NO_3)_3$ (ratio of **I** to the metal ion of 1 : 200) as well as $Cu(NO_3)_2$ and $ZnCl_2$ (1 : 20).

Spectrophotometric studies in the stationary conditions and the kinetic studies were performed using the Varian Cary 50 bio spectrophotometer (quartz cell, optical path of 2 cm). Concentration of **I** was of 2×10^{-4} mol/L (in toluene) and of 1×10^{-4} mol/L (in acetonitrile). UV irradiation was performed with the LC-4 mercury–xenon lamp (Hamamatsu). The photochromic transitions were studied using the light filtered through the UFS filter, at average power of 143 W/m^2.

1,3-Dihydro-8'-(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-ylmethylenimino)-1,3,3-trimethylspiro-{2*H*-indole-2,3'-(3*H*)-naphtho[2,1-*b*][1,4]oxazine} (I). Hot solution of 0.21 g (1 mmol) of 4-formyl-5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole in 5 mL of anhydrous ethanol was added to hot solution of 0.343 g (1 mmol) of 1,3-dihydro-8'-amino-1,3,3-trimethylspiro-{2*H*-indole-2,3'-(3*H*)-naphtho[2,1-*b*][1,4]oxazine} in 15 mL of anhydrous ethanol, and the mixture was refluxed during 3 h. Then, the mixture was cooled down to room temperature; the yellow precipitate was filtered off and washed with hot ethanol. Yield 0.4 g (76%), mp 269–271°C, R_f 0.67 (chloroform–acetone 9 : 1). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 1.36 s [3H, $C(CH_3)_2$], 1.37 s [3H, $C(CH_3)_2$], 2.38 s (3H, CH_3), 2.78 s (3H, NCH_3), 6.60 d (1H, H^7, *J* 7.4), 6.92 t (1H, H^5, *J* 7.3), 7.05 d (1H, $H^{6'}$, *J* 9.1), 7.08 d (1H, H^4, *J* 7.4), 7.18 t (1H, H^6, *J* 7.4), 7.24 m (1H, $H^{4''}$), 7.43 t (2H, $H^{3''}$, $H^{5''}$, *J* 7.9), 7.49 d.d (1H, $H^{9'}$, J_1 9.0, J_2 2.0), 7.55 d (1H, $H^{7'}$, *J* 2.0), 7.64 d (1H, $H^{5'}$, *J* 9.1), 7.78 s (1H, CH=N), 8.03 d (2H, $H^{2''}$, $H^{6''}$, *J* 8.0), 8.08 s (1H, CH=N), 8.63 d (1H, $H^{10'}$, *J* 9.2), 11.77 br.s (1H, OH). Found, %: C 75.04; H 5.60; N 13.06. $C_{33}H_{29}N_5O_2$. Calculated, %: C 75.12; H 5.54; N 13.27.

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