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Synthesis, photochromism, and complex-forming ability of *p*-tosylaminobenzylideneaminospironaphthooxazine

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New hybrid spirooxazine was synthesized from the 8´-amino-substituted spironaphthooxazine and 2-(*p*-tosylamino)benzaldehyde. Photochromism and the complex-forming ability toward Mg^{2+}, Ba^{2+}, La^{3+}, and Tb^{3+} ions of the synthesized compound and initial 8´-aminospironaphthooxazine were studied in comparison. The spectral kinetic differences in the photochromism and complex formation of these compounds were revealed.

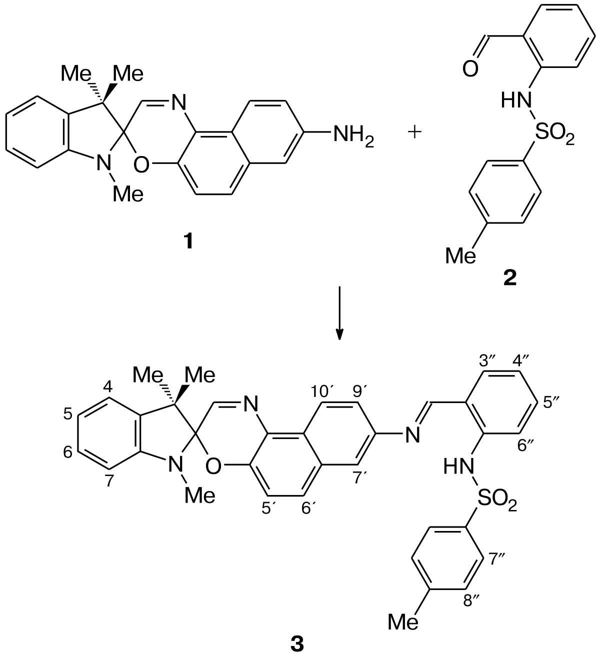
Key words: photochromism, spirooxazine, azomethine, absorption spectra, kinetics of phototransformations, complex formation with metal ions.

Interest in studying hybrid photochromic compounds has increased in the recent years due to the search for ways of extension of functional potentialities of photochromic systems.

We have previously[1—4] synthesized the spironaphthooxazine derivatives containing the salicylideneamine fragment capable of the photoinduced intramolecular proton transfer in the excited state and complex formation. The complex formation of the photoinduced merocyanine form of this compound was shown to increase the lifetime of this form, and the efficiency of complex formation of both the initial and merocyanine forms of this compound depends on the electrostatic properties of the metal cations.[4] The intramolecular processes were studied by femtosecond laser spectroscopy.[5] It was found that photon absorption results in two independent photochemical processes: intramolecular proton transfer in the excited state in the salicylidene fragment with the formation of the keto tautomer and photochromic transformations including C_{spiro}—O bond photodissociation in the oxazine fragment of the spiropyran system followed by the thermal formation of the colored *trans*-isomer of the merocyanine form. The coherent effects were also found, and a possibility of coherent control of the yield of photoreaction products by the change in the phase modulation of the exciting pulse was demonstrated.

The present work is devoted to the comparative spectral kinetic study of the photochromism and complex-forming ability toward selected metal ions of 8´-amino-

Scheme 1



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substituted spironaphthooxazine **1** and Schiff base **3**, which was synthesized for the first time from compound **1** and 2-(*p*-tosylamino)benzaldehyde (**2**) (Scheme 1).

Amino-substituted spironaphthooxazine **1** was synthesized using a known procedure,[6] and 2-(*p*-tosylamino)-benzaldehyde (**2**) was synthesized by a described procedure.[7] The structure of compound **3** was determined by IR spectroscopy, NMR spectroscopy, and elemental analysis (see Experimental).

We recorded the absorption spectra of the initial and photoinduced forms of compounds **1** and **3** in toluene and acetonitrile (Table 1, Figs 1 and 2). It was found that the both compounds manifest the photochromic properties, *i.e.*, undergo the photochromic transformations between the initial spiropyran (**A**) and photoinduced merocyanine (**B**) forms (Scheme 2).

Scheme 2

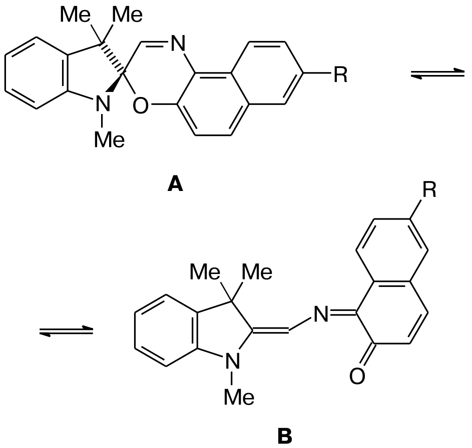


Table 1. Spectral kinetic characteristics of the photochromic transformations of spironaphthooxazines **1** and **3**

Solvent	Metal ion	λ_A^{max}	λ_B^{max}	ΔD^{ph}	k_{ddc} /s^{-1}	$T_{0.5}^{phd}$ /s
		nm				
		Spironaphthooxazine **1**				
Toluene	—	328, 390	615	0.8	0.850	73.5
MeCN	—	325, 390	625	0.25	1.400	614
MeCN	Mg^{2+}	—	640	—	—	—
MeCN	La^{3+}	—	625	—	—	—
MeCN	Tb^{3+}	—	625	—	—	—
		Spironaphthooxazine **3**				
Toluene	—	324, 390	590	0.1	0.620	510
MeCN	—	318, 390	623	0.5	1.570	151
MeCN	Ba^{2+}	318, 390	622	0.7	0.650	176
MeCN	Mg^{2+}	318, 390	620	0.9	0.300	160
MeCN	La^{3+}	316, 390	615	1.2	0.018	53.3
MeCN	Tb^{3+}	316, 390	605	1.2	0.003	36.4

Note: λ_A^{max} and λ_B^{max} are the wavelengths of the absorption band maxima of the initial (**A**) and photoinduced (**B**) forms; ΔD^{ph} is the photoinduced change in the absorbance at the absorption band maximum of the form **B** in the equilibrium state; k_{ddc} is the rate constant of spontaneous decoloration of the form **B** measured by the change in the absorbance in the dark at the maximum of the absorption band of the form **B** at 25 °C; $T_{0.5}^{phd}$ is the time during which the photoinduced absorbance at the absorption band maximum of the form **B** is halved upon the irradiation with the nonfiltered light of an LC-4 source (Hamamatsu).

The absorption spectra of the initial form **A** of spironaphthooxazine **3** exhibit a sharp increase in the intensity of the bands in the long-wavelength part of the spectrum compared to the spectra of spironaphthooxazine **1**, which is due to the introduction of the 2-tosylaminobenzylideneamine fragment into the molecule.

A comparison of the data presented in Table 1 shows that the merocyanine form **B** of these compounds has the quinoid character, because the absorption band of the photoinduced merocyanine form exhibits the bathochromic shift upon the replacement of weakly polar toluene by polar acetonitrile.[8] Accordingly, the rate of spontaneous decoloration in the dark increases. The photoinduced absorbance at the absorption band maximum of the merocyanine form shows that the efficiency

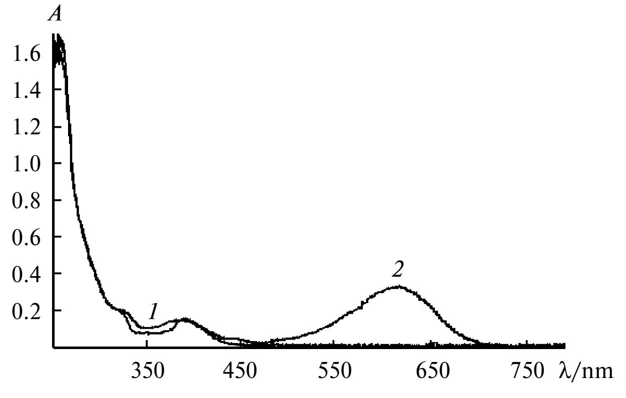


Fig. 1. Absorption spectra of a solution of compound **1** in MeCN before (*1*) and after (*2*) irradiation with the light with λ = 365 nm.

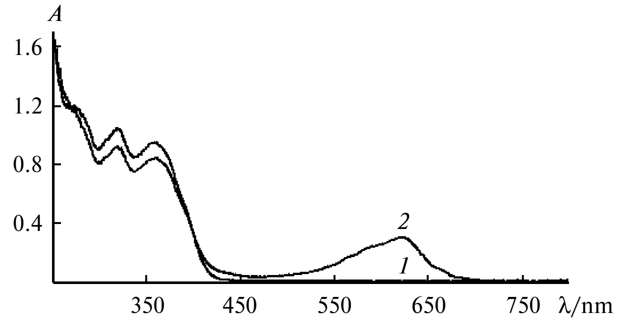


Fig. 2. Absorption spectra of a solution of compound **3** in MeCN before (*1*) and after (*2*) irradiation with the light with λ = 365 nm.

of photochromic transformations and photodegradation of compound **1** in toluene is higher than that in acetonitrile. An inverse dependence is observed in the case of spironaphthooxazine **3**. However, in the both cases, the higher the efficiency of the photodegradation, the higher the photoinduced change in the absorbance. This fact and the data of previous studies of photochromic spirooxazines[9] suggest that the photoinduced merocyanine form is characterized by the most efficient photodecomposition.

The complex formation processes of compounds **1** and **3** with the Mg^{2+}, Ba^{2+}, La^{3+}, and Tb^{3+} ions (see Table 1) were compared. No changes were observed in the absorption spectra of solutions of the initial form **A** after the metal salts were added, indicating that almost no complex formation occurs, unlike the earlier studied[4] spironaphthooxazine containing the salicylideneamine fragment.

The photoinduced merocyanine form **B** of the studied compounds participates in complex formation in different manners. In the case of compound **1**, at the low concentration of the photoinduced merocyanine form an insignificant bathochromic shift of the absorption band is observed, which increases, however, to 650 nm with the further UV-irradiation of a solution of spironaphthooxazine **1** in acetonitrile in the presence of the Tb^{3+} ions (Fig. 3). This phenomenon can be explained by the formation of a complex of the metal ion with the monomolecular merocyanine form at small exposures to the UV light followed by the aggregation of the merocyanine form.[10]

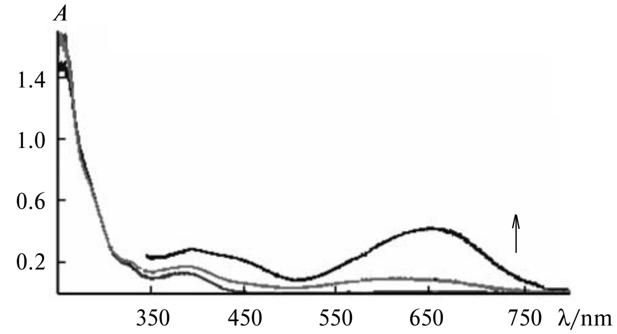


Fig. 3. Absorption spectra of a solution of compound **1** in MeCN in the presence of the Tb^{3+} ions with an increase in the UV radiation exposure.

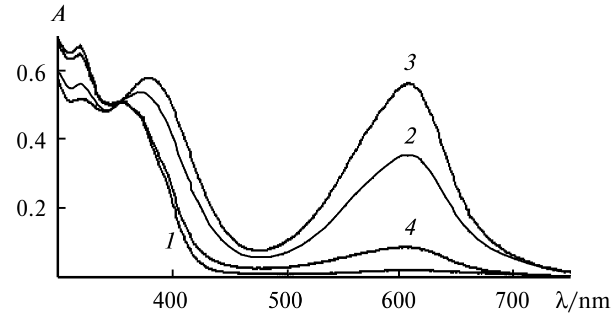


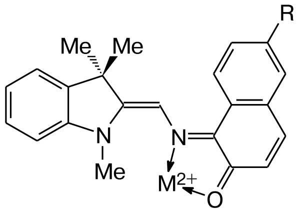
Fig. 4. Absorption spectra of a solution of compound **3** in MeCN in the presence of Tb^{3+} before (*1*) and after the consecutive UV irradiation (*2*, *3*) and dark relaxation (*4*).

In the case of compound **3**, the absorption band maximum of the merocyanine form exhibits the hypsochromic shift, whose value depends on the metal nature (see Table 1, Fig. 4).

The rate constant of dark decoloration decreases simultaneously (see Table 1). The metal cation with a higher electric charge density, in particular, Tb^{3+}, induces a more considerable hypsochromic shift of the absorption band of the photoinduced merocyanine form and inhibition of the thermal relaxation rate of the complexes of the merocyanine form compared with the cations with the lower charge density.

It should be mentioned that the metal ions affect the photodegradation process in the case of compound **3**. The Mg^{2+} and Ba^{2+} ions favor an insignificant increase in the stability of molecules **3** toward photodegradation, in spite of the increase in the photoinduced absorbance at the absorption band maximum of the photoinduced merocyanine form. This possibly indicates that these ions form complexes with molecules **3** and thus exert a positive effect on the stability of the photochromic systems toward irreversible photochemical transformations. The presence of the La^{3+} and Tb^{3+} ions decreases the photostability of compound **3**. At the same time, these ions sharply enhance the efficiency of photoaggregation of photochromic molecules. To reveal reasons for this phenomenon, further we are planning to study in more detail the complex formation processes of molecules **3** with the La^{3+} and Tb^{3+} ions.

Based on the data obtained, we can assume that the chelate complex formation in the case of the Mg^{2+} and Ba^{2+} ions occurs through the azomethinic N atom and phenoxide O atom of the photoinduced merocyanine form, decreasing the rate of dark cyclization to produce the spiro form.



Thus, the spectral kinetic study of synthesized spironaphthooxazine **3** showed that this compound has the photochromic properties, which depend on the solvent nature and the presence of metal ions. It was found for the first time that, unlike solutions of the compounds containing no metal ions, the efficiency of photodegradation is determined by the nature of ions present in the solution rather than by the photoinduced absorbance value.

Experimental

Acetonitrile and toluene (Aldrich) were used as solvents.

Complex formation processes in solutions were studied in the presence of the metal salts $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, $La(NO_3)_3$, and $Tb(NO_3)_3$ at the ligand to metal ratio 1 : 100.

The spectrophotometric study (photostationary spectra) of the studied compounds in solutions was carried out using a Cary 50 bio spectrophotometer (Varian). The kinetics of thermal decoloration and photodegradation, as well as the photoinduced change in the absorbance, were recorded with a USB2000 fiber-optical spectrometer (Ocean Optics).

The working concentration in solutions was $2 \cdot 10^{-4}$ mol L^{-1}. A quartz cell 0.2 cm thick was used for measurements. Irradiation was performed with the nonfiltered and filtered light from DRSh-250 and LC-4 lamps (Hamamatsu).

^1H NMR spectra were recorded on a Varian-300 instrument (300 MHz) at 25 °C using DMSO-d_6 as the solvent. IR spectra of the substances in Nujol were measured on a Varian Scimitar 1000 spectrometer. Elemental analyses to C, N, and H were carried out on a Perkin—Elmer 2400 automated CHN-analyzer.

1,3,3-Trimethyl-8´-[2-(*p*-tosylamino)benzylideneamino]-1,3-dihydrospiro[2*H*-indole-2,3´-[3*H*]naphtho[2,1-*b*][1,4]-oxazine] (3). Aminospirooxazine **1** (343 mg, 1 mmol) in EtOH (50 mL) was added to a hot solution of 2-(*p*-tosylamino)-benzaldehyde[7] **2** (275 mg, 1 mmol) in EtOH (50 mL). The resulting solution was refluxed for 4 h. A light green precipitate formed 24 h after was filtered off, washed with EtOH, and recrystallized from an EtOH—dioxane (2 : 1) mixture. The gray crystalline substance was obtained in a yield of 370 mg (62%), m.p. 217—219 °C. Found (%): C, 71.80; H, 5.10; N, 9.50. $C_{36}H_{32}N_4O_3S$. Calculated (%): C, 71.98; H, 5.37; N, 9.33. IR, ν/cm^{-1}: 3366 (w, br, ν(N—H)), 1631 (m, ν(C=N), spirooxazine), 1605 (s, ν(C=C) arom.), 1595 (s, ν(C=N), azomethine), 1571 (m), 1343 (s, ν(C—N)), 1270 (m, ν_{as}(S=O)), 1156 (vs, ν_s(S=O)), 1090 (s), 1082 (s), 1021 (s), 757 (s), 658 (s), 563 (s). ^1H NMR, δ: 1.33, 1.36 (both s, 3 H each, CMe_2); 2.35 (s, 3 H, CMe); 2.77 (s, 3 H, NMe); 6.58 (d, 1 H, H(7), $^3J_{6,7}$ = 7.44 Hz); 6.81 (t, 1 H, H(5), $^3J_{5,6}$ = $^3J_{4,5}$ = 7.1 Hz); 7.00—7.20 (m, 4 H); 7.25 (d, 2 H, H(8″), $^3J_{7'',8''}$ = 8.3 Hz); 7.38 (dd, 1 H, H(6), $^3J_{6,7}$ = 7.44 Hz, $^3J_{5,6}$ = 7.1 Hz); 7.52 (d, 1 H, H(6´), $^3J_{5',6'}$ = 8.6 Hz); 7.60—7.86 (m, 7 H); 8.56 (d, 1 H, H(10´), $^3J_{9',10'}$ = 9.2 Hz); 8.88 (s, 1 H, CH=N); 12.77 (s, 1 H, NH).

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