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Studies of Complex Formation of Photochromic Hybride Spirooxazine with Metal Ions

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Abstract—Spectral kinetic studies of complex formation of molecules of the hybrid spirooxazine containing spironaphthooxazine, hydroxyazomethine, and azobenzene fragments with a series of cations was carried out. Spectral and kinetic differences in the complex formation between this substance and previously studied spirooxazine derivatives were found.

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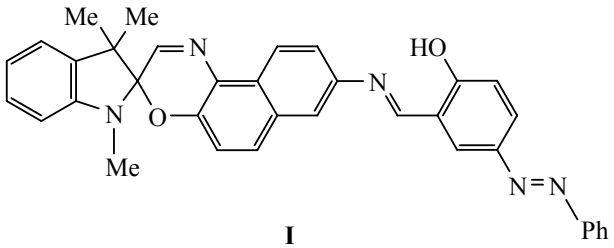
Recently the interest has increased to the investtigation of hybride photochromic compounds with the purpose of broadening of their functional possibilities [1–4]. We have lately synthesized derivatives of spirooxazine containing salicylideneimine [5] and 2-tosylaminobenzylideneimine fragments [6]. It is shown that they exhibit some specific features in photochromism and complex formation of merocyanine form of this compound with metal ions, of keto-tautomer, and in photochromic transformations of spirooxazine fragment. Complex formation of merocyanine form with metal ions leads to an increase in its lifetime, and the effectiveness of complex formation of both starting and merocyanine forms depends on the electrostatic properties of metal cations [5].

We found as a result of spectral kinetic studies of synthesized spironaphthooxazine with 2-tosylaminobenzylideneimine fragment [6] that unlike the solutions of compounds without metal ions the effectiveness of photodegradation in the presence of metal ions is determined not by the value of photoinduced optical density, but by the nature of ions present in the solution.

This article deals with the spectral kinetic studies of the complex formation of hybrid spirooxazine **I** which was synthesized for the first time. Besides spironaphthooxazine and salicylidene fragments it contains also phenylazo fragment [7]. The studies were carried out in comparison with the previously studied 8'-aminosubstituted spironaphthooxazine **II** [8].



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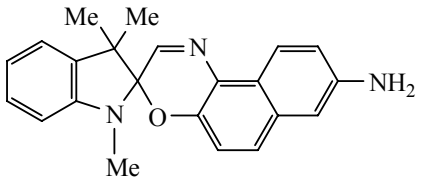


II

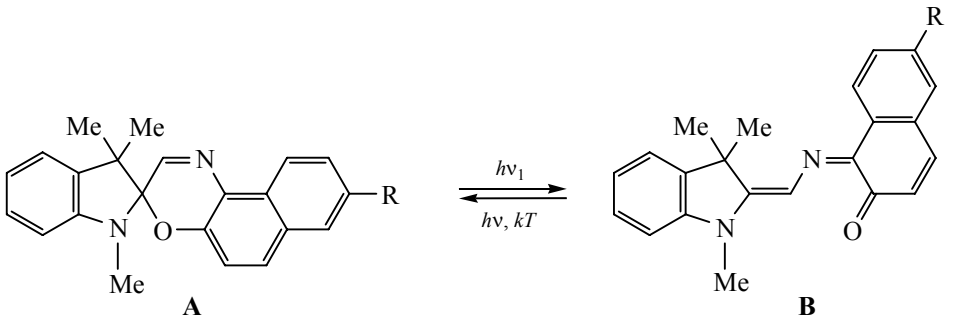
Spectral kinetic characteristics of spirooxazine **I** and its complexes with metal ions in acetonitrile[a]

M	L : M	$\lambda_{\mathbf{A}}^{max}$, nm ($D_{\mathbf{A}}$)	$\lambda_{\mathbf{B}}^{max}$, nm	$\Delta D_{\mathbf{B}}^{phot}$	$k_{\mathbf{B-A}}$, s^{-1}
–	–	320 (1.5), 345 (1.6)	620	0.08	1.0
Ca^{2+}	1 : 100	320 (1.6), 347 (1.6)	620	0.30	0.2
Zn^{2+}	1 : 10	240 (0.8), 360 (0.8)	626	0.26	0.2
Mg^{2+}	1 : 100	320 (1.6), 345 (1.6)	620	0.30	0.1
Tb^{3+}	1 : 100	356 (1.7), 454 (0.8)	595	0.40	0.0003
Cu^{2+}	1 : 10	330 (1.9), 440 (1.9)	–	–	–

[a] $\lambda_{\mathbf{A}}^{max}$ and $\lambda_{\mathbf{B}}^{max}$ are wavelengths of the absorption bands maxima of starting and photoinduced (or complex) forms of spiropyranes respectively; $D_{\mathbf{A}}$ is optical density in the maximum of the absorption band of the starting form; $D_{\mathbf{B}}$ is optical density in the maximum of the complex formed in the dark at the introduction of metal ions in solution; $\Delta D_{\mathbf{B}}^{phot}$ is the maximum value of optical density in the maximum of absorption band of photoinduced merocyanine form; $k_{\mathbf{B-A}}$, s^{-1} is the rate constant of thermal relaxation in the darkness.

The results of spectral kinetic studies of the hybrid spironaphthooxazine **I** are presented in the table and in Figs. 1–4.

As is known, spirooxazine derivatives undergo reversible photochromic transformations between the starting spiropyran (**A**) and merocyanine (**B**) forms [9].



In Fig. 1 absorption spectra of compound **I** are presented taken before and after the photoexcitation of its acetonitrile solution with the UV light.

The absorption spectrum of compound **I** differs from the spectrum of the aminosubstituted substance **II** in the range 300–400 nm due to an additional absorption of the phenylazo fragment.

The absorption band of photoinduced merocyanine form of photochrom **I** with the maximum at 659 nm is insignificantly (by 5 nm) shifted to the red side as compared to the corresponding absorption band of analog **II** [7]. *Cis-trans* isomerization of the phenylazo fragment of the hybrid compound observed during the pulse irradiation of solutions of substance **I** [7] was not clearly detected in the experimental conditions under

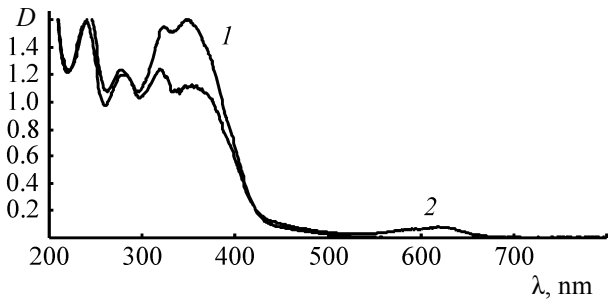


Fig. 1. Absorption spectra of solution of compound **I** in acetonitrile (*1*) before and (*2*) after irradiation with the UV light through the light filter UFS-1.

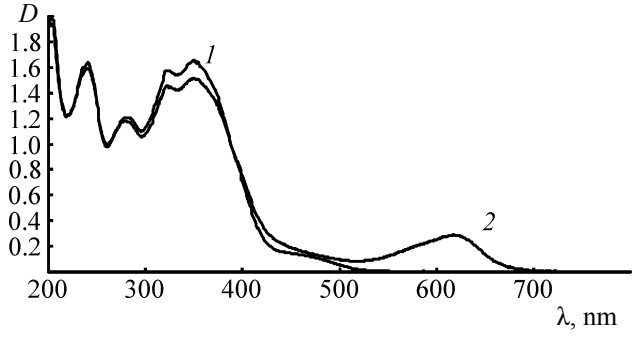


Fig. 2. Absorption spectra of compound **II** in acetonitrile in the presence of Mg^{2+} cations (*1*) before and (*2*) after irradiation with UV light through the light filter UFS-1.

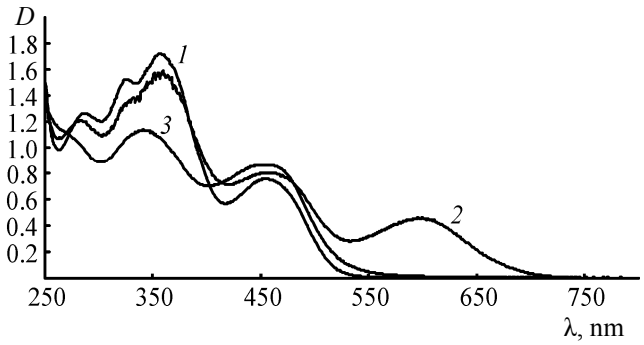


Fig. 3. Absorption spectra of solution of compound **I** in acetonitrile in the presence of Tb^{3+} (*1*) before and (*2*) after irradiation with UV light through the light filter UFS-1 and (*3*) the subsequent action of non-filtered light.

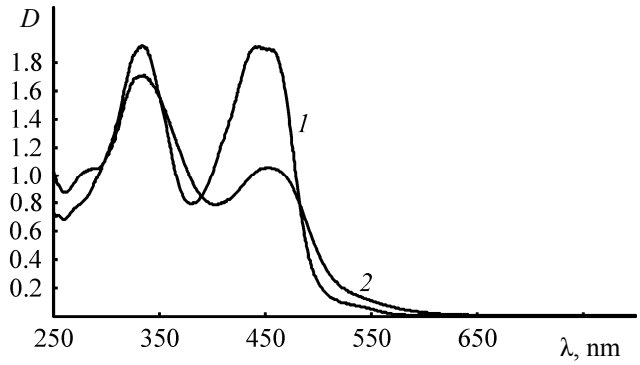


Fig. 4. Absorption spectra of solution of compound **I** in acetonitrile in the presence of Cu^{2+} cations in [L] : [M] ratio (*1*) 1 : 1 and (*2*) 1 : 10.

study probably due to overlapping of absorption bands of salicylideneamino and phenylazo fragments in the range 380–430 nm and at a high rate of thermal *cis-trans* isomerization.

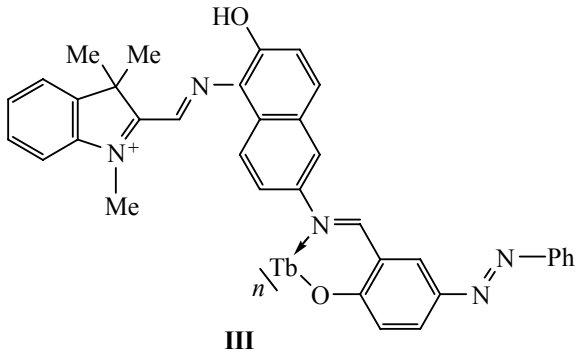
The rate constant of dark relaxation of photoinduced merocyanine form **B** at the introduction of the salicylideneimine and phenylazo fragments in the structure of the molecule decreases as compared to compound **II** [8]. It may be ascribed to the decrease in electron-donating properties of salicylideneimine fragment as compared to the amino group. It evidently provides higher value of photoinduced optical density in the maximum of the absorption band of merocyanine form ($\Delta D_{\mathbf{B}}^{\text{phot}}$) measured for compound **I**.

The presence of chelatophoric groups in the substance **I** determines the possibility of complex formation with metal ions in the spirane as well as in merocyanine form [10]. The interaction of merocyanine form of **I** with Mg^{2+}, Ca^{2+}, and Zn^{2+} metal ions unlike compound **II** [5] is seen only in the decrease in the rate of dark relaxation of merocyanine form and practically the same location of the absorption band maximum of the colored form at 620 nm (table, Fig. 2). Unlike that in the case of spirooxazine **II** the introduction of these ions not only results in a slower discoloration of solutions colored by the action of light, but also leads to a red shift of the absorption band maximum of the merocyanine form. As is known, the spectral shifts indicate the photoinduced formation of complexes of cations with phenolate oxygen atom of the merocyanine form **B**.

Unlike the reversible interaction of molecules **I** with Mg^{2+}, Ca^{2+}, and Zn^{2+} ions the introduction of Tb^{3+} ions leads to the appearance of photochemically inactive compound. At the addition of Tb^{3+} ions in acetonitrile solution of compound **I** before irradiation an absorption band appeared with a maximum at 454 nm (Fig. 3, curve *1*). No such effect was observed for the solution of spirooxazine **II** [5].

The irradiation of this solution with UV light through the light filter UFS-1 practically does not lead to any changes in the intensity of this absorption band. We consider that it shows the formation of the product of chemical interaction of spirooxazine molecules and Tb^{3+} ions which is insensitive to light. At the same time a long-wave absorption band appears with a maximum at 595 nm. It undergoes a blue shift with respect to the absorption band maximum of merocyanine form **B** (620 nm) in the spectrum of this substance (Fig. 3, curve *2*). Further prolonged irradiation of solution with the non-filtered light leads to its irreversible disappearance with the retention of the absorption band at 450 nm and with the decrease in the intensity of absorption band at 356 nm (Fig. 3, curve *3*). It may be assumed that in solution besides the obtained product of interaction of the substance **I** and Tb^{3+} ions which is insensitive to light also some molecules exist of starting photochromic spirooxazine **I**. Their photoinduced merocyanine form reacts with Tb^{3+} ions present in the solution to give complexes capable of photochromic transformations. This assumption is corroborated not only by the observed spectral shift but also by the deceleration of the dark relaxation of merocyanine form to the starting one as compared to this reaction of compound **I** in the absence of Tb^{3+} ions. At the prolonged UV irradiation photodegradation of photochromic compound takes place (Fig. 3).

Concerning the light-insensitive substance with the absorption band maximum at 450 nm it may be assumed that Tb^{3+} ions behave as a Lewis acid leading to formation of the stable complex **III** with the salicylideneimine fragment of compound **I** causing its deprotonation. The liberating proton reacts intramolecularly or intermolecularly with the spiro cycle causing its opening and the formation of a cationic dye [11].



III

Analogous light-insensitive product with the absorption band maximum at 440 nm is also formed evidenetly after introduction of Cu^{2+} ions in acetonitrile solution of compound **I** (Fig. 4).

As is seen from Fig. 4, the intensity of the absorption band at 450 nm increases with the increase in the concentration of Cu^{2+} ions. Unlike Tb^{3+} ions, Cu^{2+} ions form more stable complexes excluding the presence in solution of molecules of photochromic compound which are capable of phototransformations.

The results of the performed spectral kinetic studies of spirooxazine **I** and the comparison of the results obtained with the data of investigation of complex formation with aminosubstituted substance **II** [7] permit the following conclusions.

Spirooxazine **I** as well as the aminosubstituted substance **II** exhibit photochromic transformations of spirooxazine fragment. Unlike compound **II** in the case of the hybrid spironaphthooxazine **I** the formation of complexes with Ca^{2+}, Zn^{2+}, and Mg^{2+} was not detected spectroscopically either in the dark or while photoexcitation. But the existence of such complexes is confirmed by the deceleration of the rate of thermal relaxation of photoinduced form to the cyclic spirooxazine form in the presence of metal ions.

In the case of Tb^{3+} spirooxazine **I** besides the formation of the product insensitive to light forms also a complex of merocyanine form with metal ions. It is confirmed by the blue shift of the absorption band maximum of merocyanine form by 25 nm and the more than thousand-fold decrease in the rate constant (see the table). With Cu^{2+} ions spirooxazine **I** forms only the light-insensitive complexes.

EXPERIMENTAL

1,3-Dihydro-8'-(2-hydroxy-5-phenylazobenzylideneimino)-1,3,3-trimethylspiro{2*H*-indol-2,3'-[3*H*]-naphtho[2,1-*b*][1,4]oxazine} **I** was obtained according to the procedure described in [7]. 8'-Aminosubstituted spironaphthooxazine **II** was prepared by the procedure developed by us [8]. Purity of compounds was controlled by melting points, chromatography, and NMR spectroscopy data.

Acetonitrile from Aldrich was used as a solvent.

Investigation of complex formation in solution was carried out in the presence of metal salts $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $ZnCl_2$, and $Tb(NO_3)_3$ with L/M ratio 1 : 100, 1 : 10, 1 : 1.

Spectrophotometrical measurements (photostationary spectra) of compounds under study in solutions and investigation of kinetics of their photocoloration, photodiscoloration, photodegradation, and thermal discoloration of photoinduced form was carried out on a Cary 50 bio spectrophotometer.

The working concentration of solution was $C = 2\times10^{-4}$ M. Quartz cell of 0.2 cm was used. The irradiation was carried out with the non-filtered and filtered light of DRSh-250 and LC-4 (Hamamatsu) lamps.

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