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Photochromic properties of the bichromophore spirooxazine and its complexes with metal cations

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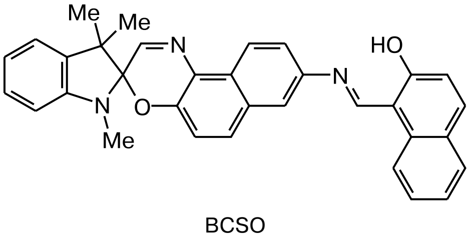
The properties of a bichromophore photochromic spirooxazine with a hydroxynaphthylideneimine fragment in position 8 were studied in solutions in the presence of alkali and alkaline earth metal salts. The changes in the absorption spectra of the initial form of this compound upon complexation are due to the electron density redistribution in the conjugation chain due to the incorporation of the metal cation into the ionophoric center of the chelating molecule. A complexation scheme was proposed and the stability constants of the resulting complexes were estimated. The complexation of the photoinduced merocyanine form of the compound increases its lifetime. This process is due to the interaction of the metal ion with both the chelating ionophoric center and the oxygen atom of the mercocyanine form. The efficiency of complexation of both the initial and the merocyanine forms depends on the electrostatic properties of the metal cations.

Key words: spironaphthooxazine, photochromic properties, complexation, absorption spectra, metal ions.

The transformation of photochromic compounds containing various ionophoric functional groups into metal ion complexes is a method for influencing their spectral and photochemical properties. These compounds could find application as selective chromo- and fluoroionophores for determination of various metal cations.[1—6] Currently, the properties of crown-containing spiropyrans, spirooxazines, and chromenes are under extensive research. However, the scope of practical use of crowned compounds is restricted by their high cost. Therefore, it is pertinent to search for photochromic compounds containing complexones of a different nature.

Here we present the results of a study of the behavior of bichromophore spirooxazine (BCSO) in solutions in the presence of alkali and alkaline earth metal salts.



BCSO

Experimental

The synthesis of BCSO was described in our previous publication.[7]

The spectrophotometric measurements were carried out in solutions in acetonitrile (Aldrich, water content 0.005%). The complexes were prepared using Mg, Ba, and Pb perchlorates (chemically pure grade). The metal salt to ligand concentration ratio (C_M/C_L) was varied from 0.1 to 100 at $C_L = 2 \cdot 10^{-4}$ mol L^{-1}. The electronic absorption spectra of the solutions were measured on a Cary 50 spectrophotometer in cells with an optical path of 0.2 cm at 25 °C. The photostationary absorption spectra were recorded on a USB2000 fiber optics spectrometer (Ocean Optics) with continuous irradiation of the solutions using a DRSh-250 gas discharge mercury lamp (λ = 365 nm). The kinetic measurements were carried out using a laboratory setup that ensured recording the kinetics of photoprocesses over time spans of down to 1 ms.

Results and Discussion

Spectroscopic properties of BCSO. The introduction of a hydroxynaphthylideneimine fragment into position 8 of spironaphthooxazine induces a shift of the long-wavelength maximum for the initial spiro form from 365 nm (for the unsubstituted compound) to 475 nm (Fig. 1),

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† Deceased.

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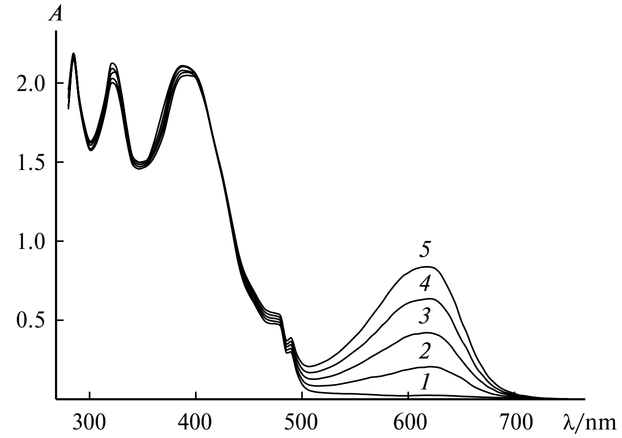


Fig. 1. Absorption spectra of BCSO in toluene before (*1*) and during irradiation of the solution with λ = 365 nm with different intensities (*2—5*).

which is due to a substantial elongation of the system of conjugated bonds.

The irradiation with light in the absorption range of the initial form brings about a new band with a peak at 620 nm due to absorption of the open merocyanine form. The kinetic measurements showed that the lifetimes of the merocyanine form are 2.8 and 0.8 s in toluene and acetonitrile, respectively. When solutions are irradiated, the absorption spectrum of BCSO has an isosbestic point (see Fig. 1), indicating the lack of a photoprocess involving proton transfer or *cis—trans* isomerization of the hydroxynaphthylideneimine fragment.

Spectral properties of BCSO complexes. The introduction of magnesium perchlorate into solutions of BCSO results, unlike that for unsubstituted spironaphthooxazine, in a change in the electronic absorption spectra of the starting spiro form (Fig. 2). This is due to the formation of complexes through interaction of the metal ion with the ionophoric fragment. Similar changes in the absorption spectra of the initial form were detected upon the addition of calcium, strontium, and barium salts.

The above metal ions have a qualitatively the same influence on the properties of BCSO complexes, resulting only in intensity redistribution in the absorption bands of the initial form (see Fig. 2). The changes in the intensity of the long-wavelength absorption bands induced by the addition of magnesium and barium salts to BCSO solutions (Fig. 3) are comparable in magnitude only in the case where the concentrations of barium salts added are much higher than the concentrations of magnesium salts. This implies that the observed effects depend on the ionic charge density. The metal cation with a higher ionic charge density interacts more efficiently with the chelating ionophore center of BCSO. Hence, the formation of complexes of this compound with metal cations was possible only due to the presence of a fragment able to bind a metal ion in the BCSO molecule.

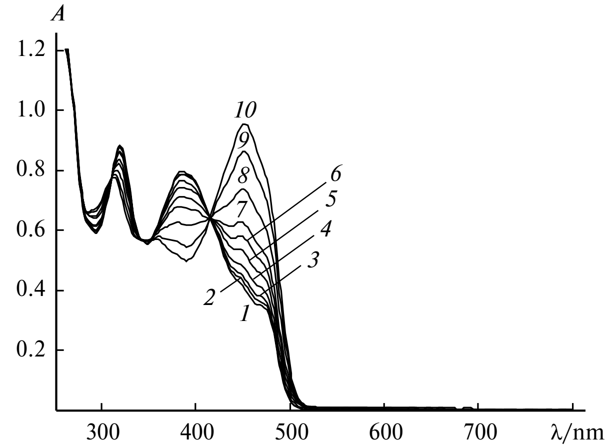


Fig. 2. Absorption spectra of BCSO solutions in acetonitrile in the absence (*1*) and in the presence of magnesium perchlorate of different concentrations: M : L = 2 (*2*), 5 (*3*), 10 (*4*), 20 (*5*), 50 (*6*), 100 (*7*), 200 (*8*), 500 (*9*), and 1000 (*10*) (C_L = $1 \cdot 10^{-4}$ mol L^{-1}).

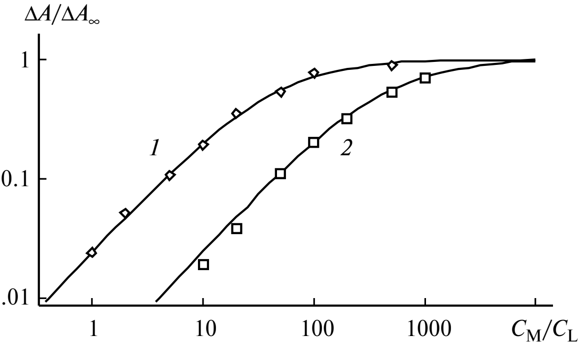


Fig. 3. Concentration dependence of the intensities of the BCSO absorption bands in acetonitrile upon the addition of magnesium (*1*) and barium (*2*) perchlorates (the dots are experimental values and the continuous lines are theoretical curves corresponding to the model $\mathrm{L} + \mathrm{M} \rightleftharpoons \mathrm{LM}$).

Elucidation of the dependence of the absorption spectra of the initial BCSO form on the concentration of metal ions added to the solution makes it possible to determine the structure of complexes and to estimate the stability constants.

As follows from the results shown in Fig. 3, the experimental data are described quite satisfactorily by the theoretical dependence[8] corresponding to the complexation model

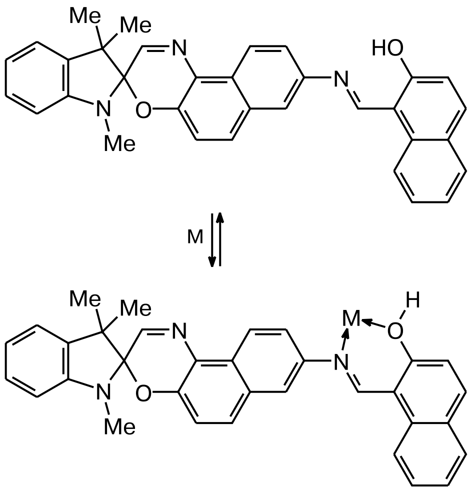
$$\mathrm{L} + \mathrm{M} \overset{K}{\rightleftharpoons} \mathrm{LM},$$

$$K = [\mathrm{LM}]/([\mathrm{L}][\mathrm{M}]),$$

with the complexation constants $\log K = 1.1$ (Ba^{2+}) and 2.1 (Mg^{2+}). The fact that the experimental curves of BCSO titration with magnesium and barium salts in acetonitrile comply with the complexation model $\mathrm{L} + \mathrm{M} \rightleftharpoons \mathrm{LM}$ (see

Fig. 3) indicates that the complexes have the formula LM (Scheme 1).

Scheme 1



The hydroxynaphthylideneimine fragment is the principal complexation center of the BCSO molecule.

Analysis of the spectroscopic data obtained for unsubstituted spirooxazine containing no hydroxynaphthylideneimine group indicates that no complexes of these compounds with magnesium cations are formed up to the concentration ratio [M] : [L] ≈ 1000.

Photochromic properties of BCSO complexes. BCSO complexes with metal cations exhibit photochromic properties. It was found that complexation retards the photocoloration process. The rate of the thermal decoloration of solutions of this compound also decreases (Fig. 4). The metal cation with a higher electrostatic charge density, for example Mg^{2+}, induces a more substantial retardation of the thermal relaxation of the complexes formed by the merocyanine form of BCSO than a cation with a lower electrostatic charge density (Ba^{2+}) (Fig. 5).

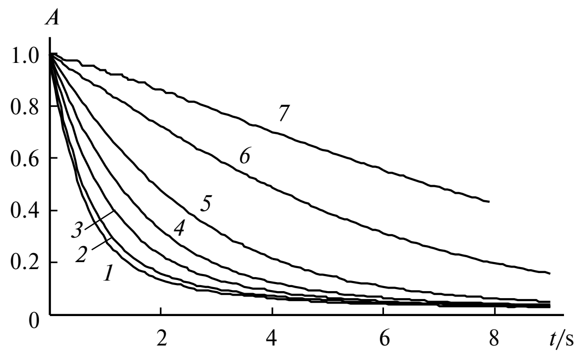


Fig. 4. Kinetics of thermal decoloration of solutions of BCSO in acetonitrile in the absence (*1*) and in the presence of magnesium perchlorate at concentration ratios of L : M = 1 : 2 (*2*), 1 : 5 (*3*), 1 : 10 (*4*), 1 : 20 (*5*), 1 : 50 (*6*), and 1 : 100 (*7*).

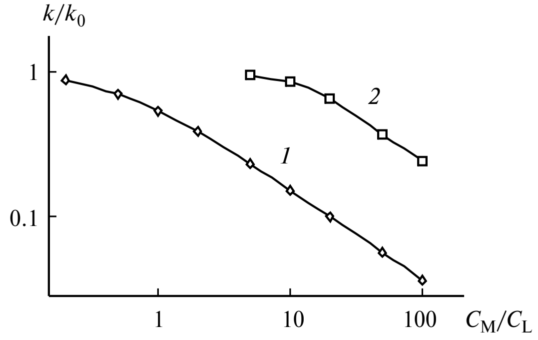


Fig. 5. Concentration dependence of the rate constant for thermal relaxation of the merocyanine form of BCSO in acetonitrile upon the addition of magnesium (*1*) and barium (*2*) perchlorate.

Comparison of the complexation of spiro- and merocyanine forms of BCSO for various concentrations of metal salts added attests to more gentle sloping of the titration curves in the case of the merocyanine form (*cf.* curves *1* in Figs 3 and 5). This is a result of involvement of the two ionophoric centers in the complexation of BCSO merocyanine form.

Thus, the increase in the lifetime of the photoinduced merocyanine form of BCSO in solutions in the presence of metal salts is due to the interaction of metal ions with both the chelating ionophoric center and the oxygen atom of the merocyanine form.

In this study, we have shown that a bichromophore photochromic compound of the spironaphthooxazine class with a new complexone, a hydroxynaphthylideneimine ionophore fragment, ensures, unlike the unsubstituted analog, an efficient complexation with not only the photoinduced merocyanine form but also the initial spiro form of spirooxazine. Due to complexation, a complexone of this type has a pronounced influence on the spectral kinetic characteristics of the photochromic transformations. The compound we studied can be synthesized rather readily using much less expensive chemicals as compared with known crown-containing spirooxazines,[7] which opens the way for using the bichromophore photochromic spirooxazine in the design of reversible chemical optical sensors.

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