# Crown-containing spironaphthoxazines and spiropyrans.
## 2*. Influence of metal cations on the photochromic properties of spironaphthoxazines linked with aza-15(18)-crown-5(6) ethers

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Spironaphthoxazines linked with aza-15(18)-crown-5(6) fragments were synthesized and studied for the first time. Addition of alkaline-earth cations to solutions of crown-containing spironaphthoxazines causes a hypsochromic shift of the absorption band of the spiro form and a bathochromic shift of the absorption band of the merocyanine form, shifts the equilibrium to the merocyanine form, and changes the lifetime of the photoexcited merocyanine form. The spectral and kinetic data were used to propose a mechanism of complexation and calculate the stability constants of the resulting complexes. The complexation involves the crown fragment and the merocyanine oxygen atom. The type of the complex is determined by the cation nature and size.

**Key words:** crown-containing spironaphthoxazines, synthesis, photochromic properties, metal ions, complexation.

Photochromic compounds possess two or more stable states; a transition between these states is followed by a change in their spectral characteristics.[2—4] An equilibrium state in such systems can be changed either by irradiation with UV or visible light or by changing the parameters of the surrounding medium. Photochromic compounds containing a complex-forming fragment can interact with metal ions, which occasionally changes the spectral characteristics of the ligands.[5—9] Such compounds make it possible to detect, even visually, the presence of metal ions in solutions and are of considerable interest for creation of efficient ionophores for selective determination of the metal ions.

Earlier,[10—13] photochromic ionophores with crown ether fragments attached to the spironaphthoxazine framework in different positions through methylene bridges of different lengths were synthesized and studied. It was shown that the influence of metal ions on the spectral and photochemical properties of these compounds is due to a possible interaction of the O atom of the merocyanine form with the metal cation located in the crown cavity. When the length of the methylene bridge is optimum, the merocyanine form of spironaphthoxazine is stabilized by effective coordination of the merocyanine O atom to the "crowned" metal cation.

To obtain spironaphthoxazine systems that would be more sensitive to the presence of metal cations in solution than the known analogs, we synthesized and studied for the first time spironaphthoxazines with azacrown fragments (CSN). For comparison, spironaphthoxazine containing no crown fragment (SN) was also tested.

### Results and Discussion

**Synthesis.** Crown-containing spironaphthoxazines **1a,b** were synthesized as described earlier[14] for 6´-amino-substituted spironaphthoxazines, which can be obtained by condensation of 2-methylideneindolenine with 4-amino-substituted 1-nitroso-2-naphthol. The latter compound can be prepared either by nucleophilic substitution of a secondary amine for the H(4) atom in 1-nitroso-2-naphthol or in two steps from sodium 1,2-naphthoquinone-4-sulfonate.

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* For Part 1, see Ref. 1.

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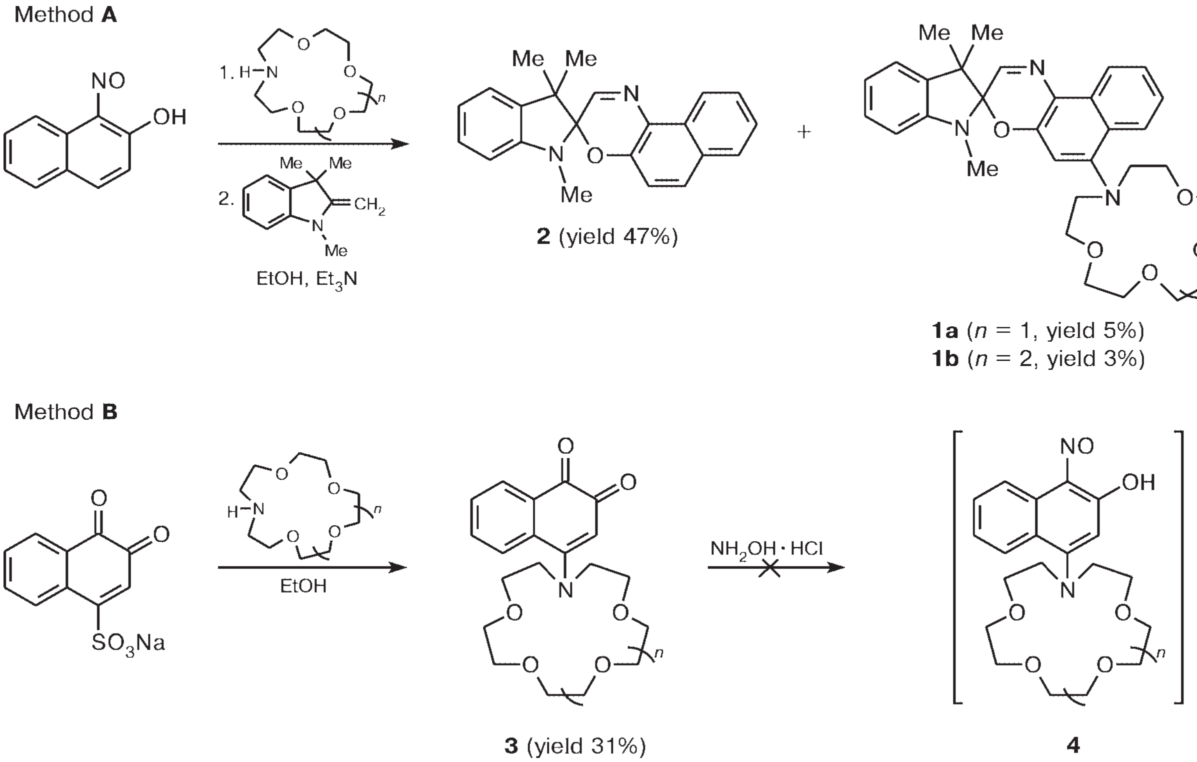
**Scheme 1**



**2** (yield 47%)

**1a** ($n$ = 1, yield 5%)
**1b** ($n$ = 2, yield 3%)

**3** (yield 31%)

**4**

We tried out both methods for the synthesis of CSNs **1a,b** (Scheme 1). The reactions of 1-nitroso-2-naphthol with aza-15(18)-crown-5(6) ethers and the subsequent reactions with indolenine were carried out in ethanol in the presence of Et$_3$N (method **A**). The yields of compounds **1a** and **1b** were low (5 and 3%, respectively); they could not be increased by varying the reaction conditions (reaction time and temperature and a ratio of the reagents). The major product was nonsubstituted SN **2**.

While following method **B**, we isolated a 1,2-naphthoquinone derivative **3** at the first stage; however, the proper conditions for its reaction with hydroxylamine to give crown-containing 1-nitroso-2-naphthol (**4**) were not found.

**Spectral and photochemical properties of CSNs 1a,b.** When irradiated with UV light, the original spiro form (SF) of CSNs **1a,b**, like the corresponding nonsubstituted SN **2**, reversibly isomerizes into colored merocyanine forms (MF) which are able to return spontaneously to the original state (Scheme 2).

Introduction of an azacrown fragment into position 6′ of the naphthalene ring (CSNs **1a,b**) results in a bathochromic shift of the absorption band of the spiro form (~13 nm) and in a hypsochromic shift of the absorption band of the merocyanine form (~28 nm), gives rise to some absorption by the starting solutions in the visible region, and causes a sixfold increase in the thermal relaxation constants of the colored form compared to the values of these parameters for unsubstituted SN **2** (Table 1). A slight shift of the equilibrium to the MF indicates that this form of the dye is stabilized by the azacrown

**Scheme 2**

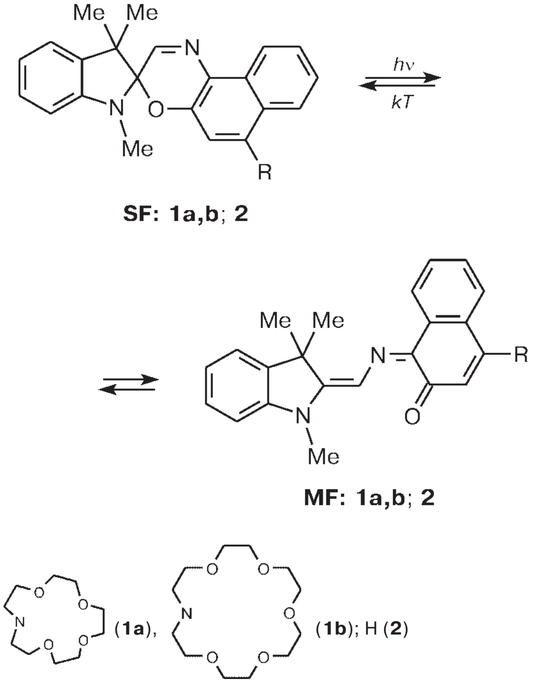


**Table 1.** Photochromic characteristics of spironaphthoxazines **1a,b** and **2** and their complexes with alkali ($Li^+$) and alkaline-earth ($Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$) ions in MeCN

| Compound | $\lambda_{SF}$[a]/nm ($\varepsilon_{SF} \cdot 10^{-4}$ /L mol$^{-1}$ cm$^{-1}$) | $\Delta\varepsilon_{SF} \cdot 10^{-4}$ [b] /L mol$^{-1}$ cm$^{-1}$ | $\lambda_{MF}$[a]/nm ($\varepsilon_{MF} \cdot 10^{-4}$ /L mol$^{-1}$ cm$^{-1}$) | $\Delta\lambda_{MF}$[c] /nm | $\Delta\varepsilon_{MF}$[b] $\cdot 10^{-4}$ /L mol$^{-1}$ cm$^{-1}$ | $k_{MF\to SF}$[d] /s$^{-1}$ |
|---|---|---|---|---|---|---|
| **1a** | 368 (1.17) | | 565 (~0.02) | | | 9.7 |
| **1a** • $Li^+$ | — | −0.07 | 580 | 15 | 0.01 | 7.7 |
| **1a** • $Mg^{2+}$ | — | −0.04 | 605 | 40 | 0.40 | 1.20 |
| **1a** • $Ca^{2+}$ | — | −0.21 | 585 | 20 | 0.08 | 1.19 |
| **1a** • $Sr^{2+}$ | — | −0.12 | 582 | 17 | 0.03 | 3.35 |
| **1a** • $Ba^{2+}$ | — | −0.09 | 575 | 10 | 0.01 | 5.12 |
| **1b** | 368 (1.20) | — | 565 (~0.02) | — | — | 9.4 |
| **1b** • $Li^+$ | — | – | 587 | 12 | 0.01 | 8.7 |
| **1b** • $Mg^{2+}$ | — | −0.01 | 606 | 41 | 0.09 | 0.83 |
| **1b** • $Ca^{2+}$ | — | −0.27 | 595 | 30 | 0.036 | 2.16 |
| **1b** • $Sr^{2+}$ | — | −0.60 | 592 | 27 | 0.020 | 0.80 |
| **1b** • $Ba^{2+}$ | — | −0.57 | 590 | 25 | 0.012 | 0.79 |
| **2** | 355 (0.56) | | 593 | — | — | 1.6 |

[a] $\lambda_{SF}(\varepsilon_{SF})$ and $\lambda_{MF}(\varepsilon_{MF})$ are the positions (extinction coefficients) of the long-wavelength absorption bands of the SF, the MF, and their complexes.

[b] $\Delta\varepsilon_{SF(MF)} = \varepsilon_{SF(MF)}$ (complex) − $\varepsilon_{SF(MF)}$ (dye) is the change in the extinction coefficient of the SF (MF) upon complexation.

[c] $\Delta\lambda_{MF} = \lambda_{MF}$ (complex) − $\lambda_{MF}$ (dye) is the shift of the absorption band of the MF upon complexation.

[d] $k_{MF\to SF}$ is the thermal relaxation constant of the MF and its complexes ($C_L = 2 \cdot 10^{-4}$ mol L$^{-1}$, $C_M/C_L = 100$, 24 °C).

fragment somewhat better than the SF. The observed changes in the spectral and kinetic parameters of CSNs **1a,b** are due to the electron-donor influence of the azacrown substituent conjugated with the π-electron system of the molecule. Analogous spectral changes were noted earlier[15] for 6´-morpholino(or -piperidino)spironaphthoxazines.

**Spectral properties of complexes formed by CSNs 1a,b.** It is known[3] that the SF and the MF of spironaphthoxazine are in equilibrium in solution (see Scheme 2). The absorption spectra of solutions of CSNs **1a,b** in the absence of metal salts virtually do not contain bands of the MF (see Table 1). This confirms that the ground-state energy levels of the SF and MF of **1a,b** are so mutually arranged that appreciable thermal population of the $S_0$ state of the merocyanine form is impossible.

In the presence of alkali and alkaline-earth cations, the spectral pattern for solutions of crown-free SN **2** remains virtually unchanged. When the same metal salts are added in the same concentration to solutions of CSNs **1a,b** in MeCN, the absorption band of their spiro forms experiences a hypsochromic shift to the UV region (Fig. 1), while their merocyanine forms begin to absorb in the visible region (Fig. 2). The shift of the band of the SF is due to coordination of its crown fragment to the metal ions. The resulting N...M coordination bond significantly reduces the conjugation of the N atom with the chromophore system of the molecule, which shortens its chromophore chain and hence causes a hypsochromic shift of the absorption band of the SF.

Appearance of the absorption bands in the visible region upon addition of alkaline-earth cations to solutions of CSNs **1a,b** in MeCN (see Table 1) suggests that the complexation stabilizes the MFs of these compounds, as well.

In the most general case, the thermodynamic equilibrium in the system crown-containing spironaphthoxazine—metal cation in solutions can be represented by Scheme 3.

Low concentrations of the MF of CSNs **1a,b** obtained after the $Li^+$, $Ba^{2+}$, $Sr^{2+}$, or $Ca^{2+}$ cation was added to

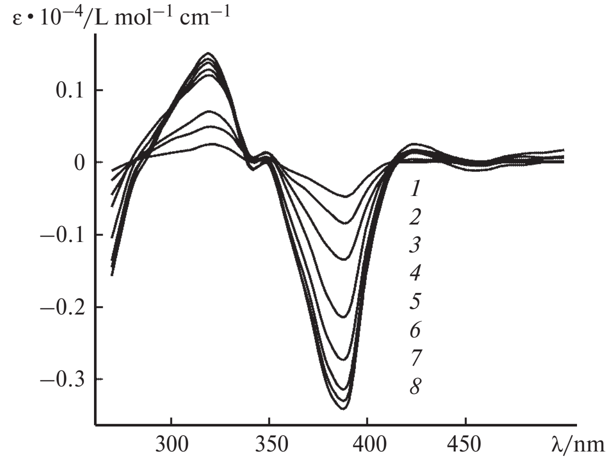


**Fig. 1.** Absorption spectra of solutions of CSN **1a** in MeCN in the presence of $Li(ClO_4)_2$ for $C_M/C_L$ = (*1*) 0.5, (*2*) 1, (*3*) 2, (*4*) 5, (*5*) 10, (*6*) 20, (*7*) 50, and (*8*) 100.

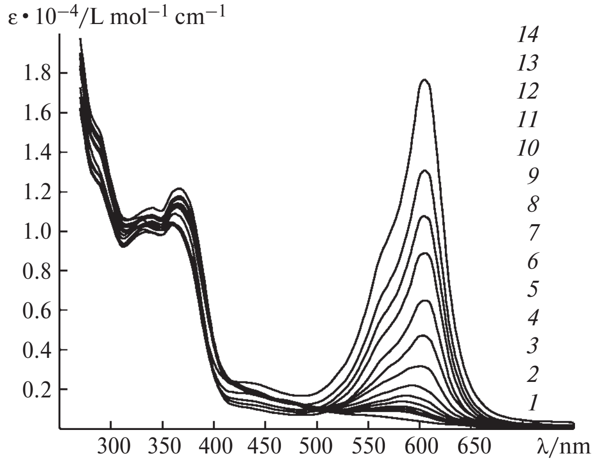


**Fig. 2.** Absorption spectra of solutions of CSN **1a** in MeCN in the presence of $Mg(ClO_4)_2$ for $C_M/C_L$ = (*1*) 0, (*2*) 0.5, (*3*) 1, (*4*) 2, (*5*) 5, (*6*) 10, (*7*) 20, (*8*) 50, (*9*) 100, (*10*) 200, (*11*) 500, (*12*) 1000, (*13*) 2000, and (*14*) 4000.

solutions enable one to ignore the cation-induced formation of the MF while studying the equilibrium in the spironaphthoxazine—metal system. In this case, the main equilibrium-determining process is the equilibrium **A** $\rightleftarrows$ **D** between the starting form **A** and its complex **D** (see Scheme 3).

Complexation constants for the SF of CSNs **1a,b** were calculated from the spectrophotometric data using the following complexation model:

$$L + M \rightleftarrows LM,\ K_{LM} = [LM]/([L][M]), \qquad (1)$$

where [L], [M], and [LM] are the concentrations of the free ligand, the free metal ion, and the complex, respectively.

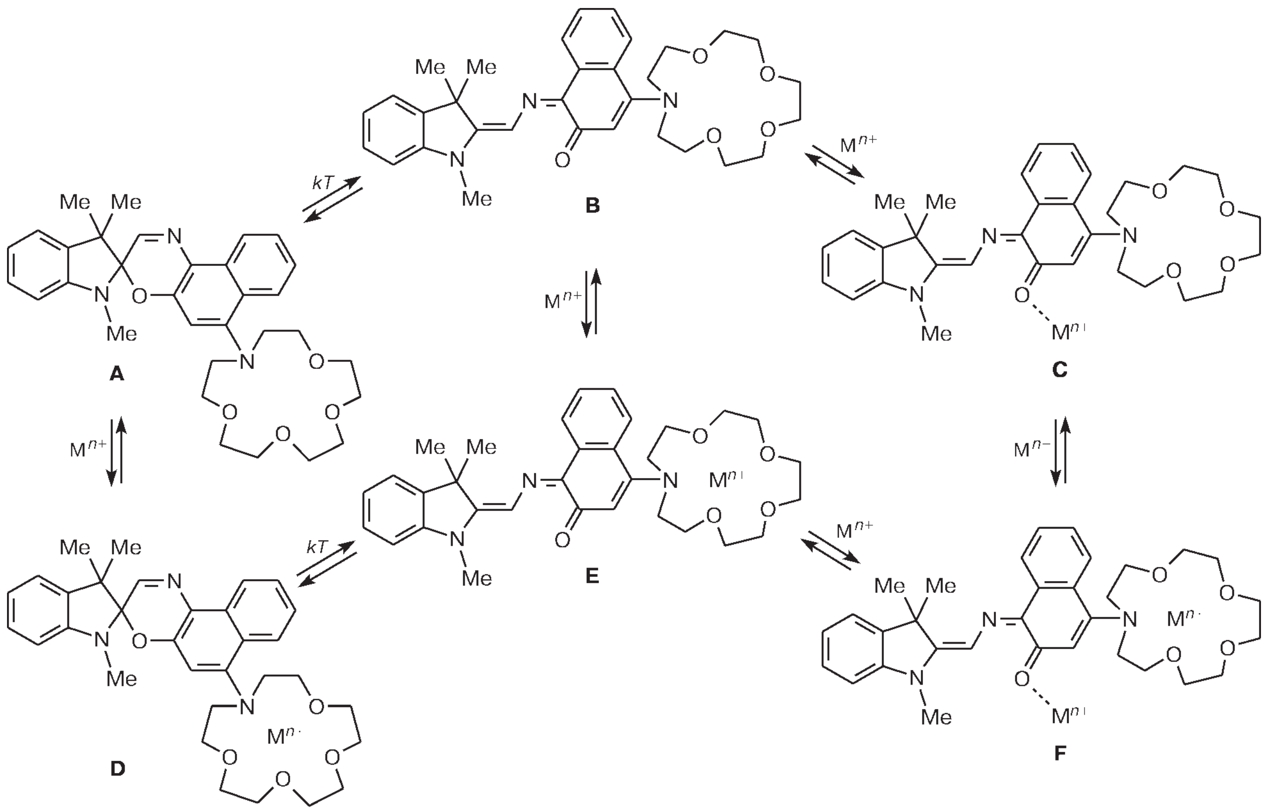
In this case, the dependence of the complexation degree (α) on the concentration of metal ions in solution is determined by the equation[16]:

$$\alpha = (A - A_0)/(A_\infty - A_0) = (C_L + C_M + 1/K_{LM}) \times$$
$$\times\ [1 - (1 - 4C_LC_M/(C_L + C_M + 1/K_{LM})^2)^{1/2}]/2C_L, \qquad (2)$$

where $A_0$, $A$, and $A_\infty$ are the optical absorption densities of the solutions in the absence and in the presence of metal cations with the concentration $C_M$ and with a concentration required for complete complexation, respectively; $C_L$ and $C_M$ are the concentrations of the ligand and the metal cation; and $K_{LM}$ is the complexation constant.

The theoretical dependences $\alpha(C_M)$ in logα *vs.* $\log(C_M/C_L)$ coordinates, which were calculated using Eq. (2), are consistent with the titration data for solutions of CSNs **1a,b** (Fig. 3). This confirms the formation of

**Scheme 3**



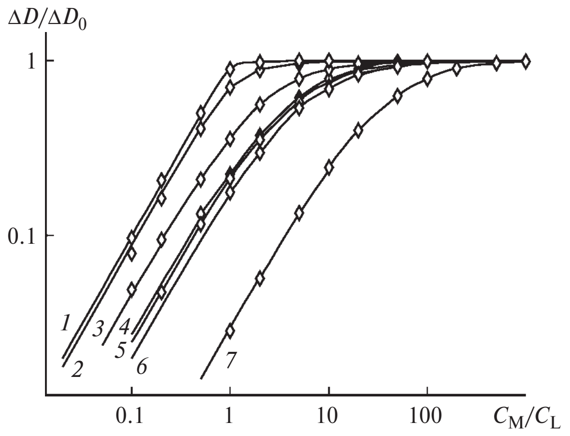


**Fig. 3.** Effect of the concentration of (*3*) $Ca^{2+}$, (*4*) $Li^+$, (*5*) $Sr^{2+}$, and (*6*) $Ba^{2+}$ perchlorates in solutions of CSN **1a** and of the concentration of (*1*) $Ba^{2+}$, (*2*) $Ca^{2+}$, and (*7*) $Mg^{2+}$ perchlorates in solutions of CSN **1b** in MeCN on the relative change in absorption at 380 nm (the experimental and theoretical curves are indicated by dotted and solid lines, respectively).

1 : 1 complexes of the SF with the $Li^+$, $Ba^{2+}$, $Sr^{2+}$, and $Ca^{2+}$ cations.

The complexation constants obtained for the spiro forms of CSNs **1a,b** ($K_D$) and $Li^+$, $Ca^{2+}$, $Sr^{2+}$, and $Ba^{2+}$ cations in acetonitrile[17] and the cation diameters (*d*) necessary for analysis of the experimental data are given in Table 2.

The hypsochromic shifts upon complexation (see Table 1) and the stability constants of the complexes of CSN **1a** with alkaline-earth cations (see Table 2) increase ($Ba^{2+} < Sr^{2+} < Ca^{2+}$) with a decrease in the cation radius; this is probably due to the better fit of the $Ca^{2+}$ size (1.98 Å) to the aza-15-crown-5 cavity (1.7—2.2 Å).[18] For the same reason, complexes of CSN **1a** with $Ca^{2+}$ and $Ba^{2+}$ are substantially more stable than those of CSN **1b** (see Table 2). The stability constants of complexes of CSN **1a** with $Li^+$ (1.36 Å) and CSN **1b** with $Mg^{2+}$ are low since the diameters of these cations are too small for efficient complexation with crown ethers of a given size.

**Table 2.** Stability constants of the complexes of spironaphthoxazines **1a,b** and **2** with alkali and alkaline-earth cations in acetonitrile

| Cation$^{n+}$ | $d$/Å | **2** | **1a** | | **1b** | |
|---|---|---|---|---|---|---|
| | | log$K_C$ | log$K_D$ | log$K_F$ | log$K_D$ | log$K_F$ |
| $Li^+$ | 1.36 | — | 3.28 | — | — | — |
| $Mg^{2+}$ | 1.32 | — | — | — | 2.2 | — |
| $Ca^{2+}$ | 1.98 | 2.2 | 3.65 | 2.4 | 4.6 | 2.3 |
| $Sr^{2+}$ | 2.24 | — | 3.22 | — | — | — |
| $Ba^{2+}$ | 2.68 | — | 3.10 | — | 5.6 | — |

*Note*. The stability constants of the complexes were determined with a measurement error of approximately ±0.1.

Unlike the complexation involving $Li^+$, $Ba^{2+}$, $Sr^{2+}$, and $Ca^{2+}$ cations, the complexation between CSN **1a** and $Mg^{2+}$ significantly shifts the equilibrium toward the colored form (see Fig. 2). In this case, UV spectral changes are due to both the formation of the SF complexes and, to a large extent, the absorption of the MF. These effects cannot be separated, which makes it impossible to use the aforesaid procedure for estimation of the complexation constants for the spiro form of CSN **1a** and $Mg^{2+}$ cations.

Complexation of CSN **1a** was also studied by NMR spectroscopy. Addition of alkaline-earth perchlorates to a solution of CSN **1a** resulted in downfield shifts of signals from protons (Table 3). Signals from the benzene protons in the indoline part experience no substantial shifts and are not given in Table 3. The greatest effect was observed for the methylene protons in the crown fragment and the protons of the naphthalene ring. It is known[3] that the

**Table 3.** $^1H$ NMR signals for CSN **1a** in $CD_3CN$ and their shifts (in parentheses) upon complexation with $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$

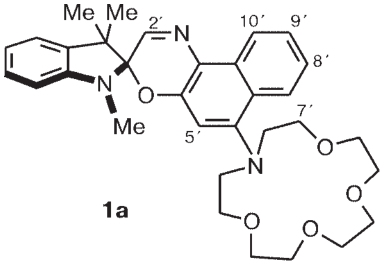
| Compound | $^1H$ NMR ($CD_3CN$), δ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $C(\underline{Me})_2$ | $N-\underline{Me}$ | H(2′) | H(10′) | H(9′) | H(8′) | H(7′) | H(5′) | $N-CH_2$[a] | $OCH_2$[a] |
| CSN **1a** | 1.34 | 2.74 | 7.70 | 8.52 | 7.55 | 7.39 | 8.30 | 6.88 | 3.40 | 3.52—3.62 |
| CSN **1a** + $Mg^{2+b}$ (SF) | 1.30 | 2.80 | 7.74 | 8.53 | 7.59 | 7.44 | 8.32 | 6.49 | 3.45 | 3.60—3.75 |
| | (−0.04) | (0.04) | (0.04) | (0.01) | (0.04) | (0.05) | (0.02) | (−0.39) | (0.05) | |
| CSN **1a** + $Mg^{2+b}$ (MF) | — | 5.44 | 9.93 | — | — | — | — | — | — | (~0.1) |
| CSN **1a** + $Sr^{2+c}$ | 1.36, 1.38 | 2.70 | 7.88 | 8.69 | 7.66 | 7.52 | 8.13 | 6.92 | 3.50 | 3.60—3.75 |
| | (0.02) | (−0.04) | (0.18) | (0.17) | (0.11) | (0.13) | (−0.17) | (0.04) | (0.10) | (~0.1) |
| CSN **1a** + $Ba^{2+c}$ | 1.34, 1.36 | 2.70 | 7.82 | 8.65 | 7.65 | 7.54 | 8.15 | 6.92 | 3.50 | 3.60—3.75 |
| | (0.02) | (−0.04) | (0.12) | (0.13) | (0.10) | (0.15) | (−0.15) | (0.04) | (0.10) | (~0.1) |

[a] Crown ether

[b] A 100-fold excess of the salt.

[c] A tenfold excess of the salt.

indoline and naphthoxazine fragments are nearly perpendicular to each other in the molecule. This accounts for spatial limitations of the complexation.



**1a**

Signals from the methylene protons in the crown fragment and from the aromatic protons are shifted more significantly for complexes with $Sr^{2+}$ and $Ba^{2+}$. Complexation with $Sr^{2+}$ shifts signals from the aromatic protons more strongly than that with $Ba^{2+}$, which correlates with the higher complexation constants of $Sr^{2+}$ (*cf.* Table 2).

Attention should be given to the upfield shifts of signals from the HC(5′) proton in a complex with $Mg^{2+}$ and from the HC(7′) proton in complexes with $Sr^{2+}$ and $Ba^{2+}$. This effect can be a result of two processes during complexation, namely, (a) a decrease in the conjugation of the lone electron pair of the N atom with the chromophore system owing to its involvement in coordination with the metal cation and (b) conformational reorganization of the crown macrocycle, which can change the conformation of the naphthoxazine fragment. X-ray diffraction data[3] showed that the conformation of the naphthoxazine fragment is very labile, being determined by steric factors even more greatly than by the electron influence of the substituents. Apparently, the chemical shifts for $Mg^{2+}$ complexes differ from those for $Sr^{2+}$ and $Ba^{2+}$ complexes because the latter cations mainly coordinate to the crown macrocycle, while the $Mg^{2+}$ cation located in the crown cavity coordinates the oxazine O atom. With a large excess of the metal, this results in the cation-induced formation of the MF.

For the most part, the NMR and UV data are fully consistent. Complexation between CSN **1a** and $Ba^{2+}$ or $Sr^{2+}$ involves the crown fragment, and addition of magnesium salts shifts the equilibrium toward the colored merocyanine form. This shift correlates with appearance of additional signals in the $^1H$ NMR spectrum, in particular, from the azomethine proton at δ 9.9 and from the N—Me group of the betaine structure of the merocyanine isomer at δ 5.44.[19]

**Cation-induced isomerization of CSNs 1a,b.** The intensities of the absorption bands in the visible region for complexes of the MF of CSNs **1a,b** depend on the nature of the metal cation and their concentration in solution (see Table 1). The illustrative absorption spectra of CSN **1a** in the presence of magnesium perchlorate in different concentrations (see Fig. 3) show that an increase in the concentration of $Mg^{2+}$ in the range $C_M/C_L < 10$ intensifies the absorption of the MF complex and shifts its band to the long-wavelength region so that its position virtually coincides with that for the MF of SN **2**. Apparently, in this range of salt concentrations, complex E is formed in solution, in which the crown N atom has no donor effect because of its involvement in coordination with the metal cation.

At higher metal concentrations, nothing but the intensity of the absorption band of the complex changes. The absorption bands of the complexes of CSNs **1a,b** with alkaline-earth cations in the visible region become less intense in order of decreasing charge density on the metal cation: $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (see Table 1). The low selectivity of the cation-induced isomerization of CSNs **1a,b** is evidence that the main process determining the shift of the equilibrium to the MF is the interaction of metal cations with the O atom of this form (the formation of complex **F**, see Scheme 3).

Thus, the much stronger coordination of the metal cations with the azacrown fragment than with the O atom of the merocyanine form accounts for the order of the formation of different complexes in solution as the metal concentration increases: $\mathbf{A}\rightarrow\mathbf{D}\rightarrow\mathbf{E}\rightarrow\mathbf{F}$. The high efficiency of interaction of the metal cations with the azacrown fragment in CSNs **1a,b** makes the formation of complex **C** highly improbable.

***Photoisomerization of CSNs 1a,b and their complexes.*** The photoisomerization of SN **2** is characterized by a monotonic decrease in the thermal relaxation constants of the MF ($k_{MF\rightarrow SF}$) with an increase in the metal concentration (Fig. 4, curves *1*, *4*). In the case of CSNs **1a,b**, this parameter is reduced more significantly for the concentrations of $Ca^{2+}$ and $Ba^{2+}$ in the range $C_M/C_L = 1$—$100$ (see Fig. 4, curves *2*, *3*, *5*, *6*). At higher concentration ratios ($C_M/C_L > 100$), the character of the observed changes in this parameter does not depend on whether the molecule contains the crown fragment or not.

A relative change in $k_{MF\rightarrow SF}$ correlates with the stability of the resulting complexes (*cf.* Table 1 and Fig. 4). Thus, in the presence of $Ca^{2+}$ and $Ba^{2+}$, $k_{MF\rightarrow SF}$ of CSN **1b** changes more substantially than that of CSN **1a**, in accordance with their complexation constants.

As demonstarted above, metal cations in low concentrations mostly coordinate the azacrown fragment. The overall scheme of thermal relaxation can be written as $\mathbf{E}\rightarrow\mathbf{D}\rightarrow\mathbf{A}$ (see Scheme 3). In this case, the rate-limiting stage of thermal decolorization is the isomerization of merocyanine complex **E** into spiro complex **D**.

At higher concentrations of metal ions in solutions of CSNs **1a,b** ($C_M/C_L > 100$), the thermal relaxation constants of the merocyanine form decrease with an increase

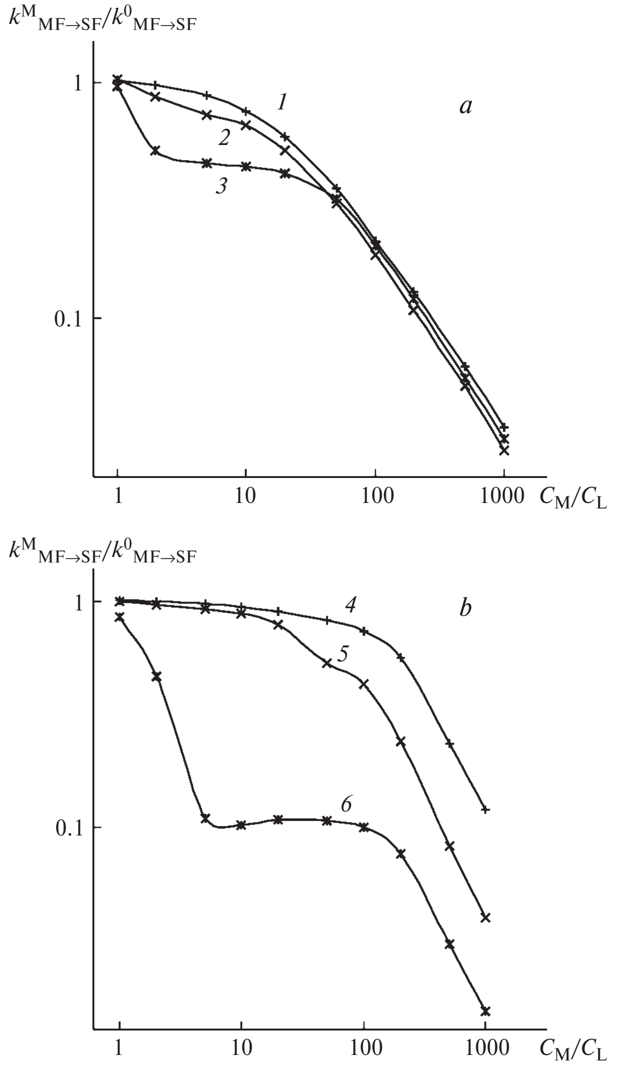


**Fig. 4.** Effect of the concentration of (*a*) $Ca^{2+}$ and (*b*) $Ba^{2+}$ perchlorates on the relative thermal relaxation constant of the MF ($k^M{}_{MF\to SF}/k^0{}_{MF\to SF}$) for **2** (*1*, *4*), **1a** (*2*, *5*), and **1b** (*3*, *6*).

in the metal concentration (see Fig. 3), as in the case of SN **2** containing no crown fragment. The equal slopes of the curves of $\log k^M{}_{MF\to SF}/k^0{}_{MF\to SF}$ ($k^M{}_{MF\to SF}$ and $k^0{}_{MF\to SF}$ are the thermal relaxation constants of CSNs **1a,b** and SN **2**, respectively) *vs.* the concentration of the metal ions proves that the same anionic center of the molecule, namely, the oxygen atom of the MF, is involved in complexation in this concentration range. Thus, at high metal concentrations, the overall scheme of thermal relaxation can be represented by **F** → **E** → **D** (see Scheme 3). In this case, the rate-limiting stage is the cleavage of the coordination bond between the metal cation and the oxygen atom of the MF (**F** → **E**).

The complexation constants for the MF of the $M_2B$ type were obtained with consideration of a large difference in efficiency between the interactions of metal cations with the azacrown fragment of the SF and with the oxygen atom of the MF. For this reason, the kinetic data can be analyzed using the following kinetic model:

$$\mathbf{E} \xrightarrow[k_1]{} \mathbf{D}, \tag{3}$$

$$\mathbf{F} \underset{k_2}{\overset{K_\mathbf{F}}{\rightleftarrows}} \mathbf{E} + \mathbf{M},\ K_\mathbf{F} = [\mathbf{F}]/([\mathbf{E}][\mathbf{M}]). \tag{4}$$

The experimental deactivation rate constant of complex **F** is determined by

$$k = (k_1 + k_2K_\mathbf{F}[\mathrm{M}])/(1 + K_\mathbf{F}[\mathrm{M}]), \tag{5}$$

where $k_1$ and $k_2$ are the deactivation rate constants of forms **E** and **F**, respectively, and $K_\mathbf{F}$ is the equilibrium constant of the process (4).

This scheme is close to that proposed previously[20] for the complexation of spiro compound containing no crown fragment and allows one, within the scope of our assumptions, to describe the complexation of CSNs **1a,b** at high metal concentrations. However, the theoretical curves based on Eq. (5) fit the experimental deactivation rate constants of photoexcited complexes only for $Ca^{2+}$ cations. The constants of complexation involving the oxygen atom of the MF of compounds **1a,b** and **2** with $Ca^{2+}$ are close ($\log K$ = 2.2—2.4), being significantly lower than the corresponding constants of complexation through the azacrown fragment of the spiro form (see Table 2).

It should be noted that the experimental dependences of the thermal relaxation constants of the colored form on the concentration of $Mg^{2+}$ and $Ba^{2+}$ cations in solution satisfy the proposed model, which can be associated with the probable formation of $LM_2$ (for $Mg^{2+}$) and $L_2M$ (for $Ba^{2+}$) complexes.

Thus, the spironaphthoxazines linked with the aza-15(18)-crown-5(6) fragments were synthesized and studied in this work for the first time. It was shown that the introduction of an azacrown fragment into the spironaphthoxazine molecule changes its spectral and photochemical properties. These changes are analogous to those produced by an electron-donor substituent (*e.g.,* the morpholine or piperidine residue) in the same position. Addition of alkaline-earth cations to solutions of CSNs **1a,b** results in a hypsochromic shift of the absorption band of the SF, shifts the equilibrium toward the MF, and changes the thermal relaxation rate of the MF. Based on the spectral and kinetic data, we proposed the scheme of complexation and calculated the stability constants of the resulting complexes. According to the data obtained, the complexation involves two centers, namely, the crown fragment and the merocyanine O atom. The complexation *via* both centers depends on the surface charge density of the metal cation; with the crown fragment as a complexation center, the size of the metal cation should fit the crown cavity. Crown ether—metal complexes are more stable than complexes involving the merocyanine O atom. Investigations of these compounds are important in a search for new types of photochromic materials that are highly sensitive to metal cations in solutions.

## Experimental

$^1$H NMR spectra were recorded on Bruker AMX-400 and Bruker DRX-500 spectrometers in $CD_3CN$ with $Me_4Si$ as the internal standard. Chemical shifts were measured with an accuracy up to 0.01 ppm, and spin-spin coupling constant with an accuracy up to 0.1 Hz. Mass spectra were recorded on a Varian MAT-311A instrument (70 eV, direct inlet of the sample into the ionization chamber). The course of the reactions was monitored by TLC on DC-Alufolien Kieselgel 60 $F_{254}$ plates (Merck). Column chromatography was carried out on Silica gel 60 silica gel (0.063—0.200 mm).

Crown-containing spironaphthoxazines were synthesized from 1,3,3-trimethyl-2-methylideneindoline (Fluka); aza-15-crown-5 and aza-18-crown-6 (Merck); and 1-nitroso-2-naphthol, sodium 1,2-naphthoquinone-4-sulfonate, and methanol (all Aldrich). The starting compounds were used without additional purification.

Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The electronic absorption spectra of the colored form were recorded on a spectrophotometer while continuously irradiating samples with light with $\lambda = 365$ nm from a DRSh-250 mercury lamp. The thermal relaxation kinetics of the colored form was studied on a kinetic setup in the time range 0.001—1000 s (photoexcitation with UV radiation generated by a pulse xenon lamp). Measurements were performed in solutions with the concentration of compounds $C_L = 2 \cdot 10^{-4}$ mol $L^{-1}$ at ~20 °C. Acetonitrile (Aldrich, water content 0.005%) was used as a solvent. Complexing agents were Li, Mg, Ca, Sr, and Ba perchlorates.

**1,3,3-Trimethyl-6´-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)spiro[indolino-2,3´-[3*H*]naphth[2,1-*b*]oxazine] (1a).**[20] ***A.*** 1-Nitroso-2-naphthol (0.393 g, 2.25 mmol) was added to a solution of aza-15-crown-5 (1 g, 4.5 mmol) in 5 mL of MeOH. The reaction mixture was heated in an atmosphere of argon at 80 °C for 6 h, and then a solution of 1,3,3-trimethyl-2-methylideneindoline (0.4 mL, 2.25 mmol) in 10 mL of MeOH was added. The reaction mixture was kept at 80 °C for 2.5 h, cooled, and concentrated. Double column chromatography gave compound **2** [20] (0.43 g, 47%) and compound **1a** (26 mg, 5%) as a viscous oil. $^1$H NMR (DMSO-$d_6$), δ: 1.34 (s, 6 H, 2 Me); 2.74 (s, 3 H, N—Me); 3.48—3.57 (m, 20 H, 2 $NCH_2$ + 4 $OCH_2$); 6.63 (d, 1 H, H(4), $J$ = 7.6 Hz); 6.84—6.92 (m, 2 H, H(2´) + H(6)); 7.13 (d, 1 H, H(7), $J$ = 7.2 Hz); 7.20 (t, 1 H, H(5), $J_1$ = 7.2 Hz, $J_2$ = 8.4 Hz); 7.41 (t, 1 H, H(8´), $J_1$ = 9.0 Hz, $J_2$ = 6.9 Hz); 7.56 (t, 1 H, H(9´), $J_1$ = 7.8 Hz, $J_2$ = 7.2 Hz); 7.71 (s, 1 H, H(5´)); 8.31 (d, 1 H, H(7´), $J$ = 8.1 Hz); 8.51 (d, 1 H, H(7´), $J$ = 8.4 Hz). Found (%): C, 70.83; H, 7.46; N, 7.05. $C_{33}H_{39}N_3O_5$. Calculated (%): C, 70.43; H, 7.20; N, 7.70.

**1,3,3-Trimethyl-6´-(1,4,7,10,13-pentaoxa-17-azacyclohexadodec-17-yl)spiro[indolino-2,3´-[3*H*]naphth[2,1-*b*]oxazine] (1b)** was obtained analogously from aza-18-crown-6 as a viscous oil. The yield of compound **1b** was 3%. $^1$H NMR (DMSO-$d_6$), δ: 1.34 (s, 6 H, 2 Me); 2.74 (s, 3 H, N—Me); 3.52 (m, 20 H, 2 $NCH_2$ + 4 $OCH_2$); 6.63 (d, 1 H, H(4), $J$ = 7.6 Hz); 6.88 (m, 2 H, H(2´) + H(6)); 7.13 (d, 1 H, H(7), $J$ = 7.2 Hz); 7.20 (t, 1 H, H(5), $J_1$ = 7.7 Hz, $J_2$ = 7.1 Hz); 7.41 (t, 1 H, H(8´), $J_1$ = 8.6 Hz, $J_2$ = 7.2 Hz); 7.56 (t, 1 H, H(9´), $J_1$ = 7.6 Hz, $J_2$ = 7.0 Hz); 7.71 (s, 1 H, H(5)); 8.31 (d, 1 H, H(7´), $J$ = 8.3 Hz); 8.51 (d, 1 H, H(7´), $J$ = 8.3 Hz). Found (%): C, 68.44; H, 6.64; N, 6.72. $C_{34}H_{43}N_3O_6 \times 0.5$ MeOH. Calculated (%): C, 68.40; H, 7.48; N, 6.93.

**4-(1,4,7,10-Tetraoxa-13-azacyclopentadec-13-yl)-1,2-naphthoquinone (3).** ***B.*** A solution of sodium 1,2-naphthoquinone-4-sulfonate (1 g, 4 mmol) and aza-15-crown-5 (1 g, 4.6 mmol) in 30 mL of water was stirred at ~20 °C for 6 h. After the reaction was completed, the products were extracted with chloroform. The solvent was removed, and the residue was recrystallized from ether. The yield of compound **3** was 0.46 g (31%), m.p. 131—146 °C. $^1$H NMR ($CD_3CN$-$d_3$), δ: 2.80—2.96 (m, 4 H, $N(CH_2)_2$); 3.05—3.25 (m, 8 H, 4 $OCH_2$); 3.28 (t, 2 H, $OCH_2$); 3.90 (t, 2 H, $OCH_2$); 6.1 (s, 1 H, H(3)); 7.50 (t, 1 H, H(6), $J$ = 7.7 Hz); 7.6 (t, 1 H, H(7), $J_1$ = 7.5 Hz, $J_2$ = 7.8 Hz); 7.83 (d, 1 H, H(5), $J$ = 7.8 Hz); 8.08 (d, 1 H, H(8), $J$ = 7.8 Hz). MS, $m/z$ ($I_{\text{rel}}$ (%)): 377 $[M]^+$ (7); 216 (59); 173 (100); 172 (87); 171 (41); 159 (83); 158 (85); 145 (37); 129 (62); 115 (42).

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