Effect of complexation on spectral and kinetic properties of crown-substituted photochromic spironaphthoxazines

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The insertion of benzo-15-crown-5 or benzo-18-crown-6 as a substituent at the 9′-position of a spironaphthoxazine molecule increases the lifetime of the open form of spironaphthoxazine by a factor of *ca.* 2. The complex formation between the crown groups and Mg^{2+} or Ba^{2+} ions changes the lifetime slightly. The addition of benzo-18-crown-6 at the 5′-position leads to an increase in the lifetime of the open form by an order of magnitude and the appearance of absorption with a maximum at 16420 cm^{-1} under dark conditions, which testifies to the stabilization of the open form. The addition of Ba^{2+} ions to this compound results in a further increase in the lifetime by *ca.* 35% due to complex formation. The luminescence of the benzo-15-crown-5-substituted compound is probably caused by both the complexation with Mg^{2+} and the photochemical reaction induced by photoactive light and is accompanied by the irreversible loss of photochromism.

Key words: spironaphthoxazine, open form, lifetime; activation energy; absorption spectrum; luminescence.

Photochromism of organic compounds has long been attracting attention of researchers. Spiropyrans have been one of the main objects of study for many years, but interest in them has recently decreased. The insertion of crown-ether substituents into spiropyran molecules stimulated the study of properties of these compounds. The appearance of absorption in the visible spectral region was observed in the presence of alkali metal salts, which was explained by the formation of complexes involving crown-ether groups.[1—3] The selectivity of the complex formation, judging from the results presented, is determined by the size of the crown-containing substituent and the ionic radii of the cations.

Many properties of spironaphthoxazines are similar to those of spiropyrans, but there are substantial differences. As compared to spiropyrans, spironaphthoxazines possess a greater number of photochromic cycles, *i.e.*, they are more stable under the action of photoactive light. The insertion of crown-ether substituents into spironaphthoxazine molecules favors the formation of their complexes with metal ions, which can change the photophysical and photochemical properties of these compounds. For example, the existence of a monoaza-12-crown-4 group at the 5′-position of a spironaphthoxazine molecule in a complex with a lithium ion stabilizes the open form of spironaphthoxazine and increases its lifetime by two orders of magnitude. The stability of the open form can be controlled within sufficiently wide limits by varying the concentration of lithium ions.[4,5]

In this work, the spectral and kinetic properties of spironaphthoxazines containing fragments of benzo-15-crown-5 and benzo-18-crown-6 ethers have been studied.

Experimental

We studied spironaphthoxazines **1—6** (see below) synthesized by procedures described previously.[6,7]

Acetonitrile from Elsiko (the content of water was 0.01%, the optical density at λ = 200 nm in a 1-cm cell was 0.4) was used as the solvent. Magnesium, barium, lithium, and potassium perchlorates preliminarily dehydrated by heating *in vacuo* to 260 °C were used for complex formation.

Absorption spectra were recorded on a Specord UV-VIS spectrophotometer attached to a Korvet computer, from which all data were passed to an IBM PC AT for processing. The sensitivity of the instrument was on the order of 0.001 of the optical density, which was achieved by using an additional rheochord and a Shch300 digital voltmeter.

The lifetimes of the open forms of spironaphthoxazines were measured on an installation with a pulse xenon lamp, and the time resolution of the installation was <1 ms. Probing was performed by the light of a KGM-70 incandescent lamp, which got to a FEU-79 photomultiplier through an MDP-3 monochromator after passing through a cell containing a solution of a sample. Then the signal was sent to the Korvet computer from the photomultiplier after passing through a U7-1 amplifier and an F7077/1 analog-digital converter. Measurements were performed at the absorption maximum of the open form (~16600 cm^{-1}) after preliminary verification that the result is independent of the choice of the wavelength in the

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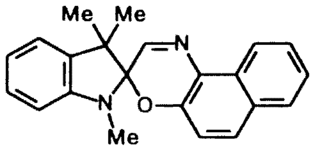

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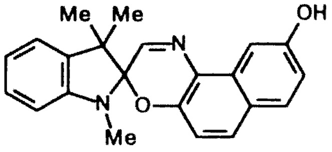

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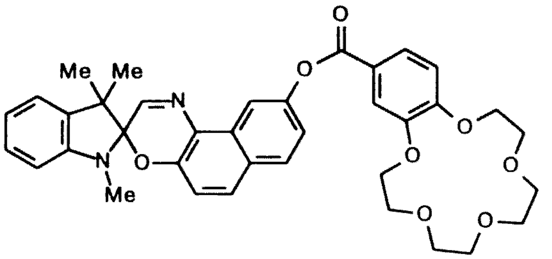

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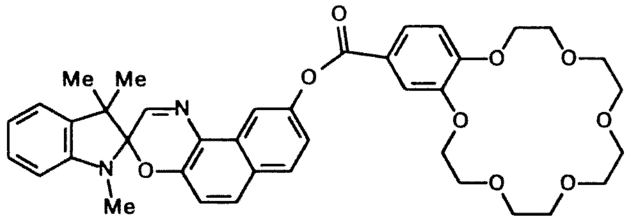

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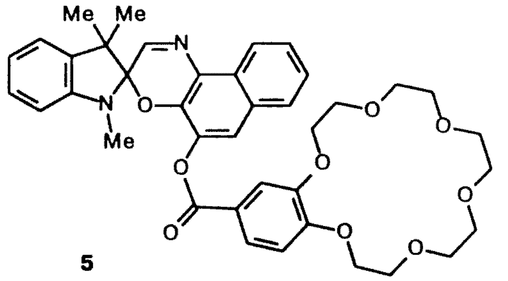

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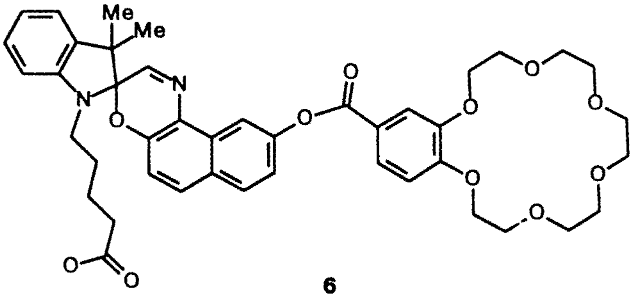

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absorption spectrum of the open form. The error of measurement of lifetimes did not exceed 5%.

Absorption spectra of the open forms of spironaphthoxazines were recorded in the photostationary states after irradiation of a solution by a DKSSh-1000 mercury lamp through a UFS-6-5 light filter on the experimental setup. All data from the experimental setup were recorded on the Korvet computer followed by computation on an IBM PC AT.

Results and Discussion

Absorption spectra in the UV region. The absorption spectra of the compounds studied in acetonitrile at 298 K are presented in Fig. 1. The insertion of the crown-ether group into the spironaphthoxazine molecule results in the appearance of two additional maxima at 33500 and 37500 cm^{-1}.

The complex formation is indicated by the fact that the absorption spectrum obtained after the addition of a salt to a solution of spironaphthoxazine is not equal to the sum of the absorption spectra of the initial compounds. The salts used are transparent in the whole spectral region; however, their addition to crown-substituted spironaphthoxazines changes the shape of the spectra. Typical changes in the spectrum of compound **6** caused by the addition of the barium salt are shown in Fig. 2. Similar changes are observed in the absorption spectrum of benzo-15-crown-5 ether in the presence of metal cations. In the case of spironaphthoxazine **2**, which contains no crown ether group, the addition of

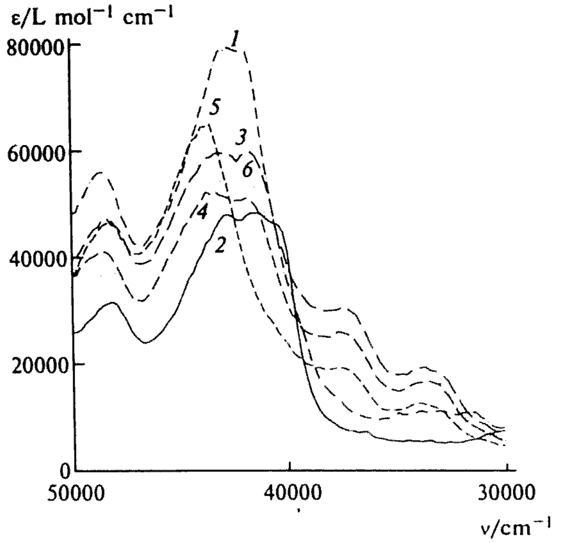


Fig. 1. Absorption spectra of compounds **1**—**6** in MeCN at 289 K. The numeration of curves (*1*—*6*) corresponds to the numbers of compounds (**1**—**6**).

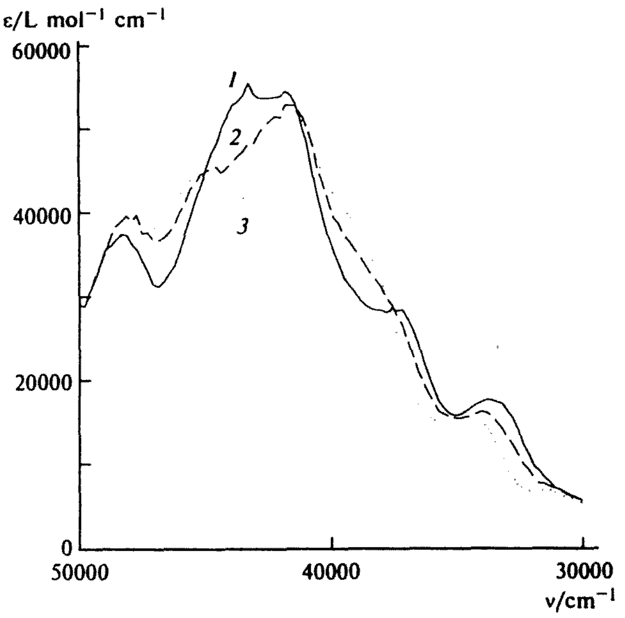


Fig. 2. Absorption spectrum of compound **6** at molar ratios $[Ba^{2+}]$: $[\mathbf{6}]$ = 0 (*1*), 0.5 (*2*), and 2 (*3*) (MeCN is the solvent, $[\mathbf{6}] = 1 \cdot 10^{-5}$ mol L^{-1}).

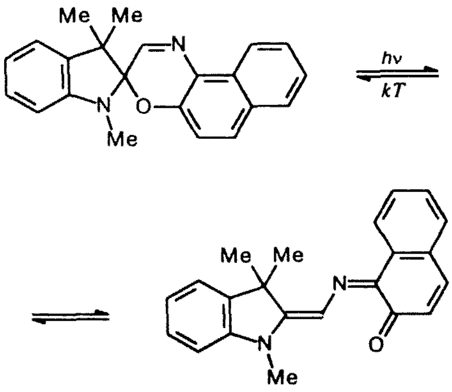
the salts did not result in a change in the shape of the spectrum. This made it possible to conclude that magnesium or barium salts react with crown-substituted spironaphthoxazine to form a complex between the metal cation and the crown ether group of spironaphthoxazine.

The maximum changes in the absorption spectra occur at a molar ratio of the salt and spironaphthoxazine equal to 2 : 1. Further increasing the concentration of cations has a slight effect on the shape of the spectrum.

Absorption spectra in the visible region. It is known that spironaphthoxazines exist in colorless closed and colored open forms. The "closed form $\rightleftharpoons$ open form" transition for compound **1** is shown in Scheme 1.

Similar transformations also occur in molecules of spironaphthoxazines **2**—**6**. In the dark, the equilibrium is always shifted considerably to the closed form, and the absorption spectra presented in Fig. 1 are assigned to the closed forms of the compounds. The only exception is spironaphthoxazine **5**: a noticeable fraction of the open form is observed along with the predominant closed structure in a solution of compound **5** in acetonitrile. The addition of barium perchlorate to this solution results in an increase in the optical absorption density of the open form at 16420 cm^{-1} (λ = 609 nm) from 0.04 to 0.053 at the molar ratio $[Ba^{2+}]$: $[\mathbf{5}]$ = 2 : 1. This testifies to additional stabilization of the open form by cations, which is likely related to the complex formation between the metal cation and the crown ether group of spironaphthoxazine and to the Coulomb interaction of the Ba^{2+} cation with the O atom.

Scheme 1



For the other compounds under the same conditions, the optical density in the range of 600 nm is not greater than 0.001, *i.e.*, the open form is not detected spectrophotometrically. The attempts to observe it in the luminescence spectra also failed, because, unlike spiropyrans, no fluorescence was observed for the open forms of any of the spironaphthoxazines.

The absorption spectra of the open forms of the compounds were measured in the photostationary states. The spectra of all spironaphthoxazines (except **5**) exhibit absorption maxima at 16750 cm^{-1} (λ = 597 nm), while that of compound **5** contains a maximum at 16420 cm^{-1} (λ = 609 nm).

The addition of metal cations does not result in any substantial change in the absorption curves of the open forms of any of the compounds studied.

Lifetime of the open form. The insertion of a crown ether substituent into a spironaphthoxazine molecule changes the lifetime of the open form. The results of the measurements of all compounds studied are presented in Table 1.

It can be seen that the insertion of benzocrown groups into a molecule of spironaphthoxazine **2** in all cases results in an increase in the lifetimes of all compounds. Compound **5** should be mentioned specially, because the lifetime of its open form is almost an order of magnitude higher than that of compound **2**. This, in particular, results in the shift of the equilibrium to the open form, which was observed in the absorption spectra in the visible region. No changes are observed when Ba^{2+} ions are added to compound **2**, but when they are added to spironaphthoxazines **3**, **4**, and **6** they show a

Table 1. Lifetime (τ) of open forms of spironaphthoxazines (SNO) **2**—**6** in acetonitrile at 294 K

Compound	τ/s		
	$[Ba^{2+}] = 0$	$[Ba^{2+}] : [SNO] = 0.5$*	$[Ba^{2+}] : [SNO] = 2.0$*
2	0.99	0.98	1.00
3	1.82	1.70	1.74
4	1.96	1.73	1.79
5	8.56	11.6	10.7
6	1.44	1.34	1.40

* Molar ratios.

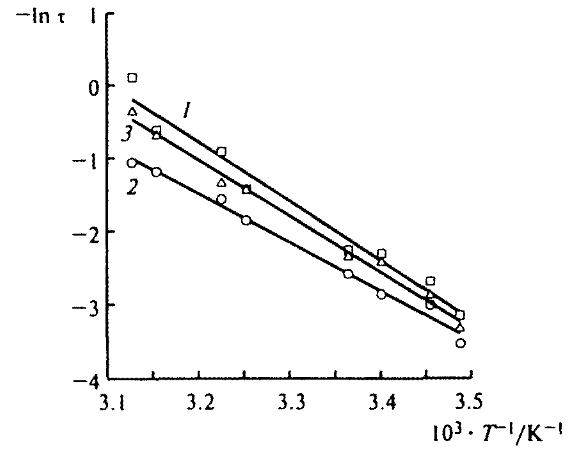


Fig. 3. Arrhenius dependences of the dark decolorization of compound **5** at molar ratios $[Ba^{2+}] : [\mathbf{5}] = 0$ (*1*), 0.5 (2), and 2 (*3*) (MeCN is the solvent, $[\mathbf{5}] = 2 \cdot 10^{-5}$ mol L^{-1}).

tendency for the lifetimes of these compounds to decrease. The opposite effect was observed for compound **5**, for which the lifetime of the open form increases by ~35% after the addition of Ba^{2+} ions at the molar ratio $[Ba^{2+}] : [\mathbf{5}] = 0.5 : 1$. Correspondingly, the absorption in the visible region increases, which is caused by the further shift in the equilibrium to the open form. An increase in the $[Ba^{2+}] : [\mathbf{5}]$ molar ratio to 2 : 1 results in a decrease in the lifetime, which may indicate the existence of complexes of different types.

The anamorphoses of the temperature dependences of the lifetimes of the open forms for compound **5** and its complexes with Ba^{2+} are presented in Fig. 3. The addition of Ba^{2+} ions to a solution of spironaphthoxazine in a ratio of 0.5 : 1 facilitates an increase in the lifetime and favors a weaker temperature dependence of this parameter (see Fig. 3, curve *2*). The addition of two moles of Ba^+ per mole of compound **5** returns the temperature dependence approximately to that observed in the absence of metal ions (see Fig. 3, curves *1* and *3*).

The addition of Mg^{2+}, Li^+, and K^+ ions results in no noticeable changes in the absorption spectrum or in the lifetime of the open form of compound **5**, although the formation of complexes of benzo-18-crown-6 ether with Li^+ and K^+ is indicated in the published data.[8]

The activation energies (E_a) of dark decolorization obtained from the data in Fig. 3 are presented in Table 2. It can be asserted with some degree of probability that both the E_a value and the lifetime of the open form are extreme for the complex of spironaphthoxazine **5** with Ba^{2+} formed after the addition of 0.5 moles of Ba^+ per mole of compound **5**.

Luminescence properties. The initial compounds did not luminesce, although the measurements were performed at the sensitivity of the spectrofluorimeter used when Raman spectra are recorded. For spironaphthoxazine **3**, the formation of a luminescent compound is observed both when Mg^{2+} ions are added and when a solution in the absence of ions is irradiated by the UV light of a xenon flash lamp or a DRSh-1000 mercury lamp through a UFS-5-5 light filter. The combined action of these factors accelerated the formation of a luminophore and was accompanied by weakening of the photochromic properties of compound **3**. This process is irreversible, and the structure of the luminophore form was not identified. Maxima of the luminescence excitation spectra and luminescence spectrum are observed at 22675 cm^{-1} (λ = 441 nm) and 18181 cm^{-1} (λ = 550 nm), respectively.

Table 2. Activation energies (E_a) of the dark reaction of returning compound **5** from the open form to the closed one in acetonitrile

Compound	[5] : [Ba^{2+}]	E_a	Δ*
		kJ mol^{-1}	
5	1.0 : 0	67.2	4.6
5 + Ba^{2+}	1.0 : 0.5	55	2.3
5 + Ba^{2+}	1.0 : 2.0	63.5	2.5

* Mean-square error.

Similar phenomena are also observed for compound **2**, but the maxima in the luminescence excitation spectra and the luminescence spectrum are considerably shifted to shorter wavelengths and exist at 27027 cm^{-1} (λ = 370 nm) and 20833 cm^{-1} (λ = 480 nm), respectively. It is likely that the crown ether substituent plays no decisive role in the formation of the luminophore, but results in a noticeable bathochromic shift in the spectra.

The appearance of luminescence is accompanied by a corresponding decrease in the photochromism of the compounds indicated.

Thus, the addition of Ba^{2+} ions to a solution of crown-containing spironaphthoxazine changes the lifetime of its open form due to the complex formation between Ba^{2+} cations and the crown ether group.

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