Crown-containing spironaphthoxazines and spiropyrans
3.* Synthesis and investigation of the merocyanine form of crown-containing spirobenzothiazolinonaphthoxazine

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A method for the synthesis of the spirobenzothiazolinonaphthoxazine, stable in the merocyanine form and containing a crown-ether fragment was developed. The complexing properties of the prepared merocyanine compound and the spectroscopic and photochromic characteristics of its complexes with alkaline earth metal cations were studied by NMR and UV spectroscopy. The results were analyzed using quantum-chemical calculations. The addition of alkaline earth metal perchlorates to a solution of a crown ether-containing merocyanine dye in MeCN results in the coordination of metal cations to two binding centers, namely, the crown-ether fragment and the merocyanine oxygen atom. This gives rise to two types of complexes, which differ substantially in their structurally. The complexation induces changes in the UV spectra and influences on the photochromic behavior of the prepared compound.

Key words: crown ether, spirobenzothiazolinonaphthoxazine, 1-[(3-methyl-6,7,9,10,12,13,15,16-octahydro[1,4,7,10,13]pentaoxacyclopentadecyno[2,3-*f*][1,3]benzothiazol-2(3*H*)-yliden)methylimino]naphthalen-2-one, alkaline earth metals, complex formation; UV spectroscopy, ^{1}H NMR spectroscopy, photochromic behavior, oxidation.

It is known that spiropyrans and spironaphthoxazines can exist in the ground state as two forms, namely, colorless (closed) or colored (merocyanine) forms. The stability of a particular spiro compound form is determined by two key factors, namely, the nature of the heterocyclic nucleus and the electronic and steric properties of substituents. For instance, indoline spiropyrans and spironaphthoxazines exist predominantly as closed (*i.e.*, colorless) forms, while both open (merocyanine) and closed forms may be stable for spiropyrans of the benzothiazolium series. In the case of spiropyrans containing a benzimidazolium nucleus, only the mercocyanine form is known.[2]

The variation of steric and electronic properties of substituents in spiro compounds of the benzothiazolium series is widely used to stabilize the open or closed form. The heterocyclic residue containing no substituents or containing electron-donating substituents (electronic factor) is favorable for stable merocyanine form. The introduction of substituents into 2-position of the oxazine nucleus (steric factor) markedly stabilizes the closed form with respect to the open form.[2] Study of the structures of the open and closed forms of a spiro compound contributes to the understanding of the photoisomerization behavior, which, in turn, helps to find ways for controlling phototransformation. This research is important regarding both the fundamental science and the manufacture of new promising photosensitive materials for optical lenses,[3] or the development of optical systems for information recording[4] and photosensitive biomaterials.[5]

Of special interest is the introduction of a crown-ether fragment into a spiro compound. Crown ethers are known to form stable complexes with various metal cations. The complex formation involving crown-containing spiro compounds allows one to affect substantially the spectroscopic and photochromic characteristics of compounds.

In this study, we synthesized stable merocyanine forms of dyes (MD) that belong to the spirobenzothiazolinonaphthoxazine series, namely, MD **1a**, serving as the model compound, and MD **1b**, containing a conjugated crown-ether fragment. The formation of complexes by

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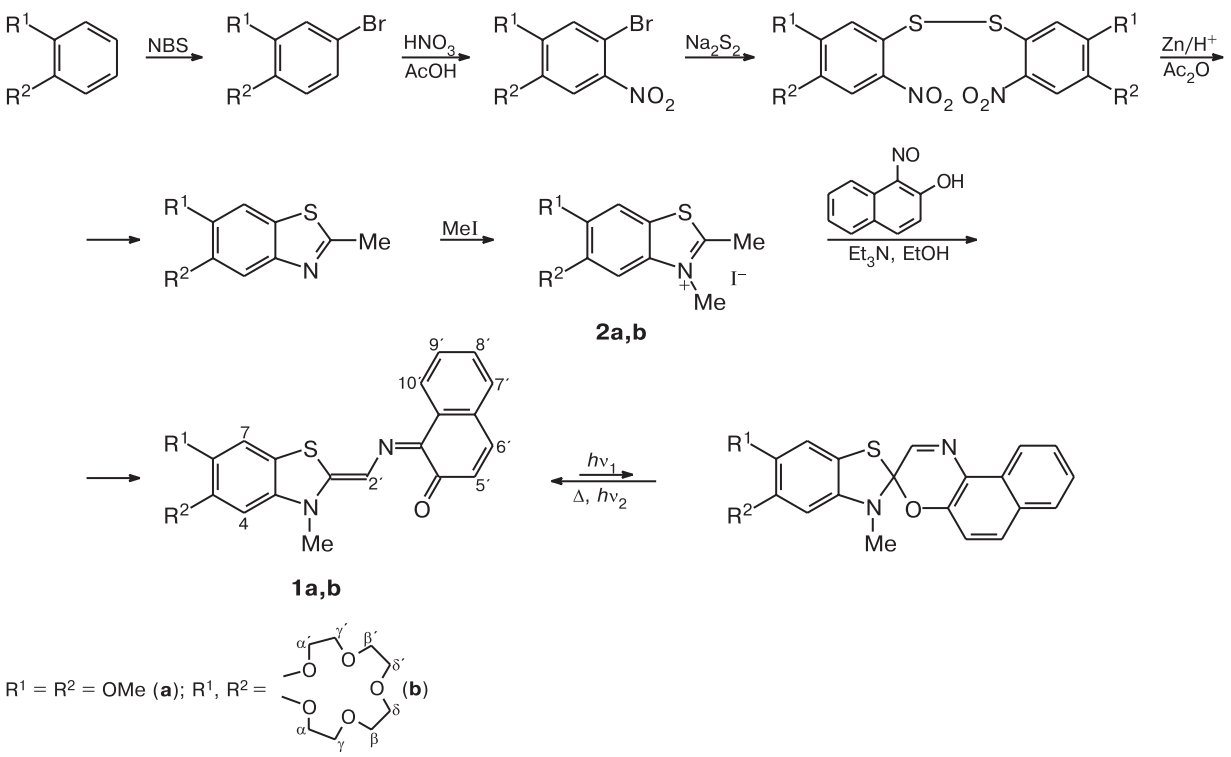
Scheme 1

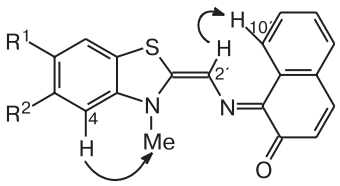


these compounds with alkaline earth metals and the effect of complexation on the capacity for photoisomerization to the spiro form were studied.

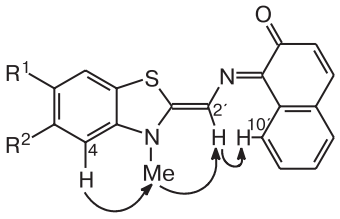
Results and Discussion

Synthesis and structure of MD 1a,b. Dyes **1a,b** were synthesized starting from substituted 2-methylbenzothiazolium salts **2a,b**, which were prepared from the corresponding benzothiazoles. Several methods have been proposed in the literature for benzothiazole synthesis.[6—8] We chose a four-step synthesis;[7,8] the large number of synthetic steps is well counterbalanced by the relatively high yield in each step and the easy accessibility of the starting compounds (Scheme 1).

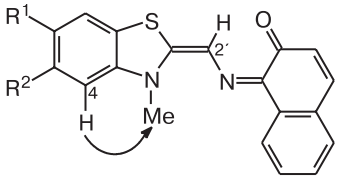
The structure of MD **1a,b** was proved on the basis of the data of ^{1}H NMR spectroscopy and COSY and NOESY techniques. The compounds **1a,b** synthesized can exist as four isomers.



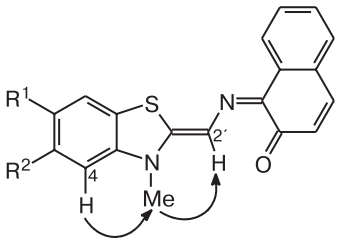
cis-trans-trans-isomer (*ctt*)



trans-trans-trans-isomer (*ttt*)



cis-trans-cis-isomer (*ctc*)



trans-trans-cis-isomer (*ttc*)

The COSY spectra of MD **1a,b** were found to exhibit cross-peaks, which allow exact assignment of the

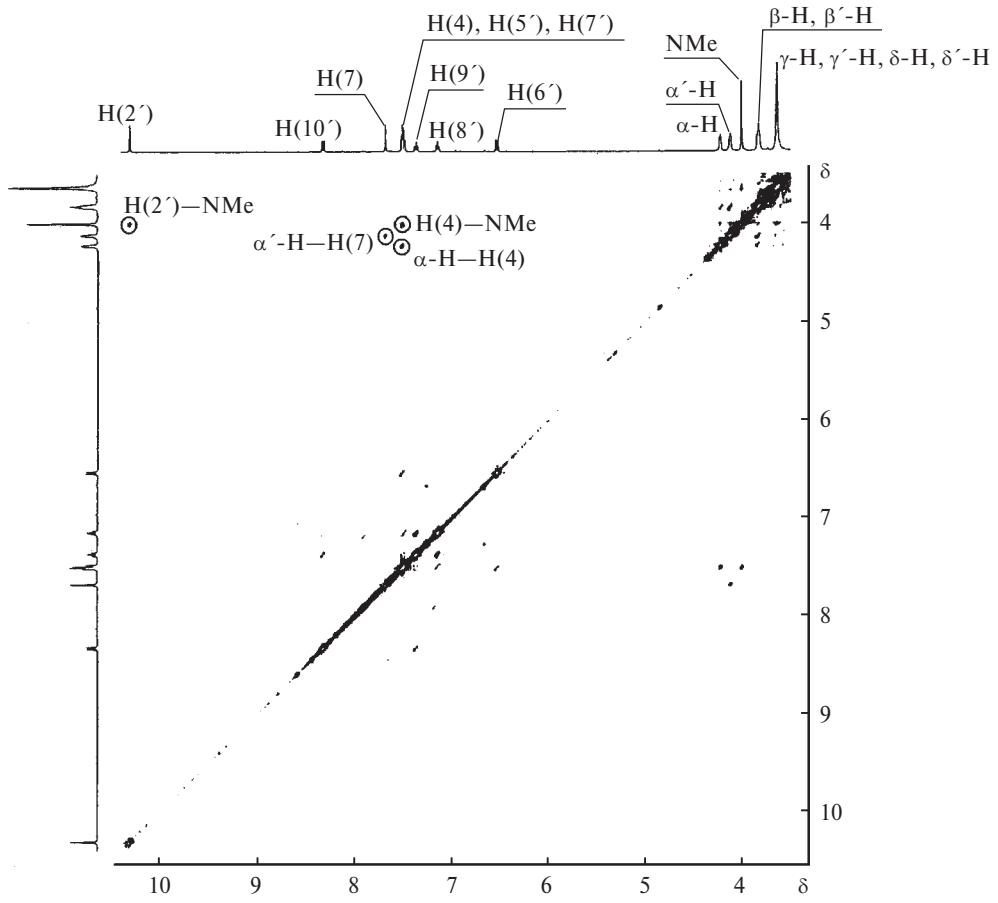


Fig. 1. NOESY ^{1}H NMR spectrum of MD **1b**.

^{1}H NMR signals (see Experimental). The NOESY spectra (Fig. 1) showed cross-peaks attesting to spatial proximity of the NMe-group protons, the H(4) proton of the benzothiazolium residue, and the H(2′) proton of the azomethine group, and in the case of **1b**, the α-H, H(4) and α′-H, H(7) protons. Among the possible isomeric structures, this situation can occur only in the *ttc*-isomer.

The compound can exist as the *ctc*-isomer only if it is mixed with the *ttc*-isomer. Since in the *ctc*-isomer, the NMe group is close in space to the H(4) proton and is remote from the H(2′) proton of the azomethine group, the spectroscopic data thus suggest that MD **1a,b** exist as mixtures of *ttc*- and *ctc*-isomers. In both isomers, the H(2′) proton is located closely to the merocyanine oxygen atom, *i.e.*, it can fall within the deshielding region of the carbonyl oxygen, which is confirmed by the low-field position of this signal (δ 10.3). The use of protic solvents capable of hydrogen bonding to oxygen of the merocyanine form may decrease the influence of the anisotropic effect of the carbonyl group on the azomethine proton and, hence, induce an upfield shift of the H(2′) signal. Indeed, this is the case on passing from DMSO-d_6 to CD_3OH; in CD_3CN, the chemical shift of the azomethine proton virtually coincides with that found in DMSO-d_6.

H(2′), δ	DMSO-d_6	CD_3CN	CD_3OH
1a	10.30	10.35	9.90
1b	10.30	10.30	10.00

In order to determine the relative stabilities of the rotational isomers of the merocyanine spironaphthoxazines, the heats of formation (ΔH_f) and the relative energies (ΔE) of rotational isomers were determined for MD **1a** as an example by semiempirical PM3 quantum-chemical calculations with a standard set of parameters[9] (Table 1). The calculations included full geometry optimization for all structures; the vibration frequencies for the compounds were also calculated in the harmonic approximation. The absence of negative values among the resulting frequencies confirms that each compound is matched by a local minimum on the potential energy surface.

The calculation of the isomer proportions at room temperature using the Boltzmann formula showed that in the gas phase, MD **1a** is an isomer mixture comprising predominantly of the *ctc* (37%) and *ttc* (33%) isomers

Table 1. Heats of formation (ΔH_f) and relative energies (ΔE) of the rotational isomers of MD **1a** and their proportions in the mixture in the gas phase according to quantum-chemical calculations

Isomer	ΔH_f	ΔE	Content
	kcal mol^{-1}		
ctt	12.45	2.52	0.124
ttt	12.17	2.24	0.152
ctc	9.93	0	0.374
ttc	10.45	0.52	0.331

Note. The relative energy of the *ctc*-isomer was taken to be zero.

(see Table 1). The C=O bond length in the naphthalene fragment in both isomers proved to be 1.22 Å, which validates the merocyanine structure of the compound.

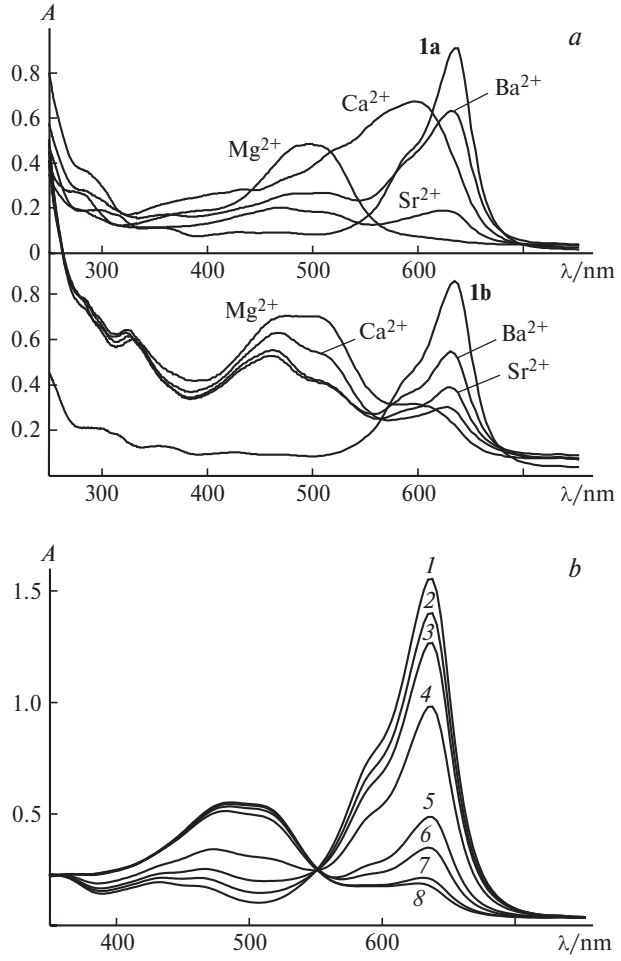


Fig. 2. Absorption spectra (MeCN, 25 °C, $C_{MD} = 4 \cdot 10^{-5}$ mol L^{-1}) of (*a*) MD **1a,b** and their complexes with various metal cations ([M^{2+}] : [**1a,b**] = 100 : 1); (*b*) MD **1b** (*1*) and its complexes with Mg^{2+} cations ([Mg^{2+}] : [**1b**] = 1 : 24 (*2*), 1 : 12 (*3*), 1 : 6 (*4*), 1 : 3 (*5*), 1 : 2 (*6*), 1 : 1 (*7*), and 2 : 1 (*8*)).

The absorption spectra of MD **1a,b** are identical in the long-wavelength region (the chromophore systems are the same) and contain an intense peak at $\lambda = 636$ nm (Fig. 2), which also confirms the existence of the stable merocyanine form for MD **1a,b**. The extinction coefficients at the long-wavelength maximum ($\lambda = 636$ nm) were 48800 and 38800 mol^{-1} cm^{-1} for MD **1a** and **1b**, respectively.

Study of complexation by ^{1}H NMR spectroscopy. The addition of alkaline earth metal perchlorates to solutions of compounds **1a,b** in MeCN entails pronounced changes in the ^{1}H NMR spectra (Fig. 3), caused by complex formation. The crown-containing MD **1b** molecule contains two sites able to coordinate metal cations, *viz.*, the crown-ether fragment and the merocyanine oxygen; therefore, generally, the complexation can be represented by Scheme 2. Compound **1a** can form only type **B** complexes.

The addition of metal salts to solutions of compounds **1a,b** induces changes in the positions of the ^{1}H NMR signals of aromatic protons, and in the case of **1b**, it also induces a downfield shift of the signals due to the crown-ether methylene protons (see Fig. 3).

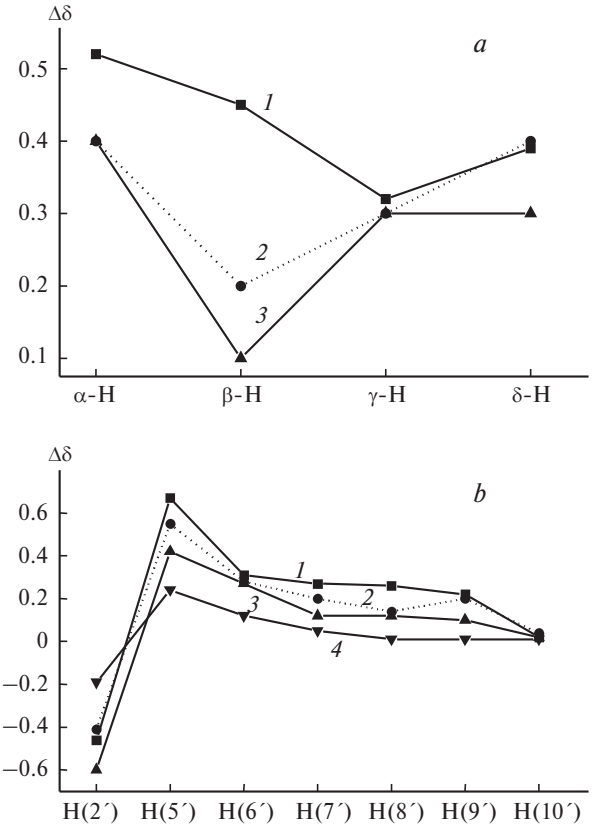
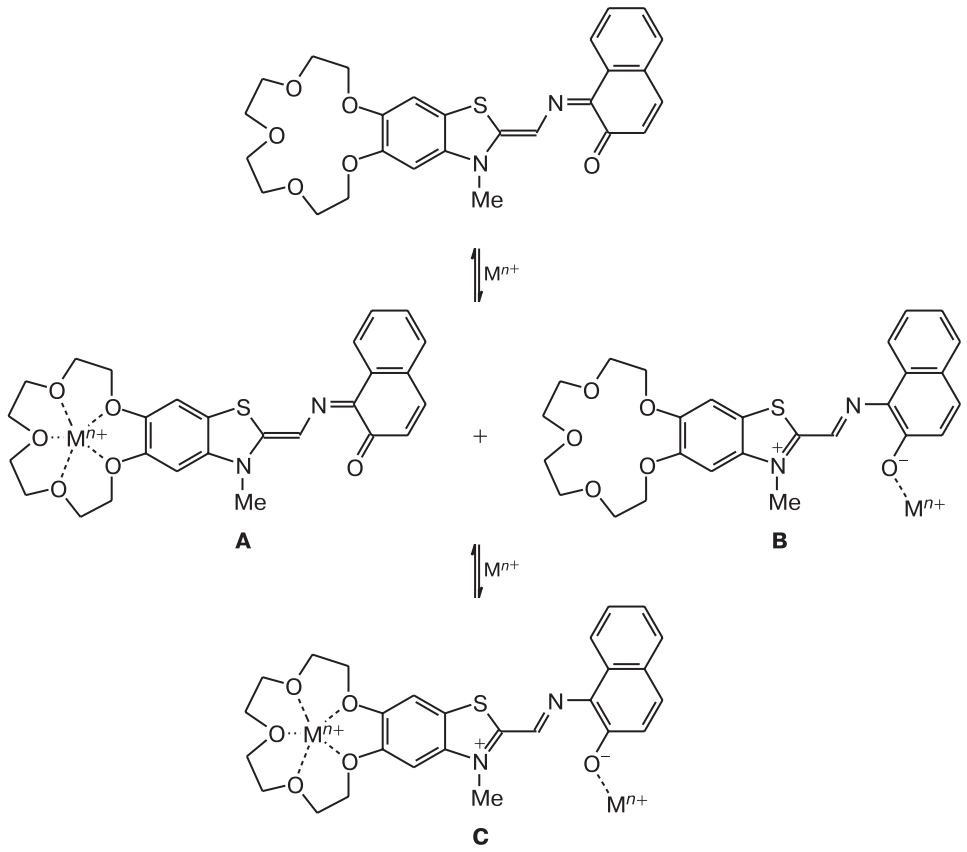


Fig. 3. Changes in the positions of the ^{1}H NMR signals (in CD_3CN) of the crown-ether moiety of MD **1b** (*a*) and the naphthalene fragment of MD **1a,b** (*b*) in the presence of Mg^{2+} (*1*, *4*), Ca^{2+} (*2*), and Ba^{2+} (*3*) cations (MD **1b**, curves *1*—*3*; MD **1a**, curve *4*).

Scheme 2



In the case of MD **1b**, the downfield shift of the proton signals corresponding to the methylene groups of the ionophoric fragment indicates that the complexation involves the crown-ether, which has been shown in our previous study for crown-containing spironaphthoxazines of different structures[10,11] (see Fig. 3, *a*, Scheme 2, complex **A**).

The signal of the azomethine H(2′) proton in MD **1a,b** undergoes a substantial upfield shift, while the proton signals of the naphthalene residues shift downfield, the most appreciable effect being observed for the H(5′) proton (see Fig. 3, *b*). This is probably due to complexation at the merocyanine oxygen atom. Indeed, the coordination of the metal cation to the O atom is expected to displace the equilibrium toward the betaine form (see Scheme 2, complex **B**). In complex **B**, the proton of the azomethine fragment does not fall any longer in the deshielding area of the carbonyl O atom; this leads to an upfield shift of the H(2′) signal (see Fig. 3, *b*). The formation of the oxygen—metal bond has a most pronounced influence on the H(5′) proton of the naphthalene residue, located in the *ortho*-position relative to the merocyanine O atom. Indeed, the signal of this proton undergoes the largest downfield shift (see Fig. 3, *b*). Finally, the betaine structure of the molecule should have an influence on the signal of the Me group at the benzothiazole N atom. In the betaine structure, the N atom is positively charged and the signals of the Me group (δ 4.30) are shifted downfield compared to the signals of the Me group in the initial merocyanine form (δ 3.90).

Thus, the data of the ^{1}H NMR spectra of compound **1b** recorded after the addition of various metal cations confirm that complexation involves both sites capable of being coordinated by metal cations. Since the studies were carried out at an equimolar ligand : metal cation ratio, one can conclude that the solution contains an equilibrium mixture of two types of complexes, **A** and **B** (see Scheme 2). The presence of an equilibrium mixture is confirmed by some signal broadening in the ^{1}H NMR spectra of the complexes formed by **1b**. The influence of the three metal cations studied (Mg^{2+}, Ca^{2+}, and Ba^{2+}) is qualitatively the same; however, it gradually decreases in this series, which may be due to the decrease in the charge density;[12] in the case of the crown-ether-containing complex, one more reason is the better fit of the Mg^{2+} cation size to the 15-crown-5 ether cavity.[13]

Optical absorption spectra and quantum-chemical calculation for MD 1a,b. The complexation of MD **1a,b** with Mg^{2+}, Ca^{2+}, and Ba^{2+} cations in MeCN in-

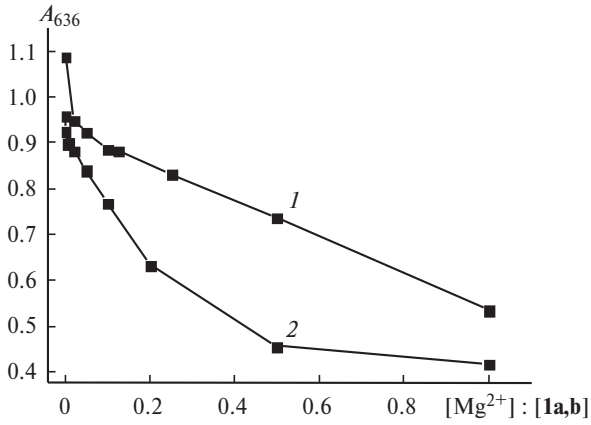


Fig. 4. Optical density of solutions of MD **1a** (*1*) and **1b** (*2*) in MeCN at $\lambda = 636$ nm in the presence of the Mg^{2+} cation at various $[Mg^{2+}] : [\mathbf{1a,b}]$ molar ratios.

duces substantial changes in the absorption spectra (see Fig. 2, *a*), which are manifested, first of all, as a decrease in the absorption at $\lambda = 636$ nm and the appearance of a typical broad band at about $\lambda = 500$ nm, these changes appearing faster for MD **1b** than for MD **1a** (Fig. 4). Apparently, this is due to the more efficient complex formation owing to the simultaneous participation of two complexation sites, the crown-ether moiety and the merocyanine oxygen. Figure 2, *a* shows the absorption spectra of free compounds **1a,b** and those in the presence of a 100-fold excess of alkaline earth metal cations. The addition of more metal cations causes virtually no further spectral changes. It can be seen from the Figure that each of the complexes MD **1a,b** formed has its own peculiar spectroscopic characteristics. A common feature is that the addition of Mg^{2+} cations gives rise to the most intense peak at $\lambda = 500$ nm, and Ba^{2+} and Sr^{2+} cations induce a less pronounced decrease in the absorption at $\lambda = 636$ nm.

Unfortunately, we could not measure the complexation constants, because the changes in the optical density observed during the titration of solutions of MD **1a,b** with metal cations are accompanied by uncontrollable protonation, oxidation, and degradation processes occurring in air (see below). Processing of the measurements results leads to relatively large discrepancies in the calculated stability constants of complexes.

In order to study the influence of complexation on the structural and electronic parameters of MD **1a,b**, to identify the energetically most favorable coordination site, and to interpret the observed shifts of the absorption bands, we carried out the PM3 calculations for the rotational isomers of **1a,b** and their complexes with Mg^{2+} in which the metal atoms are coordinated to either

Table 2. Heats of formation (ΔH_f), relative energies (ΔE), bond lengths (d), and charges on the atoms (Q) of the rotational isomers of spironaphthoxazines **1a,b** and their complexes with Mg^{2+}

Isomer	ΔH_f (ΔE) /kcal mol^{-1}	d/Å				Q/e			
		C=O	C(2)—C(2′)	C(2′)—N	N—C(3′)	N	$O_{C=O}$	O(7)	O(8)
				1a					
ctc	9.93 (0)	1.22	1.36	1.40	1.30	0.14	−0.32	−0.17	−0.20
ctc·Mg^{2+} **(B)**	368.3 (0)	1.36	1.47	1.29	1.42	0.52	−0.33	—	—
ctc·Mg^{2+} **(A)**	396.3 (28)	1.22	1.35	1.40	1.30	0.30	−0.335	—	—
ttc	10.45 (0.52)	1.22	1.36	1.40	1.30	0.17	−0.313	−0.22	−0.20
ttc·Mg^{2+} **(B)**	369 (0.7)	1.36	1.47	1.29	1.43	0.565	−0.355	—	—
ttc·Mg^{2+} **(A)**	396 (27.7)	1.23	1.35	1.40	1.30	0.334	−0.29	—	—
				1b					
ctc	103.20 (0)	1.22	1.36	1.40	1.30	0.14	−0.32	−0.17	−0.20
ctc·Mg^{2+} **(B)**	258.8 (0)	1.36	1.47	1.29	1.43	0.51	−0.33	—	—
ctc·Mg^{2+} **(A)**	314.9 (56.1)	1.22	1.35	1.40	1.30	0.23	−0.335	—	—
ttc	103.1 (0.52)	1.22	1.36	1.40	1.30	0.17	−0.31	−0.22	−0.20
ttc·Mg^{2+} **(B)**	257.4 (0.7)	1.36	1.47	1.29	1.42	0.565	−0.313	—	—
ttc·Mg^{2+} **(A)**	258.9 (27.7)	1.23	1.35	1.40	1.30	0.288	−0.295	—	—

Note. The relative energy of the *ctc*-isomer and its complex with Mg^{2+} was taken to be zero; **A** and **B** are types of complex (see Scheme 2).

methoxy-group O atoms and the crown-ether (**A**) or the merocyanine O atom (**B**) (Table 2).

According to the results, complexes **B** in which the Mg^{2+} cations are coordinated to the merocyanine O atom are thermodynamically more stable than complexes **A** in which the Mg^{2+} cation resides in the crown-ether cavity.

After coordination, complex **B** acquires a betaine structure, which shows itself as an increase in the positive charge in the benzothiazole fragment (by 0.16 *e*) and elongation of the C=O bond (1.22 Å) in the naphthalene fragment nearly to reach the C–O σ-bond length (1.36 Å). Finally, the lengths of the C(2)—C(2´), C(2´)—N, and N—C(3´) bonds, forming the chromophore system, change in such a way that the C(2)—C(2´) bond becomes longer and more similar to a single bond, the C(2´)—N bond is shortened to reach the length of a double bond, and the N—C(3´) bond is elongated to reach the single bond length. Since the initial merocyanine form is characterized by a more clear-cut averaging of the bond lengths in the conjugated system, this implies that the coordination of the metal cation to the merocyanine O atom results in a more pronounced alternation of bond lengths and, hence, in a decrease in the degree of conjugation. These changes in the structural and electronic parameters suggest that the metal coordination to the merocyanine O atom would induce a hypsochromic shift of the absorption band of the complex with respect to the band in the spectrum of the initial MD. Meanwhile, binding of the Mg^{2+} cation to the O atoms of the crown-ether moiety (complex **A**) entails no significant changes in the electron density distribution or in the bond lengths in the molecule; thus, the complexation with Mg^{2+} cations is not expected to cause any significant changes in the absorption spectrum.

Comparison of the absorption spectra of MD **1a,b** and their complexes with various metal cations (see Fig. 2, *a*) shows that the long-wavelength absorption bands actually undergo a hypsochromic shift Δν ($\Delta\nu = \nu_{complex} - \nu_{MD}$), which increases in the sequence $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$, being linearly correlated with the metal electronegativity (χ) with a good correlation coefficient (Fig. 5). Since the χ value characterizes the electron-withdrawing capacity of the element, the increase in Δν following an increase in χ implies that the MD transition into the betaine form upon coordination by the metal ion becomes more facile along the sequence $Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$. Thus, these data confirm the fact that the metal cation coordination to MD **1a,b** involves predominantly the merocyanine O atom, which is manifested as a hypsochromic shift of the absorption band of the complex, whose magnitude depends on the electronic nature of the metal cation.

Protonated MD 1a,b. In the presence of acids, the merocyanine form of the dye existing in solutions of MD **1a,b** is efficiently converted into the protonated betaine

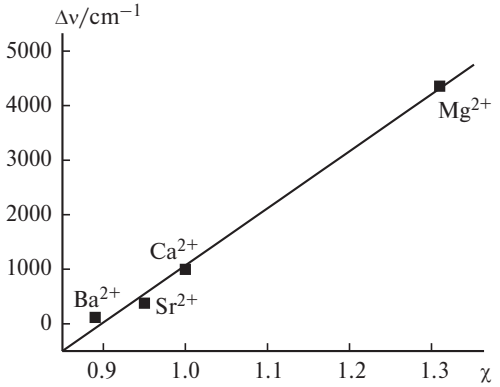
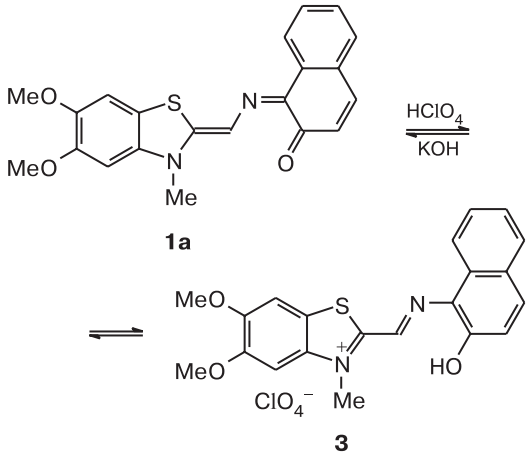


Fig. 5. Shift of the absorption band (Δν) of MD **1b** *vs.* Pauling electronegativity of the metal (χ) ($\Delta\nu = \nu_{complex} - \nu_{\mathbf{1b}}$, correlation coefficient 0.997).

structure. The concomitant changes in the absorption spectra are similar to those induced by complexation with alkaline earth metal cations. A maximum appears at about λ = 500 nm, while the absorption at λ = 636 nm decreases; however, upon subsequent addition of a solution of alkali (KOH), the maximum at λ = 500 nm disappears and the absorption at λ = 636 nm returns to the state existing before the above manipulations (with allowance for dilution). Analogous results were obtained by using acetic or perchloric acid or by passing CO_2 through solutions of MD **1a,b**.

The fact that MD **1a,b** are protonated on acidifying the solution was confirmed by isolation and characterization of compound **3** (Scheme 3).

Scheme 3

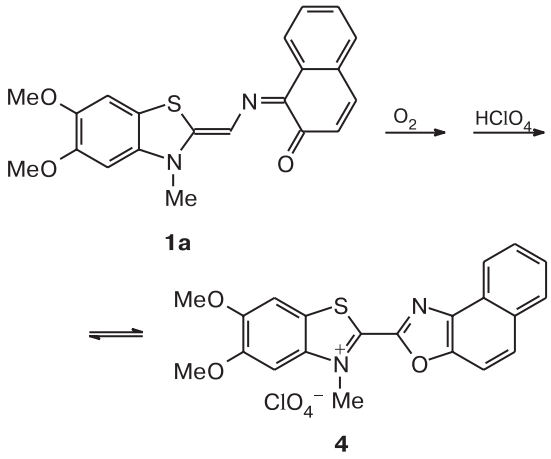


Oxidation and degradation of MD 1a,b. When solutions of MD **1a,b** are stored for several days at ~20 °C, an absorption band appears in the region of 430—470 nm, which corresponds to a new compound with intense fluorescence. The formation of the luminophore is irrevers-

ible and can be retarded by lowering the temperature or by removing oxygen from the solution.

Published data[14] lead to the suggestion that the arising fluorescing product is an oxazole derivative resulting from the oxidation of MD by atmospheric oxygen (Scheme 4). The oxidation product **4** was isolated in 8% yield after a 300-h storage of a solution of MD **1a** in MeCN and its structure was proved by a set of physicochemical methods (see Experimental).

Scheme 4



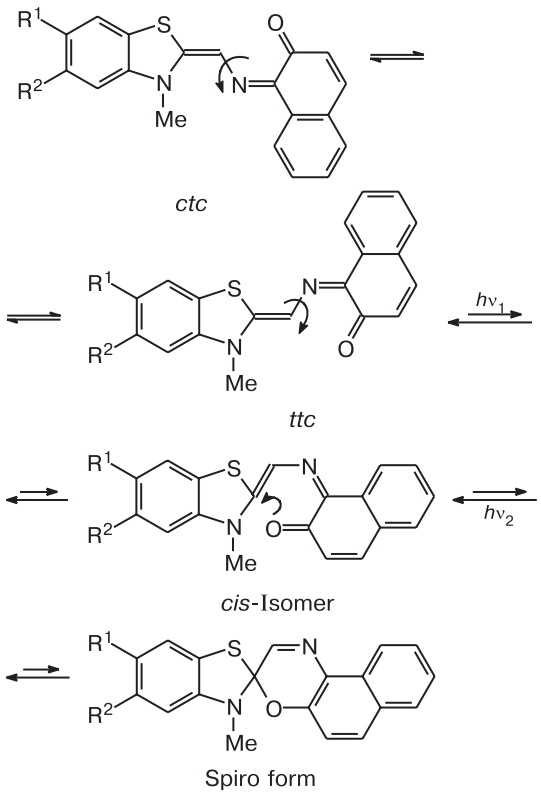
The oxidation is accompanied by intensive formation of side products whose structure was not studied. The possible mechanisms of the formation of the oxidation and degradation products from the benzothiazole MD have been described in detail previously.[14,15]

Photochromic properties of MD 1a,b. It is known that the photoinduced merocyanine form of spiropyrans and spironaphthoxazines can be converted into the cyclic form not only in the dark but also upon irradiation within the absorption band of the open form. The photochemical formation of the MD spiro form is depicted in Scheme 5.

Merocyanine dyes **1a,b** can pass to the closed form only on exposure to light. However, irradiation of solutions of these compounds by a flash of a 235-J xenon lamp with an OS14 filter (transmission of light with $\lambda > 580$ nm) does not change the absorption at $\lambda = 636$ nm, pointing to a very low quantum yield of the photoinduced discoloration. Only irradiation with a DKSSh-200 xenon lamp with an OS14 or KS11 filter (transmission of light with $\lambda > 610$ nm) for 60 s or with a DRSh-1000 mercury lamp with a OS12-5 filter (transmission of light with $\lambda > 550$ nm) for 30 s does allow one to obtain the closed forms of these compounds and to study the regularities of the photochromic process (Fig. 6).

The discoloration of MD includes two successive stages: isomerization of the *trans*-merocyanine to give

Scheme 5



the *cis*-isomer and cyclization to give the spiro form. The formation of the coordination bond between the merocyanine O atom and the metal cation can influence the photochromic process in the following way. First, coordination of the metal cation to the merocyanine O atom shifts the equilibrium between the merocyanine and betaine forms toward the latter. Since the first step of the photochromic reaction, that is, *trans*—*cis*-isomerization involves rotation around the C—N bond, an in-

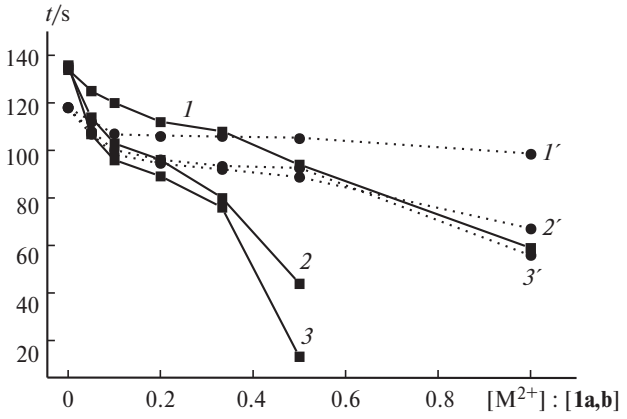


Fig. 6. Lifetime of the closed form (*t*) of MD **1a** (*1*—*3*) and **1b** (*1′*—*3′*) in MeCN *vs.* the $[M^{2+}] : [\mathbf{1a,b}]$ ratio (M^{2+} = Ba^{2+} (*1*, *1′*), Ca^{2+} (*2*, *2′*), and Mg^{2+} (*3*, *3′*)).

crease in the contribution of the betaine form hampers isomerization. Second, the coordination of oxygen to the metal prevents oxygen from participating in the cyclization giving the spiro ring. Indeed, as can be seen from Fig. 6, an increase in the metal cation concentration in a solution of MD **1a** reduces the lifetime of the closed form.

When complexation involves the crown-ether moiety, the merocyanine structure of the molecule is retained. As can be seen from the data given in Table 2, in type **A** complex, the *ttc*-isomer predominates in the mixture because, according to calculations, this isomer is more stable than the *ctc*-isomer. Both these facts should facilitate cyclization to give the spiro form.

When a metal cation is added to a solution of MD **1b** in MeCN, the metal cation is coordinated to both complexation sites. These two processes exert opposite effects on the photochromic transformation. Therefore, despite the fact that an increase in the salt concentration in a solution of MD **1b** in MeCN does reduce the lifetime of the closed form, this process is much slower than that in the case of MD **1a** (see Fig. 6).

The influence of the metal cations on the equilibrium between the closed and the open forms of MD (see Fig. 6) depends on characteristics of the cation and the resulting complex. The interaction between the merocyanine oxygen and the metal cation is determined by the charge density on the metal, *i.e.*, the complex strength decreases in the order $Ba^{2+} < Ca^{2+} < Mg^{2+}$. The effect of the cation on the lifetime of the closed form (see Fig. 6) found in our photochemical experiments decreases along the same sequence. In the complexes involving the crown-ether moiety, the correspondence of the metal cation size to the crown-ether cavity is important, in addition to the charge density. In this case, both factors act in the same direction; hence, the strength of the complexes decreases in the sequence $Ba^{2+} < Ca^{2+} < Mg^{2+}$ (see Fig. 6).

Thus, the data of the NMR and UV spectroscopy and the results of quantum-chemical calculations indicate that the addition of alkaline earth metal perchlorates to solutions of MD **1b** in MeCN results in binding of the metal cation to two complexation sites of the molecule, namely, the crown-ether moiety and the merocyanine carbonyl O atom. The complexation at the crown-ether fragment entails a decrease in the long-wavelength absorption intensity and a slight hypsochromic shift of the band; during the photochromic reaction, this process promotes the formation of the closed form. Complexation at the merocyanine O atom induces a substantial hypsochromic shift of the long-wavelength absorption band and contributes to further stabilization of the open merocyanine form. This study demonstrates the possibility of varying the spectroscopic and photochromic characteristics of spironaphthoxazines by means of complexation.

Experimental

^{1}H NMR spectra were recorded on Bruker AMX-400 and Bruker DRX-500 spectrometers. Mass spectra were run on a Varian MAT 311A instrument (70 eV) with direct sample injection into the ionization area.

The optical absorption spectra were measured on a Specord M40 spectrophotometer and the lifetimes were determined using a modernized experimental setup[16] connected to an IBM PC AT computer.

For the synthesis of spironaphthoxazines, commercial reagents and solvents (Fluka, Merck, and Aldrich) were used as received.

The reactions were monitored by TLC on DC-Alufolien Kieselgel 60 F_{254} and DC-Fertigplatten RP-18 F_{254}s plates. Column chromatography was performed using Silica gel 60 (0.063—0.200 mm) and Silica gel 60 RP-18 (0.040—0.063 mm).

1-[(3-Methyl-6,7,9,10,12,13,15,16-octahydro[1,4,7,10,13]pentaoxacyclopentadecyno[2,3-*f*][1,3]benzothiazol-2(3*H*)-ylidene)methylimino]naphthalen-2-one (1b). A mixture of benzothiazolium iodide **2b** (0.247 g, 0.5 mmol), 1-nitroso-2-naphthol (0.086 g, 0.5 mmol), EtOH (3 mL), and Et_3N (0.1 mL, 0.7 mmol) was refluxed for 2 h under argon. The reaction mixture was cooled and concentrated. Chromatographic separation gave 0.043 g (17%) of compound **1b**, m.p. 122—124 °C (decomp.). Found (%): C, 57.62; H, 5.94; N, 4.70. $C_{27}H_{28}N_2O_6S \cdot 3\,H_2O$. Calculated (%): C, 57.64; H, 6.09; N, 4.97. ^{1}H NMR (DMSO-d_6), δ: 3.64 (m, 8 H, 4 OCH_2); 3.83 (m, 4 H, 2 OCH_2); 4.00 (s, 3 H, NMe); 4.12 (m, 2 H, OCH_2); 4.22 (m, 2 H, OCH_2); 6.53 (d, 1 H, H(6′), J = 9.4 Hz); 7.15 (m, 1 H, H(8′)); 7.38 (m, 1 H, H(9′)); 7.50 (m, 3 H, H(4), H(7′), H(5′)); 7.68 (s, 1 H, H(7)); 8.32 (d, 1 H, H(10′), J = 8.2 Hz); 10.31 (s, 1 H, H(2)). MS, m/z (I_{rel} (%)): 493 $[M]^+$ (7), 492 (22), 360 (16), 169 (15), 114 (14), 58 (23), 45 (26), 44 (12), 43 (100), 42 (13), 39 (14).

1-[(3-Methyl-1,3-benzothiazol-2(3*H*)-ylidene)methylimino]naphthalen-2-one (1a) was prepared similarly to **1b** from salt **2a** and 1-nitroso-2-naphthol. Yield 44%, m.p. 188—190 °C (decomp.). Found (%): C, 62.38; H, 5.93; N, 6.84. $C_{21}H_{18}N_2O_3S \cdot 1.5\,H_2O$. Calculated (%): C, 62.20; H, 5.22; N, 6.90. ^{1}H NMR (DMSO-d_6), δ: 3.91 (s, 3 H, OMe); 3.98 (s, 3 H, OMe); 4.32 (s, 3 H, NMe); 7.13 (d, 1 H, H(6′), J = 8.9 Hz); 7.36 (m, 1 H, H(8′)); 7.54 (m, 1 H, H(9′)); 7.72 (s, 1 H, H(4)); 7.75 (d, 1 H, H(7′), J = 7.1 Hz); 7.81 (d, 1 H, H(5′), J = 8.9 Hz); 7.90 (s, 1 H, H(7)); 8.44 (d, 1 H, H(10′), J = 7.7 Hz); 10.03 (s, 1 H, H(2)). MS, m/z (I_{rel} (%)): 378 $[M]^+$ (35), 209 (65), 170 (36), 169 (100), 142 (68), 141 (72), 114 (83), 113 (52), 63 (32), 58 (56), 43 (81).

2-[(2-Hydroxy-1-naphthyl)imino]methyl-3-methyl-5,6-dimethoxy-1,3-benzothiazolium perchlorate (3). Perchloric acid (0.05 mL) was added to a solution of MD **1a** (0.05 g, 0.13 mmol) in 20 mL of MeCN. After keeping the reaction mixture for 0.5 h at ~20 °C, the solvent and excess acid were removed *in vacuo* and the residue was dried. Yield 0.06 g (quantitative), m.p. 233—237 °C. Found (%): C, 50.38; H, 3.93; N, 5.84. $C_{21}H_{19}ClN_2O_7S \cdot H_2O$. Calculated (%): C, 50.76; H, 4.26; N, 5.64. ^{1}H NMR (CD_3OD), δ: 3.95 (s, 3 H, OMe); 4.02 (s, 3 H, OMe); 4.07 (s, 3 H, NMe); 7.35 (d, 1 H, H(5′), J = 9.0 Hz); 7.50 (m, 1 H, H(8′)); 7.52 (s, 1 H, H(4)); 7.66 (m, 1 H, H(9′)); 7.70 (s, 1 H, H(7)); 7.79 (d, 1 H, H(6′), J =

8.7 Hz); 7.92 (d, 1 H, H(7´), J = 4.2 Hz); 7.96 (d, 1 H, H(10´), J = 4.3 Hz).

2-(1,3-Benzoxazol-2-yl)-3-methyl-5,6-dimethoxy-1,3-benzothiazolium perchlorate (4). A solution of MD **1a** (0.05 g, 0.13 mmol) in 20 mL of MeCN was kept in a flask in the light for 300 h. Perchloric acid (0.01 mL) was added to the reaction mixture, the solvent was evaporated, and the residue was chromatographed on a column with SiO_2 (elution with MeCN—MeOH, 1 : 1) to give 5 mg (7%) of compound **4**, m.p. 133—135 °C. Found (%): C, 52.68; H, 3.93; N, 5.64. $C_{21}H_{17}ClN_2O_7S$. Calculated (%): C, 52.90; H, 3.56; N, 5.87. ^{1}H NMR (DMSO-d_6), δ: 3.99 (s, 3 H, OMe); 4.08 (s, 3 H, OMe); 4.90 (s, 3 H, NMe); 7.53 (s, 1 H, H(2´)); 7.79 (m, 1 H, H(8´)); 7.89 (m, 1 H, H(9´)); 7.98 (s, 1 H, H(4)); 8.12 (s, 1 H, H(7)); 8.21 (d, 1 H, H(6´), J = 9.0 Hz); 8.25 (d, 1 H, H(7´), J = 8.1 Hz); 8.34 (d, 1 H, H(5´), J = 9.1 Hz); 8.63 (d, 1 H, H(10´), J = 8.1 Hz).

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