Russian Chemical Bulletin, International Edition, Vol. 51, No. 5, pp. 789—795, May, 2002

Simulation of optical response to complex formation of crown-containing 2-styrylbenzothiazoles with alkaline-earth metals

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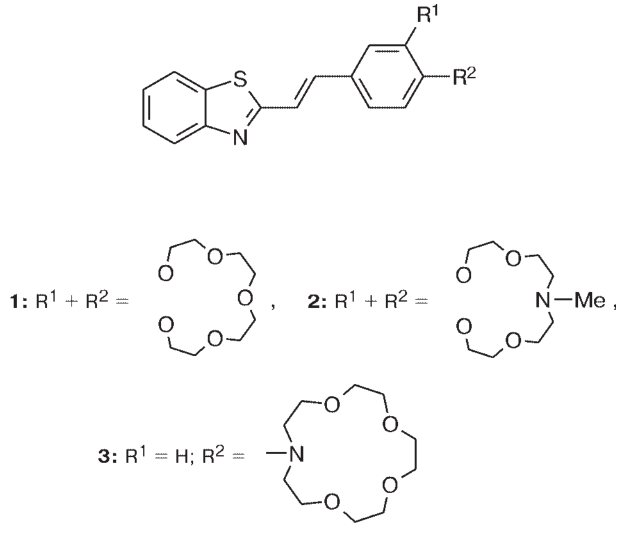
The photochromic properties and complex formation of 2-styrylbenzothiazoles containing different crown ether moieties with alkaline-earth metals were described using optical methods, NMR spectroscopy, and HPLC. The large ionochromic effect and fluorescence quenching on complex formation with alkali-earth metal cations were found for 2-styrylbenzothiazole containing the phenylazacrown ether moiety. The small ionochromic effect and fluorescence enhancement of complex formation with alkali-earth metal cations were found for 2-styrylbenzothiazole containing the benzocrown ether moiety. *cis*-Isomers of 2-styrylbenzothiazoles were stable in the dark in acetonitrile. The method for separation of *cis*-isomers of 2-styrylbenzothiazoles by HPLC was proposed.

Key words: crown ethers, 2-styrylbenzothiazoles, complex formation, UV spectroscopy, fluorescence, NMR spectroscopy.

The introduction of the crown ether moiety into the chromo- or fluorophore molecule allows a substantial change in the optical characteristics of the molecule by complex formation with metal ions.[1—6] Similar compounds named chromo- or fluoroionophores are the main element in optical sensors used for the determination of metal cations in solutions, analysis of biological liquids and industrial waste, and environmental monitoring.[7—9]

In this work, we studied a change in the electronic absorption and fluorescence spectra of crown-containing 2-styrylbenzothiazoles (CSB) **1—3** (synthesis and characteristics of the compounds were described previously[10]) in complex formation with alkaline-earth metal cations. The crown ether fragments of CSB **1—3** contain benzo-15-crown-5 (**1**), benzoaza-15-crown-5 (**2**), and phenylaza-15-crown-5 (**3**). The pair of substituents, *viz.*, benzo- or phenylazacrown ether fragment and heteroaromatic residue, along with the central C=C double bond form a common p,π-system including the electron donor (crown ether fragment) and electron acceptor (heteroaromatic residue). Taking into account this structure, we can expect that the reaction of the crown ether fragments of CSB **1—3** with metal cations substantially changes the optical characteristics. The purpose of the work was to reveal the type of the crown ether fragment at which optical responses to complex formation were maximum.



Experimental

Electronic absorption and fluorescence spectra were recorded on a Specord M-40 spectrophotometer attached to a computer and on a Shimadzu RF-5000 spectrofluorimeter at 20±1 °C. Fluorescence quantum yields (φ_{fl}) were determined by the comparison with the standard (fluorescein in a 0.01 *M* aqueous solution of KOH, λ_{exc} = 365 nm). ^{1}H NMR were obtained on a Bruker DRX-500 spectrometer in CD_3CN using Me_4Si as an internal standard. Chemical shifts were measured with an accuracy of 0.01 ppm, and SSC constants were determined with an accuracy of 0.1 Hz. HPLC studies were carried out on a Waters-600 high-pressure chromatograph.

Solutions of CSB and their complexes were irradiated with the light from a DRK-120 mercury lamp. Individual lines in

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 727—733, May, 2002.

the spectrum of this lamp were separated by glass light filters from a standard set of colored optical glasses (UFS-2 + ZhS-3, UFS-6 + BS-7, and PS-13 + ZhS-10 to separate lines at $\lambda = 313$, 365, and 405 nm, respectively). The light intensity was measured using the ferrioxalate actinometer.

Perchlorates of Mg, Ca, and Ba were dried *in vacuo* at 230 °C. Acetonitrile (specially pure grade) with the water content <0.005% was used without additional purification.

Complex formation was studied by spectrophotometric titration at 20±1 °C varying the concentration of Mg, Ca, or Ba perchlorates at a constant concentration of CSB. All experiments were carried out at the red light indoors. The absorption spectra were processed and complex formation constants were calculated using the HYPERQUAD program.[11]

Results and Discussion

Study of CSB 1—3 and their complexes with alkali-earth metals by electronic and NMR spectroscopy. The absorption spectra of CSB **1** and **2** (*trans*-isomers are implied hereinafter if no other is indicated) virtually coincide (Fig. 1, Table 1). In the case of CSB **3**, the bathochromic shift of the long wavelength absorption band by 40 nm and the hyperchromic effect (increase in the molar absorption coefficient by 16000 L mol^{-1} cm^{-1}) are observed, which is explained by a higher electron-donating capability of the crown ether substituent in compound **3** compared to **1** and **2**.

Similar to simple crown ethers, CSB **1—3** are capable of complex forming with cations of alkaline and alkaline-earth metals (Scheme 1).

The electrostatic interaction of the positively charged metal ion with heteroatoms of the crown ether fragment to a great extent decreases the electron-donating ability of the crown ether substituent, which results in the hypsochromic shift of the electronic absorption spectrum of a chromophore.

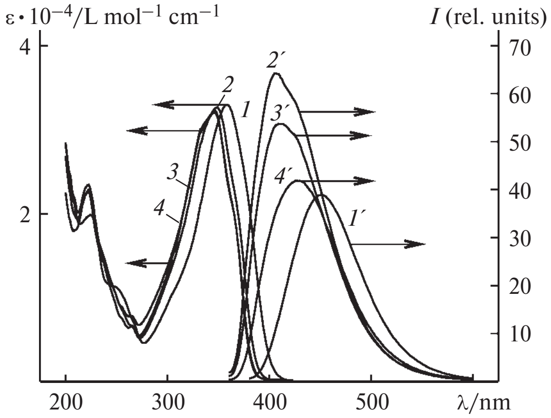


Fig. 1. Absorption (*1—4*) and fluorescence (*1′—4′*) spectra for CSB **1** (*1, 1′*, $C_0 = 2.9 \cdot 10^{-5}$ mol L^{-1}) and its complexes with Mg^{2+} (*2, 2′*, $C_M = 4.0 \cdot 10^{-3}$ mol L^{-1}), Ca^{2+} (*3, 3′*, $C_M = 4.1 \cdot 10^{-3}$ mol L^{-1}), and Ba^{2+} (*4, 4′*, $C_M = 4.0 \cdot 10^{-3}$ mol L^{-1}) in MeCN. The wavelength of fluorescence excitation is 365 nm.

Table 1. Spectral luminescence characteristics of CSB **1—3** and their complexes with the Mg^{2+}, Ca^{2+}, and Ba^{2+} cations in MeCN

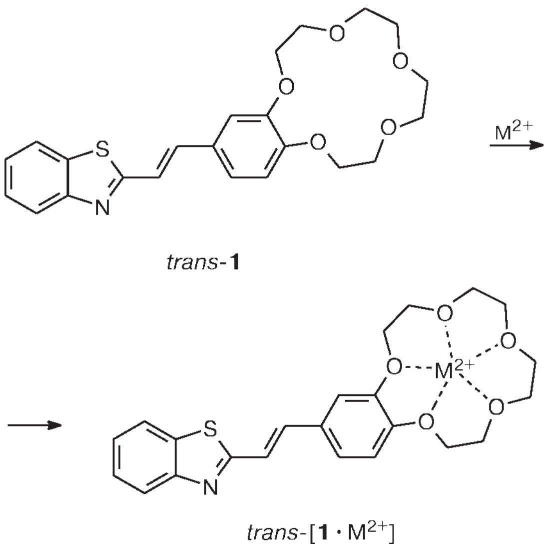
Compound	λ_{max}^{abs}/nm ($\varepsilon_{max} \cdot 10^{-4}$)^a		λ_{max}^{fl}/nm ($-\Delta\lambda$/nm)^c	φ_{fl}^b
	trans-Isomer	*cis*-Isomer		
1	358 (3.3)	350 (1.04)	452	0.024
2	357 (3.3)	349 (1.07)	448	0.025
3	399 (4.9)	399 (1.98)	505	0.066
1 · Ca^{2+}	346 (3.23)	333 (1.2)	415 (37)	0.032
2 · Ca^{2+}	346 (3.25)	330 (1.2)	433 (15)	0.026
3 · Ca^{2+}	347 (4.01)	316 (1.5)	492 (13)	0.045
1 · Mg^{2+}	346 (3.23)	—	408 (44)	0.035
2 · Mg^{2+}	352 (3.24)	—	439 (9)	0.022
3 · Mg^{2+}	346 (4.08)	—	489 (16)	0.040
1 · Ba^{2+}	349 (3.25)	—	431 (21)	0.025
2 · Ba^{2+}	349 (3.21)	—	443 (5)	0.023
3 · Ba^{2+}	357 (4.12)	—	492 (13)	0.043

[a] Wavelength of the maximum in the electronic absorption spectrum and molar absorption coefficient/L mol^{-1} cm^{-1} (in parentheses).

[b] Fluorescence quantum yield.

[c] Wavelength of the maximum in the fluorescence spectrum and $\Delta\lambda = \Delta\lambda_L - \Delta\lambda_c$ (indices "L" and "c" concern the ligand and complex, respectively).

Scheme 1



trans-**1**

trans-[**1** · M^{2+}]

M = Mg, Ca, Ba

The maximum shift of the long wavelength absorption band (LAB) is observed for CSB **3**. This effect can be caused by two factors: (a) a lone electron pair of the N atom is deduced from conjugation with the chromophoric system due to the formation of a coordination bond with the metal cation; and (b) the conformational rearrangement of the macrocycle during complex formation changes the trigonal planar configuration of the

Table 2. Stability constants of CSB complexes **1—3** with the Mg^{2+}, Ca^{2+}, and Ba^{2+} cations in MeCN at 293 K

Compound	Ion	$\log K_{11}$ ($\log K_{21}$)	Ion strength $\cdot 10^4$ /mol L^{-1}
1	Mg^{2+}	5.5±0.1	0—8
	Ca^{2+}	5.6±0.1 (10.3±0.2)	0—8
	Ba^{2+}	— (>11)	0—8
2	Mg^{2+}	5.4±0.1	0—8
	Ca^{2+}	4.9±0.1	0—8
	Ba^{2+}	5.1±0.1	0—8
3	Mg^{2+}	2.35±0.04	0—300
	Ca^{2+}	3.6±0.04	0—60
	Ba^{2+}	3.1±0.04	0—90
cis-**3**	Ca^{2+}	3.7±0.04	0—60

N atom to the pyramidal[12] one and deduces it from conjugation with the chromophoric system. Similar changes can also take place for the complex formation of CSB **1** and **2**. However, the effect is much lower because of the lower electron-donating ability of the O atom and the rigid structure of the benzocrown ether fragment.

To determine the stability constants of the CSB complexes **1—3** with alkaline-earth metal cations, we used spectrophotometric titration. Specific amounts of metal perchlorate were consecutively added to a solution with the known concentration of the dye, and the absorption spectrum was recorded after each addition. The stability constants for the complexes were determined by analysis of the spectrophotometric titration data. The results are presented in Table 2. The possibility of LM and L_2M complex formation was taken into account in the calculation (Scheme 2).

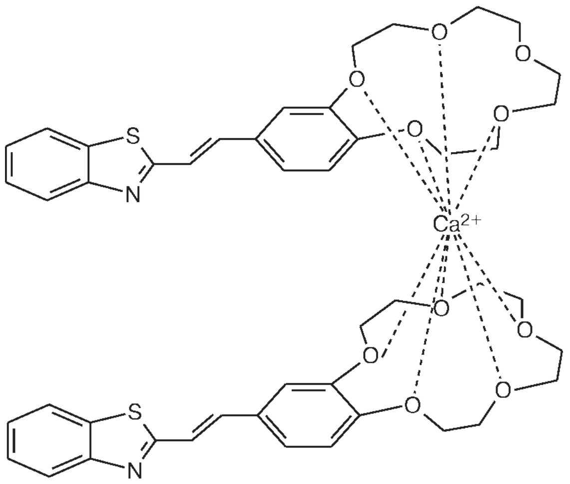
Scheme 2

$$\mathrm{L} + \mathrm{M} \underset{}{\overset{K_{11}}{\rightleftharpoons}} \mathrm{LM} \qquad K_{11} = \frac{[\mathrm{LM}]}{[\mathrm{L}]\cdot[\mathrm{M}]}$$

$$2\,\mathrm{L} + \mathrm{M} \underset{}{\overset{K_{21}}{\rightleftharpoons}} \mathrm{L_2M} \qquad K_{21} = \frac{[\mathrm{L_2M}]}{[\mathrm{L}]^2\cdot[\mathrm{M}]}$$

The complex formation constants for CSB **1** and **2** with alkaline-earth metals (see Table 2) are close and higher than the corresponding constants for CSB **3**. Since the participation of the N atom of the crown ether cycle in the formation of the chromophoric system of dye **3** is substantial, this restricts the possibility of its participation in complex formation.

The cations with a great diameter (Ca^{2+}, Ba^{2+}) and benzo-15-crown-5 derivatives are characterized by the formation of the 2 : 1 sandwich-type complexes.[13] In our experiments we found both the 1 : 1 and 2 : 1 complexes in the case of CSB **1** and Ca^{2+} cation. CSB **1** forms the 2 : 1 complex with the Ba^{2+} cation, and its stability constant is so high that cannot be detected by spectrophotometric titration, which is also related, most likely, to the formation of a stable sandwich complex.



2 **1**·Ca^{2+}

The luminescence characteristics of CSB **1—3** and their complexes with cations of alkaline-earth metals are presented in Table 1. Figure 1 presents the fluorescence spectra of CSB **1** and their complexes.

The fluorescence quantum yields of free CSB **1** and **2** (see Table 1) are identical. The N atom in the azacrown ether fragment of CSB **3** is a stronger electron donor than the O atom in the benzocrown ether macrocycle of CSB **1** or **2**, due to which the fluorescence quantum yield of CSB **3** is twice as large.

The contribution from the intramolecular charge-transfer state increases upon photoexcitation to a greater extent for CSB **3** than for **1** and **2**. Fluorescence from this state occurs with a higher efficiency than from the "locally" excited state.[14] During complex formation the metal cation interacts with the electron pair of the N atom, increasing the contribution from the intramolecular charge transfer, which results in quenching of fluorescence of CSB **3**.

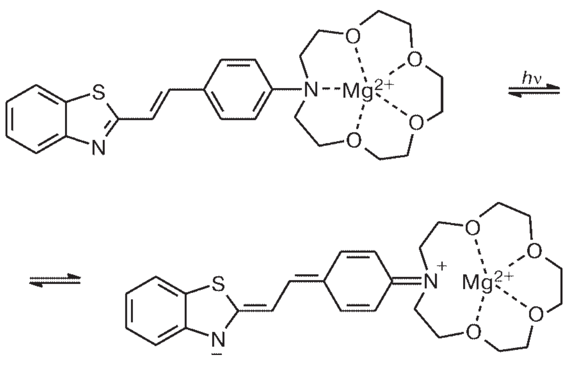
For the complex formation of CSB **2** with alkaline-earth metal cations, the fluorescence quantum yield remains almost unchanged. This indicates an insignificant participation of the O atom involved in the conjugated system of the dye in complex formation. Minor changes in the absorption spectra accompanying complex formation confirm this conclusion. Probably, the N atom in the macrocycle of CSB **2**, due to its high electron-donating ability, can efficiently be bound to the metal cation, substantially neutralizing its positive charge and decreasing the influence on the chromophoric system of the dye.

In the case of CSB **1** complex formation with the Ca^{2+} and Mg^{2+} cations, fluorescence arises. This phenomenon can be related to the fact that the conformational mobility of the macrocycle decreases upon the complex formation at the crown ether fragment, and this decreases the rate constant of nonradiative deactivation and increases the fluorescence quantum yield. Additional experiments on measuring the fluorescence lifetime are needed to confirm this hypothesis.

The hypsofluoric shifts found for CSB **2** complex formation are low and close to the corresponding hypsochromic shifts, which agrees well with the assumption about the specific coordination of the metal cation in the complex (see Table 1). CSB **1** is characterized by a combination of minor hypsochromic shifts and much larger hypsofluoric shifts accompanying the complex formation of this compound with metal cations. This phenomenon is characteristic[14] of photoexcitation processes, which can proceed with intramolecular charge transfer.

The inverse ratio of the hypsochromic to hypsofluoric shifts is observed for CSB **3** complex formation. This distinction can be due to a change in the character of metal ion coordination and its position relative to the chromophoric system of the molecule, in particular, to the cleavage of the coordination bond of the metal with the N atom of the macrocycle (photoinduced metal recoordination) (Scheme 3). Such effects have earlier been observed for styryl dyes with similar structure.[15,16]

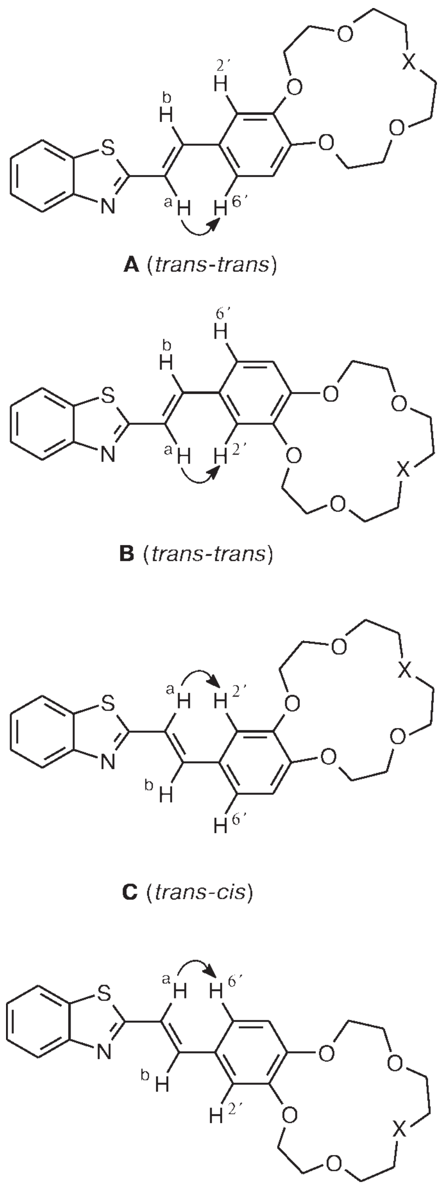
Scheme 3



Based on the SSC constants (J = 16 Hz) for olefinic protons, we conclude that CSB **1—3** are *trans*-isomers. The peaks of signals in the NMR spectrum of the initial ligands and their complexes with Ca^{2+} were assigned exactly using COSY spectroscopy. The arrangement of the structural fragments relative to each other was determined from the NOESY spectroscopic data.

Molecules of CSB **1** and **2** can exist as four isomers **A—D** (Scheme 4). The NOESY spectra of free **1** exhibit the interaction of protons of the H—C(2′) and H—C(6′) fragments with both the H_a and H_b atoms of the olefin bond. This implies that the synthesized compound can contain all four isomers. The absence of other characteristic peaks does not allow more exact choice. Only the interactions of protons of the H—C(6′) fragments with the H_a atoms appear in the spectrum of the CSB **1** complex with Ca^{2+}, *i.e.*, complex exists as a mixture of isomers **A** and **D** or one of them.

Scheme 4



A (*trans-trans*)

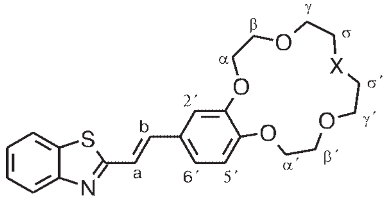
B (*trans-trans*)

C (*trans-cis*)

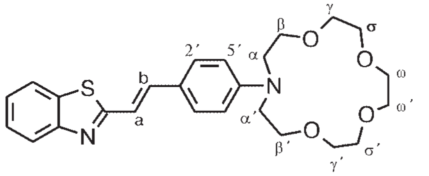
D (*trans-cis*)

The NOESY spectra of CSB **2** exhibit only the interactions of protons of the H—C(6′) and H_a fragments,

Table 3. Change in chemical shifts of protons (ppm) in the ^{1}H NMR spectrum for the complex formation of CSB **1—3** in the presence of $Ca(ClO_4)_2$



1: X = O, **2:** X = NMe



3

Compound	H_a	H_b	H—C(2′)	H—C(5′)	H—C(6′)	α,α′	β,β′	γ,γ′	σ,σ′	ω,ω′
1	0.11	0.05	0.31	0.30	0.25	0.34; 0.36	0.28	0.32	0.32	—
2	0.11	0.05	0.29	0.31	0.26	0.32; 0.27	0.26; 0.15	0.31; 0.19	0.19; 0.02	—
3	0.11	0.21	0.24	0.62	—	−0.19	0.19	0.30	0.30	0.35

Note. Conditions of spectra recording: 25 °C, ratio $Ca(ClO_4)_2$/ligand = 5/1.

and thus, conformations **B** and **C** for the free ligand are improbable.

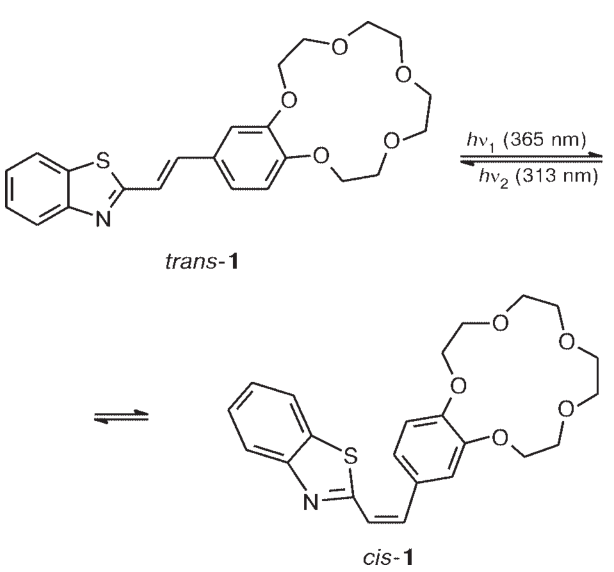
The addition of Ca perchlorate to a solution of hetarylphenylethylenes changes the chemical shifts of protons of the methylene groups, aromatic protons of benzo-, benzoaza-, and phenylazacrown ether fragments, and protons of the C=C double bond (Table 3). The influence of complex formation on the heterocyclic fragment of the molecule is low, as shown by NMR spectroscopic data. The shift of the signals from protons of the chromophoric chain (in this case, the double bond and conjugated benzene fragments of the molecule) in complex formation is more significant for CSB **3**. These data are in good agreement with the UV spectral data, according to which CSB **1** and **2** with alkaline-earth metals form stronger complexes compared to CSB **3**. However, the ionochromic effect for CSB **3** is higher than that for CSB **1** and **2**.

Changes in chemical shifts of all protons of the methylene groups in the crown ether fragment of CSB **1** are close, which can indicate the equal participation of all O atoms in complex formation. In the case of CSB **2** and **3**, the character of shifts of signals from the methylenic protons upon complex formation is more complicated and differs from the shifts for CSB **1**. When analyzing the NMR spectra of the ligands and their complexes, the effects found are determined[13] by both inherent complex formation and accompanying conformational rearrangement of the ligand. It is known[17] that for the complex formation of oxygen-containing crown ethers the metal can be localized in the cavity of the cycle. The formation of this complex is manifested in the NMR spectra as the downfield shift of the peaks from the methylenic protons compared to signals from the methylenic protons of the initial ligand. Nitrogen-containing ligands form complexes with complicated nonplanar structures in which considerable conformational rearrangement occurs. In the NMR spectrum this causes complicated changes in positions of lines from the methylene protons compared to the spectrum of the initial ligand. Similar effects take place, most likely, in our case. As follows from the data in Table 3, in the CSB **2** complex each group of the methylene protons (α, β, γ, ω) divided to two nonequivalent groups. CSB **3** is characterized by both up- and downfield shifts of lines from the methylenic protons.

***trans—cis*-Isomerization of CSB 1—3 and their complexes with alkali-earth metal cations.** When solutions of CSB **1—3** in acetonitrile are irradiated with the light with λ = 405 nm (for CSB **3**) and λ = 365 nm (for CSB **1** and **2**), absorption in the region of the long-wave band decreases with the simultaneous increase in the absorption in the short wavelength spectral region until the photostationary state is achieved. The subsequent irradiation of the resulting solution with the light with λ = 313 nm results in inverse changes in the absorption spectra up to the transition of CSB to the new photostationary state. In all cases, a distinct isosbestic point and a linear relation between the absorbances at two different wavelengths are observed. These spectral changes can be explained by reversible photochemical *trans—cis*-isomerization around the central C=C double bond (Scheme 5).

The spectra of the *cis*-isomers of CSB **1—3** were calculated from the irradiation data using the Fischer method.[18]. The absorption spectrum of the *cis*-isomer of CSB **3** is presented as an example in Fig. 2.

Scheme 5



The photochromic properties of the *cis*-isomers of CSB **1—3** and their complexes with $Ca(ClO_4)_2$ are presented in Table 1.

For CSB **1—3** the difference in the wavelengths of the absorption maxima for the *trans*- and *cis*-isomers is very low, and the $\varepsilon_c/\varepsilon_t$ ratio is rather high, which indicates an efficient conjugation in the *cis*-form between the heterocyclic group and crown ether fragment.[19] It is most likely that in *cis*-**1—3** molecules these structural fragments and C=C double bond are localized in the same plane, which provides a high efficiency of conjugation between them. The stability of the *cis*-isomers is very high: no dark isomerization was observed.

HPLC was used to analyze and separate a photostationary mixture of the *trans*- and *cis*-isomers of CSB **1—3**. Separation was performed by reverse-phase chromatography when a dual mechanism of crown ether retention[20] is realized: solvophobic interaction of the sorbate and sorbent and interaction with free silanol groups, which are present in some amount on any modified sorbent surface. In several experiments a disguising agent, *viz.*, $NaClO_4$, was added to suppress binding with silanol groups. The chromatographic conditions and retention times for the *trans*- and *cis*-isomers for CSB **1—3** are presented in Table 4. The experimental absorption spectrum of *cis*-**3** isolated from a photostationary mixture and its theoretically calculated spectrum are presented in Fig. 2.

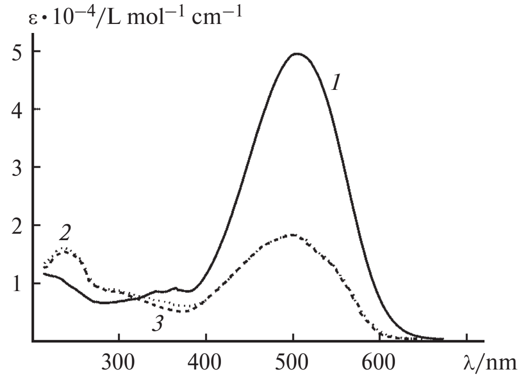


Fig. 2. Absorption spectra for *trans*- (*1*) and *cis*-isomers (*2*, *3*) of CSB **3** in acetonitrile at 293 K: *2*, spectrum calculated by the Fischer method; and *3*, spectrum of chromatographically isolated *cis*-**3**.

Based on the concentrations of the initial *trans*-isomer of CSB **3**, molar absorption coefficients for the *trans*- and *cis*-isomers, and results of HPLC analysis of the composition of a photostationary mixture of CSB **3**, we calculated the percentage content of the isomers in photostationary mixtures obtained by irradiation with the light with different wavelengths. The photostationary mixture obtained by irradiation with the light with λ = 313 nm contains 63% *cis*-isomer and 27% *trans*-isomer. In the case of irradiation with the light with λ = 365 nm, the *cis*-isomer substantially (80%) predominates.

Since *cis*-CSB **1—3** are stable in the dark, we succeeded to determine the stability constant of the *cis*-isomer of CSB **3** with the Ca^{2+} cation (see Table 2). The small difference between the complex formation constants for the *trans*- and *cis*-isomers of CSB **3** with the Ca^{2+} cation agrees with the above arguments that for *cis*—*trans*-isomerization the conjugation in the chromophore is not violated and the properties of the crown ether fragment remain unchanged.

Table 4. Chromatographic conditions and retention times of CSB **1—3**

Compound	Chromatographic conditions		Retention time/min	
	Stationary phase	Mobile phase	*trans*-Isomer	*cis*-Isomer
1	SiO_2-C16T	0.0006 *M* solution $NaClO_4$ in a MeCN—H_2O (4 : 1) mixture	11.4	9.7
2	SiO_2-C18	0.0006 *M* solution $NaClO_4$ in a MeCN—H_2O (4 : 1) mixture	6.6	5.1
3	SiO_2-CN	Hexane—ethyl acetate (4 : 1)	12	9

Thus, the obtained results show that CSB **1—3** form complexes with alkaline-earth metal cations. Complex formation changes the absorption and fluorescence spectra of CSB. The variation of the crown ether fragment structure in CSB can be used for controlling the optical response to complex formation. For example, the compounds with the phenylazacrown ether fragment exhibit a considerable ionochromic effect for binding with metal cations and fluorescence quenching (CSB **3**). The compounds with the benzocrown ether fragment are characterized by fluorescence enhancement during complex formation. Photoisomerization is efficient for all studied compounds and their complexes with alkaline-earth metal cations. However, we did not find considerable distinctions in the spectral properties and ability to complex formation for the photoisomers. The *cis*-isomers of CSB **1—3** are stable and can be isolated in the pure state by HPLC. The regularities found are significant for the development of new optical sensors.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-03-32159a and 01-03-32757) and the INTAS Foundation (Project 97-31193).

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Received March 21, 2001;
in revised form December 19, 2001