Crown-containing styryl dyes

13.* The nature of the heterocyclic moiety, complexation, and electronic absorption and fluorescence spectra of *trans*- and *cis*-isomers of photochromic 15-crown-5-ethers

S. P. Gromov, A. A. Golosov, O. A. Fedorova, D. E. Levin, and M. V. Alfimov*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
7A ul. Novatorov, 117421 Moscow, Russian Federation.
Fax: +7 (095) 936 1255

New crown ether styryl dyes containing various heterocyclic moieties and substituents were synthesized. The *cis* and *trans* isomers of crown ether styryl dyes and their complexes with metal cations were characterized by their absorption and fluorescence spectra. Based on an analysis of the spectral parameters and the shifts of the absorption and fluorescence maxima upon photoisomerization and complexation, the effects of the nature and structure of the heterocyclic moiety on the photochromism of styryl ionophores were revealed.

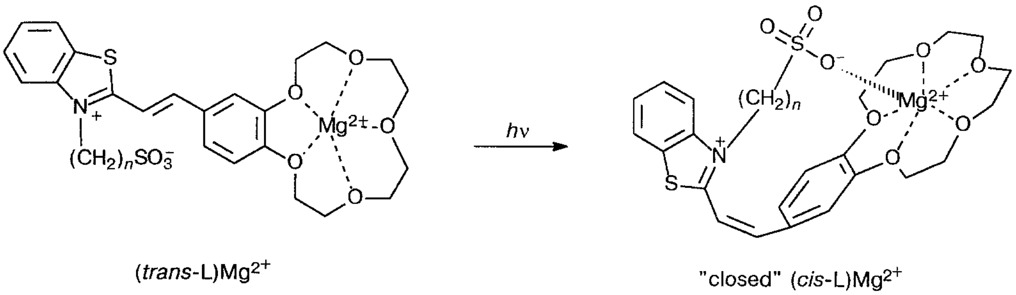
Key words: crown-containing styryl dyes, photoisomerization, complexation; electronic absorption spectra; fluorescence spectra.

To date, coupled photoisomerization and complexation reactions have been studied only for azobenzene derivatives.[2] The advantages and potentialities of photochromic crown ethers possessing a C=C double bond as the photo- and thermally switched functional group have not yet been implemented. Indeed, the significant differences between the spectral properties of complexes of *trans* and *cis* isomers of crown-containing styryl dyes with metal cations make it possible to consider them as promising components for photo-switched molecular devices.[3] These differences appear because the *cis* form contains an additional coordination bond between an anionic group of the *N*-sulfoalkyl substituent in the heterocycle of the dye and a metal ion in a cavity of the crown ether moiety. As a result, a so-called "closed" complex is formed and, simultaneously, a strong hypsochromic shift of the long-wave absorption band occurs[3,4] (Scheme 1).

We have obtained these data for styryl dyes containing benzothiazole moieties unsubstituted at the benzene cycle, in particular, for the crown-containing dye **1b** (Scheme 2).

It can be assumed that a change in the nature of the heterocyclic moiety or the introduction of substituents capable of interacting with the chromophore should have a strong effect on the spectral and complexation properties of dyes. In view of this, we synthesized a series of (15-crown-5)-containing styryl dyes (**1a—e**). The heterocyclic moieties were chosen for dyes **1a—e** from a series of the corresponding compounds with gradually increasing deviations (see Ref. 5) that relate the spectral characteristics of asymmetric styryl dyes to the electron-donating properties (basicity) of the heterocycles incorporated in these compounds. We have briefly described the synthesis of dye **1b** previously[6] (the detailed procedure has not been reported). The procedure for obtaining compound **1c** will be reported in the next communication. The desired styryl dyes **1a—e** were synthesized by condensation of betaines **2a—e** with 4-formylbenzo-

Scheme 1



(*trans*-L)Mg^{2+} "closed" (*cis*-L)Mg^{2+}

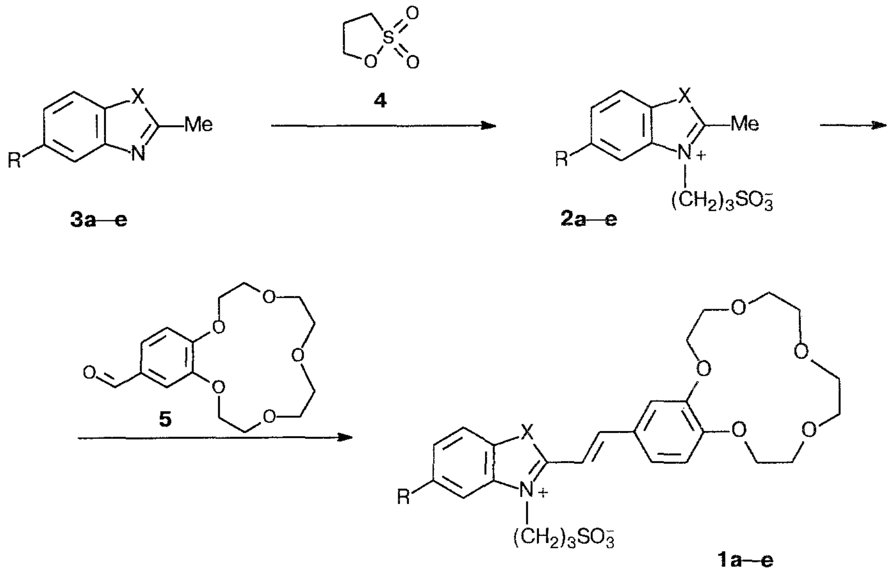
---

* For Part 12, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 129—135, January, 1995.

1066-5285/95/4401-0124 $12.50 © 1995 Plenum Publishing Corporation

Scheme 2



1—3: X = O (**a**), S (**b**, **d**, **e**), CH=CH (**c**);

R = H (**a**—**c**), Ph (**d**), MeO (**e**)

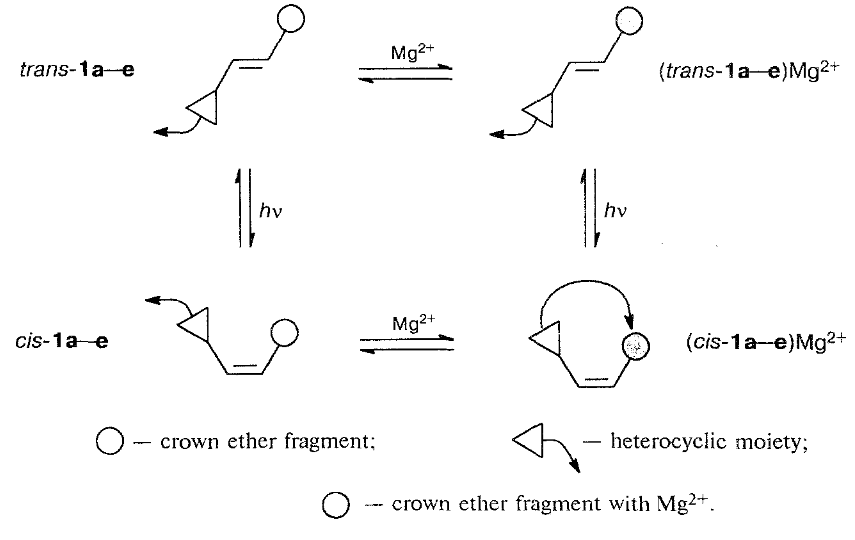
15-crown-5 (**5**) in the presence of pyridine or in acetanhydride in yields of up to 77 % (see Scheme 2).

The starting betaines **2a**—**e** were obtained by heating 2-methylbenzoxazole (**3a**), 2-methylbenzothiazole (**3b**), 2-methylquinoline (**3c**), 2-methyl-5-phenylbenzothiazole (**3d**), and 2-methyl-5-methoxybenzothiazole (**3e**), respectively, with γ-sultone (**4**) (see Ref. 7).

The structures of the resulting compounds **1a,d,e** were confirmed by ^{1}H NMR spectroscopy (see Experimental). The data of elemental analyses agree with the structures proposed. According to the ^{1}H NMR spectra, dyes **1a,d,e** exist as the *trans* forms. This conclusion can be drawn with certainty from the high coupling constant, $^3J_{trans}$ = 15.6 Hz, observed for the olefinic protons.

Dyes **1a,c**—**e** and the complexes of these ligands with Mg^{2+}, like the previously studied styryl dye **1b**,[8] undergo reversible *trans*—*cis* isomerization around the central C=C bond when irradiated (Scheme 3). The long-wave regions of the electronic absorption spectra of *trans*-**1a**—**e** contain intense bands with λ_{max} = 414—443 nm (Fig. 1, *a*). The introduction of substituents (R = Ph, MeO) at position 5 of the benzothiazole moiety in dyes **1d,e** results in a bathochromic shift of the long-wave absorption band of the *trans* isomers relative to that in the absorption spectrum of compound **1b** (Table 1). Conversely, an increase in the electron-withdrawing ability of the heterocyclic moiety results in a hypsochromic shift (**1c,b** and **1a**).

Scheme 3



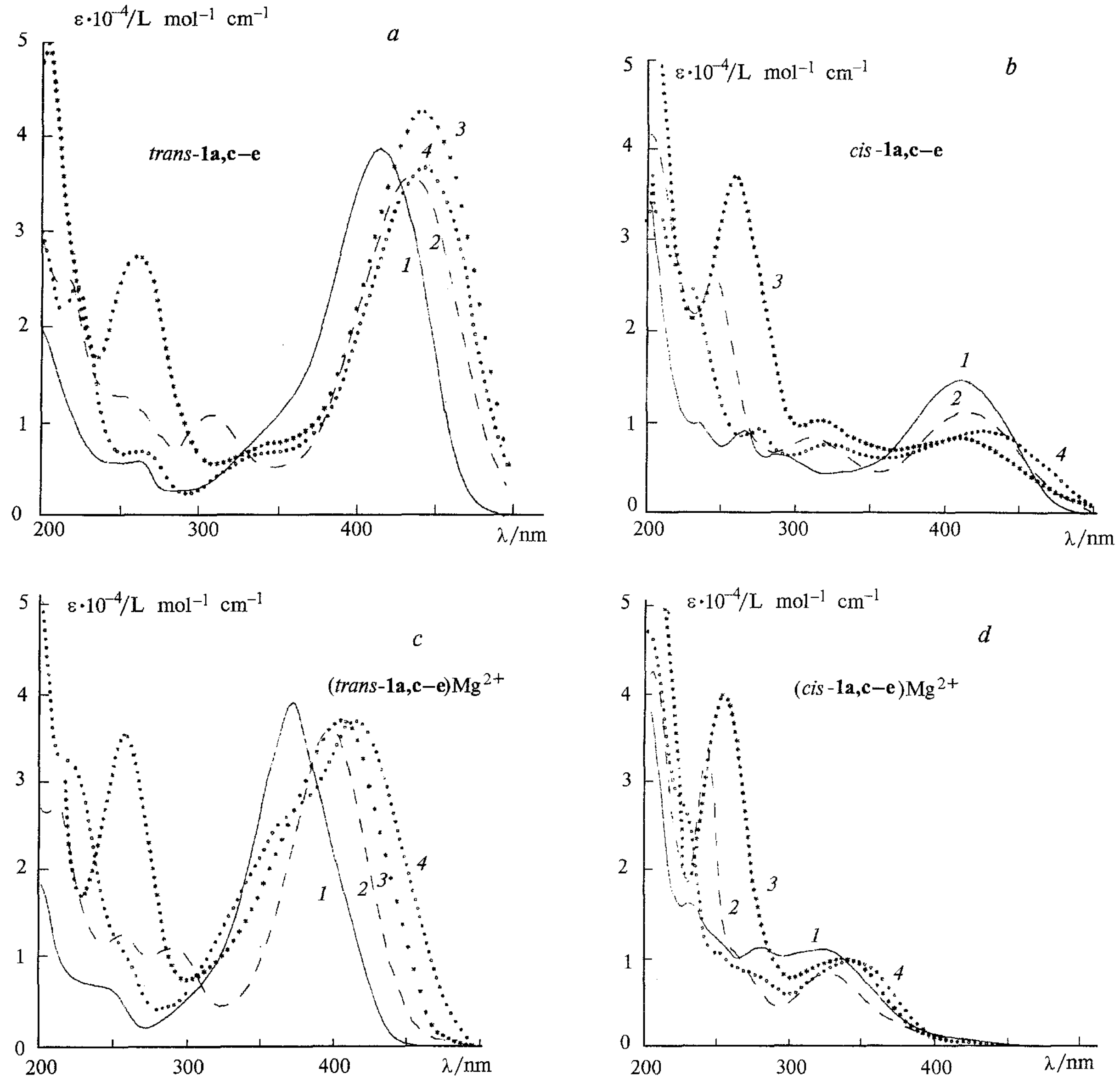


Fig. 1. Electronic absorption spectra of dyes *trans*-**1a,c—e** (*a*), *cis*-**1a,c—e** (*b*), and their complexes with Mg^{2+} (*c* and *d*, respectively, $C_M = 10^{-4}$ mol L^{-1}) in MeCN: *1*, **1a**, $C_0 = 2.04 \cdot 10^{-5}$ mol L^{-1}; *2*, **1c**, $C_0 = 2.07 \cdot 10^{-5}$ mol L^{-1}; *3*, **1d**, $C_0 = 1.49 \cdot 10^{-5}$ mol L^{-1}; *4*, **1e**, $C_0 = 1.79 \cdot 10^{-5}$ mol L^{-1}.

Table 1. Photochromic properties of *trans*-**1a—e** and *cis*-**1a—e** in MeCN

Dye	λ_{max}^{abs}/nm ($\varepsilon_{max} \cdot 10^{-4}$/L mol^{-1} cm^{-1})		Color contrast, $\Delta\lambda_{t/c}$/nm ($\Delta\varepsilon \cdot 10^{-4}$)*	$\varepsilon_c/\varepsilon_t$
	trans	*cis*		
1a	414 (3.9)	413 (1.5)	1 (2.4)	0.38
1b	435 (3.8)[6]	422 (0.89)[6]	13 (2.91)	0.23
1c	435 (3.6)	416 (1.13)	19 (2.47)	0.31
1d	442 (4.3)	406 (0.85)	36 (3.45)	0.20
1e	443 (3.7)	425 (0.93)	18 (2.77)	0.25

* $\Delta\lambda_{t/c} = \lambda_t - \lambda_c$, $\Delta\varepsilon = \varepsilon_t - \varepsilon_c$.

Using Fischer's method,[9] we calculated the absorption spectra of *cis* isomers of **1a**, **1d**, and **1e** in MeCN from the spectra of the starting *trans* isomers, taking two photostationary states (obtained by irradiation with light at λ = 365 and 436 nm) into account. The spectrum of the *cis* isomer of **1c**, for which the quantum yield of *trans—cis* photoisomerization is $\varphi_{tc} < 0.05$, was obtained by adding a small amount of water (~10 %) to the "closed" (*cis*-**1c**)Mg^{2+} (for (*trans*-**1c**)Mg^{2+}, $\varphi_{tc} = 0.4$). The (*cis*-**1c**)Mg^{2+} complex decomposed under these conditions to give the free *cis* isomer.

The maxima of the long-wave absorption bands in the spectra of *cis*-**1a—e** are shifted in the short-wave

Table 2. Luminescent characteristics of *trans*-**1a**—**e** and (*trans*-**1a**—**e**)Mg^{2+}, shifts of long-wave absorption maxima of *trans*-**1a**—**e** and fluorescence maxima of *trans*-**1a**—**e** due to complexation in MeCN

Dye	λ^f_{max}/nm	φ_f	Stokes' shift	Complex of Mg^{2+} with **1a**—**e**	λ^f_{max}/nm	φ_f	Stokes' shift	$\Delta\lambda_t^{abs}$/nm*	$\Delta\lambda_t^f$/nm*
1a	510	0.06	96	(**1a**)Mg^{2+}	475	0.014	104	43	35
1b	540[8]	0.06[8]	105	(**1b**)Mg^{2+}	501[8]	0.02[8]	108	42	39
1c	570	0.03	135	(**1c**)Mg^{2+}	505	0.07	109	39	65
1d	540	0.06	98	(**1d**)Mg^{2+}	525	0.05	118	35	15
1e	540	0.03	97	(**1e**)Mg^{2+}	535	0.10	122	30	5

* $\Delta\lambda^{abs} = \lambda_L^{abs} - \lambda_C^{abs}$, $\Delta\lambda^f = \lambda_L^f - \lambda_C^f$ (the indices L and C correspond to the ligand and the complex, respectively).

direction (relative to the maxima for the corresponding bands of the *trans* isomers) by up to 36 nm, while the ε_t^{max} values are 2.5—5 times higher than ε_c^{max} (see Table 1). The positions of the maxima of the long-wave absorption bands of compounds *cis*-**1a**—**e** differ somewhat less than those for the *trans* forms (see Fig. 1, *b*). This can be explained by assuming that the effects of the substituents are, as a whole, probably weaker in the *cis* forms due to the less effective conjugation between the heterocyclic moiety and the crown ether fragment and due to the violation of coplanarity of the chromophore owing to steric hindrance in the *cis* form. We did not observe any regular dependence of the spectral characteristics on the basicity of the heterocyclic moiety for *cis*-**1a**—**e**, as opposed to *trans*-**1a**—**e**. Calculations based on computer modeling of conformational changes in *cis*-**1b** showed[4] that the heterocyclic moiety in the *cis* form is strongly rotated relative to the plane of the double bond. The magnitude of this torsion depends not only on the basicity of the heterocycle but also on its volume.

Indeed, the color contrast in the case of *cis*-**1d** is unusually high ($\Delta\lambda_{t/c}$ = 36 nm), while the $\varepsilon_c/\varepsilon_t$ ratio is markedly lower than those for the remaining dyes studied (see Table 1). The main reason for these spectral effects is probably the considerable volume of the phenylbenzothiazole moiety, which results in greater unfolding (in comparison with *cis*-**1b**) of this moiety in the sterically strained *cis* form.

Conversely, the $\Delta\lambda_{t/c}$ value for compound **1a** is very low (1 nm), while the $\varepsilon_c/\varepsilon_t$ ratio is rather high. This can occur only if there is effective conjugation between the heterocyclic moiety and the crown ether fragment in the *cis* form. Probably, these structural fragments and the C=C double bond in *cis*-**1a** are actually located almost in the same plane, which allows highly effective conjugation between them.

The addition of $Mg(ClO_4)_2$ to *trans*-**1a,c**—**e** in MeCN results in considerable hypsochromic shifts of the maxima of the long-wave absorption bands (see Fig. 1, *c*). Similar shifts have been observed previously for crown-containing styryl dyes of the indolenine series[10] and for compound **1b**. It has been found for the latter[8] that over a wide range of C_M concentrations, this shift results from the formation of a 1 : 1 complex between the crown ether fragment of the dye and Mg^{2+}. It should be noted that the hypsochromic shift of the long-wave absorption band in the spectra of *trans* isomers of dyes **1a**—**e** due to complexation ($\Delta\lambda_t^{abs}$) gradually decreases from **1a** to **1e** (Table 2), *i.e.*, a decrease in the electron-withdrawing ability of the heterocycle and the introduction of substituents capable of interaction with the chromophore at position 5 of the benzothiazole bicycle cause a gradual decrease in the hypsochromic shift.

Unusually high hypsochromic shifts of the long-wave maxima ($\Delta\lambda_c^{abs}$ = 70—100 nm, see Fig. 1, *d*) are observed when all of the *cis*-**1a,c**—**e** form complexes with Mg^{2+} ($C_M = 10^{-4}$ mol L^{-1}). We observed a similar effect previously[6] for compound **1b**. It has been established for this compound that the hypsochromic shift results from the formation of a "closed" complex of *cis* isomer **1b** with Mg^{2+} (see Scheme 1). Due to immobilization of this twisted conformation of (*cis*-**1b**)Mg^{2+}, in which conjugation in the system of double bonds of the chromophore is violated, the long-wave absorption band of the "open" complex near λ_{max} of the complex formed by the *trans* isomer disappears almost completely.[4,6] Since compounds **1a,c**—**e** and **1b** contain the same *N*-sulfopropyl substituent and crown ether fragment, the significant hypsochromic shifts of the maxima of the long-wave absorption bands of the *cis* isomers of **1a,c**—**e** due to complexation are probably also due to the formation of "closed" forms. This is also confirmed by the similar color contrasts of the complexes of Mg^{2+} with the *cis* forms of dyes **1a**—**e** and by the almost equal $\varepsilon_c/\varepsilon_t$ values (Table 3). This allows us to assume that they

Table 3. Photochromic properties of (*trans*-**1a**—**e**)Mg^{2+} and (*cis*-**1a**—**e**)Mg^{2+} in MeCN

Complex of Mg^{2+} with **1a**—**e**	λ_{max}^{abs}/nm ($\varepsilon_{max} \cdot 10^{-4}$/L mol^{-1} cm^{-1})		Color contrast, $\Delta\lambda_{t/c}$/nm ($\Delta\varepsilon \cdot 10^{-4}$)	$\varepsilon_c/\varepsilon_t$
	trans	*cis*		
(**1a**)Mg^{2+}	371 (3.9)	320 (1.08)	51 (2.82)	0.28
(**1b**)Mg^{2+}	393 (3.6)[6]	322 (0.94)[6]	71 (2.66)	0.26
(**1c**)Mg^{2+}	396 (3.6)	330 (0.81)	66 (2.79)	0.23
(**1d**)Mg^{2+}	407 (3.7)	338 (0.98)	69 (2.72)	0.26
(**1e**)Mg^{2+}	413 (3.7)	344 (0.95)	69 (2.75)	0.26

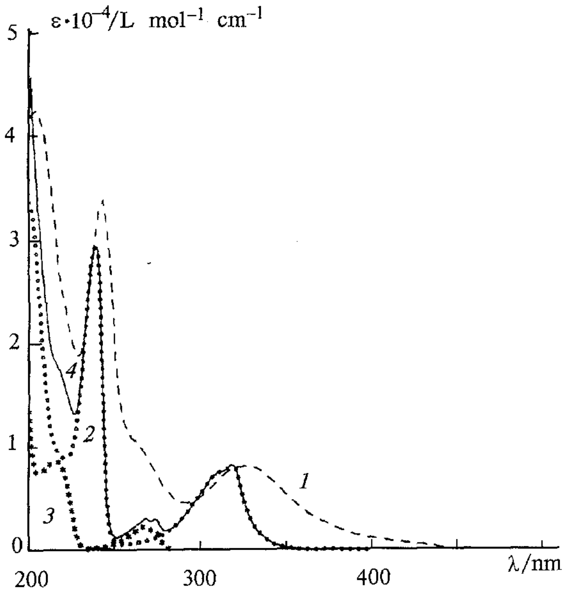


Fig. 2. Electronic absorption spectra in MeCN: *1*, the complex of *cis*-**1c** with Mg^{2+}, C_0 = 2.07 · 10^{-5} mol L^{-1} and C_M = 10^{-4} mol L^{-1}; *2*, betaine **2c**, C_0 = 2.01 · 10^{-5} mol L^{-1}; *3*, the complex of benzo-15-crown-5 with Mg^{2+}, C_0 = 10^{-4} mol L^{-1} and C_M = 10^{-2} mol L^{-1}; *4*, calculated spectrum of (*cis*-**1c**)Mg^{2+} obtained by adding the absorption spectra of betaine **2c** and that of the complex of benzo-15-crown-5 with Mg^{2+}.

have similar structures, irrespective of the nature of the heterocyclic moiety.

We attempted to estimate the degree of violation of conjugation in the chromophore when "closed" complexes of *cis*-**1a,c—e** are formed. For this purpose, we compared the absorption spectra of separate structural fragments of dyes **1a,c—e**. It was found that in all cases the spectra obtained by adding the absorption spectra of betaines **2a,c—e** with that of the complex between benzo-15-crown-5 and Mg^{2+} qualitatively reproduce the spectra of the "closed" (*cis*-**1a,c—e**)Mg^{2+}. This implies that these structural fragments in the "closed" complexes of *cis*-**1a,c—e** behave, to a significant degree, as isolated chromophores (Fig. 2). In addition, the λ_{max} values of the long-wave absorption bands of *cis*-**1a,c—e** are similar to the corresponding λ_{max} in the calculated spectra (for **1c**, λ_{max} = 329 nm (ε 8100), while in the calculated spectrum λ_{max} = 319 nm (ε 8100)). On the other hand, the integral intensity of these bands in the experimentally obtained spectra is markedly higher, probably because the long-wave charge-transfer bands[4] in "closed" complexes of *cis*-**1a,c—e** do not disappear completely. This suggests that there is some residual conjugation in the twisted conformations of "closed" complexes of *cis*-**1a,c—e** with Mg^{2+}.

We also studied the fluorescence spectra of crown-containing styryl dyes **1a,c—e**. As was expected from our previous study of the properties of compound **1b** (see Ref. 8), only *trans*-**1a,c—e** fluoresce at room temperature (Fig. 3, *a*).

The introduction of substituents (R = Ph, MeO) at position 5 of the benzothiazole heterocycle has virtually no effect on the λ_{max} values in the fluorescence spectra, unlike those in the absorption spectra. An increase in the electron-withdrawing ability of the heterocyclic moiety results in short-wave shifts of the fluorescence maxima in the series of dyes **1c**, **1b**, and **1a**. Simultaneously, the maxima of the long-wave absorption bands undergo short-wave shifts in the same order. It should be noted that the Stokes' shift is high (see Table 2). Usually, this results from a large difference between the

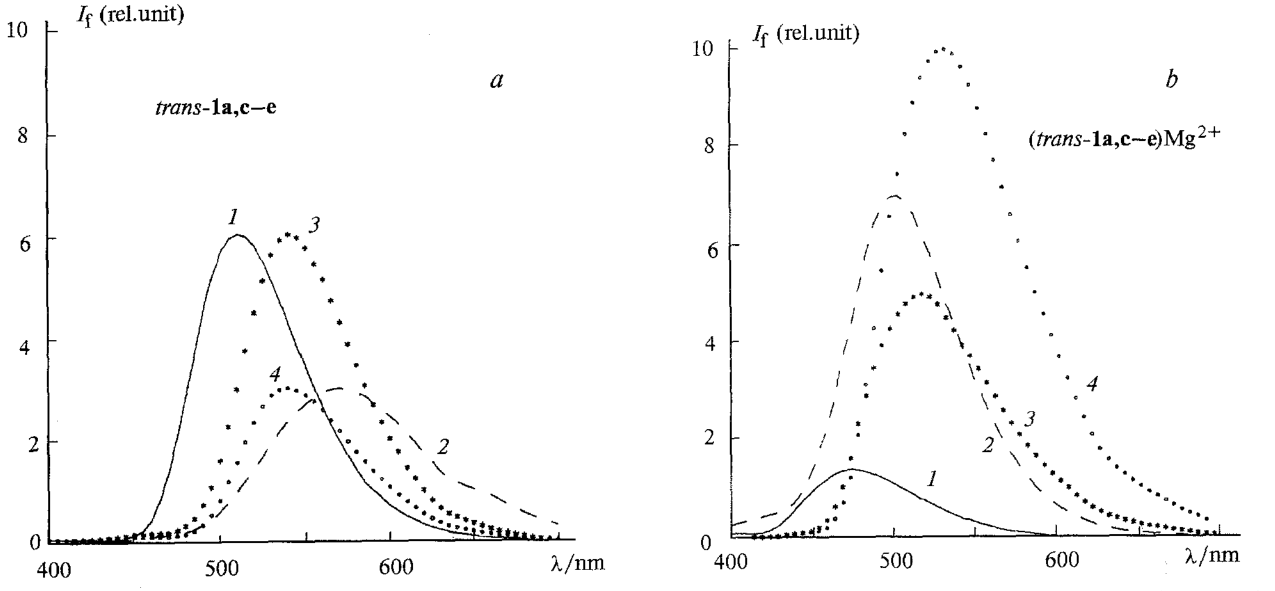


Fig. 3. Fluorescence spectra (λ_{ex} = 313 nm) of *trans*-**1a,c—e** (*a*) and their complexes with Mg^{2+} (*b*, C_M = 10^{-4} mol L^{-1}) in MeCN: *1*, **1a**, C_0 = 2.04 · 10^{-5} mol L^{-1}; *2*, **1c**, C_0 = 2.07 · 10^{-5} mol L^{-1}; *3*, **1d**, C_0 = 1.49 · 10^{-5} mol L^{-1}; *4*, **1e**, C_0 = 1.79 · 10^{-5} mol L^{-1}.

energies of the excited and ground states of dyes. The nature of the especially large Stokes' shift for compound **1c** (which is 30—40 nm greater than those for the other dyes studied) and the appearance of additional bands in its fluorescence spectrum require further investigations.

The addition of $Mg(ClO_4)_2$ to solutions of dyes **1a,c—e**, like in the case of **1b**,[8] results in fluorescence quenching (see Fig. 3, *b*). Only compounds **1c** and **1e** are an exception. The decrease in the quantum yield of fluorescence (φ_f, see Table 2) cannot be explained by a change in φ_{tc}, since the formation of dimers of the complexes[11] should manifest itself, at least, as some decrease in φ_{tc} and hence an increase in φ_f. Probably, the formation of a coordination bond between Mg^{2+} and the O atom located *para* to the central C=C bond leads to exclusion of the latter from the conjugation chain. In fact, it is known[12] that, as a rule, the introduction of a methoxy group to the conjugation chain of a chromophore increases the quantum yield of fluorescence. Hence, it can be expected that complexation with Mg^{2+} would give a reverse effect, *i.e.*, fluorescence quenching, which we indeed observed in the experiment.

The addition of Mg^{2+} cations to a solution of dye **1e** results not only in an increase in φ_f but also in an unusually small (5 nm) hypsofluoric shift of the fluorescence maximum (see Table 2). Probably, the coordination bond between the metal cation and the O atom located *para* to the C=C bond is cleaved in an excited state. The possibility of such a photo-induced cleavage of coordination bonds in complexes of crown-containing dyes has recently been considered.[13] However, in this case not only should the fluorescence maximum of *trans*-**1e** be close to λ^f_{max} of (*trans*-**1e**)Mg^{2+}, but also the quantum yield of fluorescence should equal φ_f of the free ligand, whereas it is much higher. Hence, the observed high quantum yield of fluorescence probably originates mostly from a decrease in φ_{tc}. As has already been noted, this can occur when complexes dimerize. The results of our study of the reasons for the increase in φ_f of dye **1c** following the addition of Mg^{2+} to its solution will be reported later.

It is noteworthy that both the hypsofluoric shift (15 nm) and the fluorescence quenching (see Table 2) due to complexation of compound **1d** are lower than those for compounds **1a** and **1b**. Probably, the introduction of a phenyl group at position 5 of the benzothiazole moiety also results in weakening, in the excited state, of the coordination bond between Mg^{2+} and the O atom of the crown ether fragment in the *para* position to the double bond.

Thus, we have synthesized new crown-containing styryl dyes containing various heterocyclic moieties with various substituents. We have studied the effect of the nature of the heterocyclic moiety and substituents in it on the photochromism of ionophores of the styryl series. Our results provide a basis for directed control of their spectral characteristics and complexation ability by synthetic methods.

Experimental

^1H NMR spectra (in DMSO-d_6) were obtained on a Bruker WM-400SY spectrometer using $SiMe_4$ as the internal standard. The purity of compounds was monitored by HPLC on a Milikhrom chromatograph (2×64 mm column, Separon C18, 5 μm, detection at 230 nm). The dyes were analyzed using a $MeCN—H_2O$ (85 : 15) mixture as the eluent. The dyes give one peak with retention volume 140—160 μL.

Acetonitrile was distilled over $KMnO_4$, twice over P_2O_5, and finally over CaH_2 to remove impurities and water. $Mg(ClO_4)_2$ was dried *in vacuo* at 240 °C. The solutions ($C_0 \approx 2 \cdot 10^{-5}$ mol L^{-1}) were prepared and all experiments carried out under red light in MeCN.

Electronic absorption spectra were recorded on a Shimadzu UV-3101 spectrophotometer. Stationary fluorescence spectra were measured on a Shimadzu RF-5000 spectrofluorimeter. Quantum yields of fluorescence were determined with respect to fluoresceine in a 0.01 *N* solution of KOH in EtOH as the standard[10] with excitation by light with λ = 313 nm (error ~15 %). All measurements were performed in a quartz cell whose inside surface was modified by Me_2SiCl_2 to minimize dye adsorption on the walls.[14] Solutions of compounds **1a,c,d** were photolyzed by irradiation with light from a DRSh-100 mercury lamp at wavelengths λ = 313, 365, or 436 nm.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzoxazolium betaine (1a). 4-Formylbenzo-15-crown-5 [15] (**5**) (0.064 g, 0.22 mmol) was added to a solution of 2-methyl-3-(3-sulfopropyl)benzoxazolium betaine (**2a**) (0.051 g, 0.2 mmol) in acetanhydride (5 mL), and the mixture was refluxed for 4 h. The crystals that precipitated when the reaction mixture cooled were filtered off, washed with ether, and repeatedly recrystallized from dry MeOH. Yield of dye **1a** 0.047 g (44 %), m.p. 269—271 °C. ^1H NMR, δ: 2.25 (m, 2 H, CH_2); 2.70 (m, 2 H, $CH_2SO_3^-$); 3.62 (s, 8 H, 4 CH_2O); 3.82 (m, 4 H, 2 CH_2O); 4.20 (2 m, 4 H, 2 CH_2O); 4.85 (m, 2 H, NCH_2); 7.10 (d, 1 H, HC(5')); 7.60 (d, 1 H, HC(6')); 7.76 (2 d, 2 H, HC(4), HC(7)); 7.84 (s, 1 H, HC(2')); 7.95 (d, 1 H, α-CH, ^3J_t = 15.6 Hz); 8.05 and 8.15 (2 m, 2 H, HC(5), HC(6)); 8.30 (d, 1 H, β-CH, ^3J_t = 15.6 Hz). Found (%): C, 58.38; H, 5.93; N, 2.69. $C_{26}H_{31}NO_9S$. Calculated (%): C, 58.53; H, 5.86; N, 2.62.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium betaine (1b). A mixture of 2-methyl-3-(3-sulfopropyl)benzothiazolium betaine (**2b**) (0.14 g, 0.5 mmol) and 4-formylbenzo-15-crown-5 [15] (**5**) (0.16 g, 0.55 mmol) was dissolved in dry EtOH (3 mL), pyridine (0.3 mL) was added, and the mixture was refluxed for 12 h. The dye that precipitated was filtered off and recrystallized two times from dry MeOH. Yield of dye **1b** 0.16 g (58 %), m.p. 283 °C. (Ref. 6: m.p. 283 °C). Found (%): C, 56.42; H, 5.66; N, 2.14. $C_{26}H_{31}NO_8S_2$. Calculated (%): C, 56.82; H, 5.68; N, 2.55.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)-5-phenylbenzothiazolium betaine (1d) was synthesized similarly to compound **1b**, yield 77 %, m.p. 298 °C (from methanol). ^1H NMR, δ: 2.32 (m, 2 H, CH_2); 2.71 (m, 2 H, $CH_2SO_3^-$); 3.65 (s, 8 H, 4 CH_2O); 3.82 (m, 4 H, 2 CH_2O); 4.21 (m, 2 H, CH_2O); 4.34 (m, 2 H, CH_2O); 5.22 (m, 2 H, NCH_2); 7.09 (d, 1 H, HC(5'), $J_{C(5'),C(6')}$ = 8.4 Hz); 7.47 (m, 1 H, Ph); 7.55 (m, 2 H, Ph); 7.56 (dd, 1 H, HC(6'), $J_{C(6'),C(5')}$ = 8.4 Hz, $J_{C(6'),C(2')}$ = 2.1 Hz); 7.91 (d, 2 H, Ph); 7.93 (s, 1 H, HC(2'), $J_{C(2'),C(6')}$ = 2.1 Hz); 8.05 (dd, 1 H, HC(6), $J_{C(6),C(7)}$ = 8.6 Hz, $J_{C(6),C(4)}$ = 1.8 Hz); 8.12 (d, 1 H, α-CH, ^3J_t = 15.6 Hz); 8.25 (d, 1 H, β-CH, ^3J_t = 15.6 Hz); 8.41 (d, 1 H, HC(7), $J_{C(7),C(6)}$ = 8.6 Hz); 8.58 (s, 1 H, HC(4), $J_{C(4),C(6)}$ = 1.8 Hz). Found (%): C, 56.42; H, 5.49; N, 1.96. $C_{32}H_{35}NO_8S_2 \cdot 3H_2O$. Calculated (%): C, 56.54; H, 6.08; N, 2.06.

5-Methoxy-2-[2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-16-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium betaine (1e) was synthesized similarly to compound **1b**, yield 55 %, m.p. 283 °C. ^{1}H NMR, δ: 2.27 (m, 2 H, CH_2); 2.70 (m, 2 H, $CH_2SO_3^-$); 3.64 (s, 8 H, 4 CH_2O); 3.82 (m, 4 H, 2 CH_2O); 3.99 (s, 3 H, MeO); 4.20 (m, 2 H, CH_2O); 4.31 (m, 2 H, CH_2O); 5.11 (m, 2 H, NCH_2); 7.07 (d, 1 H, HC(5′), $J_{C(5'),C(6')}$ = 8.4 Hz); 7.35 (dd, 1 H, HC(6), $J_{C(6),C(7)}$ = 8.9 Hz, $J_{C(6),C(5)}$ = 2.4 Hz); 7.52 (dd, 1 H, HC(6′), $J_{C(6'),C(5')}$ = 8.4 Hz, $J_{C(6'),C(2')}$ = 2.1 Hz); 7.84 (d, 1 H, HC(2′), $J_{C(2'),C(5')}$ = 2.1 Hz); 7.89 (m, 1 H, HC(4), $J_{C(4),C(6)}$ = 2.4 Hz); 8.02 (d, 1 H, α-CH, ^3J_t = 15.6 Hz); 8.13 (d, 1 H, β-CH, ^3J_t = 15.6 Hz); 8.17 (d, 1 H, HC(7), $J_{C(6),C(7)}$ = 8.9 Hz). Found (%): C, 52.68; H, 5.81; N, 2.23. $C_{27}H_{33}NO_9S_2 \cdot 2H_2O$. Calculated (%): C, 52.67; H, 6.06; N, 2.27.

This study was financially supported by the Russian Foundation for Basic Research (Grants No. 94-03-08-531 and 93-03-04-089) and the International Science Foundation (Grant M8Q00).

References

1. I. I. Baskin, A. A. Bagatur'yants, S. P. Gromov, and M. V. Alfimov, *Dokl. Akad. Nauk*, 1994, **335**, 313 [*Dokl. Chem.*, 1994, **335** (Engl. Transl.)].
2. S. Shinkai, in *Cation Binding by Macrocycles,* Eds. Y. Inoue and G. W. Gokel, Marcel Dekker, New York, 1990, Ch. 9.
3. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavsky, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 104 [*Dokl. Chem.*, 1991, **321** (Engl. Transl.)].
4. I. I. Baskin, K. Ya. Burstein, A. A. Bagatur'yants, S. P. Gromov, and M. V. Alfimov, *J. Mol. Struct.*, 1992, **274**, 93.
5. *The Theory of the Photographic Process*, Ed. T. H. James, Macmillan Publ., New York, 1977, Ch. 8.
6. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavsky, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 1134 [*Dokl. Chem.*, 1991, **317** (Engl. Transl.)].
7. Jpn. Pat. 6.931.573, 1967; *Chem. Abstrs.*, 1970, **72**, 121539c.
8. A. V. Barzykin, M. A. Fox, E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *J. Am. Chem. Soc.*, 1992, **114**, 6381.
9. E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.
10. S. P. Gromov, M. V. Fomina, E. N. Ushakov, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1990, **314**, 1135 [*Dokl. Chem.*, 1990, **314** (Engl. Transl.)].
11. M. V. Alfimov, S. P. Gromov, O. B. Stanislavsky, E. N. Ushakov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1449 [*Russ. Chem. Bull.*, 1993, **42**, 1385 (Engl. Transl.)].
12. B. M. Bolotin and B. M. Krasovitskii, *Organicheskie lyuminofory* [*Organic Luminophores*], Khimiya, Moscow, 1984 (in Russian).
13. M. M. Martin, P. Plaza, N. Dai Hung, Y. H. Meyer, J. Bourson, and B. Valeur, *Chem. Phys. Lett.*, 1993, **202**, 425.
14. P. I. Voskresenskii, *Tekhnika laboratornykh rabot* [*Laboratory Techniques*], Khimiya, Moscow, 1969 (in Russian).
15. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, V. V. Samoshin, N. S. Zefirov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 121 [*Russ. Chem. Bull.*, 1995, **44**, 116 (Engl. Transl.)].

Received April 22, 1994