Crown-ether styryl dyes

20.* Synthesis, spectral properties, and complex formation of photochromic dyes based on 15-crown-5-substituted benzothiazole

S. P. Gromov, D. E. Levin, K. Ya. Burshtein, V. E. Krasnovskii,*
S. N. Dmitrieva, A. A. Golosov, and M. V. Alfimov

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
7a ul. Novatorov, 117421 Moscow, Russian Federation.
Fax: 007 (095) 936 1255. E-mail: gromov@mx.icp.rssi.ru

Novel crown-containing styryl dyes (CSD) based on 15-crown-5-substituted benzothiazole with various electron-donating groups in the *para*-position of the benzene ring were synthesized. Spectral and photochemical properties of *cis*- and *trans*-isomers of CSD and their complexes with Mg^{2+} ions in solutions were studied. By analysis of spectral parameters and the magnitudes and directions of the shifts of absorption (fluorescence) maxima, the effects of substituents and complex formation on the photochromism of CSD were elucidated. Using quantum-chemical calculations, the possibility of controlling the degree of participation of either of the two chromophores in the long-wave electron transition by complex formation was analyzed.

Key words: crown-ether styryl dyes, synthesis, complex formation, photoisomerization; absorption spectra; fluorescence spectra.

Crown-containing styryl dyes (CSD) are bifunctional ethylene derivatives. Owing to their structure, they are efficient photochromic systems and photosensitive ionophores.[2] Previously it has been shown that these dyes are selective toward metal cations, depending on the ionic radius of the cation and the size of the crown-ether cavity.[3] Upon the formation of complexes, the long-wave absorption bands (LAB) and fluorescence maxima in the spectra of these dyes undergo substantial hypsochromic shifts. It was found that the variation of the nature of the heterocyclic residue or introduction of substituents, able to interact with the chromophore, into it has a strong effect on the spectral properties of the dyes and the formation of their complexes.[4,5] It seemed promising to synthesize CSD containing a crown-ether fragment in the heterocyclic part of the molecule rather than in its benzene part (as in the molecules that we have studied previously) and to study their spectral properties. Then it would be possible to change the position of the LAB of the dyes by introducing various electron-donating substituents in the benzene ring. For the type of CSD under consideration, it could be expected that upon complexation, the LAB maxima would shift to both the red and blue regions, because their molecules contain two chromophores interacting through the conjugation chain.

Therefore, we prepared a number of styryl dyes (**1a—e**) based on 15-crown-5-containing benzothiazole (Scheme 1). We also synthesized dimethoxybenzothiazole derivative **2**, which, unlike CSD **1a—e**, should not exhibit a marked tendency to the formation of complexes with metal cations.

Styryl dyes **1a—e** were prepared in 50—70% yields by condensation of the crown-containing benzothiazolium perchlorate (**3**) with *para*-substituted benzaldehydes **4a—e** carried out by refluxing in pyridine. Quaternary salt **3** was formed upon the addition of excess perchloric acid to an ethanolic solution of benzothiazolium iodide (**5**); the latter was synthesized in five steps from benzo-15-crown-5 ether (**6**) by known procedures.[6,7] Dye **2** was prepared in 50% yield similarly to compound **1b** from dimethoxybenzothiazolium perchlorate (**7**) and *p*-methoxybenzaldehyde (**4b**) (see Scheme 1). Dimethoxybenzothiazolium perchlorate **7** was synthesized by quaternization of 5,6-dimethoxy-2-methylbenzothiazole with ethyl iodide followed by the addition of excess perchloric acid to the ethanolic solution of dimethoxybenzothiazolium iodide thus formed.

The structures of the CSD **1a—e** synthesized were confirmed by ^1H NMR spectroscopy (Table 1). The data of elemental analysis correspond to the assumed structures. Judging from the spin-spin coupling constants $^3J_{trans}$ = 15.4 to 16.0 Hz for the olefinic protons,[8] molecules **1a—e** and **2** have *trans*-configurations. The distinctions in the ^1H NMR spectra of dyes **1a—e** and **2**

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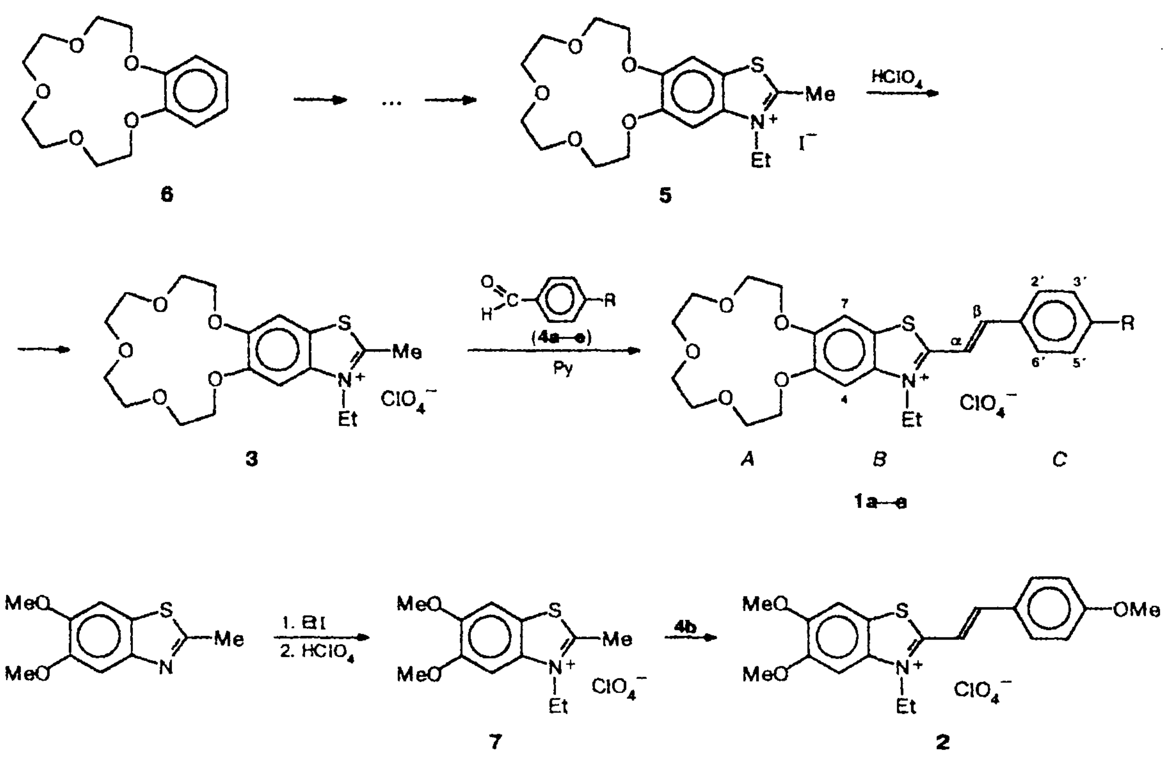
Scheme 1



1: R = H (**a**), OMe (**b**), OH (**c**), SMe (**d**), NMe$_2$ (**e**)

Table 1. ^{1}H NMR spectra of dyes **1a—e** and **2** (in DMSO-d_6)

CSD	δ (*J*/Hz)
1a	1.52 (t, 3 H, Me, $J = 7$); 3.67 (br.s, 8 H, 4 CH_2O); 3.89 (m, 4 H, 2 CH_2O); 4.25 (m, 2 H, CH_2O); 4.35 (m, 2 H, CH_2O); 4.95 (q, 2 H, NCH_2, $J = 7$); 7.56 (m, 3 H, Ph); 7.76 (s, 1 H, HC(7)); 7.90 (d, 1 H, α-CH, $^3J_{trans} = 16$); 7.93 (s, 1 H, HC(4)); 7.98 (m, 2 H, Ph); 8.06 (d, 1 H, β-CH, $^3J_{trans} = 16$)
1b	1.49 (t, 3 H, Me, $J = 7$); 3.67 (br.s, 8 H, 4 CH_2O); 3.89 (m, 7 H, 2 CH_2O, OMe); 4.23 (m, 2 H, CH_2O); 4.33 (m, 2 H, CH_2O); 4.91 (q, 2 H, NCH_2, $J = 7$); 7.11 (d, 2 H, HC(3′), HC(5′), $J_{3',2'} = J_{5',6'} = 8.8$); 7.72 (s, 1 H, HC(7)); 7.74 (d, 1 H, α-CH, $^3J_{trans} = 15.7$); 7.90 (s, 1 H, HC(4)); 7.97 (d, 2 H, HC(2′), HC(6′), $J_{2',3'} = J_{6',5'} = 8.8$); 8.01 (d, 1 H, β-CH, $^3J_{trans} = 15.7$)
1c	1.43 (t, 3 H, Me, $J = 7$); 3.63 (br.s, 8 H, 4 CH_2O); 3.84 (m, 4 H, 2 CH_2O); 4.28 (m, 2 H, CH_2O); 4.38 (m, 2 H, CH_2O); 4.88 (q, 2 H, NCH_2, $J = 7$); 6.92 (d, 2 H, HC(3′), HC(5′), $J_{3',2'} = J_{5',6'} = 8.6$); 7.71 (d, 1 H, α-CH, $^3J_{trans} = 15.6$); 7.72 (s, 1 H, HC(7)); 7.89 (d, 2 H, HC(2′), HC(6′), $J_{2',3'} = J_{6',5'} = 8.6$); 7.90 (s, 1 H, HC(4)); 8.01 (d, 1 H, β-CH, $^3J_{trans} = 15.6$); 10.50 (s, 1 H, OH)
1d	1.50 (t, 3 H, Me, $J = 7$); 2.58 (s, 3 H, SMe); 3.66 (br.s, 8 H, 4 CH_2O); 3.88 (m, 4 H, 2 CH_2O); 4.24 (m, 2 H, CH_2O); 4.34 (m, 2 H, CH_2O); 4.93 (q, 2 H, NCH_2, $J = 7$); 7.41 (d, 2 H, HC(3′), HC(5′), $J_{3',2'} = J_{5',6'} = 8.5$); 7.74 (s, 1 H, HC(7)); 7.85 (d, 1 H, α-CH, $^3J_{trans} = 15.8$); 7.92 (s, 1 H, HC(4)); 7.93 (d, 2 H, HC(2′), HC(6′), $J_{2',3'} = J_{6',5'} = 8.5$); 8.02 (d, 1 H, β-CH, $^3J_{trans} = 15.8$)
1e	1.47 (t, 3 H, Me, $J = 7$); 3.08 (s, 6 H, NMe_2); 3.65 (br.s. 8 H, 4 CH_2O); 3.85 (m, 4 H, 2 CH_2O); 4.23 (m, 2 H, CH_2O); 4.33 (m, 2 H, CH_2O); 4.82 (q, 2 H, NMe, $J = 7$); 6.83 (d, 2 H, HC(3′), HC(5′), $J_{3',2'} = J_{5',6'} = 9$); 7.5 (d, 1 H, α-CH, $^3J_{trans} = 15.4$); 7.64 (s, 1 H, CH(7)); 7.83 (s, 1 H, HC(4)); 7.84 (d, 2 H, HC(2′), HC(6′), $J_{2',3'} = J_{6',5'} = 9$); 7.91 (d, 1 H, β-CH, $^3J_{trans} = 15.4$)
2	1.50 (t, 3 H, Me, $J = 7$); 3.89 (s, 3 H, OMe); 3.96 (s, 3 H, OMe); 4.01 (s, 3 H, OMe); 4.93 (q, 2 H, NCH_2, $J = 7$); 7.11 (d, 2 H, HC(3′), HC(5′), $J_{3',2'} = J_{5',6'} = 8.8$); 7.70 (s, 1 H, HC(7)); 7.75 (d, 1 H, α-CH, $^3J_{trans} = 15.8$); 7.94 (s, 1 H, HC(4)); 7.98 (d, 2 H, HC(2′), HC(6′); $J_{2',3'} = J_{6',5'} = 8.8$); 8.02 (d, 1 H, β-CH, $^3J_{trans} = 15.8$)

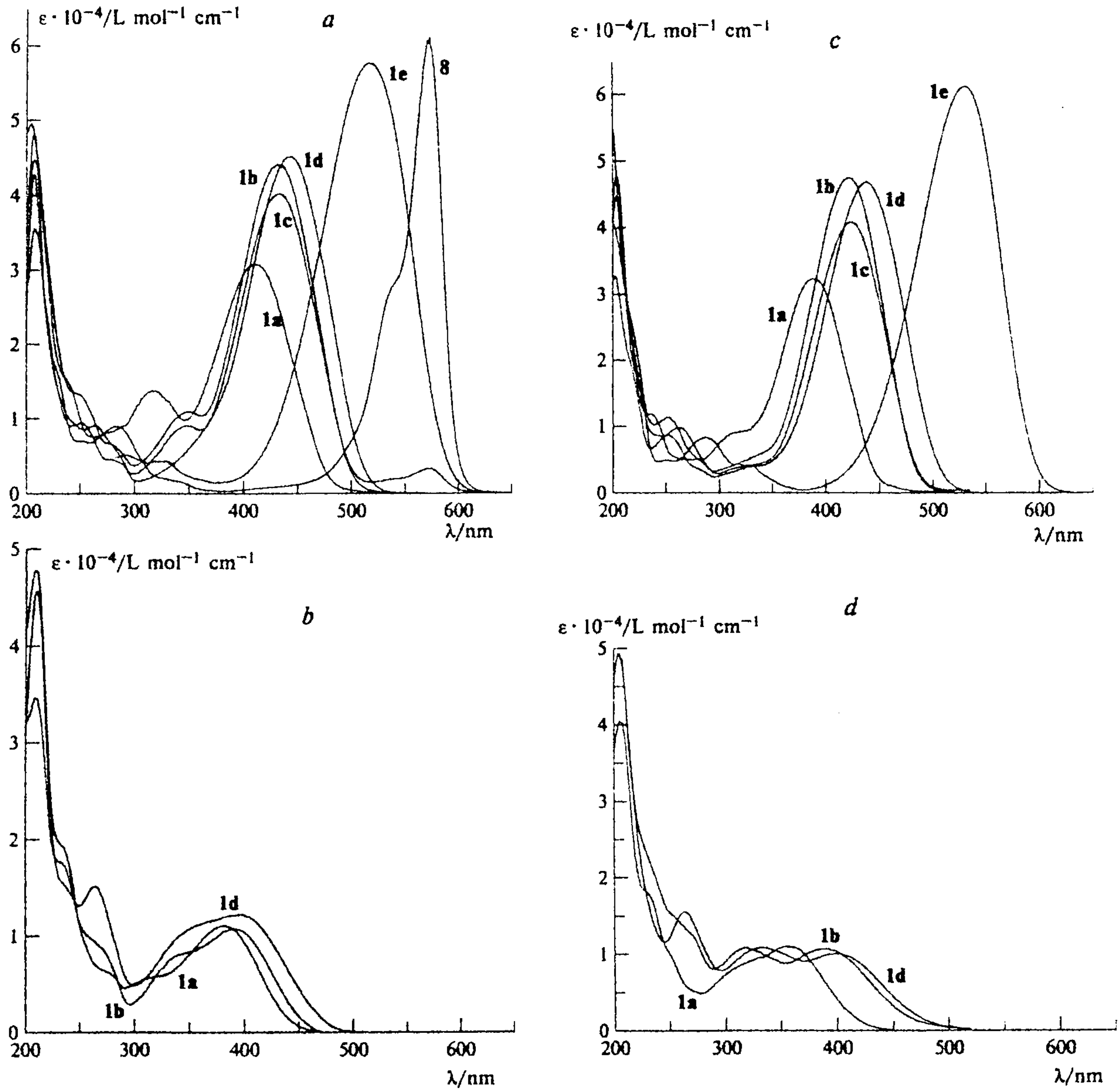


Fig. 1. Absorption spectra of CSD *trans*-**1a**—**e**, *trans*-**8** (*a*, the spectrum of *trans*-**8** was decreased by 60%), *cis*-**1a**,**b**,**d** (*b*), complexes (*trans*-**1a**—**e**) · Mg^{2+} (*c*), and (*cis*-**1a**,**b**,**d**) · Mg^{2+} (*d*) in MeCN at $C_L = 2 \cdot 10^{-5}$ mol L^{-1}, $C_{Mg} = 10^{-2}$ mol L^{-1}, $T = 295$ K. The spectrum of *trans*-**8** was obtained by adding triethylamine to a solution of *trans*-**1c** ($C_B = 0.1$ mol L^{-1}).

are due to different electron-donating abilities of substituents in the *para*-position of the benzene ring.

The absorption spectra of dyes *trans*-**1a**—**e** and *trans*-**2**, like those of the CSD studied previously (see Ref. 4) in which the benzothiazole nucleus and the crown-ether fragment are located on different sides of the double bond, exhibit an intense band with ε_{trans} 24 000—55 000 L mol^{-1} cm^{-1} in the long-wave region (Fig. 1, *a*). Our calculations have shown[9] that the LAB in the spectra of CSD correspond to an electron transition with a small charge transfer (~0.2 *e*) from the electron-donating to the withdrawing heterocyclic part of the chromophore. In the spectra of solutions of *trans*-**1a**—**e** and *trans*-**2**, this band undergoes hypsochromic shifts as the polarity of the solvent increases (Table 2). This type of behavior is characteristic of CSD (see Ref. 2) and is generally typical of highly polar polymethine dyes,[10] which exhibit

Table 2. The effect of the solvent polarity on the position of the maxima (λ^a_{max}) of the LAB for dyes *trans*-**1a**,**e**

CSD	λ^a_{max}/nm			
	H_2O	MeCN	MeOH	$CHCl_3$
trans-**1a**	403	410	413	420
trans-**1e**	497	516	520	545

Table 3. Spectral properties of the *trans*- and *cis*-isomers of dyes **1a**—**e**, **2**, and **8** and complexes (**1a**—**e**) · Mg^{2+}

Compound	*trans*-Isomer			*cis*-Isomer		*trans*-Isomer		
	λ^a_{max}	$\Delta\lambda^a$	$\varepsilon^a_{max} \cdot 10^{-4}$	λ^a_{max}	$\varepsilon^a_{max} \cdot 10^{-4}$	λ^f_{max}	$\Delta\lambda^f$	$\varphi_f \cdot 10^{-3}$
	nm		/L mol^{-1} cm^{-1}	/нм	/L mol^{-1} cm^{-1}	nm		
1a	410		3.1	381	1.1	539		11.0
1a · Mg^{2+}	389	21	3.2	360	1.1	533	6	1.5
1b	433		4.4	392	1.1	540		1.0
1b · Mg^{2+}	421	12	4.8	389	1.1	525	15	0.5
1c	432		4.0	—	—	541		0.7
1c · Mg^{2+}	425	7	4.1	—	—	523	18	0.5
1d	442		4.5	398	1.2	555		5.1
1d · Mg^{2+}	438	4	4.7	399	1.0	571	−16	4.4
1e	516		5.5	—	—	609		3.4
1e · Mg^{2+}	530	−14	6.1	—	—	613	−4	1.3
2	430		3.4	397	1.0	541		0.8
8	571		15.0	—	—	600		0.25

Note. $\Delta\lambda^{a(f)} = \lambda^{a(f)}_{max}(\text{ligand}) - \lambda^{a(f)}_{max}(\text{complex})$.

hypscochromic shifts of LAB and a decrease in ε_{max} following an increase in the solvent polarity.

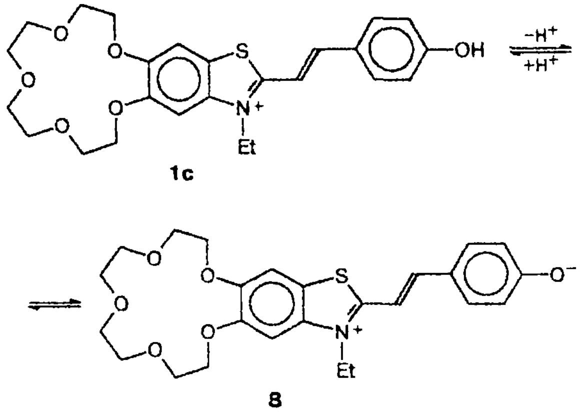
We carried out CNDO/S-CI quantum-chemical calculations[11] of the absorption spectra of dyes *trans*-**1a**,**b**,**e** and complexes (*trans*-**1a**,**b**,**e**) · Mg^{2+} using the procedure described previously.[9] To attain quantitative agreement between the calculated and experimental absorption spectra, the coefficient k_π in the expression for the resonance integral was increased to 0.7.

The experimentally observed fact that the LAB shifts hypsochromically following an increase in the solvent polarity can be explained by a substantial change in the localization of the positive charge in CSD on electron excitation. During the electron transition, solvent molecules have no time to adjust to the new distribution of electron density in CSD; therefore the benefit in energy due to solvation decreases. To reproduce this effect, in this study we used a simple quantum-chemical model of solvation, the Djano—Klopman model of solvatons,[12] which we had tested before in relation to CSD. Our calculation in terms of this model reproduced quantitatively the solvatochromic effect observed experimentally. The positions calculated for the LAB maxima for dye *trans*-**1a** were: 429 nm ($\alpha = (\varepsilon - 1)/(2\varepsilon) = 0$, gas phase), 419 nm ($\alpha = 0.2$), 411 nm ($\alpha = 0.4$), and 405 nm ($\alpha = 0.5$, the maximum possible polarity of the solvent). All the subsequent calculations were performed for $\alpha = 0.4$.

The introduction of electron-donating substituents, extending the chromophore chain and facilitating the charge transfer in the excited state, into the *para*-position of the benzene ring in CSD *trans*-**1a**—**e** results in substantial bathochromic shifts of the LAB maxima (Table 3).

In the case of dye *trans*-**1c**, the absorption spectrum contains a weak band with λ = 571 nm (ε_{trans} 2000 L mol^{-1} cm^{-1}), along with the band with λ = 432 nm (ε_{trans} 36 000 L mol^{-1} cm^{-1}). Apparently, this band is due to the presence of a minor amount of deprotonated form of the dye (R = O$^-$) in the solution of *trans*-**1c**. Since the electron-donating properties of O$^-$ are much stronger than those of the OH group, the LAB corresponding to the deprotonated form, is markedly displaced to the red region of the spectrum. This is confirmed by the fact that upon the addition of acetic acid in the concentration C_A = 0.01 mol L^{-1} to the solution of *trans*-**1c**, the band at 571 nm disappears as a result of protonation of the O$^-$ substituent (Scheme 2). The same effect is observed when $Mg(ClO_4)_2$ is added, probably due to the formation of a bond between the negatively charged O$^-$ atom and Mg^{2+}. Conversely, when triethylamine in the concentration C_B = 0.1 mol L^{-1} is added to a solution of *trans*-**1c**, the absorption band at 432 nm disappears, while the band with λ = 571 nm becomes much more intense (see Fig. 1, *a*); obviously, this is associated with the abstraction of the proton from the hydroxyl group and complete transformation of CSD *trans*-**1c** into a bipolar dye (*trans*-**8**) (ε_{trans} 150 000 L mol^{-1} cm^{-1}). The bathochromic shift of the maximum of the LAB of *trans*-**8** with respect to the corresponding band of *trans*-**1a** is 162 nm.

Scheme 2

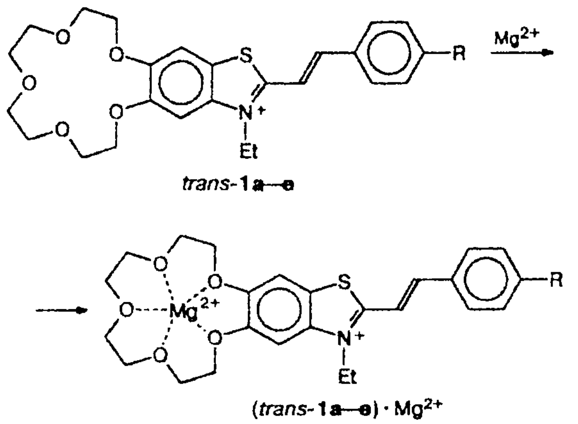


1c

8

The addition of $Mg(ClO_4)_2$ to solutions of dyes *trans*-**1a**—**e** in acetonitrile leads, as in the case of CSD studied previously (see Refs. 3 and 4), to the displacement of the LAB maxima (see Fig. 1, *c*), which is apparently due to the formation of complexes (*trans*-**1a**—**e**) · Mg^{2+} (Scheme 3).

Scheme 3



To confirm this assumption, we studied dye *trans*-**2**, which differs from *trans*-**1b** in that the benzothiazole benzene ring in its molecule contains two methoxy groups, instead of the crown-ether fragment, so that the electron-donating effect of the latter is reproduced. These dyes exhibit virtually identical absorption and fluorescence spectra. When $Mg(ClO_4)_2$ is added to a solution of CSD *trans*-**1b**, the LAB shifts hypsochromically by 12 nm, and the extinction coefficient ε increases from 44 000 (for the initial dye) to 48 000 L mol^{-1} cm^{-1} (for its complex with Mg^{2+}). In the case of CSD *trans*-**2**, the addition of $Mg(ClO_4)_2$ was not accompanied by similar spectral changes.

For all dyes *trans*-**1a**—**d**, the formation of complexes with Mg^{2+} results in hypsochromic shifts of the LAB maxima; these shifts gradually decrease as the electron-donating ability of the substituent R increases. In the case of CSD *trans*-**1e**, the electron-donating effect of the substituent (R = NMe_2) is apparently so strong that the LAB maximum undergoes a substantial bathochromic shift.

The calculated positions of the LAB maxima (Table 4) are close to experimental values and, at the qualitative level, they reflect adequately the changes in the positions of the LAB maxima of *trans*-**1a**,**b**,**e** observed upon the formation of complexes with Mg^{2+} and upon the introduction of substituents.

To elucidate the nature of the effects found, we analyzed the changes in the electronic structures of dyes *trans*-**1a**,**b**,**e** upon the electron excitation. The charges on fragments *A*, *B*, and *C* of *trans*-**1a**,**b**,**e** molecules in the ground (S_0) and the lowest singlet electron-excited (S_1) states were calculated. The results are presented in Table 5.

Table 4. Calculated positions of the LAB maxima for dyes *trans*-**1a**,**b**,**e** and complexes (*trans*-**1a**,**b**,**e**) · Mg^{2+}

Compound	λ^a_{max}	$\Delta\lambda^a$
	nm	
trans-**1a**	411	
(*trans*-**1a**) · Mg^{2+}	394	18
trans-**1b**	425	
(*trans*-**1b**) · Mg^{2+}	417	8
trans-**1e**	502	
(*trans*-**1e**) · Mg^{2+}	507	−5

Note. $\Delta\lambda^a = \lambda^a_{max}$(ligand) − λ^a_{max}(complex).

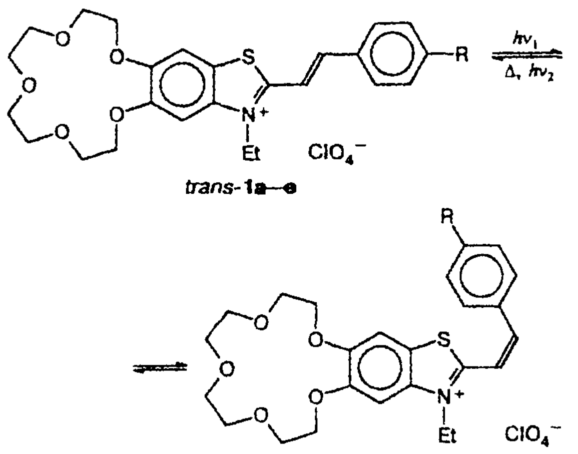
Table 5. Charge distribution (*q*/*e*) on fragments *A*, *B*, and *C* of dyes *trans*-**1a**,**b**,**e** in the ground and lower electron-excited states

CSD	State	*q* (Δ*q*) on the fragment		
		A	*B*	*C*
1a	S_0	0.24	0.48	0.28
	S_1	0.68	0.17	0.15
		(+0.44)	(−0.31)	(−0.13)
1b	S_0	0.25	0.49	0.26
	S_1	0.49	0.09	0.42
		(+0.24)	(−0.40)	(+0.16)
1e	S_0	0.26	0.50	0.24
	S_1	0.31	0.15	0.54
		(+0.05)	(−0.35)	(+0.30)

In fact, in the case of CSD *trans*-**1a** (R = H), the long-wave electron transition is accompanied by a substantial transfer of the electron density from fragment *A*, most of all, to the central part of the molecule *B*, and, to some extent, to fragment *C* of the dye, *i.e.*, upon electron excitation, the electron density is diplaced from the crown-ether moiety. Therefore, the formation of the (*trans*-**1a**) · Mg^{2+} complex is energetically more favorable in the ground state. This accounts for the experimentally observed hypsochromic shift of the LAB of *trans*-**1a** following the complexation with Mg^{2+}. When electron-donating substituents are introduced into the *para*-position of the benzene ring of fragment *C* of the dye, the character of the electron density redistribution caused by the transition to the lowest electron-excited state qualitatively changes, and, in the case of a strong electron-donating substituent such as NMe_2, the displacement of the electron density in the opposite direction, *i.e.*, toward the crown-ether moiety, predominates. Therefore, the formation of the (*trans*-**1e**) · Mg^{2+} complex in the lowest electron-excited state is energetically more favorable than that in the ground state. This results in the bathochromic shift of the LAB, which is actually observed in the experiment.

Similarly to the CSD studied previously,[3,4] dyes *trans*-**1a**—**e**, *trans*-**2** and complexes (*trans*-**1a**—**e**) · Mg^{2+} undergo reversible *trans*—*cis*-photoisomerization under irradiation (Scheme 4).

Scheme 4



trans-**1a—e**

cis-**1a—e**

The absorption spectra of dyes *cis*-**1a,b,d** and complexes (*cis*-**1a,b,d**) · Mg^{2+}, which have fairly large lifetimes, were calculated by a known procedure (see Experimental). We were not able to obtain the absorption spectra of dyes *cis*-**1c,e** and their complexes with Mg^{2+}. When the substituent R = NMe_2 is introduced into the *para*-position of the benzene ring, the degree of conjugation in fragment *C* increases. This should decrease the activation energy for the dark *cis*—*trans*-isomerization and, consequently, shorten the lifetime (τ) of CSD *cis*-**1e**. In fact, for *cis*-**1a**, $\tau = 3.5 \cdot 10^4$ s, and for *cis*-**1e**, $\tau = 250$ s. When *cis*-**1e** is bound into a complex with Mg^{2+}, the degree of conjugation in fragment *C* further increases, and hence, the lifetime of the *cis*-isomer becomes even shorter ($\tau \approx 10$ s). Probably, the short lifetimes of CSD *cis*-**1c** and its complex with Mg^{2+} ($\tau < 10$ s) make impossible observation of the changes in the absorption spectra of the corresponding *trans*-forms upon exposure to radiation. These τ values can be due to the intermediate formation of dye *cis*-**8** and its complex with Mg^{2+} as a result of the proton abstraction (see Scheme 2); the lifetimes of the latter species are presumably even shorter than those of *cis*-**1e** and (*cis*-**1e**) · Mg^{2+}.

The absorption spectra of dyes *cis*-**1a,b,d** and (*cis*-**1a,b,d**) · Mg^{2+} are shown in Fig. 1 (*b* and *d*, respectively). The maxima of the LAB in the spectra of *cis*-**1a,b,d** are shifted to the short-wave region with respect to the maxima of the corresponding bands of *trans*-isomers (by 44 nm), and ε_{cis} is 3—5 times smaller than ε_{trans} (see Table 3). The positions of the maxima of LAB for dyes *cis*-**1a,b,d** are markedly closer to one another than the positions of the LAB of *trans*-**1a,b,d**. This may be due to the fact that in *cis*-**1a,b,d**, the effects of substituents R are less pronounced than those in the molecules of *trans*-**1a,b,d**, because the efficiency of conjugation between chromophores *C* and *B* becomes weaker and coplanarity of the molecules is disturbed (*cf.* Ref. 9). Conversely, the differences between the positions of the LAB maxima of the (*cis*-**1a,b,d**) · Mg^{2+} complexes are fairly pronounced, since the degree of conjugation between chromophores *C* and *B*, apparently, markedly increases upon complex formation. This is also manifested in the fact that the formation of complexes of dyes *cis*-**1a,b** with Mg^{2+} leads to hypsochromic shifts of the LAB, which decrease as the electron-donating ability of the substituent R increases (from 21 to 3 nm). In the case of CSD *cis*-**1d**, the electron-donating effect of the substituent (R = SMe), apparently, becomes sufficiently strong to cause a bathochromic shift of the LAB maximum, although this shift is very small (−1 nm). The nature of this spectral effect may be similar to that of the effect observed on the complexation of *trans*-**1a—e** with Mg^{2+}, which we have explained by the interaction between the two chromophores.

For dyes *trans*-**1a—e**, the fluorescence spectra were recorded (Fig. 2). As should be expected,[2] the *cis*-isomers of these compounds do not fluoresce at room temperature. When electron-donating substituents are introduced into the *para*-position of the benzene ring, the fluorescence band, like the absorption band, shifts to longer wavelengths (see Table 3); however, in the case of *trans*-**1b,c** this shift with respect to *trans*-**1a** is not clearly manifested. The addition of $Mg(ClO_4)_2$ to solutions of CSD *trans*-**1a—e** in MeCN leads to quenching of the fluorescence and to displacement of λ^f_{max}: for compounds *trans*-**1a—c**, shifts to shorter wavelengths are observed, while the bands of *trans*-**1d,e** shift to longer wavelengths. It is of interest that the fluorescence spectrum of CSD *trans*-**1d** shifts to the long-wavelength region, although the LAB undergoes a hypsochromic shift. For the rest of the dyes, the absorption and fluorescence spectra move in parallel upon complexation.

The decrease in the quantum yield of fluorescence (φ_f) following the complex formation (see Table 3) cannot, apparently, be explained in our case by the change in the quantum yields of photoisomerization (φ_{tc}) upon going from CSD to their complexes with Mg^{2+}. This inference is also supported by the fact that the φ_f values for CSD are small, and the φ_{tc} values for the photoisomerization of the CSD studied and their complexes with Mg^{2+} in MeCN are close to one another and lie in the 0.5—0.7 range. The introduction of the methoxy group into the conjugation chain of the chromophore in an organic luminophor is known[13] to result normally in an increase in φ_f. Therefore, it could be expected that the formation of complexes of CSD with Mg^{2+}, in which the unshared electron pairs of the O atoms are excluded from the conjugation with the chromophore in order to participate in the formation of coordination bonds, would cause the opposite effect, *i.e.*, a decrease in φ_f, which has actually been observed in our experiments.

Thus, CSD of a new type were synthesized. The regularities of the influence of the crown-ether moiety

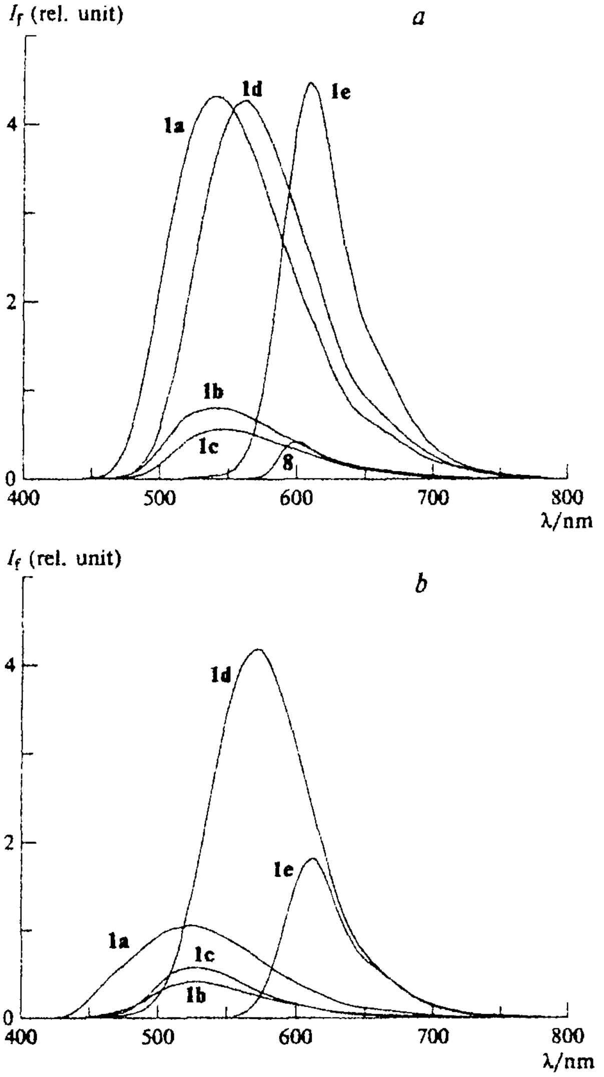


Fig. 2. Fluorescence spectra (λ_{exc} = 400 nm for CSD **1a—e**, λ_{exc} = 500 nm for *trans*-**8**) of dyes *trans*-**1a—e**, *trans*-**8** (*a*) and complexes (*trans*-**1a—e**) $\cdot$ Mg^{2+} (*b*) in MeCN at C_L = $2 \cdot 10^{-5}$ mol L^{-1}, C_{Mg} = 10^{-2} mol L^{-1}, T = 295 K. Fluorescence spectra of *trans*-**1a** was decreased twofold.

in the benzothiazole residue and of substituents in the benzene ring on the spectral and photochromic properties of CSD were studied; and the specific features of this type of dyes caused by the interaction of two chromophores were investigated. It was found that the degree to which each of the chromophores participates in the long-wave electron transition can be controlled by using complex formation. This creates the basis for the target-directed variation of spectral and photochemical properties of these dyes by virtue of their organic synthesis and complex formation.

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-200 SY spectrometer using $SiMe_4$ as the internal standard and DMSO-d_6 as the solvent. The course of the reactions was monitored by TLC on DC-Alufolien Kieselgel 60 F_{254} plates.

Acetonitrile was distilled over $KMnO_4$, twice over P_2O_5 and, finally, over CaH_2 to remove impurities and water. Methanol of the Chemicon AB company was used (HPLC). Water was distilled twice and $Mg(ClO_4)_2$ was dried *in vacuo* at 240 °C. Preparation of the solutions and all the experiments were carried out in red light; the initial concentrations of the dyes were $C_L \approx 2 \cdot 10^{-5}$ mol L^{-1}.

Solutions of CSD and their complexes with Mg^{2+} were irradiated with a DRSh-100-2 mercury lamp. Individual lines of the spectrum of this lamp were separated using glass light filters. The intensity of light was determined by a ferrioxalate actinometer.[14] All spectroscopic measurements were carried out in a quartz cell, whose inner surface was modified with Me_2SiCl_2 in order to decrease the adsorption of the dye on the walls of the cell.[15] The electronic absorption spectra were recorded on a Shimadzu UV-3101 spectrophotometer.

The *cis*-isomers of CSD do not fluoresce in solution at room temperature; therefore, the absorption spectra of dyes *cis*-**1a,b,d,e** and their complexes (*cis*-**1a,b,d**) $\cdot$ Mg^{2+} were calculated by the following procedure:[16] intensities of fluorescence of solutions of pure *trans*-isomer (I_0) and of the photosteady-state mixture obtained upon irradiation with light at λ = 365 nm (I_s) were measured, and the fraction of the *cis*-isomer in the photosteady-state mixture was determined from the formula $\alpha_s = 1 - I_s/I_0$; then the spectrum of the *cis*-isomer was calculated using the absorption spectra of the *trans*-isomer ($D_t(\lambda)$) and the photosteady-state mixture ($D_s(\lambda)$) from the equation

$$D_c(\lambda) = [D_s(\lambda) - (1 - \alpha_s) \cdot D_t(\lambda)]/\alpha_s.$$

The fluorescence spectra were measured on a Shimadzu RF-5000 spectrofluorimeter. The quantum yields of fluorescence (φ_f) were determined in relation to fluorescein in a 0.01 *N* solution of KOH in EtOH upon excitation with light with λ = 400 nm (inaccuracy –15%).

3-Ethyl-2-methyl-6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxacyclopentadecino[2,3-*f*]benzothiazolium perchlorate (3). A 57% solution of $HClO_4$ (0.72 mL, 6 mmol) was added to a solution of iodide **5** (1.01 g, 2 mmol) (see Refs. 6 and 7) in 50 mL of boiling MeOH. The solution was cooled, and the precipitate was filtered off and washed with cooled MeOH to give 0.93 g (97%) of perchlorate **3**; m.p. 197 °C (decomp.). Found (%): C, 46.17; H, 5.69; N, 2.82. $C_{18}H_{26}ClNO_9S$. Calculated (%): C, 46.20; H, 5.60; N, 2.99.

3-Ethyl-5,6-dimethoxy-2-methylbenzothiazolium perchlorate (7). A mixture of 5,6-dimethoxy-2-methylbenzothiazole (0.3 g, 1.44 mmol) and EtI (1.15 mL, 14.4 mmol) was heated in a sealed tube at 110 °C for 12 h. The tube was opened, the crystalline precipitate was washed with hot benzene and dissolved in boiling MeOH. Perchloric acid (57%, 0.5 mL) was added, the solution was cooled, and the precipitate was filtered off and washed with cooled MeOH to give 0.44 g (90%) of perchlorate **7**, m.p. 213—215 °C (decomp.). ^{1}H NMR, δ: 1.50 (t, 3 H, $NCH_2\underline{Me}$, J = 7 Hz); 3.15 (s, 3 H, Me); 3.92 (s, 3 H, OMe); 4.01 (s, 3 H, OMe); 4.77 (q, 2 H, NCH_2, J = 7 Hz); 7.72 (s, 1 H, HC(7)); 7.92 (s, 1 H, HC(4)).

Found (%): C, 42.30; H, 4.67; N, 3.89. $C_{12}H_{16}ClNO_6S$. Calculated (%): C, 42.67; H, 4.77; N, 4.15.

***trans*-3-Ethyl-2-(2-phenylethyl)-6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxacyclopentadecyno[2,3-*f*]benzothiazolium perchlorate (1a).** Perchlorate 3 (0.115 g, 0.246 mmol) was mixed with benzaldehyde (0.05 mL, 0.49 mmol), and dry pyridine (2 mL) was added. The reaction mixture was heated in an argon atmosphere for 7 h at 90 °C. The pyridine was evaporated *in vacuo*, and the residue was thoroughly washed with hot benzene and recrystallized from a 10 : 1 MeOH—MeCN mixture to give 0.09 g (65%) of salt **1a**, m.p. 224 °C (decomp.). Found (%): C, 53.93; H, 5.44; N, 2.27. $C_{25}H_{30}ClNO_9S$. Calculated (%): C, 54.02; H, 5.44; N, 2.52.

***trans*-3-Ethyl-2-[2-(4-methoxyphenyl)ethenyl]-6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxacyclopentadecyno[2,3-*f*]benzothiazolium perchlorate (1b).** Perchlorate 3 (0.05 g, 0.1 mmol) was mixed with 4-methoxybenzaldehyde **4b** (0.04 mL, 0.3 mmol), and dry pyridine (2 mL) was added. The reaction mixture was heated in an argon atmosphere for 6 h at 90 °C. The pyridine was evaporated *in vacuo*, and the residue was thoroughly washed with hot benzene and recrystallized from MeOH to give 0.044 g (70%) of salt **1b**, m.p. 243 °C (decomp.). Found (%): C, 53.40; H, 5.43; N, 2.17. $C_{26}H_{32}ClNO_{10}S$. Calculated (%): C, 53.28; H, 5.50; N, 2.39.

***trans*-3-Ethyl-2-[2-(4-hydroxyphenyl)ethenyl]-6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxacyclopentadecyno[2,3-*f*]benzothiazolium perchlorate (1c).** Perchlorate 3 (0.1 g, 0.21 mmol) was mixed with 4-hydroxybenzaldehyde **4c** (0.05 g, 0.42 mmol), and dry pyridine (2.5 mL) was added. The reaction mixture was heated in an argon atmosphere for 10 h at 90 °C. The pyridine was evaporated *in vacuo*, and the residue was thoroughly washed with hot benzene and dissolved in boiling MeOH; the solution was acidified with 57% $HClO_4$ and cooled. The precipitate was filtered off and washed with cooled MeOH to give 0.07 g (57%) of salt **1c**, m.p. 161 °C (decomp.). Found (%): C, 50.95; H, 5.14; N, 2.06. $C_{25}H_{30}ClNO_{10}S \cdot H_2O$. Calculated (%): C, 50.89; H, 5.47; N, 2.37.

***trans*-3-Ethyl-2-[2-(4-methylthiophenyl)ethenyl]-6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxacyclopentadecyno[2,3-*f*]benzothiazolium perchlorate (1d)** was synthesized from perchlorate 3 and 4-methylthiobenzaldehyde **4d**, similarly to compound **1a**. After heating of the reaction mixture for 5 h, the yield of salt **1d** was 52%, m.p. 212 °C (decomp.) (from a 10 : 1 MeOH—MeCN mixture). Found (%): C, 51.44; H, 5.27; N, 2.08. $C_{26}H_{32}ClNO_9S_2$. Calculated (%): C, 51.86; H, 5.36; N, 2.33.

***trans*-2-[2-(4-Dimethylaminophenyl)ethenyl]-3-ethyl-6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxacyclopentadecyno[2,3-*f*]benzothiazolium perchlorate (1e).** Perchlorate 3 (0.116 g, 0.25 mmol) was mixed with 4-dimethylaminobenzaldehyde **4e** (0.045 g, 0.3 mmol), and dry pyridine (3.5 mL) was added. The reaction mixture was heated in an argon atmosphere for 5 h at 90 °C and worked up as described above for CSD **1a** to give 0.082 g (55%) of salt **1e**, m.p. 184 °C (decomp.). Found (%): C, 52.39; H, 6.03; N, 4.58. $C_{27}H_{35}ClN_2O_9S \cdot H_2O$. Calculated (%): C, 52.55; H, 6.04; N, 4.54.

***trans*-3-Ethyl-2-[2-(4-methoxyphenyl)ethenyl]-5,6-dimethoxybenzothiazolium perchlorate (2)** was synthesized from perchlorate 7 and 4-methoxybenzaldehyde **4b** similarly to compound **1b**. The yield of salt **2** was 50%, m.p. 297 °C (decomp.) (from MeOH). Found (%): C, 52.75; H, 4.84; N, 2.85. $C_{20}H_{22}ClNO_7S$. Calculated (%): C, 52.69; H, 4.87; N, 3.07.

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