Crown ether styryl dyes

24.* Synthesis of multiphotochromic 15-crown-5 ethers with rigid spacers, their anion-"capped" complexes, and stereospecific [2+2] autophotocycloaddition

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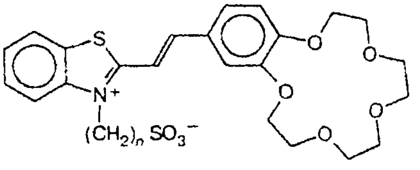
Novel styryl dyes (*trans*-**2a,b**) containing a 15-crown-5 ether moiety and an *N*-sulfobenzyl spacer were synthesized. The reactions of *trans*-**2a,b** with $Mg(ClO_4)_2$ in MeCN afford dimeric complexes. During photolysis of the latter, *trans—cis* isomerization to give anion-"capped" complexes (*cis*-**2a,b**) · Mg^{2+} and stereospecific [2+2] autocycloaddition to yield cyclobutane derivative occur in parallel. The ratio of the two transformation pathways of dyes **2a,b** depends on the spacer type. To interpret the experimental data, the molecular-mechanics and semiempirical quantum-chemical calculations were performed.

Key words: crown ether styryl dyes, synthesis, complexation, anion-"capped" complexes, [2+2] autophotocycloaddition; molecular mechanics; electronic spectra; ^1H NMR spectra.

The capability of being self-organized at the molecular level (self-assembly) in solutions to give supramolecular structures with a desired architecture and photochemical control of their properties are necessary conditions for the development of photoswitchable molecular devices.[2] Synthesis of multiphotochromic complexones able to undergo various types of molecular photoswitching is of prime importance for these purposes. Previously, we have developed a procedure for the synthesis of crown-containing styryl dyes (CSD).[3] CSD of type *trans*-**1a,b**, which can form anion-"capped" complexes upon *trans—cis*-photoizomerization owing to the interaction of the sulfo-group of the *N*-substituent (spacer) with a metal cation in the crown-ether cavity, proved to be the most promising. As a result, affinity of these compounds for metal cations can be markedly changed by exposing them to light, *i.e.*, complex formation can be controlled[4,5].



trans-**1a,b**

n = 3 (**a**), 4 (**b**)

It was also shown that the self-assembly of dimeric complexes from two molecules of *trans*-**1a,b** and two metal cations can serve as a unique tool for controlling regio- and stereoselectivities of [2+2] photocycloaddition (PCA) of CSD (see Refs. 5, 6). It can be expected that passing from spacers with flexible polymethine chains of various lengths to *N*-substituents, whose sulfo group is rigidly arranged in space, would enhance the efficiency of these interesting photochemical reactions and have an influence on the CSD transformation pathway.

In this work, using multiphotochromic 15-crown-5 ethers of the benzothiazole series **2a,b** as examples, we studied the effect of the type of rigid spacer and metal cation on the formation of anion-"capped" complexes and on the efficiency of [2+2] autophotocycloaddition of CSD.

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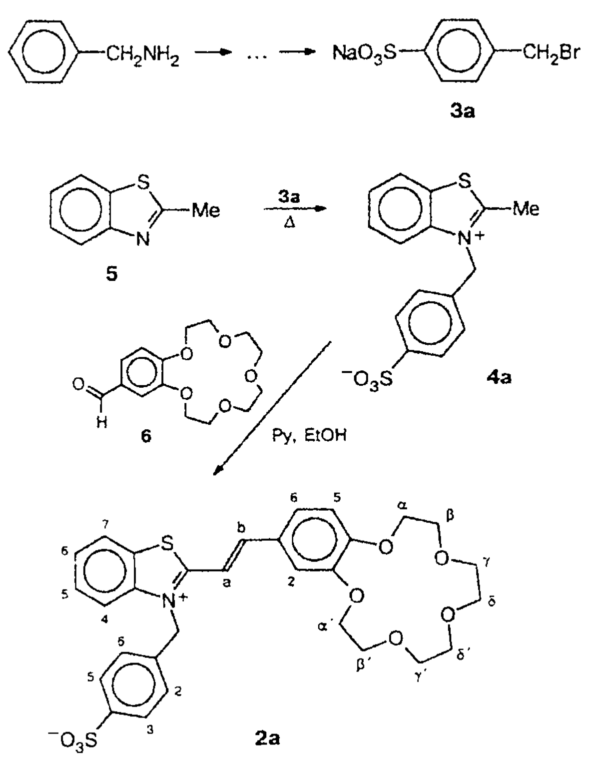
* For Part 23, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 99—107, January, 1998.

The synthesis of compounds **2a,b** is shown in Schemes 1 and 2. Sodium 4-bromomethylbenzenesulfonate (**3a**) was prepared by a known procedure.[7] The starting betaine **4a** was obtained in 65% yield by fusion together 2-methylbenzothiazole (**5**) and salt **3a** in a 2 : 1 ratio at 150 °C.

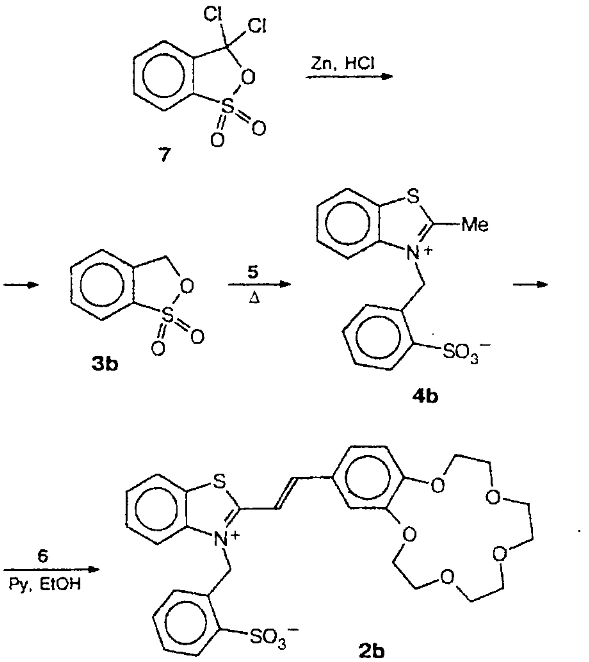
Scheme 1



These conditions are the optimum for this reaction, because variation of the conditions substantially decreases the yield of betaine **4a**. Dye **2a** was synthesized in 44% yield by the condensation of betaine **4a** with 4′-formylbenzo-15-crown-5 ether[8] (**6**) in the presence of pyridine serving as a base. When a large excess of pyridine was present, compound **2a** was not produced. In order to avoid the side formation of a cyanine dye (spectrophotometric monitoring), the reaction was carried out under an inert atmosphere. No cyanine dye was detected in the products of condensation of compounds **4a** and **6** in acetic anhydride; however, the yield of CSD **2a** in this case was 25%.

γ-Sultone **3b** was synthesized by the reduction of dichloride **7** with zinc in dilute HCl by a known procedure.[9] Betaine **4b** was prepared in 78% yield similarly to **4a** by fusion compounds **3b** and **5**. Dye **2b** was synthesized in 65% yield by the condensation of betaine **4b** with crown ether **6** in the presence of pyridine as a base. As in the previous case, an excess of pyridine markedly decreases the yield of CSD **2b** and promotes the formation of the side cyanine dye.

Scheme 2



The structure of compounds **2a,b** was proved by ^1H NMR spectroscopy (see Experimental). The *trans*-configurations of CSD **2a,b** were confirmed by the magnitudes of the spin-spin coupling constants of the olefinic protons: $^3J_{trans}$ = 15.6 Hz (see Ref. 10).

The UV spectra of the products in MeCN virtually do not differ from those reported previously for CSD *trans*-**1a,b**. The presence of a benzene ring in the *N*-substituent of CSD is manifested only as a slight bathochromic shift of the long-wavelength absorption band (LAB) (Table 1).

When Mg, Ca, or Ba perchlorate is added to a solution of CSD *trans*-**2a,b**, the LAB in their UV spectra undergo substantial hypsochromic shifts indicating that these metal cations interact with the crown-ether moiety of the dye[11] (Scheme 3).

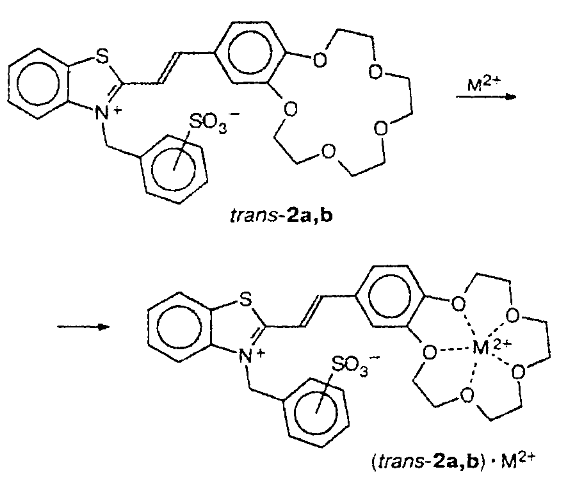
Table 1. Position of the maxima of the LAB (λ_{max}) of CSD *trans*-**1a,b** and *trans*-**2a,b** ($C_L = 2 \cdot 10^{-5}$ mol L^{-1}) in MeCN and in the presence of alkaline earth metal perchlorates ($C_M = 2 \cdot 10^{-3}$ mol L^{-1})

CSD	λ_{max} ($\Delta\lambda$)^a/nm			
	Without a salt	$Mg(ClO_4)_2$	$Ca(ClO_4)_2$	$Ba(ClO_4)_2$
trans-**1a**[b]	436	393 (43)	396 (40)	407 (29)
trans-**1b**[b]	435	395 (40)	398 (37)	406 (29)
trans-**2a**	439	397 (42)	394 (45)	406 (33)
trans-**2b**	444	404 (40)	404 (40)	416 (28)

[a] $\Delta\lambda = \lambda_{max}$(ligand) − λ_{max}(complex).

[b] See Ref. 11.

Scheme 3



M = Mg, Ca, Ba

The long-wavelength electron transition in a CSD molecule involves displacement of the electron density from the benzene ring to the heterocycle.[12] When the crown-ether moiety binds M^{2+}, this displacement (directed away from the cation) becomes energetically unfavorable. This accounts for the experimentally observed hypsochromic shift of the LAB.

For comparison, Table 1 presents the magnitudes of the hypsochromic shifts ($\Delta\lambda$) of the LAB in compounds *trans*-**2a,b**, *trans*-**1a,b** ($C_L = 2 \cdot 10^{-5}$ mol L^{-1}), and in their complexes obtained by the addition of metal perchlorates with the concentration $C_M = 2 \cdot 10^{-3}$ mol L^{-1} (under these conditions, the dye is completely bound into the complex). The $\Delta\lambda$ values depend only slightly on the structure of the *N*-substituent and change in the sequence $Mg^{2+} \geq Ca^{2+} > Ba^{2+}$. At the same time, the hypsochromic shifts observed for the complexes of *trans*-**2a** with Ca^{2+} and Ba^{2+} are much larger than those for other dyes; moreover, the $\Delta\lambda$ value observed in the case of (*trans*-**2a**) · Ca^{2+} is larger than that found for (*trans*-**2a**) · Mg^{2+}.

It was found that the patterns of the absorption spectra of the *trans*-**2a,b** complexes with Mg^{2+} ions change markedly as the concentration of the dye increases from $8 \cdot 10^{-7}$ to $9 \cdot 10^{-5}$ mol L^{-1} (Fig. 1). The concentration of CSD was varied in such a way that an excess of Mg^{2+} ions ($C_M - C_L = 1.0 \cdot 10^{-4}$ mol L^{-1}), sufficient for all the dye to be bound into the complex, was always present in the solution. In addition, the total concentration of the perchlorate anions ($C_A = 1.0 \cdot 10^{-3}$ mol L^{-1}) was kept constant by adding Et_4NClO_4 as a supporting electrolyte; this was done to ensure that a change in C_L has no effect on the equilibria of reactions of the complexes with perchlorate ions. The ionic strength of solutions varied over a very narrow range: $1.1 \cdot 10^{-3}$—$1.2 \cdot 10^{-3}$ mol L^{-1}.

If we assume that compounds *trans*-**2a,b**, like the previously studied *trans*-**1a,b**, in addition to the 1 : 1 complexes, are able to form dimeric complexes of the composition 2 : 2 with alkaline earth metal cations (Scheme 4), the spectral changes shown in Fig. 1 can be explained by a shift of the dimerization equilibrium. Figure 1 also shows the simulated absorption spectra of monomeric complexes (*trans*-**2a,b**) · Mg^{2+} and dimers [(*trans*-**2a,b**) · Mg^{2+}]$_2$. Detailed analysis of the results will be published elsewhere.

Dimerization of complexes (*trans*-**2b**) · Mg^{2+} leads to a slight decrease in the extinction coefficient (ε) and to the appearance of a long-wavelength shoulder in the absorption spectrum. The position of the maximum of

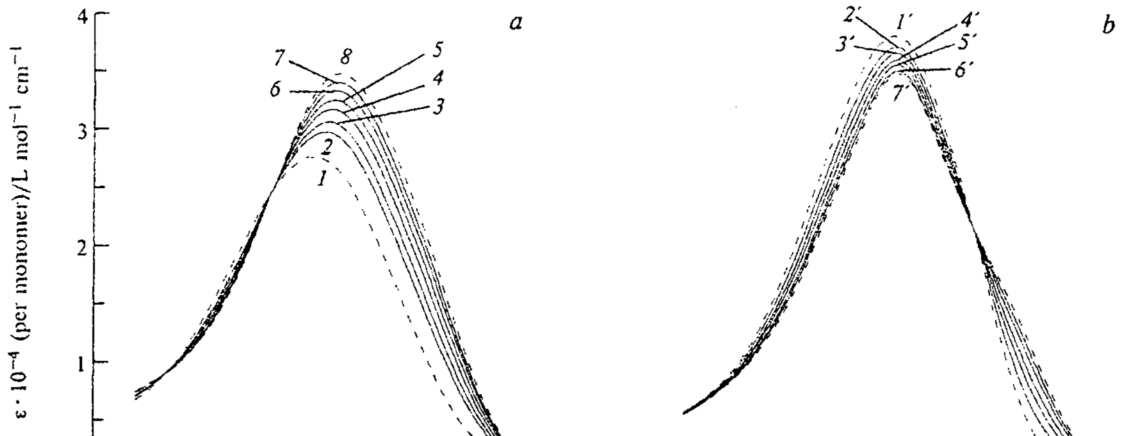
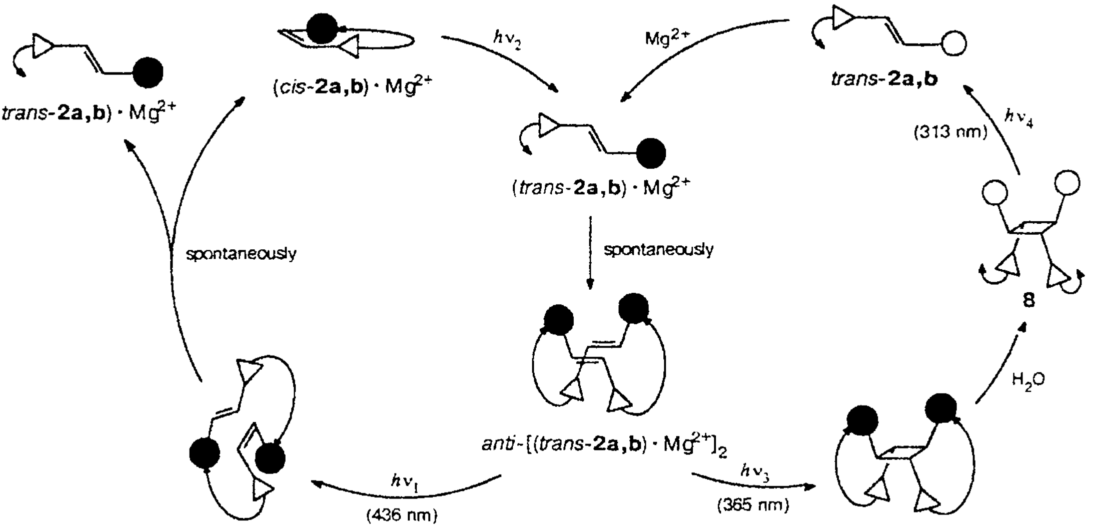


Fig. 1. Absorption spectra of complexes (*trans*-**2a**) · Mg^{2+} (*a*) and (*trans*-**2b**) · Mg^{2+} (*b*) in MeCN at various concentrations of the dyes: $C_L \cdot 10^5$/mol L^{-1} = 0.08 (*2*), 0.16 (*3*), 0.4 (*4*), 0.93 (*5*), 2.9 (*6*), 9.2 (*7*) (*trans*-**2a**); 0.08 (*2'*), 0.23 (*3'*), 0.73 (*4'*), 2.4 (*5'*), 9.0 (*6'*) (*trans*-**2b**). Dashed curves correspond to the simulated spectra of monomeric (*1*, *1'*) and dimeric (*8*, *7'*) complexes.

Scheme 4



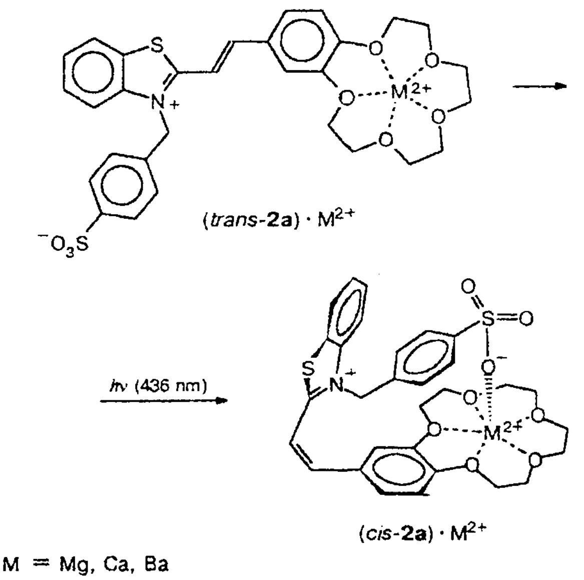
Notation. From here on, ○ is a benzo-15-crown-5 moiety; ● is a benzo-15-crown-5 moiety with Mg^{2+}; ▷ is a benzothiazole residue; ↶ is $CH_2C_6H_4SO_3^-$.

the LAB almost does not change (the bathochromic shift is ≤1 nm). However, upon dimerization of the (*trans*-**2a**) · Mg^{2+} complex, the ε value increases, and the bathochromic shift of the absorption maximum is as large as 8 nm.

Taking into account the substantial difference between the spectral changes accompanying the dimerization of the complexes of *trans*-**2a** and *trans*-**2b** and assuming that intermolecular interaction (through space) of the chromophores of the dyes makes the major contribution to these changes, we can conclude that the mutual orientations of the chromophores in the complexes [(*trans*-**2a**) · Mg^{2+}]$_2$ and [(*trans*-**2b**) · Mg^{2+}]$_2$ are different.

The complexes of *trans*-**2a,b** with alkaline earth metal cations, like the free dyes themselves, readily isomerize on exposure to blue light (see Scheme 4). The *trans—cis*-isomerization is photochemically reversible. A typical feature of these complexes is that the spectrum of the *cis*-isomer formed is strongly shifted to shorter wavelengths with respect to the spectrum of the *trans*-isomer (Figs. 2, 3). Whereas the maximum degree of photoisomerization of CSD **2a,b** in pure MeCN does not exceed 80% (according to the Fischer method[13]), in the presence of excess $Mg(ClO_4)_2$ ($1 \cdot 10^{-4}$ mol L^{-1}), the proportion of the *cis*-isomer in the *trans—cis*-photosteady state formed on exposure to light with λ = 436 nm is >99% for **2a** and ≥97% for **2b**. The same effect was found in our previous studies[4,11] for CSD **1a,b**; hence, by analogy, the effect observed here can be attributed to the formation of anion-"capped" complexes from dyes *cis*-**2a,b**; the CSD molecules in these complexes occur in nonplanar conformations in which the conjugation in the chromophore is markedly violated (Scheme 5).

Scheme 5



Using CSD **1a,b** as examples, we have shown[11] that the absorption spectra of the anion-"capped" complexes formed by the *cis*-isomers with violation of the conjugation in the chromophore exhibit an absorption band with a maximum at 240—260 nm, which does not occur in the spectra of the *cis*-isomers similar to **1a** but containing an *N*-ethyl substituent. The presence of this band in the spectra of complexes of CSD *cis*-**2a,b** with Mg^{2+} (see Figs. 2, 3) is consistent with the conclusion that in these complexes, an intramolecular coordination bond (ICB) is formed.

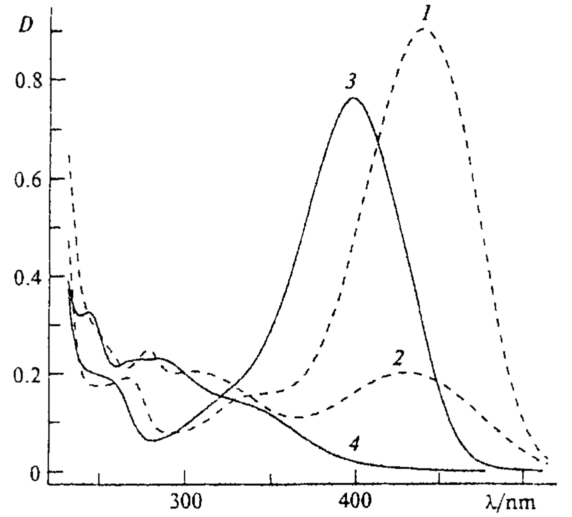


Fig. 2. Absorption spectra of individual CSD **2a** (C_L = $5 \cdot 10^{-6}$ mol L^{-1}, l = 5 cm) in MeCN: *trans*-isomer (*1*); *cis*-isomer (the spectrum was calculated by the Fischer method[13]) (*2*); in the presence of $Mg(ClO_4)_2$ (C_M = $1.1 \cdot 10^{-4}$ mol L^{-1}): *trans*-isomer (*3*); *trans—cis*-photosteady state attained under irradiation with light with λ = 436 nm (proportion of the *cis*-isomer >99%) (*4*).

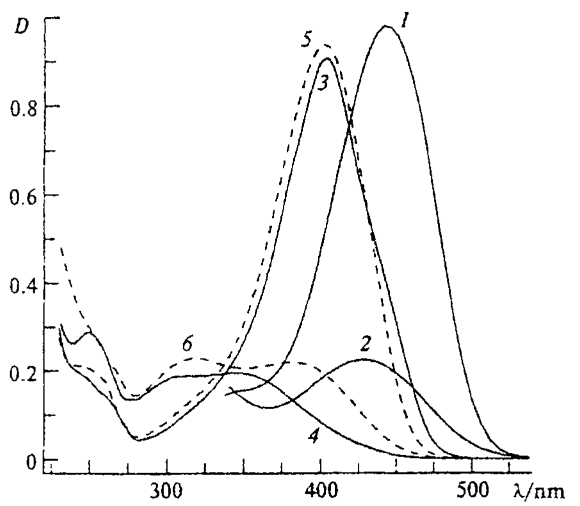
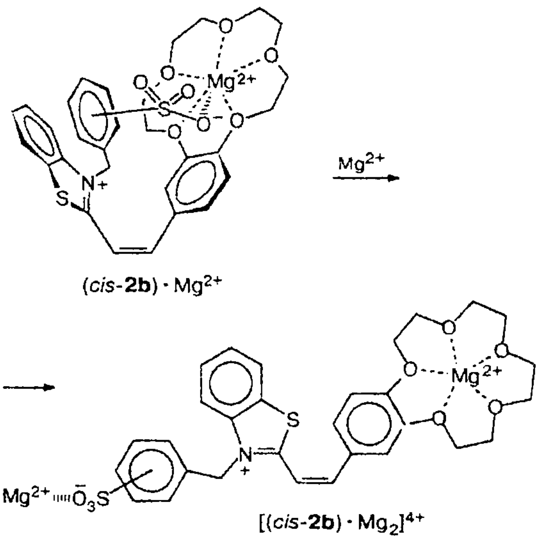


Fig. 3. Absorption spectra of individual CSD **2b** (C_L = $2.6 \cdot 10^{-5}$ mol L^{-1}, l = 1 cm) in MeCN: *trans*-isomer (*1*); *cis*-isomer (the spectrum was calculated by the Fischer method[13]) (*2*); in the presence of $Mg(ClO_4)_2$ (C_M = $1.2 \cdot 10^{-4}$ mol L^{-1}): *trans*-isomer (*3*); *trans—cis*-photosteady state attained under irradiation with light with λ = 436 nm (proportion of the *cis*-isomer ≥97%) (*4*); after addition of excess $Mg(ClO_4)_2$ (C_M = 0.2 mol L^{-1}): to the solution corresponding to curve *3* (*5*); to the solution corresponding to curve *4* (*6*).

Along with common features, the absorption spectra of the complexes of CSD *cis*-**2a,b** with Mg^{2+} also have considerable distinctions resulting apparently from the fact that the formation of the anion-"capped" complex (*cis*-**2a**) · Mg^{2+} is accompanied by stronger violation of the conjugation in the chromophore.

When a large amount of $Mg(ClO_4)_2$ (C_M = 0.2 mol L^{-1}) is added to a solution of the anion-"capped" complexes (*cis*-**2b**) · Mg^{2+}, the absorption in the long-wavelength region of the spectrum substantially increases, and the band at 240—260 nm disappears (see Fig. 3). This is apparently due to the formation of complexes $[(cis\text{-}\mathbf{2b}) \cdot Mg_2]^{4+}$ in which one of the Mg^{2+} ions is located in the crown-ether cavity, whereas the other one forms a coordination bond with the sulfo group of the spacer. When the ICB in the anion-"capped" complex (*cis*-**2b**) · Mg^{2+} is cleaved, the chromophore fragment in complex $[(cis\text{-}\mathbf{2b}) \cdot Mg_2]^{4+}$ assumes a more planar conformation, and the conjugation in it is restored (Scheme 6).

Scheme 6



In the case of anion-"capped" complex (*cis*-**2a**) · Mg^{2+}, the addition of excess $Mg(ClO_4)_2$ (C_M = 0.2 mol L^{-1}) results only in a slight shift of the equilibrium toward the complex $[(cis\text{-}\mathbf{2a}) \cdot Mg_2]^{4+}$. The anion-"capped" complex remains the major component of the equilibrium mixture.

These data indicate that anion-"capped" complex (*cis*-**2a**) · Mg^{2+} is much more stable than (*cis*-**2b**) · Mg^{2+}. Tentative results obtained by measurements of the stability constants of anion-"capped" complexes (*cis*-**2a,b**) · Mg^{2+} support this conclusion (the stability constants of the complexes formed by CSD *trans*-**2a,b** and *cis*-**2a,b** will be published later).

We also carried out comparative theoretical analysis (see Experimental) of the stabilities of anion-"capped" complexes (*cis*-**2a,b**) · Mg^{2+}: the calculated standard heat of formation of (*cis*-**2b**) · Mg^{2+} is 153.7 kcal mol^{-1}, while that for (*cis*-**2a**) · Mg^{2+} is 119.8 kcal mol^{-1}. It has been found by PM3 calculations carried out for model disubstituted benzene derivatives that transition of a sulfur group from the *ortho*- to the *para*-position in the benzene ring of the spacer decreases the standard heat of formation of the molecule by only 1.5 kcal mol^{-1}. The remaining 32.5 kcal mol^{-1} corresponds to the difference between the standard heats of formation of the anion-"capped" complexes. Thus, the stability constant of (*cis*-**2a**) · Mg^{2+} should be much greater than that of (*cis*-**2b**) · Mg^{2+}.

Calculation of the spatial structures of the complexes has shown that in anion-"capped" complex (*cis*-**2b**) · Mg^{2+}, the angle between the plane of the C=C bond (the plane of the C=C bond means the plane drawn through these two atoms and the four neighboring atoms) and the plane of the benzothiazolium residue is 35.8°, and the angle between the planes of the C=C bond and the benzene ring of the benzocrown-ether moiety is 54.0°. In the case of (*cis*-**2a**) · Mg^{2+}, these angles are 88.4° and 24.1°, respectively. Thus, the benzothiazolium residue in the structure of (*cis*-**2a**) · Mg^{2+} is located at right angle to the C=C bond indicating that there is no conjugation between the π-electron systems of the heterocycle and the rest of the molecule.

It may be expected that this difference between the spatial structures of anion-"capped" complexes (*cis*-**2a,b**) · Mg^{2+} would have an effect on their spectral properties. We simulated the electronic absorption spectra of (*cis*-**2a,b**) · Mg^{2+} using the semiempirical ZINDO/S quantum-chemical method taking into account interaction of the configurations resulting from the transfer of one electron from each of the five HOMO to each of the five LUMO. For the overlap factor of the π—π-resonance integral, we took a standard value equal to 0.64. The calculation showed that the spectra of complexes (*cis*-**2a**) · Mg^{2+} and (*cis*-**2b**) · Mg^{2+} should be appreciably different. In the case of (*cis*-**2b**) · Mg^{2+}, the LAB consists of one medium-intensity electron transition in the visible region (for the electron-vibrational $0 \rightarrow 0$ transition, the λ_{max} = 357 nm value is found, and the corresponding oscillator strength is 0.485). In the case of (*cis*-**2a**) · Mg^{2+}, the LAB is formed by two less intense electron transitions (λ_{max} = 330 and 304 nm, and the corresponding oscillator strengths are 0.065 and 0.294, *i.e.*, the total oscillator strength for the two long-wavelength transitions is 1.35 times smaller than that for one transition in (*cis*-**2b**) · Mg^{2+}). The LAB for the (*cis*-**2a**) · Mg^{2+} complex is shifted by 27 nm to shorter wavelengths in relation to the LAB of (*cis*-**2b**) · Mg^{2+}, which approximately corresponds to the experimental data (~20 nm). The pronounced difference between the spectra can be explained by the fact that the major contribution to the LAB of (*cis*-**2b**) · Mg^{2+} is made by the charge-transfer transition between the benzene ring in the crown-ether moiety and the benzothiazolium residue, whereas in the case of (*cis*-**2a**) · Mg^{2+}, this transition becomes impossible owing to the violation of the conjugation in the chromophore. The long-wavelength absorption in (*cis*-**2a**) · Mg^{2+} is caused by a set of local excitations without charge transfer between distant parts of the molecule.

When solutions of complexes of CSD **2b** with Mg^{2+} are irradiated, together with the *trans*—*cis*-isomerization, a slower PCA reaction occurs, as has been observed for **1a,b** (see Refs. 5, 6, and 11). By using light with λ = 365 nm, one can attain complete transformation of the dye into a photocycloadduct, whose absorption spectral pattern (Fig. 4) is very close to that of the photocycloadducts obtained from the complexes of CSD **1a,b**. PCA is a reversible reaction; irradiation of the photoadduct with light at λ = 313 nm gives rise to the initial dye.

It should be noted that in highly dilute solutions of CSD **2b**, PCA cannot occur by the normal bimolecular mechanism owing to short lifetimes of the excited states of molecules of this type.[14] Moreover, in the absence of metal cations, PCA does not occur even in a saturated solution of CSD **2b**. The complex of CSD *cis*-**2b** with Mg^{2+} exists in dilute solutions in the monomeric form (anion-"capped" complex); therefore, [(*trans*-**2b**) · $Mg^{2+}]_2$, whose formation was assumed previously based on the concentration dependences of the absorption spectra, remains the only possible participant of the PCA.

The ^1H NMR spectra of photoproduct **8** obtained from [(*trans*-**2b**) · $Mg^{2+}]_2$ were analyzed by the DQF-COSY and NOESY methods.[15,16] The ^1H NMR spectrum of the photoproduct exhibits two triplets at 4.26 and 5.18 ppm, which correspond to the protons of the cyclobutane ring. The absence of olefinic protons with a typical spin-spin coupling constant $^3J_{trans}$ = 15.6 Hz is additional evidence for the formation of a cyclobutane ring. As in the case of [(*trans*-**1a,b**) · $Mg^{2+}]_2$ (see Refs. 5

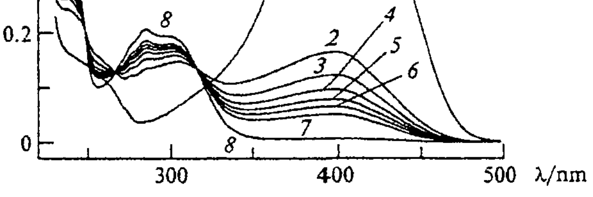
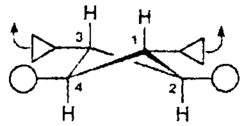


Fig. 4. Spectral changes following the photolysis of CSD *trans*-**2b** in MeCN ($C_L = 2.0 \cdot 10^{-5}$ mol L^{-1}, l = 1 cm) in the presence of $Mg(ClO_4)_2$ ($C_M = 1.2 \cdot 10^{-4}$ mol L^{-1}) by light with λ = 365 nm and with intensity $I = 2.8 \cdot 10^{15}$ cm^{-2} s^{-1}. Duration of the irradiation/min = 0 (*1*), 3 (*2*), 6 (*3*), 9 (*4*), 12 (*5*), 15 (*6*), 20 (*7*), 120 (*8*) (photocycloadduct $[\mathbf{8} \cdot Mg_2]^{4+}$).

and 6), irrespective of the initial concentration of CSD, the transformation of $[(trans\text{-}\mathbf{2b})\cdot Mg^{2+}]_2$ yields only one isomer **8**, which is responsible for an A_2B_2 type spectrum with the spin-spin coupling constant J_{AB} = 9.92 Hz.

According to the results of theoretical conformational analysis of 1,2,3,4-tetraphenylcyclobutane,[17] the magnitude of the vicinal spin-spin coupling constant in the spectrum of compound **8** (9.92 Hz) is close to this constant calculated for a conformation with equatorial substituents of the model compound (10.75 Hz); therefore, it can be concluded that cyclobutane **8** is stabilized in a conformation in which the substituents are equatorial.



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Thus, compound **8** is similar to the cycloadducts formed in the PCA involving $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$ (see Ref. 6) and exists in the conformation of a cyclobutane derivative identical to that established[17] for the product of the PCA involving a dye containing a quinoline residue substituted in position 2.

The structure of cycloadduct **8** makes it possible to conclude that complex $[(trans\text{-}\mathbf{2b})\cdot Mg^{2+}]_2$, like the previously studied $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$, is built according to the *anti*-"head-to-tail" pattern (see Scheme 5).

The quantum yield of the PCA (Φ) of *trans*-**2b** at $C_L = 2\cdot10^{-5}$ mol L^{-1} in the presence of $Mg(ClO_4)_2$ and with the excess $C_M - C_L = 1.0\cdot10^{-4}$ mol L^{-1} amounts to 0.018; within the accuracy of the measurement of Φ (~20%), it does not change upon an increase in the concentration of the dye. At the same time, in the case of the complexes of CSD *trans*-**2b** with Ca^{2+}, the Φ value at $C_L = 2\cdot10^{-5}$ mol L^{-1} is several times smaller. When C_L increases, the equilibrium of dimerization shifts toward dimeric complexes, and the quantum yield of PCA increases approaching the value found for Mg^{2+}. These results imply that the dimerization constant for complex $(trans\text{-}\mathbf{2b})\cdot Ca^{2+}$ is much smaller than that for $(trans\text{-}\mathbf{2b})\cdot Mg^{2+}$.

Prolonged irradiation of solutions of the complexes of **2a** with Mg^{2+}, Ca^{2+}, or Ba^{2+} ions with light with λ = 365 nm (and with an intensity of ~10^{16} cm^{-2} s^{-1}), unlike that for the complexes of CSD **2b**, does not lead to any changes in the absorption spectra.

Table 2 contains the quantum yields of PCA for CSD **1a,b** and **2a,b** ($C_L = 2\cdot10^{-5}$ mol L^{-1}) in the presence of $Mg(ClO_4)_2$ ($C_M = 1.2\cdot10^{-4}$ mol L^{-1}). The greatest Φ value is observed in the case of **2b**, while in the case of **2a**, the reaction does not occur. Thus, for dimeric complexes with more rigid spacers (CSD **2a,b**), the efficiency of PCA depends much more crucially on the structure of the spacer.

Table 2. Calculated energies (Q_1, Q_2) of formation of cyclobutanes from dimeric complexes, the differences between the total energies of the dimeric complexes (Q_3),[a] energies of PCA (Q_4), and the distances between the centers of the C=C bonds (R) in the *anti*-isomers of the dimeric complexes and the experimental quantum yields (Φ) of PCA for CSD **1a,b** and **2a,b** in MeCN ($C_L = 2\cdot10^{-5}$ mol L^{-1}) in the presence of $Mg(ClO_4)_2$ ($C_M = 1.2\cdot10^{-4}$ mol L^{-1})

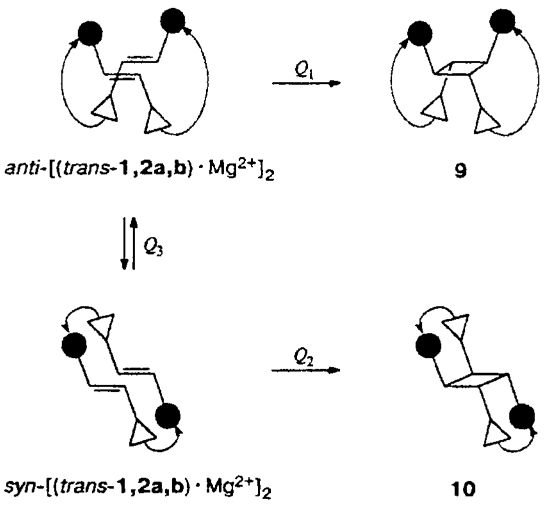
CSD	Q_1	Q_2	Q_3	Q_4	R	Φ
	kcal mol^{-1}				/Å	
1a	48.8	56.1	−2.4	51.2	8.6	0.005
1b	49.5	55.7	1.2	49.5	9.9	0.013
2a	67.6	60.6	14.1	67.6	9.9	0[b]
2b	42.6	53.3	−0.3	42.9	6.7	0.018

[a] Calculated by a molecular mechanics method.

[b] The reaction does not occur.

We carried out comparative theoretical analysis (see Experimental) of regio- and stereoselectivities of the PCA involving dimeric complexes $[(trans\text{-}\mathbf{2a,b})\cdot Mg^{2+}]_2$ and $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$. From a comparison of the calculated relative energies of formation of cyclobutanes (the difference between the total energies of cyclobutane and the dimeric complex calculated by molecular mechanics method is presented in Table 2), we found that in all cases, PCA can occur only to give cyclobutanes with structure **9** (Scheme 7). In fact, the differences between the energies of formation of cyclobutanes **9** and **10** from the most stable dimeric complex are 10.4 and 7.0 kcal mol^{-1} for irradiation of complexes *syn*-$[(trans\text{-}\mathbf{2b})\cdot Mg^{2+}]_2$ and *anti*-$[(trans\text{-}\mathbf{2a})\cdot Mg^{2+}]_2$, respectively.

Scheme 7



The energies of PCA (Q_4, see Table 2) calculated as the differences between the total energies (found by molecular mechanics method) of the most stable cyclobutane **9** and the most stable dimeric complex are 67.6 and 42.9 kcal mol^{-1} for *trans*-**2a** and *trans*-**2b**, respectively. Thus, the PCA giving cyclobutanes **9** from *anti*-[(*trans*-**2a**) · $Mg^{2+}]_2$ is energetically less favorable (ΔQ_4 = 24.7 kcal mol^{-1}) than the PCA involving *syn*-[(*trans*-**2b**) · $Mg^{2+}]_2$. In the case of dyes incorporating flexible sulfoalkyl spacers, Q_4 = 51.2 and 49.5 kcal mol^{-1} for the PCA involving *syn*-[(*trans*-**1a**) · $Mg^{2+}]_2$ and *anti*-[(*trans*-**1b**) · $Mg^{2+}]_2$, respectively. The Q_4 values for the four dyes vary in parallel with the quantum yields Φ; therefore, it can be assumed that it is these energies that act as the crucial factor determining the ease of PCA.

The mutual orientations of the C=C bonds in the *anti*-[(*trans*-**2a,b**) · $Mg^{2+}]_2$ and *anti*-[(*trans*-**1a,b**) · $Mg^{2+}]_2$ molecules are nearly identical and are favorable for the occurrence of PCA. The distances between the C=C bonds in these molecules (*R*, see Table 2) are markedly larger than the optimal distance (~4 Å). Juxtaposition of these data with the quantum yields makes it possible to conclude that the spatial structure of the dimeric complex, at least for the CSD series considered in this study, is not among the crucial factors determining the ease of PCA.

Since the PCA is a substantially endothermal reaction, according to the Bell—Evans—Polany principle, the structure of the transition state of this reaction should be closer to the structure of cyclobutane, and the factors responsible for the energy of formation of cyclobutanes should also determine the energy of the transition state and, hence, the ease of the occurrence of PCA. This statement is in line with the above-mentioned regularity (parallel variation of the energy of PCA Q_4 and the quantum yield Φ of PCA products in the series of compounds). When several bulky substituents are present, the cyclobutane ring is distorted in such a way that pseudoequatorial and pseudoaxial positions become appreciably nonequivalent, and substituents tend to occupy more favorable pseudoequatorial positions. In the case of cyclobutanes **9**, all the four bulky substituents occupy pseudoequatorial positions; this is clearly seen from the calculation of the structures of **9** (see also cyclobutane **8**). In the molecules of cyclobutanes **10**, two bulky substituents must occupy less favorable pseudoaxial positions; therefore, these structures are destabilized, in particular, due to their mutual repulsion and to the repulsion from the H atoms of the cyclobutane ring. To confirm this hypothesis, we carried out molecular mechanics calculations (MMX force field) of the relative stabilities of two stereoisomers of tetraphenylcyclobutane. We chose this particular model compound because its spatial structure is not affected by factors, other than the difference between the conformation energies of the pseudoequatorial and pseudoaxial substituents, such as relative energies of complex formation and the Coulomb energies of interaction of charged substituents, which could predetermine higher stability of one of the conformations. The energy of formation of the stereoisomer corresponding to cyclobutane **9** proved to be 6.8 kcal mol^{-1} smaller than that found for the tetraphenylcyclobutane corresponding to **10**. Note that this difference is close to the difference between the energies of cyclobutanes **9** and **10** prepared from dyes **1a,b** and **2a,b**. Thus, it can be concluded that the route of the PCA for this series of CSD is determined by the fact that the energies of formation of pseudoequatorial conformers of cyclobutane **9** from dimeric complexes are lower than the energies of formation of cyclobutanes **10** containing pseudoaxial substituents.

Thus, variation of the structure of the spacer makes it possible to change fundamentally the ratio of the two transformation pathways for multiphotochromic CSD, namely, the formation of a strong anion-"capped" complex and the PCA. These transformations studied simultaneously demonstrate new prospects for using CSD as structural units in the development of molecular photoswitchable devices.

Experimental

^1H NMR spectra were recorded on Bruker WM-500, Bruker AMX-400, and Bruker AC-200 spectrometers (500.13, 400.13, and 200.13 MHz, respectively) at 300 and 313 K. Chemical shifts were measured with an accuracy of 0.01 ppm, and spin-spin coupling constants were determined with an accuracy of 0.1 Hz.

UV spectra were recorded on a Specord M40 spectrophotometer. Solutions were irradiated using individual lines of the spectrum of a DRSh-250 mercury lamp. The intensity of the actinic light was measured using a PP-1 chamber receiver. The quantum yields of PCA were determined by the procedure described previously.[6] Solutions of the dyes and their complexes were prepared in red light. Spectral and photochemical studies were carried out at 25 °C in quartz cells (*l* = 5, 1, and 0.2 cm), whose inner surface was modified by hydrophobic groups.[6]

The calculations were carried out by the following procedure. Once the initial models of (*cis*-**2a,b**) · Mg^{2+}, dimeric complexes [(*trans*-**1a,b**) · $Mg^{2+}]_2$ and [(*trans*-**2a,b**) · $Mg^{2+}]_2$, and the corresponding cyclobutane derivatives had been constructed, their geometries were optimized by a molecular mechanics method using the MMX force field. For each of the models, 100 conformations were obtained by random distortion of the geometry. Each of the conformations was also optimized by molecular mechanics using the MMX force field. Of the 100 conformations thus obtained, one with the lowest energy was selected. In the case of (*cis*-**2a,b**) · Mg^{2+}, the selected conformation was optimized by the semiempirical PM3 quantum-chemical method.

The purity of the compounds was checked by HPLC using a Milikhrom chromatograph (a 2 × 64 mm column, Separon C18, 5 mm, detection at 230 nm). The betaines derived from heterocyclic bases and dyes were analyzed using a 85 : 15 $MeCN—H_2O$ mixture as the eluent. The compounds obtained exhibited peaks with retention volumes of 100—120 mL and 140—160 mL for betaines and dyes, respectively.

Mg, Ca, and Ba perchlorates were dried *in vacuo* at 230 °C; Et_4NClO_4 used as the supporting electrolyte was dried *in vacuo* at 40 °C. Acetonitrile used for spectroscopy was purified by a known[18] procedure.

2-Methyl-3-(4-sulfobenzyl)benzothiazolium betaine (4a). A mixture of 2-methylbenzothiazole **5** (0.6 g, 4 mmol) and sodium *p*-bromomethylbenzenesulfonate **3a** (0.55 g, 2 mmol) was fused together for 6 h at 150 °C. The product was washed successively with boiling C_6H_6 and cold MeOH and recrystallized from water. The yield of **4a** was 0.415 g (62%), m.p. 262—265 °C (decomp.). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 3.27 (s, 3 H, Me); 6.08 (s, 2 H, CH_2N); 7.27 (d, 2 H, H(2), sulfobenzyl H(6)); 7.60 (d, 2 H, H(3), sulfobenzyl H(5)); 7.81 (m, 2 H, H(5), benzothiazole H(6)); 8.18, 8.48 (2 d, 2 H, H(4), benzothiazole H(7)). Found (%): C, 53.82; H, 4.07; N, 4.06. $C_{15}H_{13}NO_3S_2 \cdot H_2O$. Calculated (%): C, 53.41; H, 4.49; N, 4.15.

2-Methyl-3-(2-sulfobenzyl)benzothiazolium betaine (4b). A mixture of 2-methylbenzothiazole **5** (0.3 g, 2 mmol) and γ-sultone **3b** (0.17 g, 1 mmol) was fused together for 4 h at 150 °C. The reaction product was refluxed with benzene and Me_2CO, and the precipitate was filtered off. The yield of **4b** was 0.25 g (78%), m.p. 300 °C (decomp.). ^{1}H NMR (200 MHz, DMSO-d_6), δ: 3.17 (s, 3 H, Me); 6.36 (s, 2 H, CH_2N); 6.66 (d, 1 H, sulfobenzyl H(6), J = 7.8 Hz); 7.39, 7.53 (2 m, 2 H, H(4), sulfobenzyl H(5)); 7.74—7.84 (m, benzothiazole 2 H); 7.93 (m, benzothiazole 1 H); 8.05 (d, sulfobenzyl 1 H, J = 7.8 Hz); 8.27 (m, benzothiazole 1 H). Found (%): C, 56.84; H, 4.12; N, 4.38. $C_{15}H_{13}NO_3S_2$. Calculated (%): C, 56.42; H, 4.11; N, 4.39.

trans*-2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecyn-16-yl)ethenyl]-3-(4-sulfobenzyl)benzothiazolium betaine (2a).** ***A. A mixture of betaine **4a** (0.64 g, 1.9 mmol) and 4′-formylbenzo-15-crown-5 ether **6** (0.65 g, 2.2 mmol) was placed into a flask equipped with a reflux condenser and with a pipe for the supply of an inert gas, 20 mL of anhydrous EtOH was added, and the system was purged with Ar. Then pyridine (7.2 mL, 89 mmol) was added dropwise, and the mixture was held for 5 h at 90 °C in a flow of Ar. Then the mixture was cooled and diluted with ether, and the precipitate was filtered off and recrystallized several times from MeOH. The yield of **2a** was 0.54 g (44%), m.p. 255—257 °C. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 3.74 (br.s, 8 H, γ,γ', δ,δ'-CH_2O); 3.92 (m, 4 H, β,β'-CH_2O); 4.30 (s, 4 H, α,α'-CH_2O); 6.35 (s, 2 H, CH_2N); 7.23 (d, 1 H, benzocrown-ether H(5), $J_{H(5),H(6)}$ = 8.4 Hz); 7.41 (d, 2 H, H(2), sulfobenzyl H(6), J = 8.2 Hz); 7.71 (d, 2 H, H(3), sulfobenzyl H(5), J = 8.2 Hz); 7.72 (m, 1 H, benzocrown-ether H(6)); 7.75 (m, 1 H, benzocrown-ether H(2)); 7.87 (m, 2 H, H(5), benzothiazole H(6)); 8.09 (d, 1 H, H_a, $^3J_{trans}$ = 15.6 Hz); 8.22 (d, 1 H, benzothiazole H(4), $J_{H(4),H(5)}$ = 8.3 Hz); 8.33 (d, 1 H, H_b, $^3J_{trans}$ = 15.6 Hz); 8.53 (d, 1 H, benzothiazole H(7), $J_{H(7),H(6)}$ = 8.0 Hz). Found (%): C, 54.98; H, 5.31; N, 2.03. $C_{30}H_{31}NO_8S_2 \cdot 3H_2O$. Calculated (%): C, 55.28; H, 5.73; N, 2.15.

B. A mixture of betaine **4a** (0.64 g, 1.9 mmol) and 4′-formylbenzo-15-crown-5 ether **6** (0.65 g, 2.2 mmol) in 5 mL of acetic anhydride was heated for 5 h at 140 °C. Then the mixture was cooled and diluted with ether, and the precipitate was filtered off and recrystallized several times from MeOH. The yield of **2a** was 0.31 g (25%), m.p. 256—257 °C.

***trans*-2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecyn-16-yl)ethenyl]-3-(2-sulfobenzyl)benzothiazolium betaine (2b).** Dye **2b** was prepared according to procedure *A* given above for compound **2a**; yield 65%, m.p. 262—263 °C. ^{1}H NMR (200 MHz, DMSO-d_6), δ: 3.64 (br.s, 8 H, γ,γ', δ,δ'-CH_2O); 3.82 (m, 4 H, β,β'-CH_2O); 4.20 (m, 4 H, α,α'-CH_2O); 6.55 (s, 2 H, CH_2N); 6.69 (d, 1 H, sulfobenzyl H(6), $J_{H(6),H(5)}$ = 7.4 Hz); 7.05 (d, 1 H, benzocrown-ether H(5), $J_{H(5),H(6)}$ = 8.4); 7.21, 7.32 (2 t, 2 H, H(5), sulfobenzyl H(4)); 7.49 (d, 1 H, benzocrown-ether H(6), $J_{H(6),H(5)}$ = 8.4 Hz); 7.74—7.84 (b, 3 H, benzocrown-ether H(2), H(5), benzothiazole H(6)); 7.94 (d, 1 H, sulfobenzyl H(3), $J_{H(3),H(4)}$ = 7.6 Hz); 8.11 (br.s, 2 H, H_a, H_b); 8.42, 8.52 (2 d, 2 H, H(4), benzothiazole H(7)). Found (%): C, 57.91; H, 5.31; N, 1.94. $C_{30}H_{31}NO_8S_2 \cdot 1.5H_2O$. Calculated (%): C, 57.68; H, 5.49; N, 2.24.

1-*cis*-3-Di[3-(2-sulfobenzyl)benzothiazolium-2-yl]-*trans*-2-*trans*-4-di(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecyn-16-yl)cyclobutane (8). A solution of compound *trans*-**2b** (6 mg, 0.01 mmol) and $Mg(ClO_4)_2$ (2.5 mg, 0.011 mmol) in 10 mL of MeCN was irradiated in a quartz cell with light with λ = 365 nm until the dye was entirely consumed (monitoring by spectrophotometry). Then the solvent was evaporated *in vacuo*, and the dry residue was dissolved in 0.5 mL of MeCN-d_3. Prior to recording of the ^{1}H NMR spectrum, about 5% (v/v) D_2O was added to the solution.* ^{1}H NMR (400 MHz, MeCN-d_3 + D_2O (5%)), δ: 3.70, 3.73 (2 m, 16 H, 2 γ,γ', δ,δ'-CH_2O); 3.84, 3.89 (2 m, 8 H, 2 β,β'-CH_2O); 4.03, 4.18 (2 m, 8 H, 2 α,α'-CH_2O); 4.26 (t, 2 H, H(2), cyclobutane H(4), $^3J_{H(2),H(1)}$ = $^3J_{H(2),H(3)}$ = $^3J_{H(4),H(1)}$ = $^3J_{H(4),H(3)}$ = 9.92 Hz); 5.18 (t, 2 H, H(1), cyclobutane H(3), $^3J_{H(1),H(2)}$ = $^3J_{H(1),H(4)}$ = $^3J_{H(3),H(2)}$ = $^3J_{H(3),H(4)}$ = 9.92 Hz); 6.09 (s, 4 H, 2 CH_2N); 6.29 (d, 2 H, sulfobenzyl 2 H(6), $^3J_{H(6),H(5)}$ = 7.7); 6.60 (d, 2 H, benzocrown-ether 2 H(5), $^3J_{H(5),H(6)}$ = 8.4 Hz); 6.89 (d, 2 H, benzocrown-ether 2 H(6), $^3J_{H(6),H(5)}$ = 8.4 Hz); 6.99 (t, 2 H, sulfobenzyl 2 H(5), $^3J_{H(5),H(6)}$ = $^3J_{H(5),H(4)}$ = 7.7 Hz); 7.17 (s, 2 H, benzocrown-ether 2 H(2)); 7.29 (t, 2 H, sulfobenzyl 2 H(4), $^3J_{H(4),H(5)}$ = $^3J_{H(4),H(3)}$ = 7.7 Hz); 7.78 (t, 2 H, benzothiazole 2 H(5)); 7.82 (m, 4 H, sulfobenzyl 2 H(3), benzothiazole 2 H(4), $^3J_{H(3),H(4)}$ = 7.7 Hz); 7.84 (m, 2 H, benzothiazole 2 H(6), $^3J_{H(6),H(7)}$ = 8.1 Hz); 8.39 (d, 2 H, benzothiazole 2 H(7), $^3J_{H(7),H(6)}$ = 8.1 Hz).

This work was carried out with financial support of the Russian Foundation for Basic Research (Projects No. 95-03-09090 and 97-03-32968), the INTAS (Grant 95-IN-RU-237), and the CRDF (Grant RC2-137).

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* Under these conditions, the crown ether moieties cannot form complexes with Mg^{2+} ions, which are strongly solvated by D_2O.

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Received June 25, 1997