Reviews

Supramolecular organic photochemistry of crown-ether-containing styryl dyes

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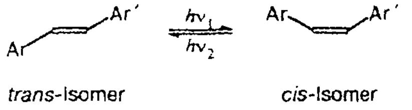
The data on the molecular design, spectral properties, photochemistry and complexation of photochromic crown ethers containing a C=C bond are described systematically and generalized. Prospects for the practical application of these compounds are considered.

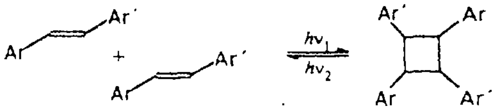
Key words: crown-ether-containing styryl dyes, *trans—cis*-photoisomerization, complexation, anion-"capped" complexes, dimeric complexes, stereospecific [2+2]-photocycloaddition.

Natural photosensitive systems participate in photosynthesis, vision, phototropism, and phototaxis phenomena. In these systems, light acts as the triggering mechanism actuating a whole series of vital processes.[1] The molecules of photosensitive systems should incorporate an "antenna" to absorb photons and a fragment capable of changing its reactivity thereafter.

Among the artificial photosensitive systems, compounds in which the role of the photoantenna is played by the N=N bond able to undergo only one type of transformation under the action of light, *viz.*, reversible *trans—cis-* and *cis—trans*-isomerization, have been studied most comprehensively. [2,3]

In the case of compounds with C=C bonds, along with photoisomerization, other reversible photochemical (photoswitchable) processes, for example, [2+2]-photocycloaddition giving cyclobutane derivatives, can also occur.[2]





Another important advantage of these compounds is that they are readily accessible.

Crown compounds, which have served as the basis for the synthetic analogs of enzymes[4,5] and some photosensitive systems,[3] can be mentioned among the most interesting and promising fragments responsive to variations of the molecular structure upon photoswitching.

Crown compounds contain several heteroatoms with unshared electron pairs, which can participate in the formation of coordination bonds with metal cations. The ability of crown compounds to form complexes depends markedly on their molecular and spatial structures.

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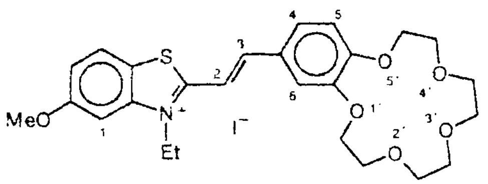
Therefore, the "photochemical behavior in the absence and in the presence of metal ions is one of the most intriguing aspects of unsaturated crown compounds".[6] However, the advantages and potential of crown-ether-containing unsaturated compounds with photoswitchable C=C bonds have not been employed so far.

We have chosen styryl dyes, which, like stilbene, contain two aromatic substituents at the C=C bond, as the objects of investigation.[7] These compounds are characterized by high quantum yields of photoisomerization, which is accompanied by substantial changes of the chromophore structure and is characterized by high extent of photoreversibility. If crown-ether and styryl-dye moieties are bound by covalent bonds in such a way that one or two heteroatoms of the macrocycle are conjugated with the chromophore, it may be expected that the additivity in the manifestation of the specific properties of these crown-containing styryl dyes (CSD) would be violated. Thus, photostructural transformations in the dye moiety would result in a change in the efficiency of binding metal cations by the crown-ether moiety, whereas the complexation, in turn, would change the spectral and photochemical characteristics of the dye moiety.

Conjugated reactions of this type, apparently, can occur in supramolecular structures resulting from the self-assembly[8,9] involving CSD molecules; this can be used for the design and synthesis of previously unknown types of photochemical and photophysical molecular devices.[10] The selective irradiation with light, which is easy to perform, could serve as the most promising way of controlling these devices.

The structure of CSD

We have synthesized a number of compounds of this new type[11] and have studied their spectral and photochemical properties for the first time. The structure of one of these compounds, *trans*-**1**, was established by X-ray diffraction analysis (Fig. 1).[12,13]



trans-**1**

The chromogen of this molecule is planar, apparently due to the strong conjugation between the benzothiazole residue, the ethylene bond, the benzene ring, and two oxygen atoms of the benzocrown-ether moiety, and is characterized by a high degree of leveling of the orders of the π-bonds in the chromophore.

The planar structure of the chromogen in *trans*-**1** results in the appearance of nonvalence interactions, which are manifested as a decrease in some interatomic distances with respect to the sums of the van der Waals radii of the corresponding atoms and as distortion of some angles. The existence of nonvalence interactions of H(2) with H(6), the S atom with H(3), H(3) with H(4), and of the H atoms in the ethyl group with H(1) and H(2) indicates that the molecule of *trans*-**1** is substantially sterically strained. All these features of the structure of the dye moiety in *trans*-**1** are apparently common to all CSD and can affect their spectral and photochemical properties.

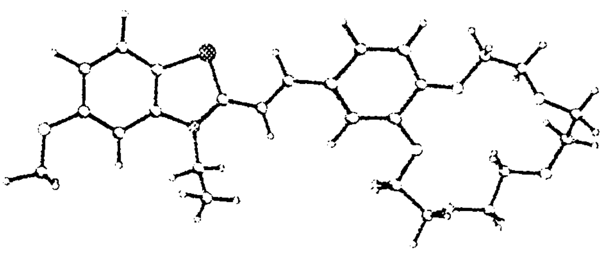


Fig. 1. Structure of *trans*-**1** projected onto the least overlap plane.

Yet another peculiar feature in the structure of *trans*-**1** that distinguishes it from, for example, benzo-15-crown-5 ether is that the unshared electron pairs of the O(2′), O(3′), and O(4′) atoms of the macrocycle are directed outward from its cavity, which implies that for a metal cation to be bound efficiently in a complex, the conformation of the ring must change. This feature may be due to the electron-withdrawing effect of the dye moiety on the O atoms linked to the benzene ring in the crown-ether fragment.

Electronic spectra and dark and photoinduced formation of complexes of CSD

Crown-containing styryl dyes possess deep and intense color in the yellow (420—460 nm) and red (520—550 nm) regions, which is associated with the fact that an O (or N) atom of the crown-ether moiety is located in the *para*-position with respect to the double bond.[11] Judging by the magnitude of the spin-spin coupling constant (^3J = 15.6—16.7 Hz) for the olefinic protons, the solution configuration of the double bond in all the CSD synthesized is *trans*. A substantial hypsochromic shift of the long-wavelength absorption band (LAB) and an increase in the Stokes shift of the fluorescence spectrum following an increase in the polarity of the solvent are common properties of CSD.

For example, when an aqueous solution of *trans*-**2** is irradiated with light with λ = 436 nm, absorption in the region of LAB decreases, whereas absorption in the short-wavelength region of the spectrum simultaneously increases until a photosteady state is attained. When the same solution is exposed to light with λ = 365 nm, the reverse change in the spectrum occurs up to the transi-

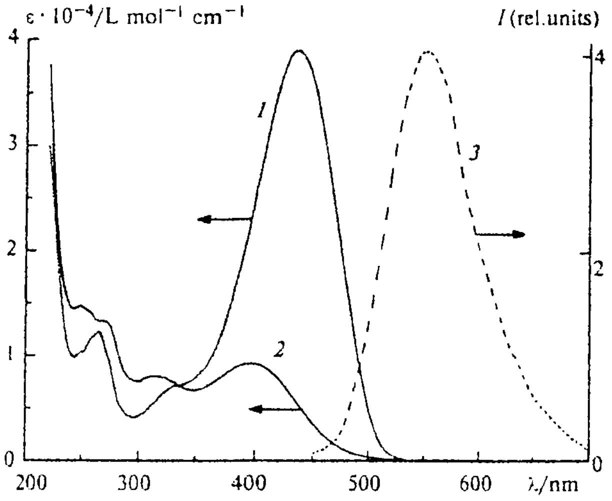
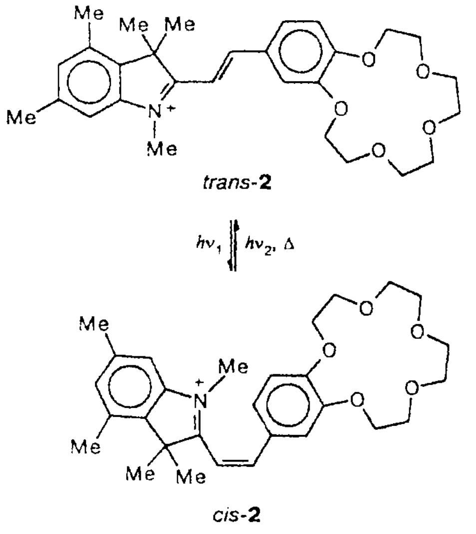


Fig. 2. Electronic absorption spectra of *trans-* (*1*) and *cis*-isomers (*2*) of CSD 2 and non-corrected fluorescence spectrum of the *trans*-isomer (*3*). Water, T = 295 K.

tion into a new photosteady state. These spectral changes are due to the occurrence of reversible photochemical *trans*—*cis*-isomerization (Fig. 2) (Scheme 1).[14]

Scheme 1



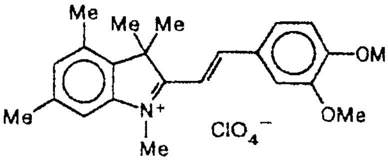
trans-**2**

cis-**2**

The quantum yields of both forward and reverse photoisomerization in polar solvents are similar for all CSD and lie in the range of 0.4—0.5 (see Ref. 7). The efficiency of the photoreaction does not depend on the presence of atmospheric oxygen in the solution.

After irradiation of CSD in solutions, the initial spectral pattern is rapidly restored in the dark owing to the thermal *cis*—*trans*-isomerization.

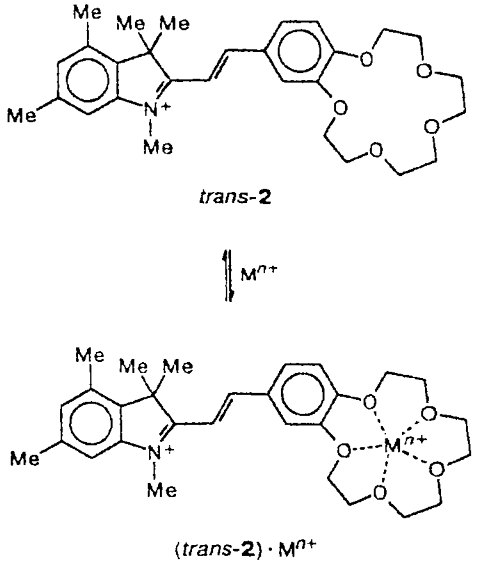
A comparative study of CSD 2 and its analog 3 shows that the macrocyclic fragment does not exert any specific effect on the spectral and photochemical properties of the dyes.[14]



trans-**3**

The difference between these compounds became obvious when the formation of complexes in MeCN was studied (Scheme 2). It was found that the addition of alkaline earth metal perchlorates to solutions of *trans*-**2** resulted in a substantial hypsochromic shift of the LAB, whereas the addition of the same metal salts to a solution of *trans*-**3** resulted in only minor spectral changes.

Scheme 2



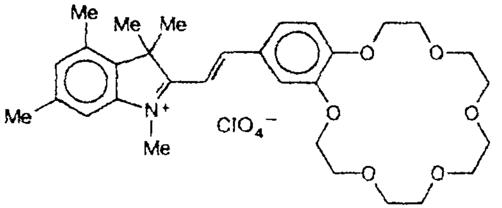
trans-**2**

(*trans*-**2**) · M^{n+}

Our calculations showed[15,16] that the LAB in the electronic spectra of CSD refer to an electron transition with a small charge transfer (~0.2 e) from the benzocrown ether (donor) on the heterocyclic moiety (acceptor). When the crown-ether fragment is bound to a metal cation, the Coulomb interaction appears, and this displacement of electron density becomes energetically unfavorable (the electron density moves away from the cation). This accounts for the experimentally observed hypsochromic shift of the LAB.

When alkaline earth metal perchlorates are added to solutions of *cis*-CSD, the LAB normally also shifts hypsochromically; however, in this case, the shifts are markedly smaller than those of the LAB of the *trans*-isomers. This is apparently due to the violation of the efficient conjugation in the nonplanar *cis*-isomer of CSD.

Taking into account the known[17] empirical rules for simpler crown ethers, it should be expected that the displacement of the LAB following the complexation of CSD would depend on the spatial matching of the sizes of the crown-ether cavity and the metal ion, the charge density on the metal cation, and the nature of the solvent. In fact, in the presence of Mg^{2+}, the LAB of *trans*-**2** in MeCN shifts by more than 40 nm (Table 1). However, the shift of the LAB of *trans*-**4** following the addition of Mg^{2+} is only 1 nm. The size of the cavity of the 15-crown-5-ether fragment in *trans*-**2**, apparently, matches best the size of Mg^{2+}, and this accounts for its efficient interaction with the electron-donating oxygen atoms of the crown ether including the oxygen atom conjugated with the chromophore. Similarly, when Eu^{3+} is added to a solution of *trans*-**4**, which incorporates an 18-crown-6-ether moiety, the LAB undergoes a substantial hypsochromic shift by 44 nm. Of alkaline earth metal cations, Sr^{2+} matches the crown-ether cavity of *trans*-**4** to the greatest degree (see Ref. 18).



trans-**4**

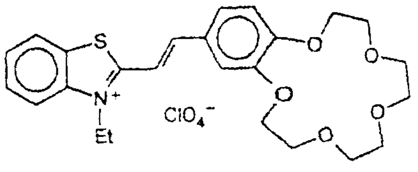
Comparison of alkali and alkaline earth metal cations indicates that the latter produce much larger shifts of the LAB. Correspondingly, in the case of trivalent cations with even higher charge densities, the shifts become even larger.

It should be noted that the shifts of the absorption bands of CSD decrease markedly on going from MeCN to MeOH. Probably, this is due to the fact that MeOH molecules compete with crown ethers for the complex formation to a greater extent than MeCN.

Table 1. Variation of the positions of the LAB maxima of *trans*-**2**,**4** ($C_L = 1 \cdot 10^{-5}$ mol L^{-1}) following the formation of complexes ($C_M = 1 \cdot 10^{-3}$ mol L^{-1}) in MeCN and MeOH

$M^{n+}X^-$	$\lambda_L - \lambda_{LM}$/nm		
	trans-**2** in MeCN	*trans*-**4** in MeCN	*trans*-**4** in MeOH
$LiClO_4$	15	1	0
$NaClO_4$	11	8	8
$KClO_4$	8	13	2
KSCN	3	11	3
$CsClO_4$	3	5	4
NH_4ClO_4	4	13	4
$Mg(ClO_4)_2$	42	1	2
$Ca(ClO_4)_2$	39	26	4
$Sr(ClO_4)_2$	33	29	23
$Ba(ClO_4)_2$	28	27	27
$Eu(ClO_4)_3$	2	44	3
$Tb(ClO_4)_3$	1	34	2

It can be assumed that in the series Mg^{2+}, Ca^{2+}, Ba^{2+}, the constants of the complex formation vary in parallel with the magnitudes of the hypsochromic shifts of the LAB in the spectra of the corresponding complexes with CSD. To verify this hypothesis, we measured the stability constants of the complexes of *trans*-**5** with these ions.[19]



trans-**5**

The simplest scheme of the complex formation (Scheme 3), where L is a dye molecule, M is a metal cation, and K_1 is the stability constant of the complex, is described by the equation

$$C_M/\alpha C_L = 1 + (K_1C_L)^{-1}\cdot(1-\alpha)^{-1}, \qquad (1)$$

where α is the degree of complexation calculated from the formula $\alpha = (D_L - D)/(D_L - D_{LM})$ (D_L, D, and D_{LM} are the optical density of the initial solution, the current optical density, and that corresponding to the complete binding of the components in the complex).

Scheme 3

$$L^+ + M^{2+} \xrightleftharpoons{K_1} (LM)^{3+}$$

Equation (1) in the $C_M/\alpha C_L$ *vs* $(1-\alpha)^{-1}$ coordinates is a straight line with a slope of $(K_1C_L)^{-1}$ and with the intercept on the ordinate axis equal to unity. Below, all the experimental data on titration by solutions of metal salts are presented in these coordinates, because each extension of Scheme 3 results in a deviation of the corresponding plot from linearity. In particular, the nonlinear character of the dependence of α on C_M in the interaction of *trans*-**5** with Mg^{2+}, Ca^{2+}, and Ba^{2+} (Fig. 3) was explained by invoking an additional process, *viz.*, the interaction of the perchlorate anion (A^-) with the triple-charged complex cation $(LM)^{3+}$ (Scheme 4) (K_i is the constant of the ion pair formation).

Scheme 4

$$(LM)^{3+} + A^- \xrightleftharpoons{K_i} (LMA)^{2+}$$

The formation of $(LM)^{3+}\ldots ClO_4^-$ ion pairs was also confirmed in the experiments on titration in the presence of tetraethylammonium perchlorate (at a constant concentration of the anions).

The solid lines in Fig. 3 show the theoretical plots, calculated taking into account this additional equilib-

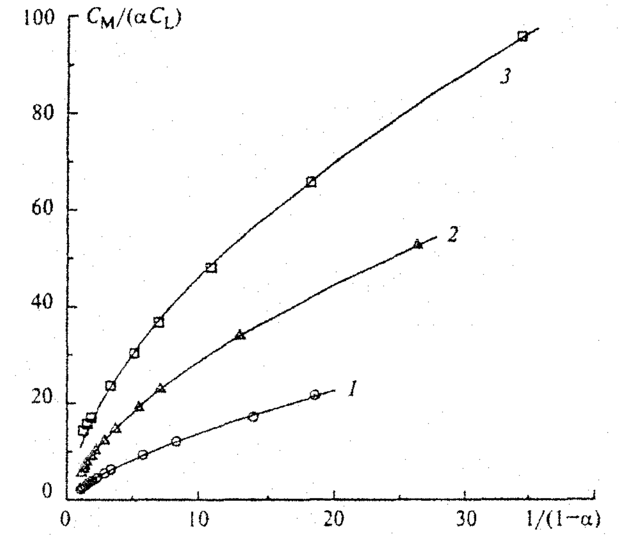


Fig. 3. Dependences of the degree of complexation α on the concentration C_M of the salt added at the coordinates of Eq. (1) for *trans*-5 and ions: Mg^{2+} ($C_L = 2.1 \cdot 10^{-5}$ mol L^{-1}) (*1*), Ca^{2+} ($C_L = 2.0 \cdot 10^{-5}$ mol L^{-1}) (*2*), Ba^{2+} ($C_L = 2.0 \cdot 10^{-5}$ mol L^{-1}) (*3*). MeCN, $T = 295$ K.

rium. The resulting K_1 and K_i constants are listed in Table 2.

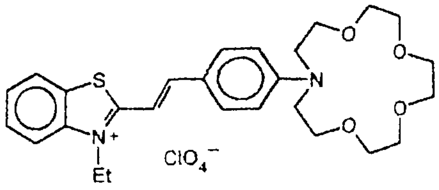
These data imply that the magnitudes of the shifts of the LAB vary in parallel with the $\log K_1$ values for the complexes of *trans*-5 with metal ions. This regularity makes it possible to estimate qualitatively the efficiency of binding of CSD by various metal cations, at least, for the dyes whose macroheterocyclic moiety contains only O atoms.

It should be noted that for *trans*-5 the stability of 1 : 1 complex of Mg^{2+} ions with L is almost three orders of magnitude lower than that in the case of benzo-15-crown-5 ether (B15C5) ($\log K_1$ 7.2, see Ref. 19). This can be due to the fact that on going from B15C5 to CSD, the electron density on those O atoms of the crown-ether moiety that are bound directly to the benzene ring markedly decreases, due to the strong electron-withdrawing effect of the positively charged heterocyclic residue.

It was of interest to study styryl dyes containing an *N*-phenylaza-15-crown-5 moiety in place of the benzo-crown moiety. Upon this replacement, the LAB of the CSD shifts bathochromically (by almost 90 nm in the case of *trans*-**6**), because the unshared electron pair of the nitrogen atom of the crown-ether fragment is involved in the conjugation with the chromophore.[20]

Table 2. Stability constants of complexes and changes in the positions of the LAB maxima of *trans*-5 in the presence of alkaline earth metal perchlorates ($C_M = 1 \cdot 10^{-2}$ mol L^{-1}) in MeCN at $T = 295$ K

Cation	$C_L \cdot 10^5$ /mol L^{-1}	$\lg K_1$	$\lg K_i$	$\lambda_L - \lambda_{LM}$ /nm
Mg^{2+}	2.1	4.5	2.8	39
Ca^{2+}	2.0	4.0	2.8	36
Ba^{2+}	2.0	3.7	2.8	28



trans-**6**

Figure 4 shows the dependence of the absorption spectrum of *trans*-**6** on the concentration of Ca^{2+} ions. The substantial ionochromic effect observed in this system, like that observed in the case of *trans*-**2**, can be attributed to the formation of complexes between the metal cation and the crown-ether moiety of the dye.

The stability constant of the complex of *trans*-**6** with Ca^{2+} ($\log K = 2.4$) measured by us within the framework of the simplest complex-formation scheme (see Scheme 3) is an effective value, because association of the triple-charged complex with the ClO_4^- ion was not taken into account in the calculations. However, it can be shown that the dependence of D on C_M under the experimental conditions is described fairly accurately by Eq. (1) with the following effective constant:

$$K \approx K_{LM}(1 + K_{LMA}C_L)/(1 + K_{MA}C_L). \tag{2}$$

In order to compare the abilities of the crown-ether-fragments of *trans*-5 and *trans*-**6** to form complexes with Ca^{2+}, one can estimate the effective constant K for *trans*-5 in a similar way using the values $\log K_{LM} = 4.0$ and $\log K_{LMA} = 2.8$ (see Table 2). The resulting value ($\log K \approx 4.8$) indicates that on going from *trans*-5 to

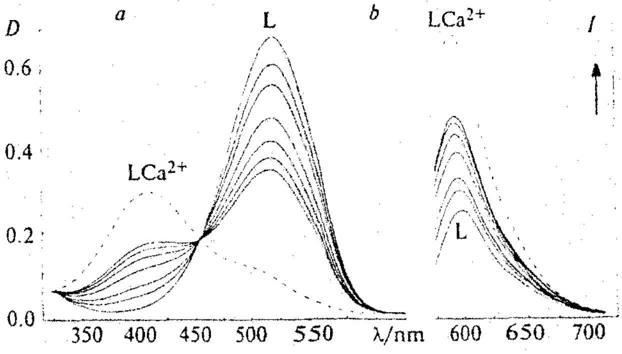


Fig. 4. Dependence of the absorption (*a*) and fluorescence (*b*) spectra of *trans*-**6** ($C_L = 1.0 \cdot 10^{-5}$ mol L^{-1}) in MeCN on the concentration of Ca^{2+} ions (C_M/C_L = 50, 100, 200, 300, 400, 500) at a constant concentration of perchlorate ions C_A = 0.01 mol L^{-1}. The dashed line shows the calculated spectra of the complex.

trans-**6**, the stability of the complexes decreases by more than two orders of magnitude. The same is true for ordinary crown ethers, benzo-15-crown-5 ($\log K_{LM}$ = 6.6, see Ref. 19) and *N*-phenylaza-15-crown-5 ($\log K_{LM}$ = 3.23, see Ref. 21). The fact that the complexes of *trans*-**6** are less stable than those of *N*-phenylaza-15-crown-5 can be explained by the strong electron-withdrawing effect of the positively charged benzothiazole residue in the dye molecule.

Exposure of solutions of *trans*-**6** to visible light results in spectral changes typical of *trans—cis*-isomerization. The *cis*-isomer thus formed is unstable and is converted into the corresponding *trans*-isomer in the dark.[22] The rate constant of the dark *cis—trans*-isomerization is more than three orders of magnitude higher than that in the case of CSD like *trans*-**5** (k_{c-t} = $2 \cdot 10^{-5}$ s^{-1}, see Ref. 23). This is due to the fact that the degree of conjugation in the chromophore fragment of *cis*-**6** is higher than that in *cis*-**5** owing to the nitrogen atom with an unshared electron pair in the *para*-position to the C=C bond.

When a solution of $Ca(ClO_4)_2$ with a concentration of 0.05 mol L^{-1} is added to a solution of compound **6** (C_L = $1.0 \cdot 10^{-5}$ mol L^{-1}), k_{c-t} decreases to $6.4 \cdot 10^{-4}$ s^{-1} (by a factor of 50). Apparently, this attests to the formation of a relatively strong coordination bond in (*cis*-**6**) · Ca^{2+} between the metal cation and the nitrogen atom of the azacrown-ether moiety, leading to a decrease in the degree to which the nitrogen atom participates in the conjugation with the chromophore.

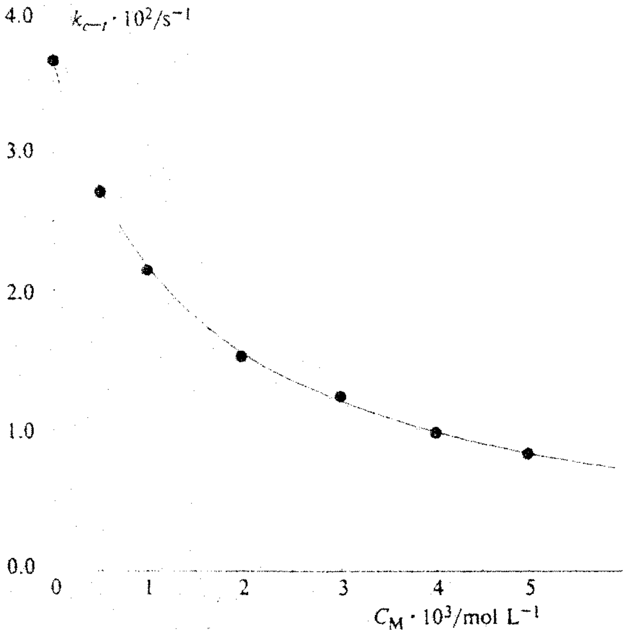


Fig. 5. Experimental (dots) and theoretical (Eq. (1)) (the curve) dependences of the rate constant for the dark *cis—trans*-isomerization in MeCN of dye **6** (C_L = $1.0 \cdot 10^{-5}$ mol L^{-1}) on the concentration of Ca^{2+} ions at a constant concentration of ClO_4^- (C_A = 0.01 mol L^{-1}).

In the case of (*cis*-**6**) · Ca^{2+}, the kinetics of the dark *cis—trans*-isomerization (Fig. 5) that was monitored using the variation of the optical density of the solution at 522 nm corresponded exactly to a first-order equation. This dependence was analyzed in terms of Scheme 3.

The data obtained for C_M = 0.05 mol L^{-1} indicate that the k_{c-t} value at the complete complexation is much lower than that for free *cis*-**6**. Therefore, for degrees of complexation varying from 0 to 0.8, the ratio of the concentration of the free *cis*-isomer to its overall concentration in the solution can be taken as being equal to the ratio of the current k_{c-t} value to k^0_{c-t} at C_M = 0. Taking into account the fact that in the experiments C_M was greater than C_L, the following approximate equation corresponding to Scheme 3 can be written:

$$k_{c-t} \approx k^0_{c-t}/(1 + KC_M). \quad (3)$$

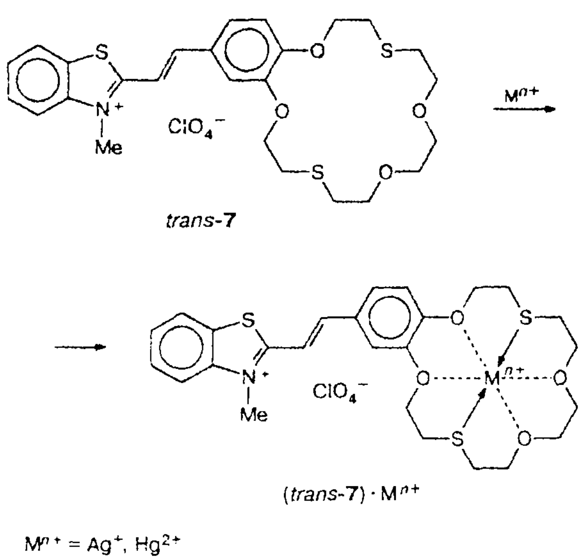
It can be seen from Fig. 5 that the experimental points fit well the theoretical curve. The stability constant $\log K$ of the complex of *cis*-**6** with Ca^{2+} obtained by approximation is 2.85.

When *trans*-**6** is converted into the *cis*-form, the stability of its complexes increases ~2.5-fold. Apparently, this relatively small difference is due to the weakening of the electron-withdrawing effect of the positively charged benzothiazole residue on the binding of metal cations, because it is known that in *cis*-alkenes the effects of substituents are less efficiently transferred through C=C bonds than in the corresponding *trans*-isomers. The violation of conjugation in *cis*-**6** owing to its non-planar structure can provide one more reason for this weakening.

Thiacrown compounds have been little studied, despite the fact that they possess substantial advantages over oxygen- and nitrogen-containing crown compounds, because they are more prone to form complexes with heavy and transition metals.[24] For example, the addition of alkali or alkaline earth metal (Na, K, Mg, Ca) nitrates to *trans*-**7** in MeOH (Scheme 5) does not result in any substantial changes in the absorption spectra, since the dithiacrown-ether moiety is virtually incapable of binding ions having low affinities for sulfur-containing ligands. On the other hand, when silver and mercury(II) nitrates or perchlorates are added as solutions of the same concentration in MeOH, the LAB of *trans*-**7** shift hypsochromically by 12 and 20 nm, as a result of the formation of (*trans*-**7**) · M^{n+} complexes (see Ref. 25).

It is noteworthy that the hypsochromic shift of the LAB of *trans*-**7** with Hg^{2+} in MeCN is not much larger than the corresponding shift in the case of a CSD containing a benzo-18-crown-6 moiety, although the constants of complexation of mercury(II) ions with dithiacrown ethers differ appreciably from those with crown ethers;[26] in particular, for the 1,10-dithia-18-crown-6 ether and Hg^{2+}, $\log K_1$ amounts to 19.5 in 0.5 *M* HNO_3.[27] As noted above, the greatest effect on

Scheme 5

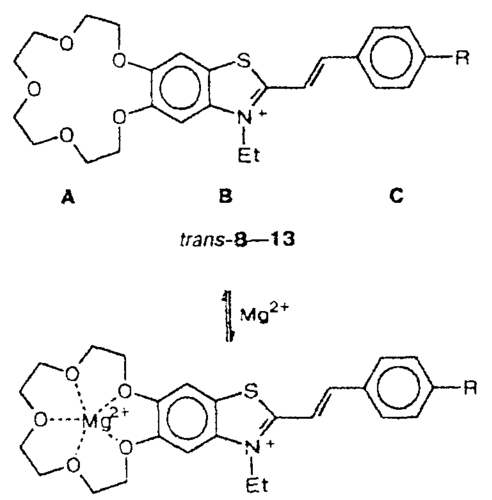


the chromophore system of CSD during complexation is exerted by the interaction of the cation with the O atom incorporated in the conjugation chain of the chromophore. Apparently, the S atoms of the dithiacrown-ether moiety of *trans*-7 form very strong bonds with Hg^{2+} and thus cause its coordination saturation, and this hampers the efficient interaction of Hg^{2+} with the O atoms conjugated with the benzene ring. This results in the complexation-induced hypsochromic shifts of the LAB being relatively small compared, for example, to those for Mg^{2+} and *trans*-5. At the same time, the bonds of Hg^{2+} with the S atoms of the dithiacrown moiety of the CSD are so strong that the shifts of the LAB are observed even in the presence of water.

The $\log K_1$ value found for *trans*-7 and Ag^+ in MeCN in terms of the simplest scheme of complex formation (3) is equal to 4.8. It was impossible to determine the stability constant of the *trans*-7 · Hg^{2+} complex by direct titration, due to its very high magnitude; therefore, titration by a solution of a competing ligand was used (see below). The resulting value of the K_1/K_c ratio for (*trans*-7) · Hg^{2+} was 0.040. Thus, the stability constant of this complex K_1 is 25 times smaller than the constant K_c of the complex of benzodithia-18-crown-6 with Hg^{2+}. This can be explained by the fact that on going to the dye, the electron density on the O atoms attached to the benzene nucleus in the crown-ether ring decreases due to the electron-withdrawing effect of the positively charged benzothiazole residue. However, the stability constant of (*trans*-5) · Mg^{2+} is almost three orders of magnitude lower than that for the corresponding complex containing benzo-15-crown-5 (see Ref. 19). These differences between the properties of the two types of CSD are due to the high strengths of the two coordination bonds between the S atoms and Hg^{2+}. Conversely, the coordination bonds of the O atoms with Hg^{2+} are relatively weak, which greatly decreases the effect of the positively charged benzothiazolium residue on the complex-forming properties of the macrocyclic moiety. Apparently, this also accounts for the fact that the hypsochromic shifts of LAB cannot be used as an adequate estimate of the efficiency of binding of metal ions by CSD of this type.

Now we consider the spectral properties and complex formation of *trans*-**8**—**13** (Scheme 6), which contain a crown-ether fragment in the heterocyclic rather than in the benzene part of the molecule.

Scheme 6



R = H (**8**), OMe (**9**), OH (**10**), SMe (**11**), NMe_2 (**12**), O^- (**13**)

The positions of the LAB of these CSD can be markedly changed by introducing various substituents in the *para*-position of the benzene ring (Fig. 6).[28] For example, in the case of the strongest electron-donating substituent R = O^- (*trans*-**13**, λ = 571 nm), the LAB is displaced by 162 nm with respect to that for dye *trans*-**8** (R = H).

The changes in the positions of the LAB maxima ($\lambda_L - \lambda_{LM}$/nm) of *trans*-**8**—**12** ($C_L = 2 \cdot 10^{-5}$ mol L^{-1}) following the addition of $Mg(ClO_4)_2$ (C_M = $1 \cdot 10^{-2}$ mol L^{-1}) in MeCN are given below.

trans-**8**	*trans*-**9**	*trans*-**10**	*trans*-**11**	*trans*-**12**
21	12	7	4	−14

When *trans*-**8**—**11** are bound in complexes with Mg^{2+}, the hypsochromic shifts of the LAB gradually decrease as the electron-donating character of the substituent R increases, while in the case of *trans*-**12**, complexation leads to a bathochromic shift. The CNDO/S-CI quantum-chemical calculations have shown that at R = H (*trans*-**8**), the long-wavelength electron transition is accompanied by a substantial transfer of the electron density from fragment **A** mostly to the central fragment **B** and, to some extent, to the fragment **C**. Thus, the formation of (*trans*-**8**) · Mg^{2+} is energetically more fa-

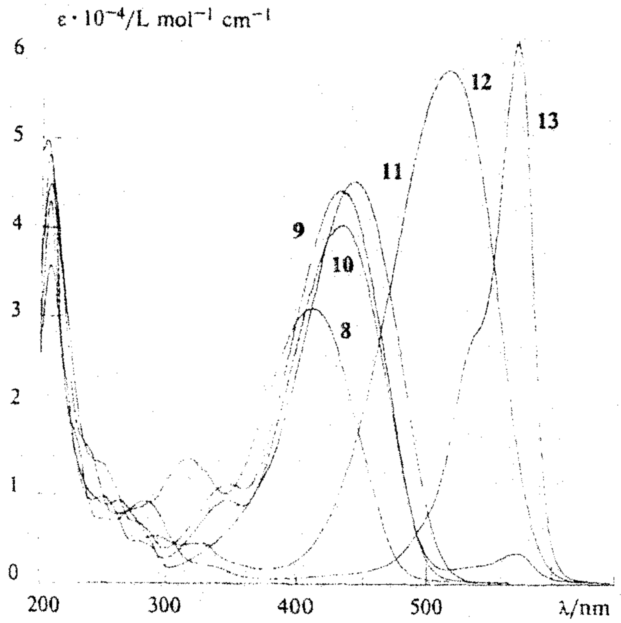


Fig. 6. Absorption spectra of complexes *trans*-**8**—**13** (the spectrum of *trans*-**13** was scaled 2.5-fold) in MeCN at C_L = $2 \cdot 10^{-5}$ mol L^{-1}, C_M = $1 \cdot 10^{-2}$ mol L^{-1} and T = 295 K. The spectrum of *trans*-**13** was obtained by adding NEt_3 to C_B = 0.1 mol L^{-1} to a solution of *trans*-**10**.

vorable in the ground state. This accounts for the experimentally observed hypsochromic shift of the LAB upon complexation. Conversely, in the case of strong electron-donating substituents such as NMe_2 (*trans*-**12**), the transition to the lowest electron-excited state results in the predominant displacement of the electron density in the opposite direction, *i.e.*, from fragment C toward the crown-ether moiety. Therefore, the energy of formation of the complex of *trans*-**12** with Mg^{2+} in the lowest electron-excited state is larger than that in the ground state, which is responsible for the experimentally observed bathochromic shift of the LAB.

The introduction of electron-donating substituents R into the *para*-position of the benzene ring (**8**—**12**) leads to an increase in the degree of conjugation between the benzene ring and the positively charged heterocyclic fragment, and this results in the increase in the rate of the dark *cis*—*trans*-isomerization. In fact, the lifetime τ of *cis*-**8** is $3.5 \cdot 10^4$ s, while in the case of *cis*-**12**, τ = 250 s. The lifetimes of (*cis*-**8**—**12**) · Mg^{2+} are even smaller than those of *cis*-**8**—**12**, which distinguishes these compounds from the CSD containing benzocrown-ether fragments.

The *trans*-isomers of CSD weakly fluoresce in MeCN and MeOH at 293 K (quantum yield of fluorescence φ_f = 0.002—0.1),[29,30] whereas *cis*-CSD exhibit no fluorescence at all. The intensity of fluorescence of *trans*-CSD markedly increases as the temperature decreases (up to φ_f = 0.6 at 173 K).[29] An increase in the electron-donating abilities of the heterocyclic residue and the crown-ether fragment of CSD results in displacement of the fluorescence bands to longer wavelengths and in an increase in φ_f. The lifetimes of the fluorescence of CSD increase from 150 ps in MeOH to 2.3 ns in glycerol.[31] We attribute the observed variations in the fluorescence lifetimes to the barrier *trans*—*cis*-isomerization occurring in the singlet electron excited state.

The addition of alkali and alkaline earth metal salts leads, as a rule, to displacement of the fluorescence maxima λ_f to shorter wavelengths and to quenching of fluorescence. The decrease in φ_f cannot be explained by the change in the quantum yield of photoisomerization φ_{tc}, because the formation of complexes of CSD is not accompanied by a substantial change in φ_{tc}. The introduction of a methoxy group into the conjugation chain of the chromophore of an organic luminophor is known to result normally in an increase in φ_f (see Ref. 32). Therefore, it could be expected that the formation of complexes with metal ions during which the unshared electron pairs of the O atoms participate in the formation of coordination bonds and are thus eliminated from conjugation with the chromophore would cause the opposite effect, *i.e.*, a decrease in φ_f; we actually observed this in our experiments.[29]

In some cases, unusual behavior of CSD was observed, *viz.*, the position of λ_f changed only slightly after the addition of metal salts.[29] The fact that the fluorescence spectra shift slightly or not at all after the complex formation, whereas the LAB is displaced substantially, as has been observed, for example, for *trans*-**14** and Na^+ (see Fig. 7), probably can be explained by a change in the character of coordination of a metal ion and its position in the macroheterocycle (Scheme 7). When dye *trans*-**14** passes to the first excited state, the electron density on the O atom incorporated in the chromophore

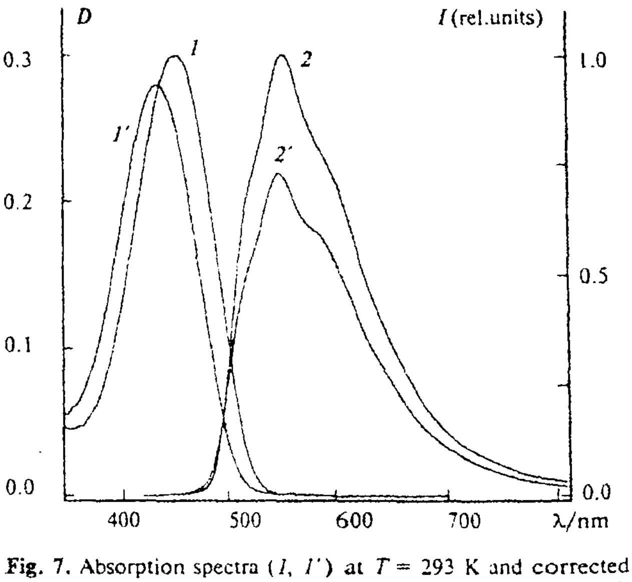
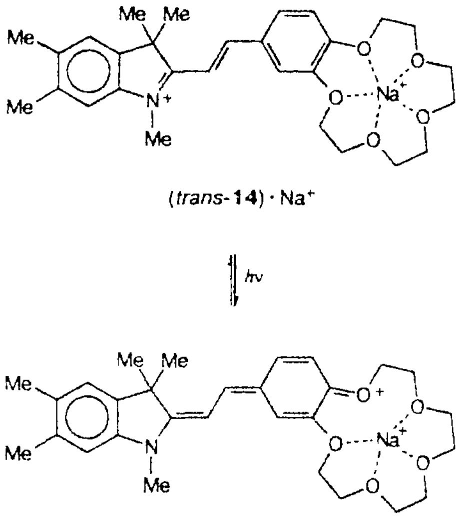


Fig. 7. Absorption spectra (*1*, *1'*) at T = 293 K and corrected fluorescence spectra (*2*, *2'*) at 173 K of *trans*-**14** in EtOH. Concentrations $NaClO_4$ = 0 (*1*, *2*) and 0.01 mol L^{-1} (*1'*, *2'*).

Scheme 7



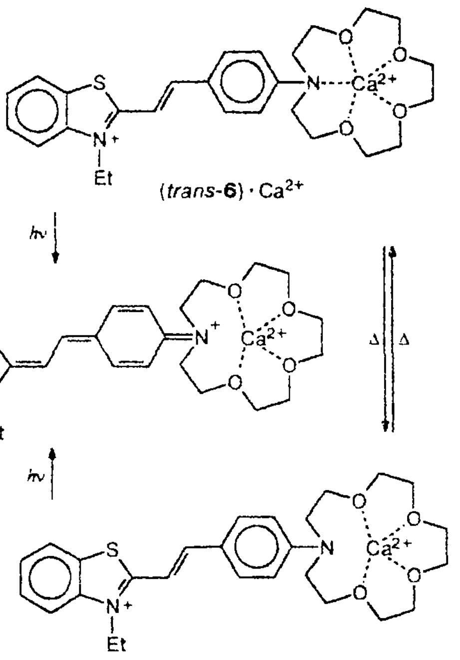
and located in the *para*-position with respect to the C=C bond decreases, and this weakens the coordination bond of metal ion with this O atom. Consequently, the equilibrium position of the metal ion in the macroheterocycle changes, and now it is predominantly bound to four of the five O atoms in the 15-crown-5 fragment. Thus, the observed phenomenon can be defined as photoinduced recoordination of the metal cation.

We observed an interesting example of recoordination in the ground and excited states for *trans*-**6** (see Ref. 20). Our analysis of the absorption spectral pattern (see Fig. 4, *a*) has shown that the long-wavelength shoulder at the band with a maximum at 410 nm cannot be attributed to the residual absorption of the free ligand. This conclusion is confirmed by the fact that the calculated spectrum virtually coincides with the experimental spectrum recorded after the addition of a large amount of $Ca(ClO_4)_2$ (C_M = 0.5 mol L^{-1}) to a solution of *trans*-**6**.

Apparently, the origin of the low-intensity band can be explained by the occurrence of a thermodynamic equilibrium between two forms of the complex. In the major form, responsible for the LAB with a maximum at 410 nm, the Ca^{2+} ion interacts efficiently with the nitrogen atom of the crown-ether moiety. In the other form, the coordination bond with the N atom is weakened, but the interaction with the O atoms is retained (Scheme 8). In the latter case, the effect of the cation on the electronic structure of the chromophore is much weaker.

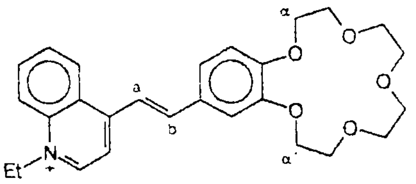
Figure 4, *b* presents the dependence of the fluorescence spectrum of *trans*-**6** on the concentration of Ca^{2+} ions. Since upon the photoexcitation of *trans*-**6**, the electron density on the N atom decreases, it can be assumed that in the excited state, the equilibrium shifts toward the complex in which the corresponding coordination bond is absent. This form of the complex, apparently, makes the major contribution to the fluorescence spectrum, and, therefore, the position of the fluorescence band of *trans*-**6** changes only slightly upon complexation.

Scheme 8



¹H NMR spectra of CSD complexes with metal ions

NMR spectroscopy provides vast information on the structures and reactivities of metal complexes.[33] We have shown that the addition of alkali and alkaline earth metal salts to solutions of CSD in MeCN-d_3 results in downfield shifts of all signals in the ¹H NMR spectra of the ligands.[34] The signals for the protons of the methylene groups, especially those located in the α- and α′-positions of the crown-ether fragment, are shifted to the greatest extent (see, for example, Fig. 8).[34,35]



trans-**15**

For the protons remote from the crown-ether fragment, the changes in the corresponding chemical shifts are smaller (see the chemical shifts for the protons of the benzene ring of the benzocrown-ether moiety), but they are still quite noticeable for H(a) and H(b). This can be

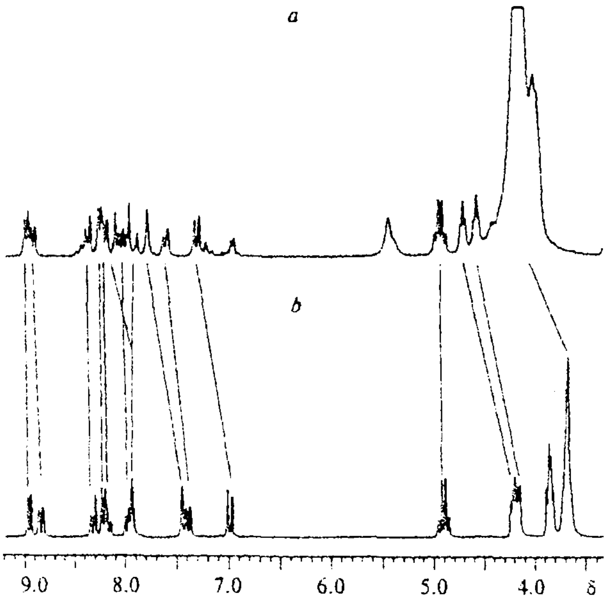
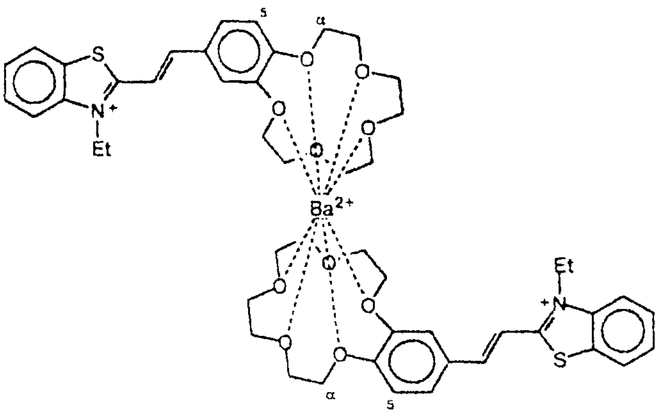


Fig. 8. ^{1}H NMR spectra of (*trans*-15) · Mg^{2+} (*a*) and *trans*-15 (*b*) in MeCN-d_3 at T = 295 K. The signals of the same protons are linked with straight lines.

due to the effective transfer of the electron-withdrawing effect of the metal cation bound in the complex along the conjugation chain of the chromophore.

The changes in the chemical shifts of the protons of CSD in MeCN-d_3 are much larger than in methanol-d_4, which may suggest that in the former solvent the complexes are more stable. In the study of the complexation of CSD, we have observed a correlation between some ^{1}H NMR and UV spectral parameters, which points to the common nature of these spectral effects. The best correlation can be followed between the displacement of LAB and the changes in the chemical shifts of the protons of the α, α′ methylene groups, which are directly bound to the conjugation chain of the chromophore. It should be noted that the ^{1}H NMR method enables the detection of more subtle changes in the structures of CSD caused by complexation.

^{1}H NMR titration proved to be especially efficient for the investigation of the stoichiometry of the formation of complexes by CSD, because it allows this process to be investigated at markedly higher concentrations of the dye ($C_L > 10^{-2}$ mol L^{-1}) than UV spectroscopy.[34] For example, analysis of the ^{1}H NMR spectra of *trans*-5 in the presence of $Ba(ClO_4)_2$ has shown that the change in the monotonic character of the dependence of Δδ on $[Ba^{2+}]/[L]$ for the signals of all the protons is observed at $[Ba^{2+}]/[L]$ values of approximately 0.5 and 1.0 (Fig. 9). Apparently, in the former case, a coordination compound is formed in which M/L = 0.5 and the Ba^{2+} ion is located between the crown-ether cavities of two *trans*-5 molecules, thus forming a sandwich-type structure.



The second point corresponds to the coordination compound of the composition BaL that has been detected previously by UV spectroscopy (see Ref. 19); this complex has a structure of a semi-sandwich or, which is less likely due to the large ionic radius of Ba^{2+}, an inclusive structure.

We have also prepared complexes of Cu^{2+} with a number of nitrogen- and sulfur-containing crown compounds, which are the main fragments of the CSD under consideration, and have studied the effects of the nature of the heteroatom and the size of the macroheterocycle on the electronic structures of the complexes by ESR and optical spectroscopy.[36] The fractions of the unpaired electron in the σ- and π-type orbitals of Cu^{2+} and of the ligands were estimated in terms of the MO LCAO method from *g*- and *A*-tensors and the optical data. The

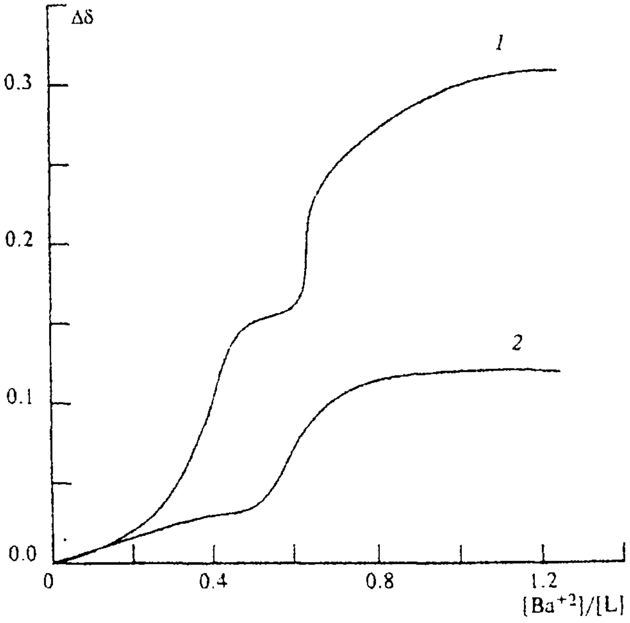


Fig. 9. Dependence of the shifts of the signals of α-CH_2 (*1*) and H(5) (*2*) in ^{1}H NMR spectrum of *trans*-5 on the ratio of the $Ba(ClO_4)_2$ and *trans*-5 concentrations in MeCN-d_3 at T = 295 K.

σ- and π-bonds in the complexes under consideration are more covalent than those in the complexes of crown ethers containing only O atoms. Thus, ESR spectroscopy can become a useful tool for the investigation of the complexes of CSD with paramagnetic metal ions.

Study of CSD and their complexes with metal ions by Raman spectroscopy

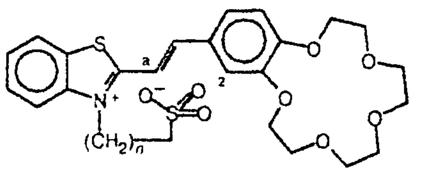
Raman spectra of CSD of the benzothiazole and indolenine series in the 300—1750 cm^{-1} range were recorded using several excitation wavelengths.[37—39] The formation of a complex between a dye molecule and the Mg^{2+} ion in MeCN results in the intramolecular transfer of the electron density. This is manifested in the Raman spectrum as a low-frequency shift of the line assigned to the Ph—O vibrations in the crown-ether fragment and high-frequency shifts of several lines associated with the Ph—N$^+$=C—C=C—Ph fragment incorporating the benzene ring and the C=C and $^+$N=C bonds. These changes in the Raman frequencies correlate with the previously observed changes in the positions of the LAB maxima depending on the structure of CSD and following the complex formation with Mg^{2+} or variation of the solvent polarity.

The results demonstrate that the Raman spectra are sensitive to the changes in the structure and in the character of the bonds in these photochromic ionophores caused by binding metal ions, and indicate that this method can provide much information when applied to studies of complex conjugated processes of photoisomerization and complexation of CSD.

Absorption spectra and complex-forming properties of *cis*-isomers of betaines of CSD; the formation of the anion-"capped" complexes

It is known that ionophores containing a crown-ether moiety and a functional group in a spatially accessible position that acts as an additional ligand in the formation of complexes (laryate crown ethers) are more efficient receptors of metal cations.[40] We suggested that the synthesis of a CSD with anionic terminal groups would make it possible to prepare photochromic crown ethers, able to "put on" their "anionic cap" in the *cis*-form and to "take it off" in the *trans*-form during photoirradiation; this, in turn, would enable one to control the binding of metal cations by virtue of light. For this purpose, we synthesized betaines of CSD *trans*-**16**—**18** (see Refs. 41—43), whose sulfo group can act under certain conditions as an additional ligand in the formation of complexes with alkaline earth metal cations.

According to ^{1}H NMR data, in a MeCN-d$_3$ solution, compounds **16**—**18** exist in the *trans*-configuration. The sulfo group in the *N*-substituent forms an intramolecular ion pair with the positively charged N atom of the heterocyclic ring. This is indicated by the substantial changes in the chemical shifts of the H(a) and H(2) protons following the addition, to a solution of *trans*-**17**,**18** in MeCN-d$_3$, of a small amount of D$_2$O, which apparently leads to dissociation of the ion pair. At the same time, the chemical shifts of protons of *trans*-**5** remain virtually unchanged under the same conditions.[35]



trans-**16**—**18**

n = 1 (**16**), 2 (**17**), 3 (**18**)

From the absorption spectra shown in Fig. 10, it can be seen that in MeCN the LAB maxima of free *trans*-**17** and *cis*-**17** are spaced only 15 nm apart. However, the hypsochromic shift of the LAB of the (*cis*-**17**) · Mg^{2+} complex with respect to that of (*trans*-**17**) · Mg^{2+} reaches[41,42] 70 nm. The same situation is observed in the case of complexes with Ca^{2+} and Ba^{2+} ions. The LAB maxima of *cis*-**17** and its complexes with Ba^{2+}, Ca^{2+}, and Mg^{2+} ions occur at 421, 338, 325, and 321 nm, respectively.

The stability constants for (*cis*-**17**,**18**) · Mg^{2+} are so great that they are beyond the range of sensitivity of

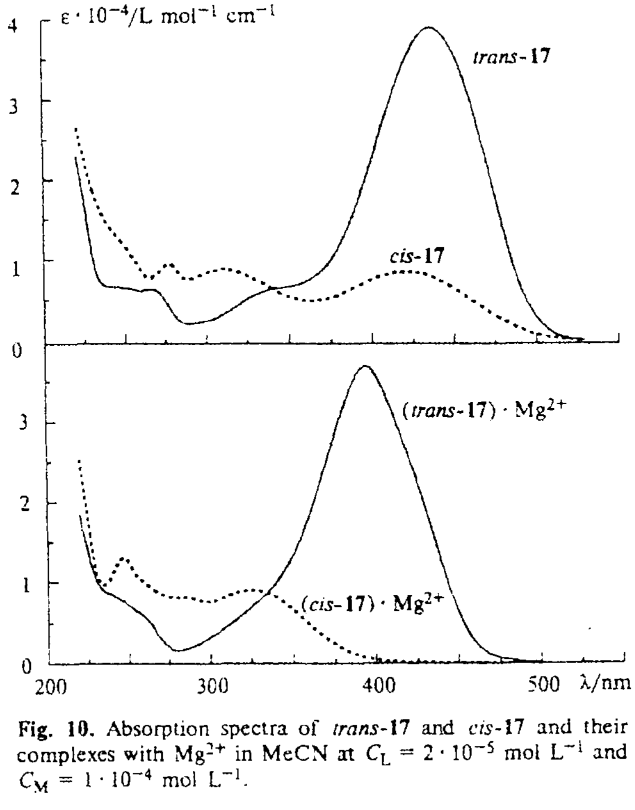


Fig. 10. Absorption spectra of *trans*-**17** and *cis*-**17** and their complexes with Mg^{2+} in MeCN at C_L = 2 · 10^{-5} mol L^{-1} and C_M = 1 · 10^{-4} mol L^{-1}.

direct titration by a solution of $Mg(ClO_4)_2$; therefore, to measure these constants, titration by a solution of a competing ligand was used. In addition to the reaction shown in Scheme 3, this system includes an equilibrium with the competing ligand (L^1) (Scheme 9).

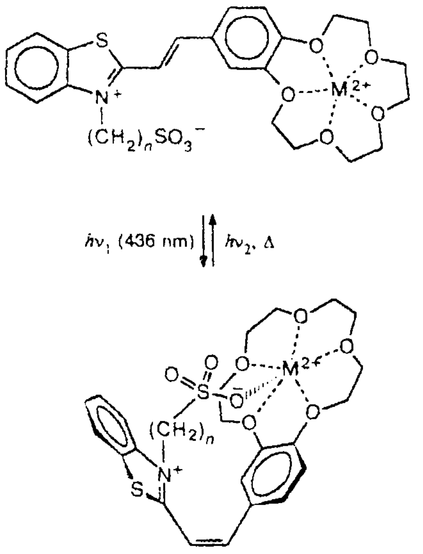
Scheme 9

$$L^1 + M^{2+} \xrightleftharpoons{K_c} (L^1M)^{2+}$$

For this purpose, we used B15C5; the stability constant of its complex with Mg^{2+} was measured preliminarily using direct titration by a solution of a metal salt.

The experimental plots for the degree of complexation of *cis*-**17** and *cis*-**18** against the concentration of B15C5 added were in good agreement with the theoretical curves calculated in terms of the accepted scheme. The $\log K_c$ values found in this way for complexes (*cis*-**17**) · Mg^{2+} and (*cis*-**18**) · Mg^{2+} were 9.4 and 10.3, respectively. The effects observed were attributed to the formation of an intramolecular coordination bond (IntraCB) between the sulfo group and the cation located in the crown-ether cavity in (*cis*-**17,18**) · Mg^{2+} (Scheme 10).

Scheme 10

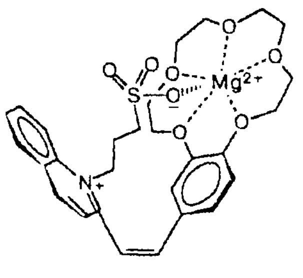


Anion-"capped"
(*cis*-**17,18**) · M^{2+}

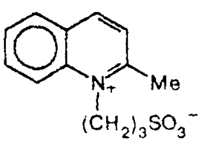
The increase in the stability of complexes with an IntraCB on going from (*cis*-**17**) · Mg^{2+} to (*cis*-**18**) · Mg^{2+} is due to the fact that the steric strain in the chelate macrocycle decreases as its size increases.[43] Owing to the relatively short length of the *N*-ω-sulfoalkyl substituent (spacer), the coordination bond can be formed only when some parts of the chromophore are substantially twisted around the single C—C bonds (ethylene fragment—heterocyclic residue and ethylene fragment—benzocrown-ether residue) and, hence, when the conjugation in the chromophore is largely violated. Apparently, it is the stabilization of the twisted conformation in *cis*-**17,18** that accounts for the spectral changes observed after the formation of the anion-"capped" (*cis*-**17,18**) · Mg^{2+}.

We studied the nature of these changes using molecular mechanics by computer simulation of the complexes of *cis*-CSD with metal cations and using quantum-chemical calculations of the absorption spectra of (*cis*-**17,18**) · Mg^{2+}. We found that the hypsochromic shifts of the LAB of these complexes are not actually the same, but they are due to the dramatic decrease in the intensity of the charge-transfer band caused by the break of conjugation in the chromophore.[44]

In order to estimate experimentally the extent to which the conjugation in the chromophore is violated after the formation of the anion-"capped" complexes by *cis*-isomers of CSD, we compared their spectra with those obtained by the addition of the absorption spectra of the betaines derived from heterocyclic bases to the spectrum of the complex of B15C5 with Mg^{2+}. In all cases, the resulting theoretical spectra reproduced qualitatively the absorption spectra of the anion-"capped" complexes of CSD (see, for example, Fig. 11). However, the integral intensities of the bands in the experimental spectra were much higher; probably, this was due to the fact that the long-wavelength charge-transfer bands of the anion-"capped" complexes of CSD do not disappear completely, which indicates that in the twisted conformations of the anion-"capped" complexes of CSD with Mg^{2+}, some residual conjugation is retained (see Ref. 45).



(*cis*-**19**) · Mg^{2+}



20

When the concentration of $Mg(ClO_4)_2$ in the solution of the anion-"capped" (*cis*-**17**) · Mg^{2+} (C_L = $2 \cdot 10^{-5}$ mol L^{-1}) increases to $C_M > 1 \cdot 10^{-2}$ mol L^{-1}, an abrupt increase in the absorption in the long-wavelength region of the spectrum begins, and at C_M = 0.5 mol L^{-1} the spectral pattern becomes absolutely different. These spectral changes have been attributed to the destruction of the IntraCB caused by the interaction of the sulfo group with excess Mg^{2+} ions. When the IntraCB are cleaved, a nearly planar conformation of the chromophore

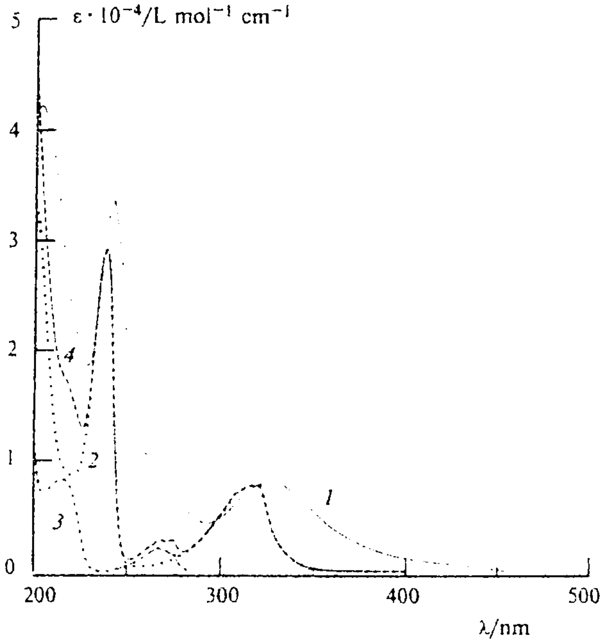
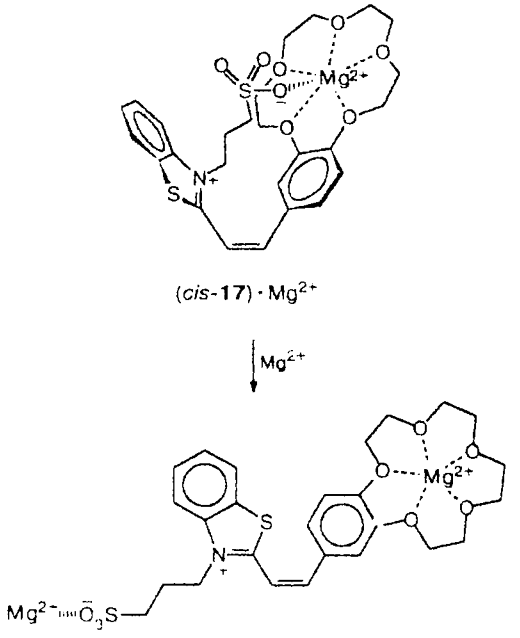


Fig. 11. Absorption spectra in MeCN: complex of *cis*-**19** with Mg^{2+}, C_L = 2.07 · 10^{-5} mol L^{-1} and C_M = 1 · 10^{-4} mol L^{-1} (*1*); betaine **20**, C_0 = 2.01 · 10^{-5} mol L^{-1} (*2*); complex B15C5 with Mg^{2+}, C_0 = 10^{-5} mol L^{-1} and C_M = 10^{-2} mol L^{-1} (*3*); the theoretical spectrum of (*cis*-**19**) · Mg^{2+} obtained by addition of the absorption spectra of betaine **20** and the complex of B15C5 with Mg^{2+} (*4*).

is restored and, hence, the conjugation in the chromophore is also restored[41] (Scheme 11).

Scheme 11



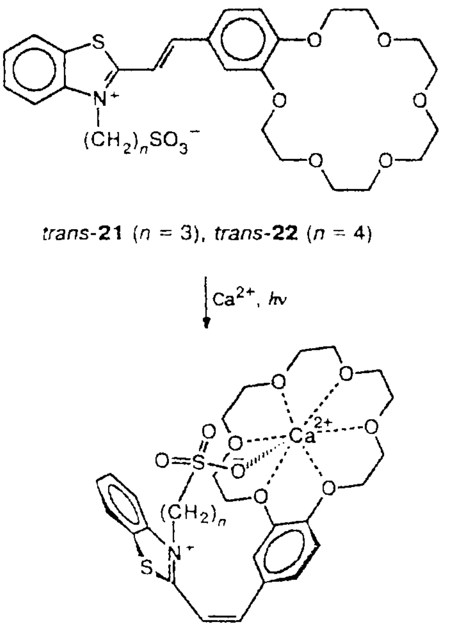
Conversely, the absorption spectra of (*cis*-**5**) · Mg^{2+} and (*cis*-**16**) · Mg^{2+} virtually do not depend on the excessive concentration of $Mg(ClO_4)_2$ and are similar to the corresponding spectrum of (*cis*-**17**) · Mg^{2+}, obtained at C_M = 0.5 mol L^{-1}. This is due to the fact that although the structures of the chromophores in *cis*-**5** and *cis*-**16** are identical to that in *cis*-**17**, the formation of IntraCB in the complexes of these compounds with Mg^{2+} is impossible, because *cis*-**5** contains no sulfogroup and *cis*-**16** incorporates too short a spacer.

The spectral parameters of the complexes of *cis*-**18** generally coincide with those described above for the complexes of *cis*-**17**. Therefore, it was concluded that, first, an IntraCB can also be formed in the complexes of *cis*-**18**, and, second, the length of the *N*-4-sulfobutyl spacer is still insufficient for the IntraCB to be formed without substantial twisting of the chromophore fragments.

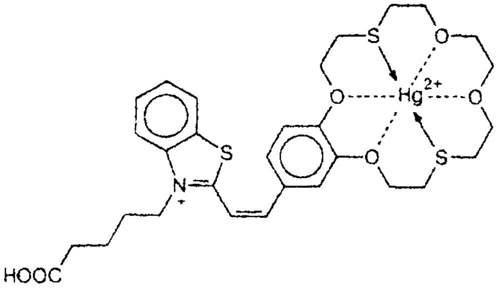
The synthesis of the anion-"capped" complexes of *cis*-CSD is an ion-selective reaction. In fact, the addition of $Mg(ClO_4)_2$ to solutions of *cis*-**21**,**22**, unlike its addition to *cis*-**17**,**18**, does not lead to any considerable changes in the absorption spectra, because the crown-ether moiety of *cis*-**21**,**22** is virtually unable to bind a Mg^{2+} ion, whose diameter is much smaller than the cavity of 18-crown-6.

Conversely, in the case of complexes of *cis*-**21**,**22** with Ca^{2+}, the equilibrium in dilute solutions is completely shifted toward the anion-"capped" complexes, in which the formation of IntraCB results in twisting of the fragments of CSD accompanied by disturbance of the conjugation in the chromophore (Scheme 12). In this case, too, due to the presence of IntraCB, (*cis*-**21**,**22**) · Ca^{2+} is much more stable than (*trans*-**21**,**22**) · Ca^{2+} (see Ref. 46).

Scheme 12



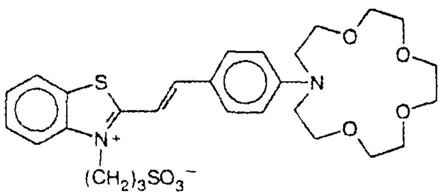
Crown-ether containing styryl dye *cis*-**23** contains a dithiacrown-ether moiety capable of forming selectively complexes with Hg^{2+} and an *N*-4-carboxybutyl substituent as a spacer. Study of the spectral properties of complex (*cis*-**23**) · Hg^{2+} makes it possible to conclude that the conjugation in the chromophore of this complex is not disturbed and the structure of the chromophore is nearly planar.[25] Apparently, in MeCN, the carboxyl group of *cis*-**23** cannot dissociate and thus cannot form an anion-"capped" complex.



(*cis*-**23**) · Hg^{2+}

The anion-"capped" complexes considered above were obtained by exposure of solutions of the complexes of *trans*-CSD with metal cations to light with λ = 436 nm.[41,43]

Synthesis and study of CSD capable of molecular photoswitching in the red region of the spectrum is of principal importance. The introduction of a donor nitrogen atom having a lone electron pair into the *para*-position with respect to the C=C bond in the chromophore of CSD makes it possible to accomplish a photochromic transition in this region. Using the photochromic dye *trans*-**24** as an example, we studied the effect of the N atom in the crown-ether moiety and the nature of metal cation on the photoisomerization and the formation of anion-"capped" complexes.[22]



trans-**24**

When C_M/C_L = 1.5 (M = Ca^{2+}) and the content of *cis*-**24** is no more than 20% of the overall concentration of the dye, the plot for the variation of the optical density of the solution in the dark is monoexponential. The rate constant for the *cis—trans*-isomerization is equal to $9.0 \cdot 10^{-4}$ s^{-1}. By substituting this value in formula (3), one can estimate the lower limit for the stability constants of complexes of *cis*-**24** with Ca^{2+} as $\log K > 6.3$, *i.e.*, on going from *cis*-**6** to *cis*-**24**, the stability of the complexes increases by more than three orders of magnitude. This effect can probably be explained by the formation of IntraCB in the complexes of *cis*-**24** between the Ca^{2+} ion located in the crown-ether cavity and the sulfo group of the spacer.

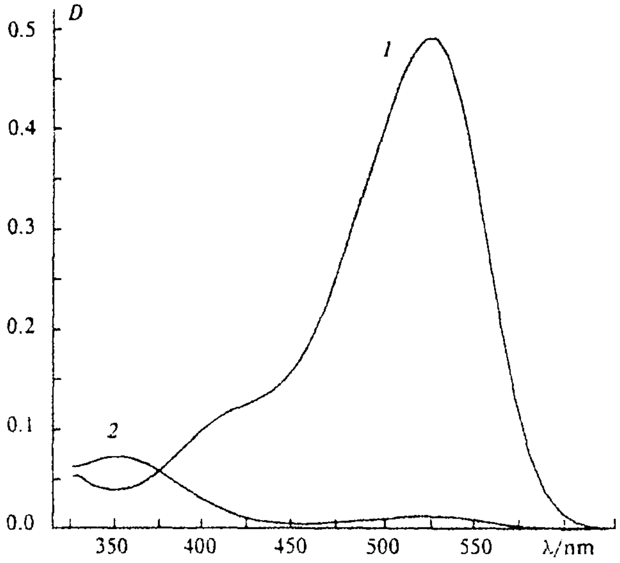


Fig. 12. Absorption spectra of dye **24** in MeCN (C_L = $1.0 \cdot 10^{-5}$ mol L^{-1}) in the presence of $Ca(ClO_4)_2$ at C_M/C_L = 100; *trans*-isomer (*1*), *trans—cis*-photosteady state formed upon irradiation with light with λ = 546 nm and an intensity of ~$1 \cdot 10^{16}$ cm^{-2} s^{-1} (*2*).

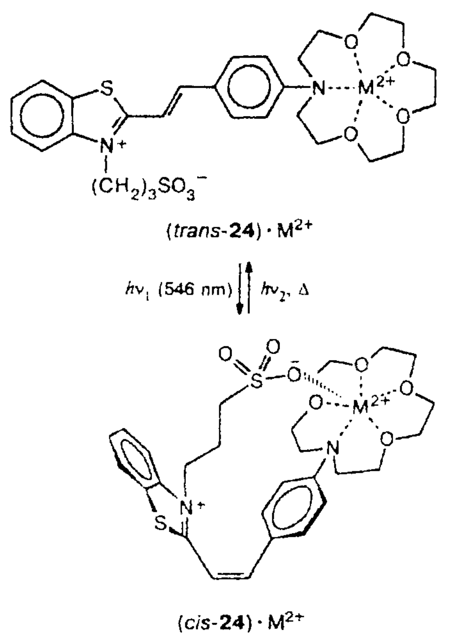
When a solution of **24** containing Ca^{2+} is irradiated with light with λ = 546 nm under the conditions in which the equilibrium involving the *trans*-isomer is shifted toward the monomeric complexes (at $C_L = 1 \cdot 10^{-5}$ mol L^{-1} and $C_M = 1 \cdot 10^{-3}$ mol L^{-1}), a *trans—cis*-photosteady state is established; it can be seen from Fig. 12 that it is markedly shifted toward the *cis*-isomer (>97%).

The spectrum of (*cis*-**24**) · Ca^{2+} exhibits a medium-intensity band with a maximum at 350—360 nm; the residual absorption in the long-wavelength region of the spectrum is extremely weak. The great hypsochromic shift, equal to 170 nm, observed on going from (*cis*-**24**) · Ca^{2+} to (*trans*-**24**) · Ca^{2+} (Scheme 13), as in the case of dyes **17** and **18**, may be due to the formation of an anion-"capped" complex in which the dye molecule acquires a twisted conformation with substantial disturbance of the conjugation in the chromophore.[22]

Alkaline earth metal cations have a considerable inhibitory effect on the *cis—trans*-isomerization of **24**, which indicates that these cations react with the azacrown-ether fragment of *cis*-**24** and that anion-"capped" complexes are formed. The maximum effect is observed in the case of Ca^{2+} ions, which are known[47] to form the most stable complexes with aza-15-crown-5 ethers in the series of alkaline earth metal cations.

When the concentrations of the complexes of *cis*-**17**,**18** with Mg^{2+}, Ca^{2+}, and Ba^{2+} in MeCN are increased to $C_L > 10^{-2}$ mol L^{-1} and in the presence of a

Scheme 13



M = Ca, Ba, Mg

slight excess of $M(ClO_4)_2$, the absorption spectrum undergoes changes similar to those observed after the addition of a large excess of the salt. This effect was attributed to the cleavage of IntraCB accompanied by restoration of the nearly planar conformation of the chromophore. It was suggested that this cleavage occurs owing to the formation of dimeric complexes $[(cis\text{-}\mathbf{17,18}) \cdot M^{2+}]_2$ containing two intermolecular coordination bonds (InterCB) (see Refs. 23 and 48).

When the concentrated solution of $[(cis\text{-}\mathbf{17,18}) \cdot M^{2+}]_2$ is diluted to $C_L \approx 10^{-5}$ mol L^{-1}, the absorption spectrum typical of anion-"capped" complexes containing IntraCB is restored (see Fig. 13).

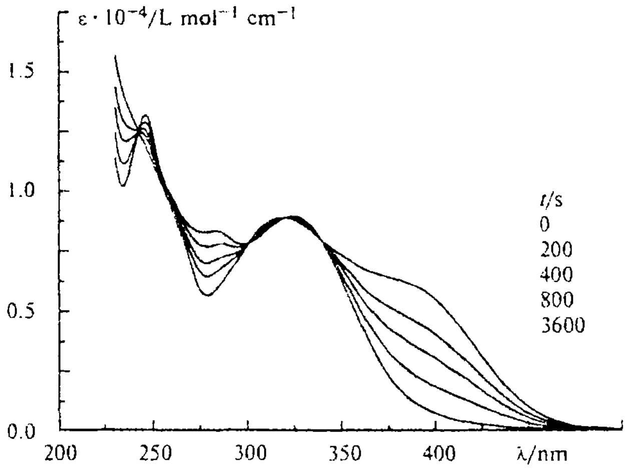
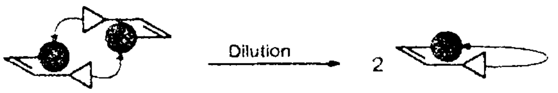


Fig. 13. Time variation of the absorption spectrum of $[(cis\text{-}\mathbf{17}) \cdot Mg^{2+}]_2$ after dilution of a solution with $C_L = 2.2 \cdot 10^{-3}$ mol L^{-1} to $C_L = 5.9 \cdot 10^{-5}$ mol L^{-1} with excess $Mg(ClO_4)_2$ ($C_M = 1 \cdot 10^{-4}$ mol L^{-1}) in MeCN at $T = 295$ K.

The time dependence of the optical density at any wavelength is described adequately by the first-order kinetics with a rate constant of $k_d = 1.8 \cdot 10^{-3}$ s^{-1}, which does not depend on the concentration of the solution in the $10^{-5} < C_L < 10^{-4}$ mol L^{-1} range. The k_d value for $[(cis\text{-}\mathbf{18}) \cdot Mg^{2+}]_2$ under similar experimental conditions is virtually identical to that given above for $[(cis\text{-}\mathbf{17}) \cdot Mg^{2+}]_2$.

When $Mg(ClO_4)_2$ is added to a dilute solution of *cis*-**17**,**18**, the absorption spectrum assumes instantaneously the shape typical of the monomeric anion-"capped" complex with an IntraCB. Therefore, the formation of an IntraCB is not the rate-determining step in the dark reaction observed after the dilution of a concentrated solution of $[(cis\text{-}\mathbf{17,18}) \cdot Mg^{2+}]_2$. It was thus concluded that the dark reaction is limited by the rate of transition of the dimeric complexes to monomeric (*i.e.*, dissociation of dimers) (Scheme 14) and that the measured k_d values are rate constants for the dissociation of $[(cis\text{-}\mathbf{17,18}) \cdot Mg^{2+}]_2$.

Scheme 14



● — the fragment of the benzocrown-ether with M^{n+};

▷ — heterocyclic residue;

⌒ — spacer

In the case of dimeric complexes of *cis*-**17**,**18** with Ca^{2+} and Ba^{2+} ions, the k_d values proved to be much larger than those for Mg^{2+}. The time that passed from the dilution of the solutions to the beginning of recording the spectrum (5—10 s) exceeded the lifetimes of these dimeric complexes.

Formation of complexes by *trans*-isomers of CSD betaines and their self-assembly in the dimeric complexes

Our X-ray diffraction study of *trans*-**1** has shown that in the single crystal the molecules of the dye are arranged in "head-to-tail" pairs, so that the double bonds are located one above the other (Fig. 14).[12,13] It could be suggested that in the case of solutions of the *trans*-isomers of CSD betaines, dimerization may be facilitated by the formation of InterCB between the sulfo group of one dye molecule and the metal cation located in the crown-ether cavity of the other dye molecule.

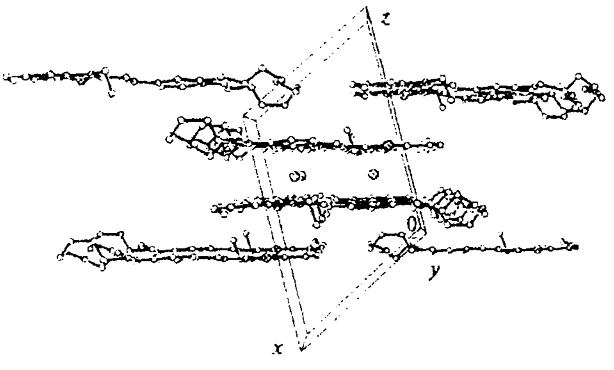


Fig. 14. The mode of packing (without hydrogen atoms) of *trans*-**1** and iodide anions in a single crystal projected onto a ($x0z$) plane.

After short-term irradiation of dilute solutions of (*trans*-**17**,**18**) · Mg^{2+}, slow changes in their absorption spectra occur in the dark (Fig. 15) (see Refs. 23 and 48). The time dependence of the optical density at any wavelength is described adequately by first-order kinetics with a rate constant equal to $1.5 \cdot 10^{-3}$ s^{-1}, which is independent of the degree of *trans*—*cis*-photoisomerization. This rate constant is very close to the k_d value measured for [(*cis*-**17**) · Mg^{2+}]$_2$.

It was thus concluded that (*trans*-**17**,**18**) · Mg^{2+} complexes apparently form dimers even in dilute solutions owing to two InterCB similar to those arising in the dimeric complexes of the *cis*-isomers; these InterCB are retained during *trans*—*cis*-photoisomerization. The dimeric complexes that are formed in this reaction and incorporate the molecules of the *cis*-isomer slowly dissociate, because in the case of the *cis*-isomer the equilibrium in a dilute solution is completely shifted toward monomeric anion-"capped" complexes. It is this process that accounts for the dark changes in the absorption spectra after the irradiation of solutions of [(*trans*-**17**,**18**) · Mg^{2+}]$_2$ (Scheme 15).

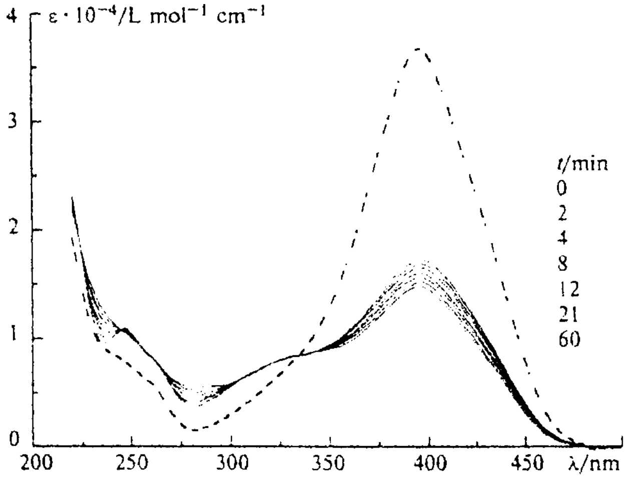
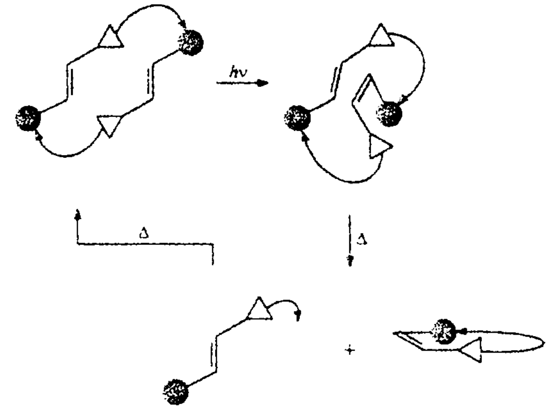


Fig. 15. Dark variations of the absorption spectrum after irradiation of the solution of [(*trans*-**17**) · Mg^{2+}]$_2$ (C_L = $2 \cdot 10^{-5}$ mol L^{-1}, C_M = $1.2 \cdot 10^{-4}$ mol L^{-1}) in MeCN with light with λ = 436 nm for 5 s (I = $6 \cdot 10^{15}$ cm^{-2} s^{-1}) at T = 295 K. The spectrum of the initial solution is shown with the dashed line.

Scheme 15



According to the above assumption, the amplitude of the dark changes in the optical density at a particular wavelength should be determined by the degree of dimerization of the complexes of *trans*-CSD with metal ions in the initial solution (before irradiation). Experimental dependences of this amplitude on the initial concentration of (*trans*-**17**,**18**) · Mg^{2+} made it possible to estimate the equilibrium dimerization constants ($\log K_d$) as 5.5 and 7.0, respectively.[19] Evidently, the substantial increase in the stability of dimeric complexes on going from [(*trans*-**17**) · Mg^{2+}]$_2$ to [(*trans*-**18**) · Mg^{2+}]$_2$ can be explained by the decrease in the steric strain following an increase in the size of the pseudomacro ring consisting of two *trans*-**17**,**18** molecules and two Mg^{2+} ions.

In a study of surface-enhanced Raman scattering of *trans*-**17**,**18** and their complexes with Mg^{2+} in the 10^{-4} to 10^{-8} mol L^{-1} range of concentrations, it was shown that the dimers can also be formed on the surface of silver upon adsorption on an electrochemical electrode.[49] It was found that in the case of *trans*-**17**, at C_L = 10^{-5} mol L^{-1} in MeCN and at C_M/C_L = 3—9, the (*trans*-**17**) · Mg^{2+} complexes are joined into the [(*trans*-**17**) · Mg^{2+}]$_2$ dimers in the "head-to-tail" manner. A considerable excess of Mg^{2+} ($C_M/C_L > 100$) results in the dissociation of the dimeric complexes to give (*trans*-**17**) · $2Mg^{2+}$.

It was found that the dimerization process (Scheme 16) should be taken into account, in addition to the equilibrium shown in Scheme 3, in the determination of the stability constants K_1 for (*trans*-**17**,**18**) · Mg^{2+}.

The reaction with ClO_4^- was not considered in the calculations; it can be neglected due to the very high stability of (*trans*-**17**,**18**) · Mg^{2+}.

The experimental complex formation plots obtained for (*trans*-**16**) · Mg^{2+} and the stability constants calcu-

Scheme 16

$$(LM)^{2+} + (LM)^{2+} \xrightleftharpoons{K_d} (LM)_2^{4+}$$

lated from them were virtually identical to those obtained for (*trans*-**5**) · Mg^{2+}.

Analysis of experimental dependences of α on C_M for the reactions of *trans*-**17**,**18** with Ca^{2+} and Ba^{2+} ions showed that the scheme of the processes must also include the formation of sandwich-like complexes of L with M^{2+} of the composition 2 : 1 (Scheme 17).

Scheme 17

$$(LM)^{2+} + L \xrightleftharpoons{K_2} (L_2M)^{2+}$$

The fact that the consumption of *trans*-**17**,**18** at relatively small α is much larger than that of the $Ba(ClO_4)_2$ added can serve as reliable proof of the formation of (*trans*-**17**,**18**)$_2$ · Ba^{2+}. It has been suggested that in this case, the dimerization of complexes may be neglected in the calculation of the stability constants. Therefore, the K_1 and K_2 constants (Table 3) were calculated taking into account only the equilibrium processes shown in Schemes 3 and 17.

To study the formation of complexes of *trans*-**17**,**18** with Mg^{2+}, titration of solutions of complexes with a solution of a competing ligand (B15C5) was used, as in the case of anion-"capped" complexes (*cis*-**17**,**18**) · Mg^{2+}. The reaction scheme for this system includes the equilibrium shown in Scheme 9 in addition to the processes presented in Schemes 3 and 16.

To illustrate this, the experimental dependence of α on the concentration C_c of the competing reagent added for (*trans*-**17**) · Mg^{2+} is given in Fig. 16 by dots. Approximation of this dependence to the theoretical curve was carried out using the K_d constant found by the photochemical method. This best approximation is shown by the solid line.

Table 3. Stability constants of the complexes of *trans*-**16**—**18** and B15C5 with alkaline earth metal cations in MeCN at T = 295 K

CSD	M^{2+}	$C_L \cdot 10^{-5}$ /mol L^{-1}	lgK_1*	lgK_i	lgK_2
B15C5	Mg^{2+}	1.0	7.2 (7.3)	—	—
trans-**16**	Mg^{2+}	2.2	4.7	—	—
	Ca^{2+}	2.1	4.0	2.7	—
	Ba^{2+}	2.0	3.7	2.9	—
trans-**17**	Mg^{2+}	0.4	6.7 (6.65)	—	—
	Ca^{2+}	1.9	6.0	—	3.7
	Ba^{2+}	2.0	5.7	—	5.0
trans-**18**	Mg^{2+}	0.4	6.6 (6.7)	—	—
	Ca^{2+}	2.1	6.0	—	3.7
	Ba^{2+}	2.0	5.7	—	5.0

* The logK_1 values found by titration with a solution of a competing ligand are given in parentheses.

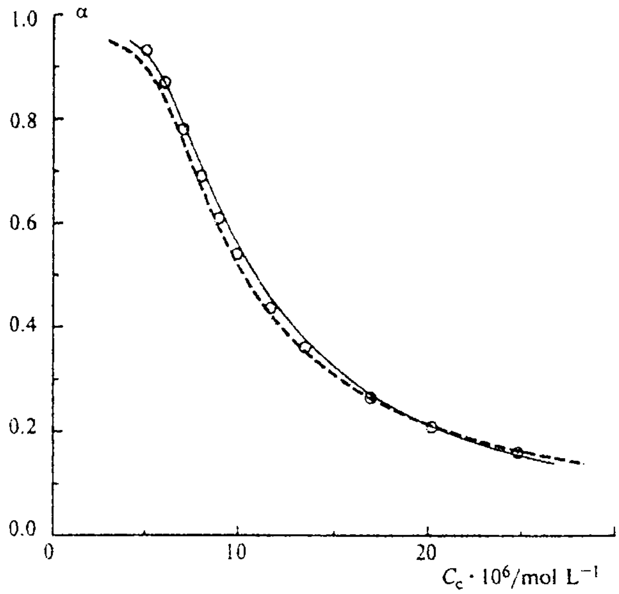


Fig. 16. Dependence of the degree of complexation of *trans*-**17** with Mg^{2+} on the concentration of the competing B15C5 (C_c) at constant $C_L = 4.2 \cdot 10^{-6}$ mol L^{-1} and $C_M = 1.0 \cdot 10^{-5}$ mol L^{-1} in MeCN at T = 295 K (dots). The continuous and dashed lines are approximations of the experimental plots obtained using Scheme 16 and the simplified scheme including only equilibria 3 and 9.

The K_1 values calculated for *trans*-**17** and B15C5 are in good agreement with the corresponding values found in the direct titration experiments (see Table 3). Similar results were also obtained for (*trans*-**18**) · Mg^{2+}.

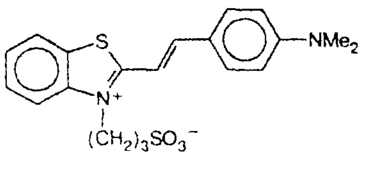
The introduction of a sulfo group in position 2 of the *N*-ethyl substituent in a CSD (*i.e.*, going from *trans*-**5** to *trans*-**16**) has virtually no effect on the stability constants of L · M^{2+} (1 : 1) complexes. However, an increase in the length of the spacer even by one methylene unit (going to *trans*-**17**) results in a dramatic increase in K_1. When the length of the spacer is increased by one more methylene unit (*trans*-**18**), the K_1 value scarcely changes. The stability of the 2 : 1 (sandwich) complexes of CSD with Ba^{2+} also does not change on going from *trans*-**17** to *trans*-**18**. For *trans*-**5** and *trans*-**16**, we could not determine the K_2 values. However, experimental results showed that K_2, like K_1, sharply increases on going from *trans*-**16** to *trans*-**17**.

Apparently, the fact that the stability of L · M^{2+} (1 : 1 and 2 : 1) complexes depends nonmonotonically on the length of the *N*-ω-sulfoalkyl spacer can be explained by the formation of an intramolecular ion pair between the sulfo group and the quaternary N atom of the benzothiazole residue or, what is less likely, between this group and the metal cation located in the crown-ether cavity.

It can be seen from Tables 2 and 3 that for *trans*-**5**,**16**—**18** the K_1 values decrease as the ion diameter in the series Mg^{2+}, Ca^{2+}, Ba^{2+} increases. These results confirm the assumption based on the analysis of spectral shifts upon complexation ($\lambda_L - \lambda_{LM}$) that the crown-ether cavity in *trans*-**5**,**16**—**18** matches best the size of Mg^{2+}.

The dependences of the absorption and fluorescence spectra of *trans*-**24** on the concentration of Ca^{2+} were even more complicated. Analysis of these dependences has shown[20] that the addition of small quantities of Ca^{2+} ions leads to the formation of aggregates containing up to four dye molecules per metal cation. In these aggregates, the cation does not interact with the crown-ether fragments but is bound only to the sulfo groups in *trans*-**24** molecules. As the concentration of Ca^{2+} increases, the degree of aggregation first increases and then the equilibrium shifts toward monomeric complexes A—LM, MA—L, and MA—LM, where A—L is the molecule of *trans*-**24** (A is the sulfo group, L is the azacrown-ether fragment, and M is the metal cation).

One of the reasons for the cation-induced aggregation of *trans*-**24** is, apparently, that the azacrown-ether moiety is less prone to bind Ca^{2+} ions than the sulfo-group. A similar cation-induced aggregation effect was observed for dye *trans*-**25**.



trans-**25**

The aggregation of *trans*-**24**,**25** molecules can also be promoted by other double-charged cations such as Mg^{2+}, Ba^{2+}, or Zn^{2+}. Conversely, the single-charged Na^+ cation did not cause aggregation of these dyes.

Regio- and stereospecific cation-dependent [2+2]-autophotocycloaddition of the *trans*-isomers of CSD betaines

The stereochemistry of the main product of concerted [2π+2π]-photocycloaddition (PCA) of alkenes, which involves the lowest singlet excited state of one of the two reacting molecules, is determined taking into account the orbital symmetry and orbital overlap.[50,51] In solution, these intermolecular reactions occur with low quantum yields because of the fast deactivation of the excited state, which is caused by the occurrence of competing processes, first of all, by *trans*—*cis*-photoisomerization and fluorescence. Intermolecular PCA reactions occurring by a concerted mechanism have, as a rule, low regio- and stereoselectivity, because the reacting molecules can be differently oriented with respect to each other and because both *trans*- and *cis*-isomers of the alkenes are involved in the process owing to the photoisomerization occurring in parallel.[51]

The regio- and stereoselective PCA of ethylene derivatives in molecular organized microsystems has been studied most comprehensively. In this case, stereoselectivity of the process results from a particular orientation of molecules in the cavity of a matrix (in an ordinary or liquid crystal, in a micelle, on silica gel surface, or in a "guest—host" complex).[52]

Spontaneous assembly of alkenes in a supramolecular structure in which the reactants are pre-organized in such a way that their mutual orientation is favorable for the formation of only one cyclobutane isomer in a high yield could be a promising tool for controlling the regio- and stereoselectivity of PCA as well as its efficiency. Under certain conditions, $[(trans\text{-}\mathbf{17},\mathbf{18}) \cdot Mg^{2+}]_2$ complexes can serve as intermediates for the synthesis of photocycloadducts. One may expect that the photocycloaddition would follow the "head-to-tail" pattern, according to the most probable orientation of the molecules in the dimeric complexes.

In fact, upon exposure of solutions of $[(trans\text{-}\mathbf{17},\mathbf{18}) \cdot Mg^{2+}]_2$ to light with λ = 365 nm, along with fast *trans*—*cis*- and *cis*—*trans*-photoisomerization, a relatively slow photoreaction occurs.[53,54] Unlike the *trans*- and *cis*-isomers of $(\mathbf{17},\mathbf{18}) \cdot Mg^{2+}$, the products of this reaction do not absorb light with λ = 365 nm (Fig. 17); therefore prolonged photolysis leads to almost complete phototransformation of the initial CSD. The photoreaction is reversible, because irradiation of the reaction products with light with λ = 313 nm affords the initial CSD.

The structures of the photolysis products **26** and **27** (Scheme 18) obtained from $[(trans\text{-}\mathbf{17},\mathbf{18}) \cdot Mg^{2+}]_2$, respectively, were established using the ^1H NMR COSY and NOESY spectroscopic techniques. For this purpose, D_2O was added to solutions of complexes of **26** and **27**

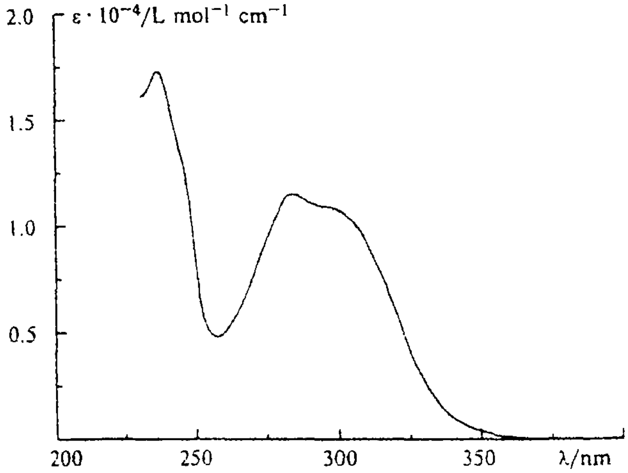
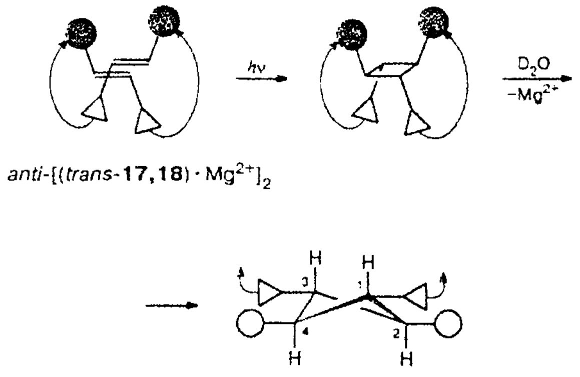


Fig. 17. Absorption spectrum of the photoproduct resulting from photolysis of a solution of $[(trans\text{-}\mathbf{17}) \cdot Mg^{2+}]_2$ ($C_L = 2.0 \cdot 10^{-5}$ mol L^{-1}, $C_M = 1.2 \cdot 10^{-4}$ mol L^{-1}) in MeCN with light with λ = 365 nm at $T = 295$ K.

with Mg^{2+} in $MeCN-d_3$. Under these conditions, the ether fragment cannot form complexes with the Mg^{2+} ions strongly solvated with D_2O molecules. Irrespective of the initial CSD concentration, only one of the 11 theoretically possible isomers of cyclobutane derivatives **26** and **27** is formed; this compound exhibits an A_2B_2 type spectrum with the spin-spin coupling constant of J_{AB} = 9.9 Hz.

Scheme 18



anti-[(*trans*-**17,18**)·Mg^{2+}]$_2$

26, 27

○ — the benzocrown-ether moiety

The conformational analysis of the model compound, 1,2,3,4-tetraphenylcyclobutane, that we have carried out by molecular mechanics has shown[55] that for the isomers like **26** and **27**, the energy of the conformer with equatorial substituents is 5.6 kcal mol^{-1} lower than that of the conformer with axial substituents. The conformation with equatorial substituents is characterized by an internal dihedral angle in the cyclobutane ring of 22.6° and by a proton vicinal spin-spin coupling constant of 10.75 Hz (calculated using the Carplus equation). The corresponding values for the conformation with axial substituents are equal to 17.6° and 2.2 Hz. The fact that the experimental vicinal spin-spin coupling constants in compounds **26** and **27** are close to the corresponding constant calculated for the conformation with equatorial substituents of the model compound makes it possible to conclude that compounds **26** and **27** are stable in the conformations with equatorial substituents.

The cyclobutanes **26** and **27** obtained can be used as a new promising type of host molecules (photoswitchable receptors). In the conformation with axial crown-ether fragments, these compounds would probably exhibit high selectivity with respect to metal ions with large diameters or even to relatively small organic cations.

Assuming a concerted mechanism of [2π+2π]-cycloaddition, it can be concluded that compounds **26** and **27** are formed from the [(*trans*-**17,18**)·Mg^{2+}]$_2$ complexes with a cross arrangement of the molecules corresponding to the *anti*-"head-to-tail" type.

To confirm the fact that only dimeric complexes of *trans*-CSD participate in PCA, some additional experiments were carried out. Figure 18 shows the dependences of the relative concentration of *cis*-**18** incorporated in the dimeric complexes in the *trans*—*cis*-photosteady state (C_{rel}) and the quantum yield of the consumption of CSD in PCA (Φ) on the light intensity. It can be seen that as the light intensity decreases, the C_{rel} value sharply drops, whereas Φ slightly increases. This proves that the molecules of *cis*-**18** bound into the dimeric complexes are not involved in PCA.

The failure of *cis*-**17,18** to undergo PCA, probably, can be explained by the large distance between the double bonds and by their unfavorable mutual orientation in the supramolecular [(*cis*-**17,18**)·Mg^{2+}]$_2$ and (*cis*-**17,18**)·Mg^{2+}·(*trans*-**17,18**)·Mg^{2+} complexes.

The dependence of the quantum yield in the [2+2]-auto-PCA on the concentration of the complexes of **17** with Mg^{2+} under irradiation with light with λ = 365 nm and an intensity of $3.7\cdot10^{15}$ cm^{-2} s^{-1} in MeCN (the constant excess of $Mg(ClO_4)_2$ was $1\cdot10^{-4}$ mol L^{-1}) is given below.

C_L /mol L^{-1}	$5\cdot10^{-6}$	$2.4\cdot10^{-5}$	$4.5\cdot10^{-5}$	$2.1\cdot10^{-4}$	$2\cdot10^{-3}$
Φ	0.0022	0.0043	0.0052	0.0051	0.0055

Analysis of the dependence of the quantum yield of the consumption of **17** in the PCA on the concentration of the complexes showed that cyclobutane is formed only from the dimeric complex. Since the supramolecular complexes containing molecules of the *cis*-isomer do not participate in PCA, this dimer is [(*trans*-**17**)·Mg^{2+}]$_2$. The ~2.5-fold decrease in the quantum yields of PCA in the $5\cdot10^{-5}$—$5\cdot10^{-6}$ mol L^{-1} concentration range can

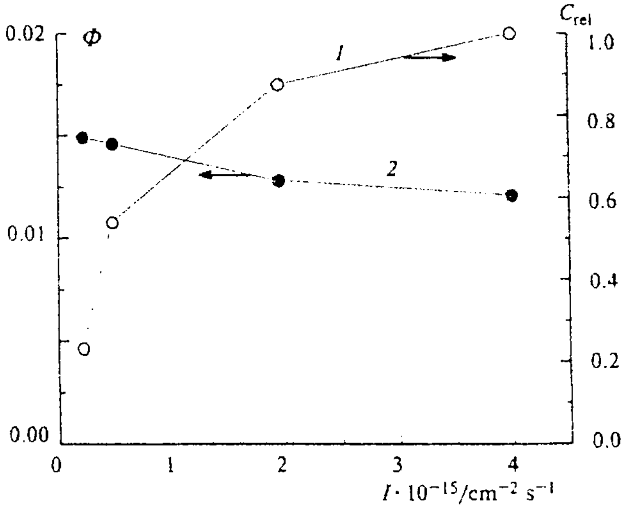


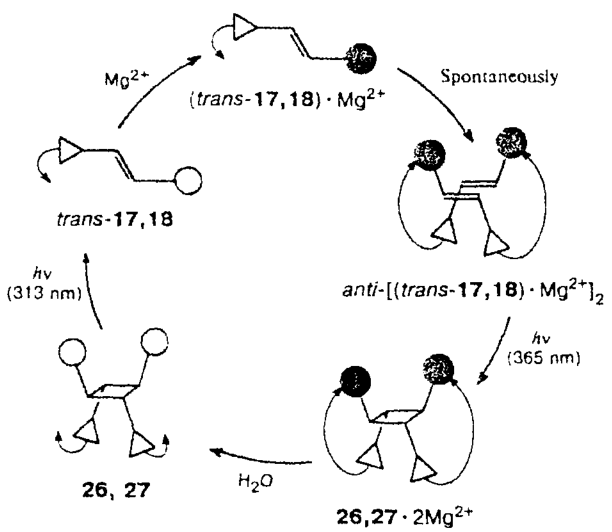
Fig. 18. Dependence of the relative concentration of (*cis*-**18**)·Mg^{2+} incorporated in the dimeric complexes, in the *trans*—*cis*-photosteady state C_{rel} (*1*) and dependence of the quantum yield of PCA Φ (*2*) on the intensity of the light with λ = 365 nm in MeCN + 0.08% H_2O at an excessive concentration of $Mg(ClO_4)_2$ of $1\cdot10^{-4}$ mol L^{-1} (*T* = 295 K).

probably be explained by the decrease in the degree of dimerization of (*trans*-**17**) · Mg^{2+}.

In the case of (*trans*-**17,18**) · Mg^{2+}, the Φ values measured at $C_L = 4.5 \cdot 10^{-5}$ mol L^{-1} and light intensity $I = 3.7 \cdot 10^{15}$ cm^{-2} s^{-1} are 0.005 and 0.013, respectively. The increase in Φ on going to *trans*-**18** can be explained by the fact that the increase in the length of the spacer results apparently in a decrease in the steric restrictions to the interaction between the CSD molecules incorporated in the dimeric complexes.

The auto-PCA of *trans*-**17,18** observed upon irradiation with light and in the presence of $Mg(ClO_4)_2$ can be represented as the following general scheme (Scheme 19).

Scheme 19



The complexes of *trans*-**17,18** with Ca^{2+} and Ba^{2+} also undergo the PCA reaction. In the case of Ca^{2+}, the Φ value measured at $C_L = 2 \cdot 10^{-5}$ mol L^{-1} amounts to 0.001 for *trans*-**17** and 0.01 for *trans*-**18**. The decrease in Φ on going from Mg^{2+} to Ca^{2+} is probably due to the fact that the equilibrium dimerization constants for complexes of *trans*-**17,18** with Ca^{2+} are lower and, therefore, the degree of dimerization at a particular concentration of the dye is smaller.

It should be noted that *trans*-**16**—**18** and *trans*-**5** in the absence of alkaline earth metal cation and the complexes of *trans*-**5,16** with Mg^{2+}, Ca^{2+}, or Ba^{2+} do not undergo PCA under the conditions described above; this can be explained by the high degree of conjugation involving the C=C bond in the dyes and by the Coulomb repulsion between the positively charged molecular fragments that prevents them from approaching each other. In the case of complexes of *trans*-**5,16** with M^{2+}, there are other factors hampering the PCA, *viz.*, the absence of a sulfoalkyl spacer or its insufficient length, which makes the formation of dimers impossible. The promoting effect of alkaline earth metal salts on the PCA of low-reactivity ethylene derivatives has not been described previously and, in our opinion, it is of interest by itself.

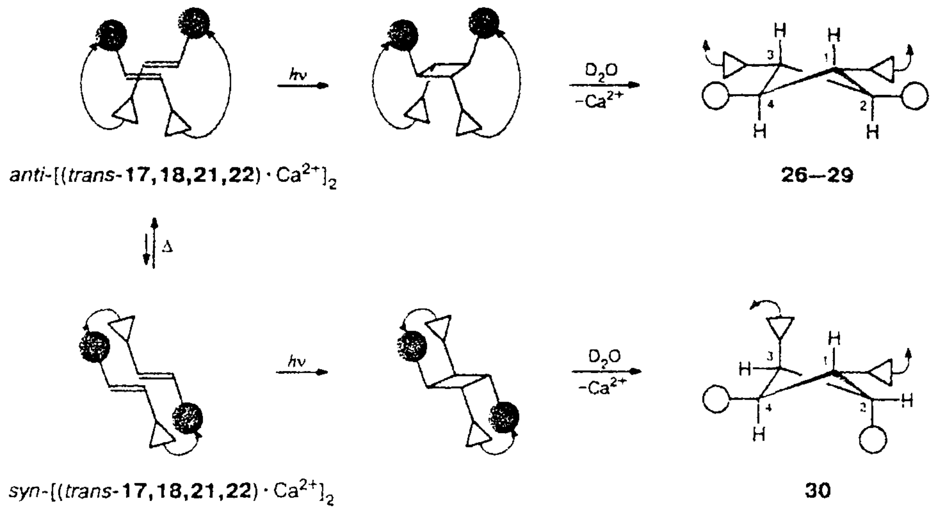
The effect of alkaline earth metal ions on the auto-PCA of CSD cannot be explained by the template effect,[56] which implies that the metal cation is bound directly to the reaction centers of the reacting molecules, thus facilitating the reaction. In our opinion, the accumulation of CSD in the reaction area and the effect on the mutual orientation of the molecules, similar to that observed, for example, in the crystalline state without metal cations, are of crucial importance in this case.[12]

The molecular-mechanic procedure we developed for computer simulation of the [2+2]-auto-PCA of the dimeric complexes of CSD with metal cations made it possible to establish the relationship between the regio- and stereoselectivity of the formation of crown-containing cyclobutane derivatives and the spatial structures of the dimeric complexes of CSD with M^{2+}.[57] Thus, we can predict the formation of isomeric dimers in which the CSD molecules are arranged by the *anti*-"head-to-tail" type or precisely one above the other (*syn*-"head-to-tail," Scheme 20), and to predict the formation of cyclobutane derivatives of the corresponding structures after irradiation. In fact, using ^1H NMR spectroscopy, among the photoproducts obtained from [(*trans*-**17,18,21,22**) · Ca^{2+}]$_2$ (**26**, **27**, and **29** from *trans*-**17,18**, and **22**, respectively), in the case of **21**, we detected[46] two isomeric crown-containing cyclobutane derivatives (**28** and **30**) in a ratio of 2 : 1.

The cyclobutane region in the spectrum of **28** and **29** is similar to the corresponding part of the spectrum of **26** and **27**; it is also an A_2B_2-type spectrum with the spin-spin coupling constant J_{AB} = 9.85 Hz. The cyclobutane protons in **30** are responsible for an AA'BB' pattern in the ^1H NMR spectrum with the following set of vicinal spin-spin coupling constants: $^3J_{H(1),H(2)} = {}^3J_{H(3),H(4)} = 10.54$ Hz, $^3J_{H(3),H(2)} = {}^3J_{H(1),H(4)} = 7.74$ Hz; this is in good agreement with constants of 10.5 and 7.7 Hz found previously for a 1,2,3,4-tetrasubstituted cyclobutane[58] and also with the values of vicinal constants calculated using molecular mechanics. These calculations showed[55] that 1,2,3,4-tetraphenylcyclobutane with an arrangement of substituents similar to that in **30** is characterized, after fast conformational averaging due to the low energy barrier, by the vicinal constants $^3J_{cis}$ = 8.97 and $^3J_{trans}$ = 6.78 Hz, which are also in good agreement with the set of the experimental vicinal coupling constants found for compound **30**.

The formation of two isomeric derivatives **28** and **30** in the PCA is the only example found by us in which the rigorous stereospecificity observed previously for the PCA reactions of CSD was violated; evidently, this is due to the fact that in this case, the overall quantum yield of the reaction is low (see below). In both dimeric complexes, *anti*- and *syn*-[(*trans*-**21**) · Ca^{2+}]$_2$, the C=C bonds in *trans*-**21** probably are arranged unfavorably with respect to each other, and this hampers both the

Scheme 20



efficient occurrence of the PCA and its high stereospecificity.

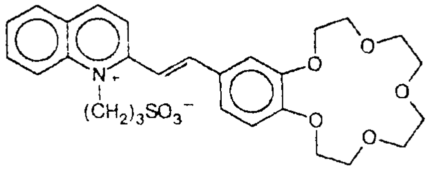
The quantum yields in the PCA involving complexes of *trans*-**17,18,21,22** with Ca^{2+} were determined at $C_L = 2.0 \cdot 10^{-5}$ mol L^{-1} and $C_M = 1.2 \cdot 10^{-4}$ mol L^{-1} from the kinetics of the consumption of CSD during irradiation with light with $\lambda = 365$ nm. The values for the quantum yields in the PCA (Φ), based on the overall absorbance of the dye at the irradiation wavelength, are listed below.

CSD	**17**	**18**	**21**	**22**
Φ	0.001	0.01	0.0004	0.06

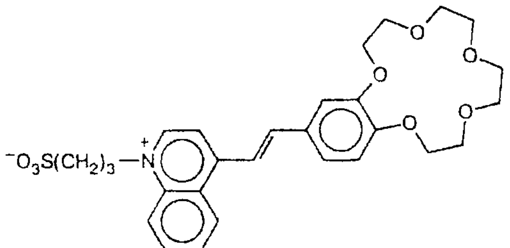
As noted above, the dimeric complexes of CSD with M^{2+} have a pseudomacrocyclic structure. Therefore, the increase in the efficiency of the PCA of *trans*-**17,18,21,22** containing different crown-ether fragments following an increase in the length of the spacer might be attributed to the decrease in the steric strain in the pseudomacrocycle. However, the fact that for CSD with spacers of various lengths, the dependences of Φ on the size of the crown-ether cavity are opposite in sign prompts one to think that a significant role belongs to the fine adjustment in the mutual orientation of the reacting C=C bonds in the dimeric complex preorganized for the auto-PCA.

It should also be noted that *trans*-**21,22**, unlike *trans*-**17,18**, do not enter into auto-PCA in the presence of Mg^{2+} under the conditions described above. Thus, the variation of the size of the crown-ether fragment makes it possible to change the ion selectivity of the PCA and to control the efficiency of the interaction.

It may be assumed that the variation of the structure of the heterocyclic residue would permit the supramolecular spatial structure of the dimeric complex to be changed in such a way as to control the efficiency of the interaction and the stereochemistry of the final product. For this purpose, we carried out[55] a comparative study of isomeric CSD of the quinolinium series containing 15-crown-5 fragments: *trans*-**19** and *trans*-**31**.



trans-**19**



trans-**31**

Examination of the molecular models of the dimeric complexes based on *trans*-**19** and Mg^{2+} showed that the sulfopropyl spacer is sufficiently long for the formation of *anti*-[(*trans*-**19**) · $Mg^{2+}]_2$ with cross "head-to-tail" arrangement of molecules of **19** similar to the dimeric complexes based on *trans*-**17,18** and Mg^{2+}.

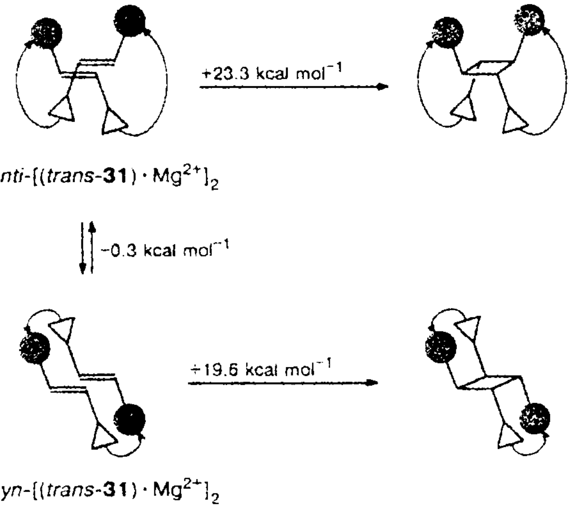
When a solution of *trans*-**19** in MeCN containing $Mg(ClO_4)_2$ is irradiated with light with $\lambda = 405$ nm, the absorption spectrum rapidly changes until a photosteady state, caused by the reversible *trans*—*cis*-photoisomerization of (*trans*-**19**) · Mg^{2+}, is established. Upon further irradiation, the absorption spectrum of the reaction solution undergoes very slow changes that are associated with the auto-PCA of *trans*-**19**. The overall quantum yield in the PCA of *trans*-**19** (Φ) is ~0.0007; it was estimated from the kinetics of the decay of the optical density of the reaction solution at 405 nm (the product of the PCA does not absorb in this region of the spectrum).

Analysis of the ^{1}H NMR spectra of the reaction product performed using COSY and NOESY techniques showed that, as in the case of *trans*-**17**,**18**, only one isomer of the cyclobutane derivative is formed, irrespective of the initial concentration of *trans*-**19**; this isomer is responsible for an A_2B_2 type spectrum with a spin-spin coupling constant J_{AB} of 9.85 Hz, and its structure is similar to that of the crown-containing cyclobutanes **26** and **27**.

When a solution of *trans*-**31** in MeCN containing Mg(ClO$_4$)$_2$ is irradiated with light with λ = 405 nm, the spectral changes cannot be divided into fast and slow stages. The quantum yield in the PCA involving the complex of *trans*-**31** with Ca^{2+} and occurring under irradiation with light with λ = 436 nm is markedly higher (Φ = 0.15) than that in the case of *trans*-**19** and is comparable with the quantum yield in the *trans—cis*-photoisomerization of *trans*-**31**. This implies that the complexes of this dye are dimerized to a large extent even at relatively high dilution and, evidently, the steric structure of the dimeric complex is quite favorable for the PCA.

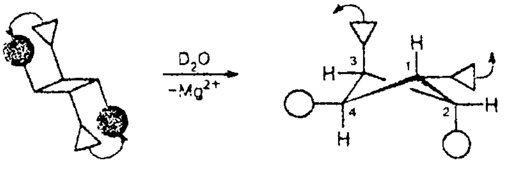
Our procedure of computer simulation of [2+2]-auto-PCA of CSD made it possible to predict the stereochemistry of the crown-containing cyclobutane derivative expected as a result of the PCA involving one of the two calculated predominant conformations of [(*trans*-**31**)·Mg^{2+}]$_2$ in which the *trans*-**31** molecules are arranged exactly one above the other according to the *syn*-"head-to-tail" type[59] (Scheme 21).

Scheme 21



Analysis of Scheme 21 leads to three main conclusions: (1) the reaction mixture can contain both *syn*- and *anti*-[(*trans*-**31**)·Mg^{2+}]$_2$; (2) apparently, crown-containing cyclobutane **32** will be formed as the major reaction product (Scheme 22), *i.e.*, unlike the previous cases, the PCA will occur in the dimeric complex of the *syn*-"head-to-tail" type; (3) the quantum yield is likely to be markedly higher than that observed in the previous cases, since PCA becomes much less endothermic. These conclusions were confirmed experimentally.

Scheme 22



32

Using ^{1}H NMR spectroscopy, the cyclobutane derivative resulting from the PCA of compound **31** in the presence of magnesium or calcium perchlorate was identified as compound **32** (the spectrum is described by an AA′BB′ type spin system with the following set of vicinal spin-spin coupling constants: ${}^3J_{H(1),H(2)}$ = ${}^3J_{H(3),H(4)}$ = 10.29 Hz and ${}^3J_{H(1),H(4)}$ = ${}^3J_{H(2),H(3)}$ = 7.61 Hz). No photoproducts other than **32** were detected.

The two latter theoretical predictions can be illustrated by the comparison of the spatial structures of *syn*- and *anti*-[(*trans*-**31**)·Mg^{2+}]$_2$ (Fig. 19), which makes it possible to understand why the PCA is highly efficient and stereospecific in this case. The C=C bonds in *syn*-[(*trans*-**31**)·Mg^{2+}]$_2$ are nearly parallel to each other, whereas in *anti*-[(*trans*-**31**)·Mg^{2+}]$_2$ they are almost perpendicular to each other and moreover they lie in nearly perpendicular planes; this prevents these bonds from approaching each other and makes the formation of a non-strained four-membered ring impossible. Thus, steric requirements predetermine the formation of compound **32** in the auto-PCA. The distance between the C=C bonds in *syn*-[(*trans*-**31**)·Mg^{2+}]$_2$ (5.5—6.5 Å) is much smaller than that in *anti*-[(*trans*-**17**)·Mg^{2+}]$_2$ (6.5—7 Å) or *anti*-[(*trans*-**22**)·Ca^{2+}]$_2$ (7.4 Å); therefore, it may be expected that the quantum yield of cyclobutane **32** will markedly increase. Thus, both factors, *viz.*, the relative energy and the geometry, act here in the same direction.

According to our calculations,[57] the *syn*-[(*trans*-**31**)·Mg^{2+}]$_2$ and *anti*-[(*trans*-**31**)·Mg^{2+}]$_2$ complexes correspond to fairly deep potential energy minima and the relative energy of their formation is small; this suggests that both dimeric complexes exist in solution. In fact, the ^{1}H NMR spectrum of (*trans*-**31**)·Mg^{2+} exhibits two groups of signals corresponding to the two forms of [(*trans*-**31**)·Mg^{2+}]$_2$ in a ratio of 10 : 3 (Fig. 20).[35] It follows from the 2D NOESY spectrum that these two forms exist in a dynamic equilibrium with each other,

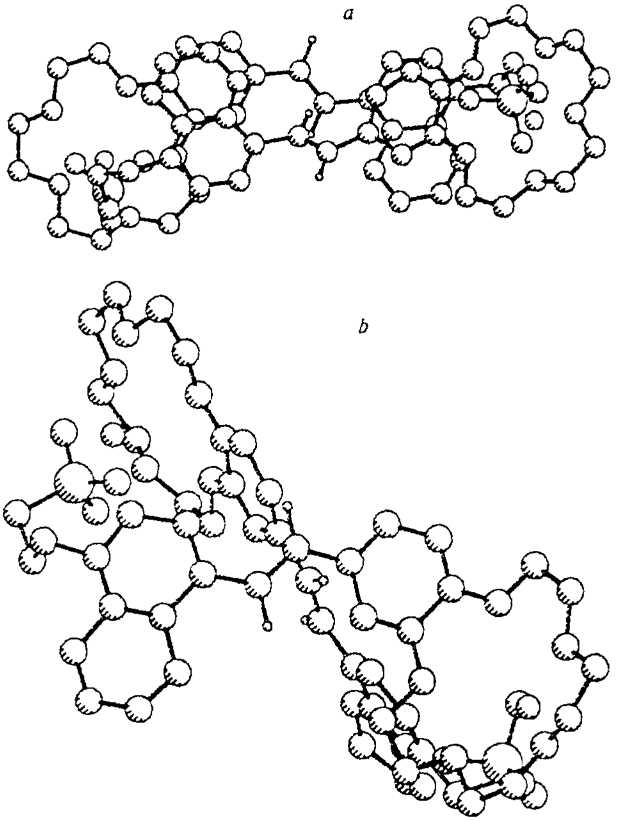


Fig. 19. Spatial structures of *syn*-[(*trans*-**31**) · Mg^{2+}]$_2$ (*a*) and *anti*-[(*trans*-**31**) · Mg^{2+}]$_2$ (*b*). Only those H atoms that are bound to the C atoms of the central C=C bond are shown.

and their lifetimes on the NMR time scale are sufficiently long for them to be observed separately at room temperature. The point of coalescence of these two forms is 70 °C, which corresponds to an activation barrier of 16—17 kcal mol^{-1}.

To confirm the fact that it is [(*trans*-**31**) · Mg^{2+}]$_2$ that is formed in the complexation, we carried out comparative analysis of the ^1H NMR spectra of *trans*-**31** and *trans*-**15**, which is a complete analogue of *trans*-**31** except that it cannot form dimeric complexes, because it contains no *N*-ω-sulfoalkyl group. The chemical shifts of the protons in *trans*-**31** and *trans*-**15** virtually coincide. Upon the formation of a complex with $Mg(ClO_4)_2$, all the signals for *trans*-**15** shift downfield. The closer a proton to Mg^{2+}, the larger the shift of its signal (see Fig. 8).

From a comparison of the changes in the chemical shifts of (*trans*-**15**) · Mg^{2+} and the two forms of [(*trans*-**31**) · Mg^{2+}]$_2$, it can be seen that upon complexation, almost all the signals of aromatic protons and the signals of the protons at the C=C bond in compound *trans*-**31** are displaced upfield. This is in good agreement with the assumption that [(*trans*-**31**) · Mg^{2+}]$_2$ is formed according to the "head-to-tail" type with a plane-parallel arrangement of the aromatic rings at which the benzene part of the benzocrown-ether moiety of one molecule falls into the shielding cone of the heteroaromatic moiety of the second molecule and *vice versa*. From a more detailed analysis of the ^1H NMR spectra, it was also found that the complex present in smaller amounts has the structure of *syn*-[(*trans*-**31**) · Mg^{2+}]$_2$.

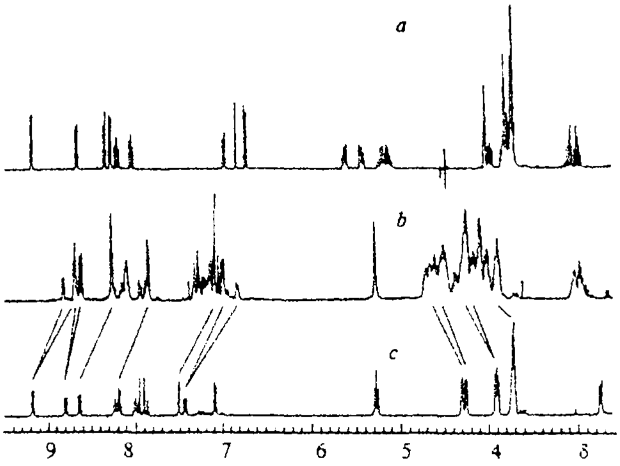


Fig. 20. ^1H NMR spectra of the crown-containing cyclobutane **32** (*a*) in D_2O, *syn*- and *anti*-[(*trans*-**31**) · Mg^{2+}]$_2$ (*b*), and *trans*-**31** (*c*) in MeCN-d_3 at T = 295 K. The lines show the variation of the chemical shifts of the protons in *trans*-**31** following the formation of the complex with $Mg(ClO_4)_2$.

Thus, target-directed variation of the structure of the heterocyclic residue and the crown-ether fragment and the length of the sulfoalkyl spacer makes it possible to change basically the route of the ion-selective PCA reaction and to control the efficiency of interaction and the stereochemistry of the final product. The transformations studied also demonstrate new prospects for using CSD in the self-assembly into photoswitchable molecular devices,[60] for example, as synthons for stereospecific photochemical synthesis of a new promising type of host molecules (photoswitchable receptors), *viz.*, crown-containing cyclobutanes.

Photoinduced reactions and complex formation of CSD in polymer layers and in Langmuir—Blodgett films

Previously, a series of photosensitive polymers containing azobenzene or spiropyran fragments have been synthesized;[61] these polymers made it possible to control, for example, the viscosities and pH of solutions and the polarities of the film surface. All these phenomena were due to photoinduced changes of the chromophore groups.

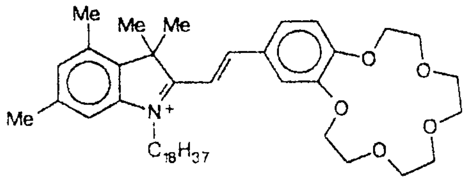
The use of a hydrophilic polymeric support can be promising for controlling photochemically the extraction of metal salts from aqueous solutions. Hydrophilic polymers containing photochromic and chromogenic ionophores can also be used for the development of film optical sensors for metal ions.

For this purpose, we studied *trans—cis*-photoisomerization of *trans*-**14** in polyvinylbutyral (PVB) films and polyacrylamide hydrogels.[62]

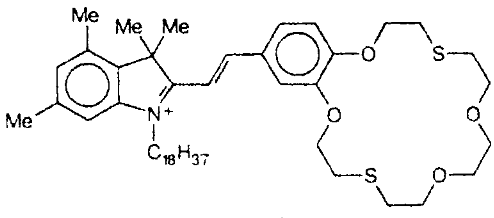
The main specific feature of the photoisomerization in a PVB film is that the interconversion is not complete. About 30% of the CSD dissolved in the film is involved in the photoreaction. This result is adequately interpreted in terms of the theory of free "space". Photochemical reactions of *trans*-**14** in the polyacrylamide gel, like those in solution, occurred with complete retention of the photochromic properties of the dye.

The preparation and study of ion-selective ultrathin films from crown ethers is a relatively new field of science that is being rapidly developed.[6,63,64] These films can find application for the elaboration of optical sensors, sensitive units in ion-selective electrodes, and unique tools for the investigation of ion transport through biological and model membranes. Nevertheless, only a few studies devoted to the monolayers and Langmuir—Blodgett (LB) films of crown ethers have been published. This is due to the fact that these compounds are incapable of forming stable monolayers on an air—water interface owing to the non-balanced ratio between the hydrophilic and hydrophobic parts of their molecules. Modification of crown ethers with long hydrocarbon chains permits synthesis of their surface-active derivatives, which can easily be converted into monolayers and LB films.[65—67] Amphiphilic CSD can be used for self-assembly of promising supramolecular structures by virtue of the LB technique; this would make it possible to control complex formation and photochemical reactions.

We were the first to obtain ultrathin films from amphiphilic *trans*-**33** using the LB technique[68] and to study the effect of metal cations on their photochemical and spectral characteristics.



trans-**33**



trans-**34**

Using the surface plasmon resonance technique, the extremely high, selective sensitivity of LB films based on amphiphilic *trans*-**34** containing benzodithia-18-crown-6 fragment to mercury vapor has been demonstrated.[69] The established correlations between the structure of CSD and their properties in solutions allowed us to accomplish the target-directed synthesis of new amphiphilic CSD and to predict the possibility of *trans—cis*-photoisomerization, aggregation, and PCA; later, these processes were actually observed in the monolayers and LB films of these compounds.[70,71]

* * *

The functional potentialities of CSD were not studied before our works. We were able to discover a number of novel effects and to study the mechanism of the processes involved; the most promising among the latter are the ion-selective formation of anion-"capped" complexes and stereospecific ion-selective auto-PCA of CSD. The results make it possible to predict the possibility of synthesizing CSD suitable for the development of selective chromo- and fluoroionophores, including those for cations with large ion radii, relatively small organic cations, and heavy metal cations; photochromic ionophores for photocontrolled ion transport through membranes; polymeric and LB films with photoreversible properties; photoreversible synzimes and molecular devices for molecular electronics. We hope that the supramolecular organic photochemistry of CSD will be further developed and that these systems will find practical use.

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