Crown ether styryl dyes
18.* Synthesis, anion-"capped" complexes, and ion-selective stereospecific [2+2] autophotocycloaddition of photochromic 18-crown-6 ethers

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New crown ether styryl dyes (*trans*-**1c,d**) containing the 18-crown-6 ether fragment were synthesized. Interaction of *trans*-**1c,d** dyes, as well as their analogs, *trans*-**1a,b** containing the 15-crown-5 ether fragment, with $Ca(ClO_4)_2$ in MeCN afforded supramolecular structures (dimeric complexes). Competing reactions, *trans-cis*-photoisomerization with the formation of anion-"capped" complexes of *cis*-**1a—d** and [2+2] autophotocycloaddition with the formation of cyclobutane derivatives **8a—d** and **9c**, were observed on photolysis of solutions of complexes of *trans*-**1a—d** with Ca^{2+}. Preorganization of *trans*-isomers in dimeric complexes with Ca^{2+} determined the regio- and stereoselectivity of each of the two directions of the photocycloaddition and the efficiency of the reaction.

Key words: crown ether styryl dyes; synthesis; complexation; anion-"capped" complexes; [2+2] photocycloaddition; cyclobutane derivatives; ^1H NMR spectra.

The ability for self-organization in solution on the molecular level (spontaneous assembling) with the formation of supramolecular structures with the desired architecture and the ability to be photocontrolled are the necessary conditions for creation of photo-switched molecular devices.[2] Earlier we have found that in the course of photoisomerization caused by irradiation, complexes of crown-containing styryl dyes (CSD) are able to take off the "anionic cap" in the *trans*-form and put it on in the *cis*-form. This, in turn, permitted us to achieve photocontrol over binding of cations of alkaline-earth metals.[3] In addition, it has been shown that self-assembly of dimeric complexes from two CSD molecules and two metal cations, affording a favorable mutual space orientation of molecules, may become a unique instrument for the control of regio- and stereoselectivity of [2+2] photocycloaddition (PCA) of CSD (see Ref. 4). This opens wide possibilities for using CSD as synthons for stereospecific photochemical synthesis of crown-containing cyclobutanes, a new promising type of host molecules (receptors). These reactions were discovered to be photochemically reversible that allows one to carry out not only assembly but, when needed, disassembly of the receptor molecules synthesized. Directed molecular engineering of supramolecular structures based on CSD allows one to expect the increase in efficiency of these interesting photoreactions and to control the stereochemistry of the end products.[5]

In the present work we studied the influence of the size of the crown ether cavity and the nature of the metal cation on the photoisomerization and [2+2] autophotocycloaddition of CSD by the example of photochromic 15-crown-5 and 18-crown-6 ethers of benzothiazole series **1a—d**.

The syntheses of CSD **1a** (see Ref. 6) and **1b** (briefly, without a detailed procedure)[7] were described by us earlier. CSD **1a—d** were synthesized by condensation of betaines **2a,b** with 4-formylbenzo-15(18)-crown-5(6) ethers[8] (**3a,b**) in the presence of pyridine in up to 60 % yields. The starting betaines **2a,b** were obtained by heating of 2-methylbenzothiazole (**4**) with γ-sultone (**5a**) and δ-sultone (**5b**), respectively, in up to 25 % yields (Scheme 1). The low yield of betaines **2a,b** probably results from steric hindrance which appear on quaternization of the heterocyclic base due to the presence of the methyl group in position 2 of the thiazole cycle of **4**.

* For Part 17 see Ref. 1.

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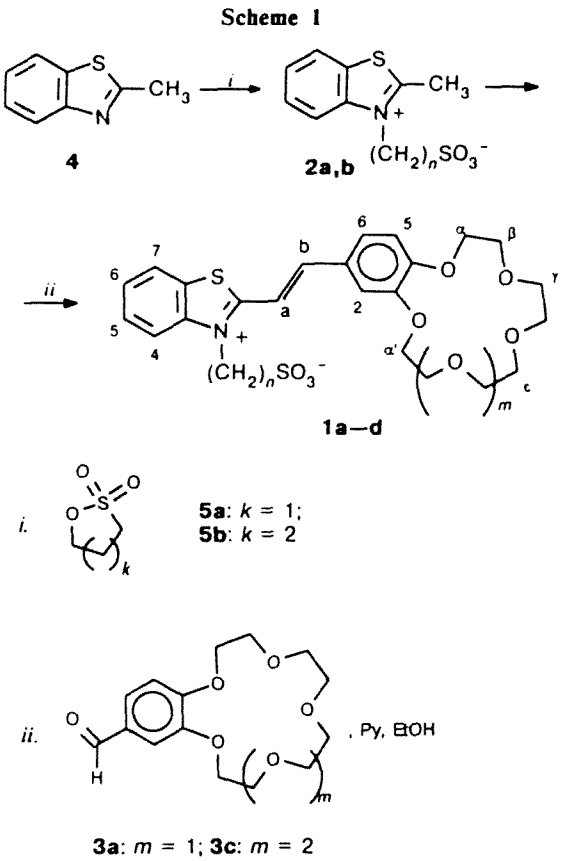
Scheme 1



1, **2**: n = 3 (**a**, **c**), 4 (**b**, **d**);
1, **3**: m = 1 (**a**, **b**), 2 (**c**, **d**)

The structure of compounds **1c,d** obtained was confirmed by ^{1}H NMR spectroscopy (see Experimental). The elementary analysis data correspond to the proposed structures. Judging from the coupling constants $^3J_{trans}$ = 15.6 Hz (see Ref. 9) for olefin protons, CSD **1c,d** obtained have *trans*-configuration.

The electron absorption spectra of *trans*-**1c,d** in MeCN are practically similar to those of *trans*-**1a,b** (see Ref. 7), since the chromophore part of all of the compounds is identical. Unlike the case with *trans*-**1a,b**, addition of $Mg(ClO_4)_2$ at concentration C_M = $1.2 \cdot 10^{-4}$ mol L^{-1} into a solution of *trans*-**1c,d** with C_L = $2.0 \cdot 10^{-5}$ mol L^{-1} does not lead to a noticeable change in the absorption spectrum since the crown ether fragment of dyes **1c,d** is almost incapable of binding the Mg^{2+} ion whose diameter is significantly smaller than the cavity size of the 18-crown-6 ether.

At the same time, addition of $Ca(ClO_4)_2$ at the same concentration results in a hypsochromic shift of the long-wave absorption band (LAB) of *trans*-**1c,d** from 436 to 410 nm and from 435 to 412 nm, respectively.

Shifting of the electron density from the benzene ring to the heterocycle occurs in the CSD molecule during the long-wave electron transition.[10] When the crown ether fragment binds Ca^{2+} ion, such shifting of the electron density outward from the cation becomes energy unprofitable. This explains the experimentally observed hypsochromic shift of the LAB.

Further increase in the concentration of $Ca(ClO_4)_2$ in solution does not result in noticeable spectral changes; therefore, one may conclude that under the given above conditions, *trans*-**1c,d**, as well as *trans*-**1a,b** (see Ref. 1), are almost completely transformed into complexes with Ca^{2+} ions (weak spectral changes observed with the increase in $C_M > 1 \cdot 10^{-3}$ mol L^{-1} may be due to a change in complex composition). The data on the stability of the complexes of *trans*-**1c,d** with Ca^{2+} obtained by the standard spectrophotometric titration method showed that the apparent stability constants of these complexes are so high that they lie beyond the sensitivity limit of this method ($\log K > 7$).

Thus, the complexes of *trans*-**1a—d** with Ca^{2+} are convenient objects for comparative photochemical investigation since they can be obtained under similar conditions at relatively low concentrations of dye and metal salt.

Reversible competitive reactions of *trans-cis*-photoisomerization and photocycloaddition (PCA) are observed on photolysis of solutions of the complexes **1a—d** with Ca^{2+}. Similar reactions proceed in the case of the previously studied complexes of **1a,b** with Mg^{2+}.[3,4,7]

In the spectra of (*cis*-**1a—d**)·Ca^{2+} formed as the result of photoisomerization, the LAB are located in a significantly shorter-wave region than those of the starting complexes of *trans*-**1a—d** with Ca^{2+} (Fig. 1). Such unusually strong photochromic effect in the *trans-cis*-photoisomerization, as in the case of the complexes of **1a,b** with Mg^{2+} (see Ref. 3 and 7), may result from the formation of an intramolecular coordination bond (ICB) in the *cis*-form between the sulfo group of the

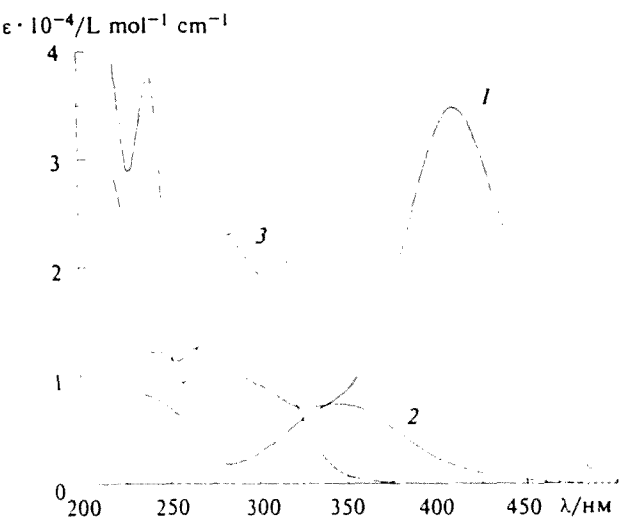
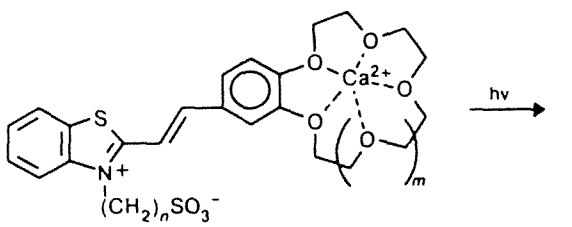


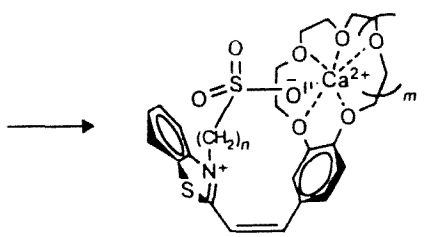
Fig. 1. Absorption spectra of (*trans*-**1d**)·Ca^{2+} (*1*), (*cis*-**1d**)·Ca^{2+} (*2*), and **8d**·$2Ca^{2+}$ cycloadduct (*3*) in MeCN (C_L = $2.0 \cdot 10^{-5}$ mol L^{-1}, C_M = $1.2 \cdot 10^{-4}$ mol L^{-1}) at 295 K.

N-substituent and the cation located in the cavity of the crown ether fragment (Scheme 2). Due to the relatively small length of the *N*-substituent (spacer), the formation of anion-"capped" complex is probably accompanied by significant twisting of separate fragments of the chromophore around ordinary bonds (ethylene fragment — benzothiazole residue and ethylene fragment — benzocrown ether residue). The twisting causes distortion of conjugation in the chain of chromophore atoms which results in a hypsochromic shift of LAB of (*cis*-**1a—d**)·Ca^{2+}.

Scheme 2



(*trans*-**1a—d**)·Ca^{2+}



(*cis*-**1a—d**)·Ca^{2+}

The conclusion about the formation of an ICB is confirmed by the fact that the absorption in the long-wave region of the spectra increases significantly when large amounts of $Ca(ClO_4)_2$ (C_M > 0.1 mol L^{-1}) are added to a solution of (*cis*-**1a—d**)·Ca^{2+}. The same effect was observed previously for (*cis*-**1a**)·Mg^{2+} (see Ref. 3) and was attributed to the rupture of the ICB in the complex due to the interaction of the sulfo group with an additional metal cation with the formation of the (*cis*-**1a**)·$2Mg^{2+}$ complex where conformation of the *cis*-isomer of the dye becomes more planar, and this results in restoration of conjugation in the chromophore and, respectively, in the increase in long-wave absorption.

Earlier we have shown by the example of (*cis*-**1a,b**)·Mg^{2+} that the existence of ICB, in addition to the strong photochromic effect, provides significantly higher stability of the *cis*-isomer complexes as compared with that of the *trans*-isomer complexes.[7] Using these effects, we were able to obtain pure anion-"capped" (*cis*-**1a—d**)·Ca^{2+} complexes also in the case of **1a—d**.

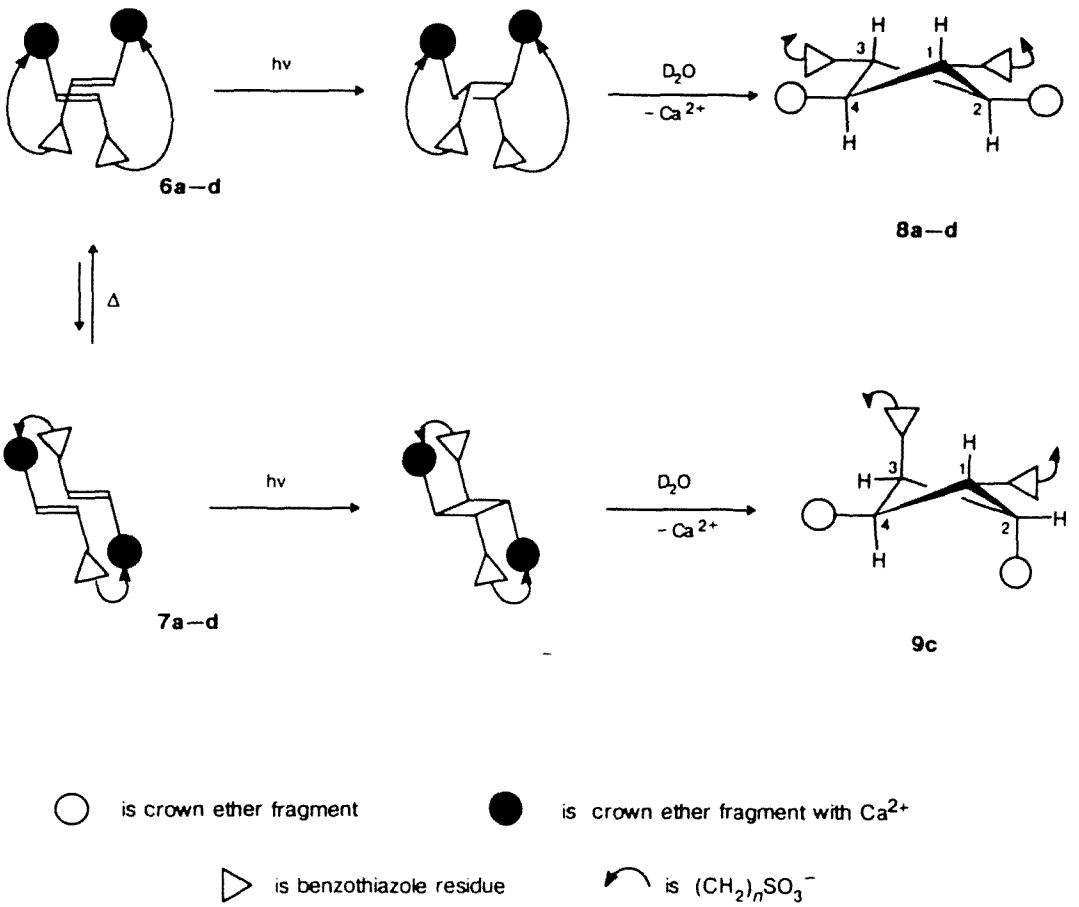
(*cis*-**1a—d**)·Ca^{2+} complexes were obtained by irradiation of solutions of the complexes of *trans*-**1a,c** with Ca^{2+} (λ = 436 nm). For such irradiation, the *trans-cis*-photostationary state is shifted toward the *cis*-isomer for more than 99 %. In this case, only trace amounts of cycloadduct are formed in the period of establishment of the *trans-cis*-photostationary state since the quantum yield (Φ) of the PCA reaction, competing with photoisomerization, is low.

In the case of the complexes of *trans*-**1b,d** with Ca^{2+}, the Φ value for PCA is significantly higher; therefore, the procedure for the preparation of (*cis*-**1b,d**)·Ca^{2+} was modified in the following way. A solution of *trans*-**1b,d** (C_L = $2.0 \cdot 10^{-5}$ mol L^{-1}) was transformed into *trans-cis*-photostationary state by irradiation with light at 436 nm. The content of *cis*-**1b,d** in this case was approximately 80 % (determined by Fischer method).[11] Then $Ca(ClO_4)_2$ in 1 : 2 ratio with respect to the dye was added to the solutions. Under these conditions, Ca^{2+} ions are completely bound with *cis*-**1b,d** and *trans*-**1b,d** remain in the unbound state. Irradiation of solution followed by the addition of $Ca(ClO_4)_2$ in 1 : 2 ratio with respect to the dye which remained unbound, was repeated several times until *trans*-**1b,d** was completely transferred into (*cis*-**1b,d**)·Ca^{2+}. Such a procedure allowed us to obtain pure (*cis*-**1b,d**)·Ca^{2+} since *trans*-**1b,d** remained in a free form in all irradiation stages and, therefore, did not take part in PCA.

Prolonged photolysis of solutions of the complexes **1a—d** with Ca^{2+} by light with a shorter wavelength λ = 365 nm which is absorbed by both isomeric forms of the complexes, results in total consumption of CSD due to the PCA reaction competing with photoisomerization (the exceptions are complexes of **1c** with Ca^{2+} for which the total consumption of the dye is not achieved because the quantum yield of PCA is low). As an example, Fig. 1 presents the electron absorption spectrum of the cycloadduct complex obtained on photolysis of the complexes of **1d** with Ca^{2+}. For the comparison, the absorption spectra of the complexes of *trans*- and *cis*-**1d** with Ca^{2+} are also given. When the obtained complexes of cycloadducts with Ca^{2+} are irradiated with light with λ = 313 nm, the formation of complexes of the starting dyes occurs until a complex photostationary state stemming from the existence of reversible reactions of photoisomerization and PCA is reached.

It should be noted that in very diluted solutions of the complexes **1a—d** with Ca^{2+} (at C_L ~10^{-5} mol L^{-1}) the PCA reaction cannot proceed according to the usual bimolecular mechanism due to the small lifetime of the excited state $\tau < 10^{-10}$ s (see Ref. 12). Even if we propose that the reaction is diffusion controlled, the maximum theoretical quantum yield of PCA under these conditions cannot exceed 10^{-5}, whereas the experimental Φ values (see below) for the complexes of **1a—d** with Ca^{2+} lie within $4 \cdot 10^{-4}$ — $6 \cdot 10^{-2}$ interval. This allows us to conclude that only aggregated species take part in the PCA. Since the (*cis*-**1a—d**)·Ca^{2+} complexes, as was shown above, are in the monomeric form, only the aggregated complexes of *trans*-**1a—d** with Ca^{2+} can be such species.

Scheme 3



One may assume that the complexes of *trans*-**1a—d** with Ca^{2+}, similar to that of *trans*-**1a,b** with Mg^{2+}, form pseudomacrocyclic dimeric structures in MeCN[4,12,13] which have two additional coordination bonds between sulfopropyl or sulfobutyl spacers and two cations in cavities of crown ether fragments.

Examination of molecular models of such supramolecules based on *trans*-**1a—d** and Ca^{2+} showed that, similar to $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$ (see Ref. 4), the most probable space structures for these compounds are structures of "head-to-tail" type with crossed arrangement of molecules (**6a—d**) (anti-"head-to-tail", Scheme 3). It is evident that the existence of $[(trans\text{-}\mathbf{1a—d})\cdot Ca^{2+}]_2$ may lead to regio- and stereoselective PCA with the formation of the corresponding cyclobutane derivatives.

As we have already shown by the example of CSD of the quinoline series,[5] the structure of the cycloadducts is not changed when passing from Mg^{2+} to Ca^{2+}; therefore, the **8a,b** structure, which was reliably established earlier for the photoproducts obtained from $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$ (see Ref. 4), was attributed to the photoproducts obtained from $[(trans\text{-}\mathbf{1a,b})\cdot Ca^{2+}]_2$.

Analysis of ^1H NMR spectra of all photoproducts obtained from $[(trans\text{-}\mathbf{1c,d})\cdot Ca^{2+}]_2$ was carried out using COSY and NOESY spectroscopy (for preparation of samples for ^1H NMR see Experimental). Like $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$ (see Ref. 4), only one isomer (**8d**) from 11 theoretically possible cyclobutane derivatives is formed from $[(trans\text{-}\mathbf{1d})\cdot Ca^{2+}]_2$, irrespective of the starting CSD concentration. Its ^1H NMR spectrum is of A_2B_2 type with coupling constant J_{AB} = 9.73 Hz.

The results of the theoretical conformation analysis, previously carried by us by the example of 1,2,3,4-tetraphenylcyclobutane,[5] allow us to make a conclusion about the stability of compound **8d** in the conformation of equatorial arrangement of substituents. This conclusion is based on the fact that the values of the experimental vicinal coupling constant in **8d** and the corresponding constant, calculated for the conformation of the model compound with equatorial substituents, are close (9.73 and 10.75 Hz, respectively). This means that the structure of the **8d** product is similar to that of cycloadducts **8a,b** which are formed from $[(trans\text{-}\mathbf{1a,b})\cdot Mg^{2+}]_2$ as the result of PCA (see Ref. 4), and to the conformation of the cyclobutane derivative obtained in the PCA reaction of the CSD containing quinoline residue substituted at position 2 (see Ref. 5).

Not long ago we proposed the procedure for computer modeling of [2+2] autoPCA of dimeric complexes of CSD with metal cations.[14] This procedure, based on

molecular mechanics, allowed us to determine the correlation between regio- and stereoselectivity of formation of cyclobutane derivatives and space structures of dimeric complexes of CSD with M^{2+}, to predict the possibility of formation of isomers with anti-"head-to-tail" arrangement of CSD molecules (**6a—d**) and with arrangement of molecules directly one over the other (**7a—d**) (*syn*-"head-to-tail", Scheme 3), as well as the formation of cyclobutane derivatives with corresponding structures on irradiation.

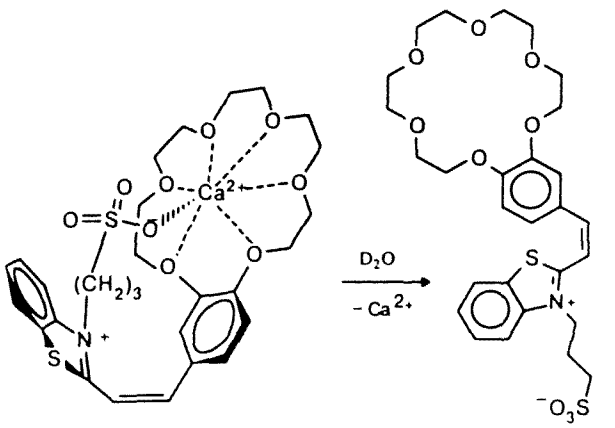
Actually, using ^{1}H NMR spectroscopy, among the three photoproducts obtained from $[(trans\text{-}\mathbf{1c})\cdot Ca^{2+}]_2$, we found two isomeric cyclobutane derivatives **8c**, **9c**, and *cis*-**1c** in the ratio 2 : 1 : 1.6. The cyclobutane part of the spectrum of **8c** is similar to the corresponding part of the **8d** spectrum and is also attributed to the A_2B_2 type with coupling constant J_{AB} = 9.85 Hz. The ^{1}H NMR spectrum of cyclobutane **9c** protons is described by a spin system of AA'BB' type with the set of vicinal coupling constants $^3J_{H(1),H(2)} = {}^3J_{H(3),H(4)}$ = 10.54 Hz and $^3J_{H(3),H(2)} = {}^3J_{H(1),H(4)}$ = 7.74 Hz. This set of vicinal constants is in good correlation with the values of the constants 10.29 and 7.61 Hz obtained earlier for the crown-containing 1,2,3,4-tetrasubstituted cyclobutane,[5] and with the values of the vicinal constants[15] calculated using molecular mechanics.[16] These calculations showed that 1,2,3,4-tetraphenylcyclobutane, in which the substituents are arranged as in the **9c** structure, has the vicinal constants $^3J_{cis}$ = 8.97 and $^3J_{trans}$ = 7.68 Hz after quick conformation averaging due to a low energy barrier; these constants are also in good correlation with the set of experimental coupling constants in **9c**.

The existence of two isomeric cyclobutane derivatives **8c** and **9c** among PCA products is the first example of violation of strict stereospecificity, which we observed earlier for the PCA reaction of CSD (see Ref. 4,5) that is probably due to the low total quantum yield of the reaction (see below). The C=C double bonds of *trans*-**1c** in both dimeric complexes **6c** and **7c** may be arranged in an unfavorable manner relative to each other, thus lowering both the efficiency of the PCA and its stereospecificity.

The analysis of the spectrum of the third photoproduct showed that the compound obtained is free CSD **1c** in the *cis*-configuration with coupling constant $^3J_{cis}$ = 12.0 Hz (see Ref. 9) typical of olefin protons (Scheme 4).

The presence of *cis*-**1c** in the reaction mixture may be explained by the fact that the dye cannot be completely consumed due to the low quantum yield of the PCA. In order to simplify the interpretation of ^{1}H NMR spectrum, the residue of $\mathbf{1c}\cdot Ca^{2+}$ containing CSD in the form of a mixture of *cis*- and *trans*-isomers was completely transformed into $(cis\text{-}\mathbf{1c})\cdot Ca^{2+}$ by irradiation with light at λ = 436 nm (see above). To date this is the only case in which a CSD is observed in its *cis*-form using ^{1}H NMR.

Scheme 4



$(cis\text{-}\mathbf{1c})\cdot Ca^{2+}$ *cis*-**1c**

The quantum yields of PCA for the complexes of *trans*-**1a—d** with Ca^{2+} were measured at $C_L = 2.0\cdot10^{-5}$ mol L^{-1} and $C_M = 1.2\cdot10^{-4}$ mol L^{-1} by kinetics of CSD consumption on irradiation with light at λ = 365 nm. CSD concentration was monitored by the absorption spectrum of a solution at 360—430 nm which is the sum of the absorption spectra of complexes of *trans*- and *cis*-isomers.

The quantum yields of PCA obtained with respect to total absorption of a dye at irradiation wavelength are the following:

CSD	**1a**	**1b**	**1c**	**1d**
Φ	0.001	0.01	0.0004	0.06

As can be seen, an increase in the size of the crown ether cavity in CSD containing a sulfopropyl spacer results in a noticeable lowering of the quantum yield of the auto-CPA reaction in complexes of CSD with Ca^{2+}, whereas a significant increase in the efficiency of this reaction is observed in the case of the sulfobutyl spacer. It is evident that the effects observed cannot be explained by the electron-donating effect of the additional methylene group in the sulfobutyl spacer.

Since the PCA reaction occurs only with the participation of $[(trans\text{-}\mathbf{1a—d})\cdot Ca^{2+}]_2$, the obtained dependence of Φ on the cavity size of the crown ether fragment and the spacer length might be, in principle, explained by the different degrees of dimerization of $(trans\text{-}\mathbf{1a—d})\cdot Ca^{2+}$ under these experimental conditions. Preliminary data on measuring degrees of dimerization allowed us to estimate the elementary quantum yields of the PCA with respect to the absorption of $[(trans\text{-}\mathbf{1a—d})\cdot Ca^{2+}]_2$ only (the results will be published later). It turned out that the elementary quantum yields, as well as the Φ values, fall into the order *trans*-**1d** > *trans*-**1b** > *trans*-**1a** > *trans*-**1c**, but this dependence is less sharp. Hence, the series of Φ values

obtained cannot be explained only by the different degrees of dimerization of *trans*-**1a—d**·Ca^{2+}.

As was previously mentioned by us,[1] dimeric complexes of CSD with M^{2+} have pseudomacrocyclic structure. Therefore, the increase in the efficiency of PCA for *trans*-**1a—d** containing different crown ether fragments, as the spacer length increases, might be attributed to the decrease in steric hindrance in the pseudomacrocycle. However, for CSD containing spacers with different lengths, the dependences of Φ on the cavity size of the crown ether fragment are opposite in sign, suggesting the important role of the factor of mutual orientation for the reacting C=C bonds in dimeric complex preorganized for the auto-PCA.

It should also be noted that CSD **1a—d** in the absence of metal cations under the above conditions do not enter the auto-PCA reaction. The effect of promoting the PCA reaction with alkaline-earth metal salts for aryl- and diarylethylenes with low reactivities was never described previously, and, in our opinion, it is of obvious theoretical interest.

The influence of Ca^{2+} ions on the auto-PCA reaction of CSD studied by us cannot be explained by the template effect[17] where a metal cation is bound directly to reaction centers of reacting molecules that favors the reaction. In our case, the effect of concentrating CSD in the reaction area and the effect of mutual orientation play the decisive role, as in the case of other models, *e.g.*, in a crystal state in the absence of metal cations.[18]

Thus, altering the structure of crown ether fragment also allows one to change the ionic selectivity of the formation of anion-"capped" complexes and that of the PCA reaction and to control the efficiency of PCA. The transformations studied demonstrate simultaneously new possibilities in the application of CSD as synthons for stereospecific photochemical synthesis of new type of host molecules (receptors).

Experimental

^{1}H NMR spectra were obtained on Bruker AMX-400 and Bruker AC-200 spectrometers with working frequencies 400.13 and 200.13 MHz at 300 K. Chemical shifts and coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. To record the ^{1}H NMR spectra of free photoproducts, photoreactions were completed, MeCN was evaporated, dry residues obtained were dissolved in MeCN-d_3, and D_2O was added to the solutions (5 % by volume). Under these conditions, the crown ether fragment is not able to form complexes with Ca^{2+} ions, which are strongly solvated by D_2O molecules. The analysis of the cyclobutane subspectrum was carried out using the CALM iteration program. The CALM program is a version of the UEAITR program adapted for personal computers (see Ref. 19). The mean-square deviation of the calculation was 0.027 Hz.

Electron absorption spectra of solutions were recorded on a Specord-M40 spectrophotometer. MeCN for the spectral studies was distilled with $KMnO_4$, twice over P_2O_5, and then once over CaH_2. $Ca(ClO_4)_2$ was dried *in vacuo* at 230 °C. Solutions of dyes and their complexes were irradiated with a DRSh-250 mercury lamp. Glass filters were used to separate individual spectral lines of the lamp. The intensity of actinic light was measured with a PP-1 radiation detector.

The purity of compounds was controlled by HPLC chromatography on a Milikhrom chromatograph (2×64 mm column, Separon C18, 5 mm, detection at 230 nm). The dyes were analyzed using a MeCN—H_2O (85 : 15) mixture as the eluent. The dyes give one peak with retention volume 140—160 mL.

2-Methyl-3-(3-sulfopropyl)benzothiazolium betaine (2a). A mixture of 2-methylbenzothiazole (**4**) (2.24 g, 1.91 mL, 0.015 mol) and γ-propansultone (**5a**) (1.95 g, 1.4 mL, 0.016 mol) in benzene (10 mL) was refluxed for 20 h. The residue formed was filtered off, washed with hot benzene and Me_2CO, and crystallized from abs. EtOH to give 1 g (25 %) of betaine **2a**, m.p. 276—278 °C (*cf.* Ref. 20). ^{1}H NMR (DMSO-d_6, 400 MHz), δ: 2.19 (m, 2 H, CH_2); 2.63 (m, 2 H, $CH_2SO_3^-$); 3.19 (s, 3 H, CH_3); 4.94 (m, 2 H, CH_2N); 7.78 and 7.88 (2 m, 2 H, H(C-5), H(C-6), J = 8.5, 8.2, 7.3 Hz); 8.40 and 8.44 (m, 2 H, H(C-4), H(C-7), J = 8.5, 8.2 Hz). Found (%): C, 48.81; H, 4.73; N, 5.04. $C_{11}H_{13}NO_3S_2$. Calculated (%): C, 48.69; H, 4.83; N, 5.16.

2-Methyl-3-(4-sulfopropyl)benzothiazolium betaine (2b) was synthesized similarly to compound **2a**, yield 25 %, m.p. 294 °C (*cf.* Ref. 21). ^{1}H NMR (DMSO-d_6, 400 MHz), δ: 1.78 (m, 2 H, CH_2); 1.97 (m, 2 H, CH_2); 2.50 (m, 2 H, $CH_2SO_3^-$); 3.23 (s, 3 H, CH_3); 4.76 (m, 2 H, CH_2N); 7.79 and 7.89 (2 m, 2 H, H(C-5), H(C-6)); 8.43 (m, 2 H, H(C-4), H(C-7)). Found (%): C, 50.65; H, 5.17; N, 4.79. $C_{12}H_{15}NO_3S_2$. Calculated (%): C, 50.51; H, 5.30; N, 4.91.

***trans*-2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-19-yl)ethenyl]-3-(4-sulfobutyl)benzothiazolium betaine (1b).** A mixture of betaine **2b** (0.12 g, 0.48 mmol) and 4-formylbenzo-15-crown-5 (**3a**) (0.16 g, 0.55 mmol) was dissolved in abs. EtOH, then pyridine (0.1 mL) was added, and the mixture was refluxed for 10 h. The product precipitated was filtered off, boiled with hexane to remove the crown ether **3a**, which does not enter the reaction, and then crystallized from abs. MeOH to obtain 0.12 g (45 %) of **1b**, m.p. 318 °C (*cf.* Ref. 7). Found (%): C, 54.19; H, 5.92; N, 2.27. $C_{27}H_{33}NO_8S_2 \cdot 2H_2O$. Calculated (%): C, 54.08; H, 6.22; N, 2.34.

***trans*-2-[2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-19-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium betaine (1c)** was synthesized similarly to compound **1b**, yield 60 %, m.p. 314 °C (from MeOH). ^{1}H NMR (CD_3CN, 400 MHz), δ: 2.40 (m, 2 H, CH_2); 2.83 (m, 2 H, $CH_2SO_3^-$); 3.6—3.75 (m, 12 H, g,γ′, δ,δ′, ε,ε′-CH_2O); 3.88 and 3.94 (2 m, 4 H, β,β′-CH_2O); 4.29 (m, 2 H, α′-CH_2O); 4.62 (m, 2 H, α-CH_2O); 5.14 (m, 2 H, CH_2N); 7.09 (d, 1 H, H(C-5) of benzocrown, $J_{H(5),H(6)}$ = 8.4 Hz); 7.41 (dd, 1 H, H(C-6) of benzocrown, $J_{H(6),H(5)}$ = 8.4 Hz, $J_{H(6),H(2)}$ = 1.8 Hz); 7.75 and 7.84 (2 m, 2 H, H(C-5), H(C-6) of benzothiazole, J = 8.4, 8.3 Hz); 8.05 (d, 1 H, H(C_b), $^3J_{trans}$ = 15.6 Hz); 8.09 and 8.18 (2 d, 2 H, H(C-7), H(C-4) of benzothiazole, J = 8.4, 8.3 Hz); 8.20 (d, 1 H, H(C-2) of benzocrown, $J_{H(2),H(6)}$ = 1.8 Hz); 8.51 (d, 1 H, H(C_a), $^3J_{trans}$ = 15.6 Hz). Found (%): C, 54.89; H, 6.27; N, 2.14. $C_{28}H_{35}NO_9S_2 \cdot H_2O$. Calculated (%): C, 54.98; H, 6.10; N, 2.29.

***trans*-2-[2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-19-yl)ethenyl]-3-(4-sulfobutyl)benzothiazolium betaine (1d)** was synthesized similarly to compound **1b**, yield 42 %, m.p. 185—187 °C. ^{1}H NMR (CD_3CN, 400 MHz), δ: 2.09 (m, 2 H, CH_2); 2.27 (m, 2 H, CH_2); 2.88 (m, 2 H, $CH_2SO_3^-$); 3.6—3.73 (m, 12 H, g,γ′, δ,δ′, ε,ε′-CH_2O); 3.89 and 3.97 (2 m, 4 H,

β,β'-CH_2O); 4.30 (m, 2 H, α'-CH_2O); 4.58 (m, 2 H, α-CH_2O); 4.93 (m, 2 H, CH_2N); 7.09 (d, 1 H, H(C-5) of benzocrown, $J_{H(5),H(6)}$ = 8.4 Hz); 7.38 (dd, 1 H, H(C-6) of benzocrown, $J_{H(6),H(5)}$ = 8.4 Hz, $J_{H(6),H(2)}$ = 1.8 Hz); 7.74 and 7.84 (2 m, 2 H, H(C-5), H(C-6) of benzothiazole, J = 8.5, 8.0 Hz); 8.01 (d, 1 H, H(C_b), $^3J_{trans}$ = 15.6 Hz); 8.08 and 8.18 (2 d, 2 H, H(C-7), H(C-4) of benzothiazole, J = 8.5, 8.0 Hz); 8.27 (d, 1 H, H(C-2) of benzocrown, $J_{H(2),H(6)}$ = 1.8 Hz); 8.48 (d, 1 H, H(C_a), $^3J_{trans}$ = 15.6 Hz). Found (%): C, 57.26; H, 6.02; N, 2.39. $C_{29}H_{37}NO_9S_2$. Calculated (%): C, 57.31; H, 6.14; N, 2.30.

Preparation of photoproducts 8c, 9c, and *cis*-1c (general procedure). A solution of CSD **1c** (C_L = $2 \cdot 10^{-3}$ mol L^{-1}) and $Ca(ClO_4)_2$ (C_M = $2.1 \cdot 10^{-3}$ mol L^{-1}) in MeCN was irradiated with a DRSh-250 mercury lamp at λ = 365 nm for 1 day. After that the solution was additionally irradiated with light at λ = 436 nm for 10 min, and MeCN was evaporated *in vacuo*.

1,*cis*-3-di[3-(3-Sulfopropyl)benzothiazolium-2-yl]-*trans*-2-*trans*-4-di(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-19-yl)cyclobutane dibetaine (8c). ^{1}H NMR (CD_3CN+D_2O (5 %), 400 MHz), δ: 1.73 (m, 4 H, 2 CH_2); 2.26 (m, 4 H, 2 $CH_2SO_3^-$); 3.80 (m, 8 H, 2 ε,ε'-CH_2O); 3.70—4.45 (m, 32 H, 2 α,α', β,β', g,γ', δ,δ'-CH_2O); 4.27 (t, 2 H, H(C-2), H(C-4) of cyclobutane, $^3J_{H(2),H(1)} = {}^3J_{H(2),H(3)} = {}^3J_{H(4),H(1)} = {}^3J_{H(4),H(3)}$ = 9.85 Hz); 4.40 (m, 4 H, 2 CH_2N); 5.02 (t, 2 H, H(C-1), H(C-3) of cyclobutane, $^3J_{H(1),H(2)} = {}^3J_{H(1),H(4)} = {}^3J_{H(3),H(2)} = {}^3J_{H(3),H(4)}$ = 9.85 Hz); 7.22 (d, 2 H, 2 H(C-5) of benzocrown, $J_{H(5),H(6)}$ = 8.4 Hz); 7.37 (d, 2 H, 2 H(C-2) of benzocrown, $J_{H(2),H(6)}$ = 1.9 Hz); 7.68 (dd, 2 H, 2 H(C-6) of benzocrown); 7.85 and 7.92 (2 m, 4 H, 2 H(C-5), 2 H(C-6) of benzothiazole, J = 8.5, 8.1 Hz); 8.19 and 8.33 (2 d, 4 H, 2 H(C-7), 2 H(C-4) of benzothiazole, J = 8.5, 8.1 Hz).

1,*trans*-3-di[3-(3-Sulfopropyl)benzothiazolium-2-yl]-*trans*-2-*cis*-4-di(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-19-yl)cyclobutane dibetaine (9c). ^{1}H NMR (CD_3CN+D_2O (5 %), 400 MHz), δ: 3.70—4.45 (m, 40 H, 2 α,α',β,β',γ,γ',δ,δ',ε,ε'-CH_2O); 5.30 (m, 2 H, H(C-2), H(C-4) of cyclobutane, $^4J_{H(2),H(4)}$ = 0.58±0.01 Hz; 5.67 (m, 2 H, H(C-1), H(C-3) of cyclobutane, $^3J_{H(3),H(2)} = {}^3J_{H(1),H(4)}$ = 7.74±0.01 Hz, $^3J_{H(1),H(2)} = {}^3J_{H(3),H(4)}$ = 10.54±0.01 Hz, $^4J_{H(1),H(3)}$ = 0.60±0.01 Hz); 6.90 (d, 2 H, 2 H(C-5) of benzocrown); 7.17 (dd, 2 H, 2 H(C-6) of benzocrown); 7.32 (d, 2 H, 2 H(C-2) of benzocrown); 7.78 and 7.82 (2 m, 4 H, 2 H(C-5), 2 H(C-6) of benzothiazole); 8.09 and 8.32 (2 d, 4 H, 2 H(C-7), 2 H(C-4) of benzothiazole, $J = J$ = 8.2 Hz). We were not able to make an unambiguous assignment of the protons of CH_2, $CH_2SO_3^-$, and CH_2N groups since their position is masked by the corresponding protons of compounds **8c** and *cis*-**1c**.

***cis*-2-[2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-19-yl)ethenyl]-3-(3-sulfopropyl)benzothiazolium betaine (*cis*-1c).** ^{1}H NMR (CD_3CN+D_2O (5 %), 400 MHz), δ: 1.51 (m, 2 H, CH_2); 2.62 (m, 2 H, $CH_2SO_3^-$); 3.7—4.45 (m, 16 H, α,α',β,β',γ,γ',δ,δ'-CH_2O); 3.76 (m, 4 H, ε,ε'-CH_2O); 4.50 (m, 2 H, CH_2N); 6.81 (dd, 1 H, H(C-6) of benzocrown); 6.87 (d, 1 H, H(C-5) of benzocrown); 6.87 (d, 1 H, H(C-a), $^3J_{cis}$ = 12.0 Hz); 7.14 (d, 1 H, H(C-2) of benzocrown, $J_{H(2),H(6)}$ = 1.8 Hz); 7.65 (d, 1 H, H(C-b), $^3J_{cis}$ = 12.0 Hz); 7.83 and 7.91 (2 m, 2 H, H(C-5), H(C-6) of benzothiazole); 8.18 and 8.25 (2 d, 2 H, H(C-7), H(C-4) of benzothiazole, J = 8.2, 8.5 Hz).

1,*cis*-3-di[3-(4-Sulfobutyl)benzothiazolium-2-yl]-*trans*-2-*trans*-4-di(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-19-yl)cyclobutane dibetaine (8d). A solution of CSD **1d** (C_L = $2 \cdot 10^{-3}$ mol L^{-1}) and $Ca(ClO_4)_2$ (C_M = $2.1 \cdot 10^{-3}$ mol L^{-1}) in MeCN was irradiated with a DRSh-250 mercury lamp at λ = 365 nm. After complete comsumption of the dye (spectrophotometric control) MeCN was evaporated *in vacuo*. ^{1}H NMR (CD_3CN+D_2O (5 %), 400 MHz), δ: 1.18 (m, 4 H, 2 CH_2); 1.50 (m, 4 H, 2 CH_2); 2.25 (m, 4 H, 2 $CH_2SO_3^-$); 3.82—3.98 (m, 24 H, 2 g,γ',δ,δ',ε,ε'-CH_2O); 4.07 (2 m, 8 H, 2 β,β'-CH_2O); 4.32 and 4.62 (2 m, 8 H, 2 α,α'-CH_2O); 4.36 (m, 4 H, 2 CH_2N); 4.41 (t, 2 H, H(C-2), H(C-4) of cyclobutane, $^3J_{H(2),H(1)} = {}^3J_{H(2),H(3)} = {}^3J_{H(4),H(1)} = {}^3J_{H(4),H(3)}$ = 9.73 Hz); 5.01 (t, 2 H, H(C-1), H(C-3) of cyclobutane, $^3J_{H(1),H(2)} = {}^3J_{H(1),H(4)} = {}^3J_{H(3),H(2)} = {}^3J_{H(3),H(4)}$ = 9.73 Hz); 7.18 (d, 2 H, 2 H(C-5) of benzocrown, $J_{H(5),H(6)}$ = 8.5 Hz); 7.50 (dd, 2 H, 2 H(C-6) of benzocrown, $J_{H(6),H(5)}$ = 8.5 Hz, $J_{H(6),H(2)}$ = 1.8 Hz); 7.59 (d, 2 H, 2 H(C-2) of benzocrown, $J_{H(2),H(6)}$ = 1.8 Hz); 7.83 and 7.90 (2 m, 4 H, 2 H(C-5), 2 H(C-6) of benzothiazole, J = 8.5, 8.2 Hz); 8.10 and 8.31 (2 d, 4 H, 2 H(C-7), 2 H(C-4) of benzothiazole, J = 8.5, 8.2 Hz).

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References

1. O. B. Stanislavskii, E. N. Ushakov, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 605 [*Russ. Chem. Bull.*, 1996, **46** (Engl. Transl.)].
2. M. V. Alfimov and S. P. Gromov, *Supramolecular Chemistry*, ed. V. Balzani and L. De Cola, NATO ASI Ser., 1992, 343.
3. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, I. K. Lednev, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **317**, 1134 [*Dokl. Chem.*, 1991, **317** (Engl. Transl.)].
4. M. V. Alfimov, S. P. Gromov, O. B. Stanislavskii, E. N. Ushakov, and O. A. Fedorova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1449 [*Russ. Chem. Bull.*, 1993, **42**, 1385 (Engl. Transl.)].
5. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, A. V. Buevich, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2225 [*Russ. Chem. Bull.*, 1995, **44** (Engl. Transl.)].
6. S. P. Gromov, A. A. Golosov, O. A. Fedorova, D. E. Levin, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 129 [*Russ. Chem. Bull.*, 1995, **44**, 124 (Engl. Transl.)].
7. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavskii, and M. V. Alfimov, *Dokl. Akad. Nauk SSSR*, 1991, **321**, 104 [*Dokl. Chem.*, 1991, **321** (Engl. Transl.)].
8. S. P. Gromov, O. A. Fedorova, A. I. Vedernikov, V. V. Samoshin, N. S. Zefirov, and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 121 [*Russ. Chem. Bull.*, 1995, **44**, 116 (Engl. Transl.)].
9. H. Gunther, NMR *Spectroscopy. An Introduction*, J. Wiley and Sons, 1980, Chapter 2.

10. I. I. Baskin, K. Ya. Burstein, A. A. Bagatur'yants, S. P. Gromov, and M. V. Alfimov, *J. Mol. Structure*, 1992, **274**, 93.
11. E. Fischer, *J. Phys. Chem.*, 1967, **71**, 3704.
12. A. V. Barzykin, M. A. Fox, E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *J. Am. Chem. Soc.*, 1992, **114**, 6381.
13. E. N. Ushakov, O. B. Stanislavskii, S. P. Gromov, O. A. Fedorova, and M. V. Alfimov, *Dokl. Akad. Nauk*, 1992, **323**, 702 [*Dokl. Chem.*, 1992, **323** (Engl. Transl.)].
14. I. I. Baskin, A. A. Bagatur'yants, S. P. Gromov, and M. V. Alfimov, *Dokl. Akad. Nauk*, 1994, **335**, 313 [*Dokl. Chem.*, 1994, **335** (Engl. Transl.)].
15. C. A. G. Haasnoot, F. A. A. M. de Leeuw, and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
16. N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.
17. R. Hoss and F. Vögtle, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 375.
18. S. P. Gromov, O. A. Fedorova, M. V. Alfimov, V. V. Tkachev, and L. O. Atovmyan, *Dokl. Akad. Nauk*, 1991, **319**, 1141 [*Dokl. Chem.*, 1991, **319** (Engl. Transl.)].
19. R. B. Johannsen, J. A. Feretti, and R. K. Harris, *J. Magn. Reson.*, 1970, **3**, 84.
20. H. Kampfer and M. Hase, Ger. Offen. DE 28 03 493 A 1, 1979; *Chem. Abstr.*, 1980, **92**, 76478q.
21. H. Kampfer, Eur. Pat. 0 055 428, 1982; *Chem. Abstr.*, 1982, **97**, 182387q.

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