Crown-ether styryl dyes

15.* Synthesis and two pathways of regio- and stereospecific cation-dependent [2+2]-autophotocycloaddition of chromogenic 15-crown-5-ether betaines of quinoline series

S. P. Gromov,[a]★ O. A. Fedorova,[a] E. N. Ushakov,[b] A. V. Buevich,[c] and M. V. Alfimov[a]

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

[b]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 (096) 515 3588*

[c]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Seiences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328*

Styryl dyes (**4a,b**) containing a 15-crown-5 fragment and isomeric 2- and 4-quinolinium residues with an *N*-sulfopropyl substituent undergo [2+2]-autophotocycloaddition to give cyclobutane derivatives (**9a,b**) in acetonitrile only in the presence of $Mg(ClO_4)_2$ or $Ca(ClO_4)_2$. The stereospecificity of both pathways of photocycloaddition and its efficiency are explained by the preorganization of the supramolecular dimers derived from the *trans*-isomers of the dyes when they are bound into complexes with Mg and Ca cations.

Key words: crown ether styryl dyes; complex-formation; [2+2]-photocycloaddition; cyclobutane derivatives; ^1H NMR spectra.

The stereochemistry of the major product of the concerted [2π+2π]-photocycloaddition (PCA) of alkenes, which involves the lowest singlet excited state of one of the two reacting molecules, is determined by taking into account the orbital symmetry and orbital overlap.[2,3] In solution, these intermolecular transformations are characterized by low quantum yields, since interaction between the reactants is a bimolecular reaction, and the excited state is rapidly deactivated, due to the occurrence of competing processes, first of all, *trans-cis*-photoisomerization. Intermolecular PCA reactions occurring by a concerted mechanism normally have low regio- and stereoselectivities, because reacting molecules can have various mutual arrangements, and photoisomerization, occurring in parallel, involves both *trans*- and *cis*- isomers of alkenes.[3]

A promising tool for controlling the regio- and stereoselectivity of PCA as well as its efficiency may be provided by spontaneous assembling of alkenes into a supramolecular structure with such a preorganization of reactants that the mutual spatial arrangement of molecules would be favorable for the formation of only one cyclobutane isomer in a high yield.

We realized this situation using crown ether styryl dyes (CSD, **1**), which form supramolecular dimers (**2**) with a crossed arrangement of molecules (*anti*-"head-to-tail") in the presence of Mg^{2+} ions, due to intermolecular interaction between the sulfo group of one of the molecules and a Mg^{2+} ion located in the crown cavity of the other molecule.[4] It was shown that photoirradiation of solutions of dimer **2** results in stereospecific PCA giving only one of the 11 possible derivatives of cyclobutane (**3**), which is expected in conformity with the concerted suprafacial (s,s) addition of the reactants.

One may have suggested that variation of the structure of the heterocyclic residue would make it possible to change the supramolecular spatial structure of the dimer in a desired direction and thus to control the efficiency of interaction and stereochemistry of the final product of PCA.

Therefore, we synthesized isomeric chromogenic 15-crown-5-ethers of the quinoline series (**4a,b**). CSD **4a,b** were prepared by condensation of betaines (**5a,b**) with 4-formylbenzo-15-crown-5 (**6**) in the presence of pyridine in 41 % and 12 % yields, respectively.

Efficient formation of CSD **4b** in the latter case is probably hampered by the lower C—H acidity of the methyl group in position 4 of the pyridine ring of **5b** and by steric hindrances caused by the benzene ring located

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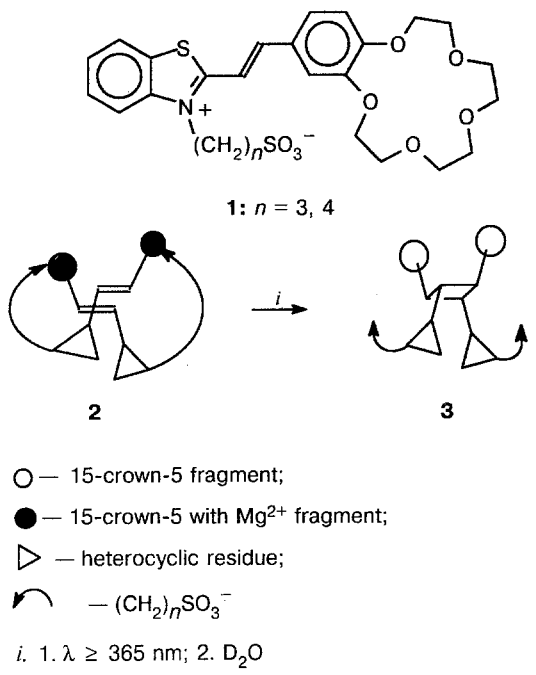
Scheme 1



in the *ortho*-position with respect to this methyl group (Scheme 2).

The starting betaines **5a,b** were obtained by heating 2-methylquinoline (**7a**) or 4-methylquinoline (**7b**) with γ-sultone (**8**) in 20 % or 75 % yield, respectively. The substantially lower yield of betaine **5a** is apparently due to steric restrictions arising during quaternization of the heterocyclic base owing to the presence of the methyl group in position 2 of the pyridine ring of compound **7a**.

The structures of the resulting compounds **4a,b** were confirmed by ^{1}H NMR spectroscopy (see Experimental). The data of elemental analysis correspond to the assumed structures. Judging from the coupling constants of olefinic protons, $^3J_{trans}$ = 15.6 to 15.8 Hz (see Ref. 5), the resulting CSD **4a,b** have the *trans*-configuration.

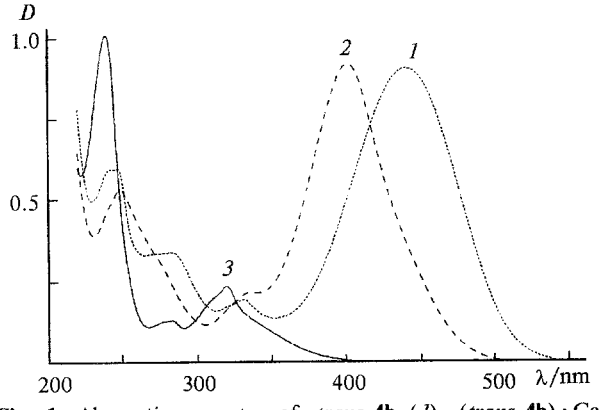
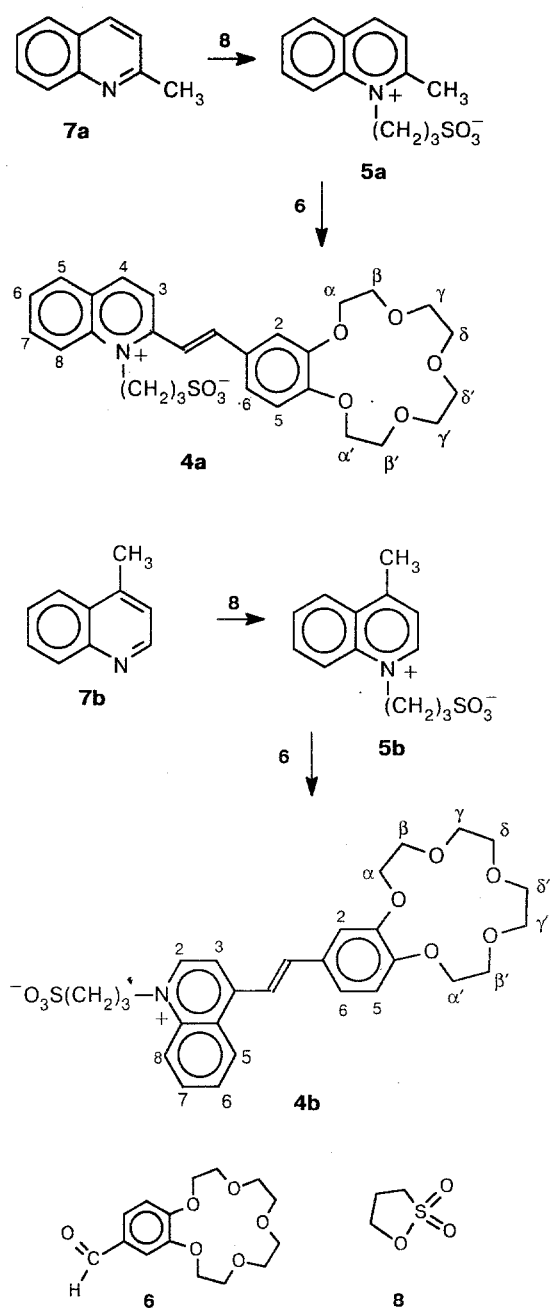


Fig. 1. Absorption spectra of *trans*-**4b** (*1*), (*trans*-**4b**) · Ca^{2+} (*2*), and cycloadduct **9b** · $2Ca^{2+}$ (*3*) in MeCN in a 1 cm thick cell at 295 K and $C_M = 1 \cdot 10^{-4}$ mol L^{-1} (*2*, *3*).

Scheme 2



Solutions of CSD **4a,b** in MeCN are colored intense yellow, which is responsible for long-wavelength bands with maxima at 435 nm for **4a** and 441 nm for **4b** in their absorption spectra (Fig. 1). When alkaline earth metal perchlorates are added into these solutions, substantial hypsochromic shifts of absorption bands are observed (on the addition of $Mg(ClO_4)_2$, these shifts are 39 nm for **4a** and 40 nm for **4b**). The long-wavelength band in the electronic absorption spectra of CSD contains a substantial admixture of a configuration with charge transfer from the benzene ring to the heterocyclic

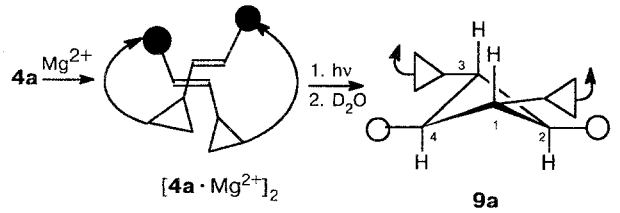
ring.[6] Binding the crown-ether moiety to Mg^{2+} or Ca^{2+} cations results in appearance of Coulomb interaction, which makes this displacement of the electron density energetically unfavorable (the electron density shifts from the cation). This accounts for the experimentally observed hypsochromic shift in the electronic absorption spectrum.

An examination of molecular models of dimeric complexes based on CSD **4a** and Mg^{2+} showed that the sulfopropyl group is long enough for two additonal coordination bonds with metal cations to be formed, the "head-to-tail" configuration with crossed arrangement of **4a** molecules (*anti*-"head-to-tail," see Scheme 3) being the most likely form of the dimer.

When a MeCN solution of **4a** containing $Mg(ClO_4)_2$ with concentrations of the dye and the metal salt of $C_L = 2 \cdot 10^{-3}$ mol L^{-1} and $C_M = 2.5 \cdot 10^{-3}$ mol L^{-1}, respectively, is irradiated in a 0.01 cm thick cell with light having $\lambda = 405$ nm and the intensity $I = 3.5 \cdot 10^{15}$ $cm^{-2} \cdot s^{-1}$, the absorption spectrum changes rapidly, until a photo steady state, caused by reversible *trans-cis*-photoisomerization of (*trans*-**4a**) · Mg^{2+}, is established. During subsequent irradiation the absorption spectrum of the reaction solution undergoes very slow variations, that we attribute to the process of autoPCA of **4a** molecules. The overall quantum yield in the PCA of **4a** (Φ) under these conditions was ~0.0007, as was estimated from kinetics of the decay of the optical density of the reaction solution at 405 nm, occurring after establishment of the photo steady state in the *trans-cis*-photoisomerization (the product of PCA does not absorb in this spectral region).

^1H NMR spectra of the reaction product were analyzed using COSY and NOESY spectroscopies. As in the case of CSD **1**, irrespective of the initial concentration of **4a**, only one isomer of cyclobutane derivative (**9a**) is formed (Scheme 3); it exhibits an A_2B_2 type spectrum with a spin-spin coupling constant J_{AB} of 9.85 Hz. Theoretical conformational analysis, which we carried out by molecular mechanics[7] in relation to 1,2,3,4-tetraphenylcyclobutane, showed that the energy of the conformation with equatorial substituents of an isomer of the **9a** type is lower than that of the conformation with axial substituents by 5.6 kcal mol^{-1}.

Scheme 3

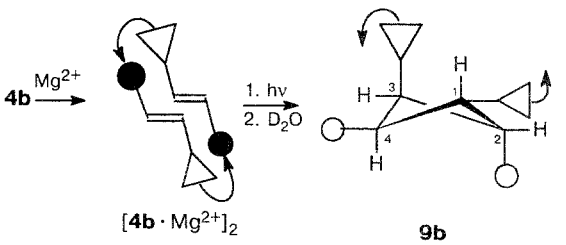


The conformation with equatorial substituents is characterized by an internal dihedral angle in the cyclobutane ring of 22.6° and a proton vicinal spin-spin coupling constant of 10.75 Hz (calculated from the Carplus equation[8]). For the conformation with axial substituents, the corresponding parameters are 17.6° and 2.2 Hz. The fact that the experimental vicinal coupling constant of compound **9a** is close to the corresponding constant calculated for the conformation with equatorial substituents of the model compound (9.85 and 10.75 Hz, respectively) allows one to conclude that compound **9a** is stable as a conformation with the equatorial arrangement of substituents.

When a solution of **4b** in MeCN with $C_L = 2 \cdot 10^{-3}$ mol L^{-1} containing $Mg(ClO_4)_2$ with $C_M = 2.5 \cdot 10^{-3}$ mol L^{-1} is irradiated with light having a wavelength of 405 nm, variations in the absorption spectrum cannot be divided into rapid and slow steps. In the case of **4b**, the quantum yield of PCA reaction is much higher than that for **4a** and is comparable to quantum yields of *trans-cis*-photoisomerization of **4b**, therefore the procedure used above to measure the quantum yield of the consumption of dye **4a** in PCA, cannot be applied now. In addition, to exclude participation of *cis*-**4b** in PCA, the reaction was carried out in a dilute solution with a concentration of **4b** · Mg^{2+} or **4b** · Ca^{2+} of no more than $1 \cdot 10^{-4}$ mol L^{-1}. Under these conditions, almost all complexes *cis*-**4b** are monomeric (due to the same reasons as in the case of CSD **1**).[4] We determined the quantum yield of PCA for Ca^{2+} complex **4b** ($C_L = 1.1 \cdot 10^{-5}$ mol L^{-1}, $C_M = 1 \cdot 10^{-4}$ mol L^{-1}) irradiated with light having $\lambda = 436$ nm (the procedure of the measurements is presented in the Experimental). The high value of quantum yield ($\Phi = 0.15$) indicates that degree of dimerization of the complexes of this dye remains rather high even in very dilute solutions and that the spatial structure of dimeric complexes is probably rather favorable for the PCA reaction.

Recently we suggested a molecular-mechanic procedure for computer simulation of [2+2]-autoPCA of CSD complexes with metal cations.[9] This procedure allowed us to predict the stereochemistry of the cyclobutane derivative expected in conformity with the calculated predominant conformation of the dimer [(*trans*-**4b**) · Mg^{2+}]$_2$, in which **4b** molecules are arranged precisely one above the other (*syn*-"head-to-tail," see Scheme 4).

Scheme 4

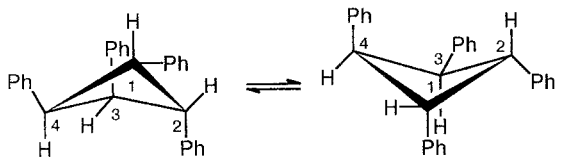


In fact, by using ^{1}H NMR spectroscopy, structure **9b** was ascribed to the cyclobutane derivative obtained from **4b** *via* the PCA reaction in the presence of magnesium or calcium perchlorate. In both cases, no photoproducts were detected among the reaction products, apart from **9b**.

The ^{1}H NMR spectrum of the cyclobutane protons of compound **9b** is described by a spin system of the AA′BB′ type with the following set of vicinal 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. This set of vicinal coupling constants correlates well with the constants of the previously studied 1,2,3,4-tetrasubstituted cyclobutane, which are equal to 10.5 and 7.7 Hz.[10]

The conclusion concerning the relative arrangement of the substituents in cyclobutane **9b** is also supported by theoretical calculations of vicinal constants[8] carried out by us based on the geometry of this molecule determined by molecular mechanics. These calculations showed that 1,2,3,4-tetraphenylcyclobutane with an arrangement of substituents similar to that in structure **9b** has internal dihedral angles of 20.6—20.7° and vicinal constants $^3J_{H(1),H(2)trans} = 10.91$, $^3J_{H(1),H(4)cis} = 8.85$, $^3J_{H(2),H(3)cis} = 9.09$, and $^3J_{H(3),H(4)trans} = 2.65$ Hz. At ambient temperature, due to the low energy barrier, rapid conformational averaging of this compound occurs (Scheme 5). This results in averaging of the experimentally observed NMR parameters: $^3J_{trans} = 7.68$, $^3J_{cis} = 8.97$ Hz. This set of coupling constants corresponds well to experimental vicinal constants of compound **9b**.

Scheme 5



In conclusion, it should be noted that in the absence of alkaline earth metal cations, CSD **4a,b** do not undergo PCA under the above conditions; this can readily be explained by high degree of conjugation involving the double C=C bond in dye molecules and by Coulomb repulsion between the positively charged molecular fragments, which prevents them from moving closer together.

The influence of Mg^{2+} and Ca^{2+} ions on the autoPCA reaction of CSD cannot be explained by the template effect,[11] when a metal cation directly bound to the reaction centers of the reacting molecules facilitates a reaction. In our case, the crucial factors are probably that CSD is concentrated in the region where the reaction occurs and the effect of mutual orientation, as in the case of other models, for example, having no metal cations in the crystalline state.[12,13]

Thus, directed modification of the structure of the heterocyclic residue makes it possible to change principally the direction of PCA and to control the efficiency of interaction and stereochemistry of the final product. In addition, the transformations studied demonstrate new possibilities in the use of CSD as synthons for stereospecific photochemical synthesis of a promising new type of host molecules (receptors).

Experimental

^{1}H NMR spectra were recorded on Bruker AMX-400 and Bruker AC-200 spectrometers (operating at 400.13 and 200.13 MHz) at 300 K. Chemical shifts were measured with an accuracy of 0.01 ppm, and spin-spin coupling constants were determined with an accuracy of 0.1 Hz. Electronic absorption spectra were obtained on a Specord M40 spectrophotometer. Solutions of the dyes and their complexes for spectrophotometric studies were prepared in MeCN, which was initially purified by distillation over $KMnO_4$, then by two distillations over P_2O_5, and finally by distillation over CaH_2. $Mg(ClO_4)_2$ and $Ca(ClO_4)_2$ were dried *in vacuo* at 230 °C. Irradiation was carried out with the light of a DRSh-250 mercury lamp. To isolate individual lines of the spectrum of this lamp, glass filters were used. The intensity of the actinic light was measured using a PP-1 chamber receiver.

Overall quantum yields Φ of PCA in dilute solutions of **4b** containing Ca^{2+} were estimated by the following procedure. An initial solution of the complex ($C_L = 1.1 \cdot 10^{-5}$ mol L^{-1}, $C_M = 1 \cdot 10^{-4}$ mol L^{-1}) in a 1 cm thick cell was irradiated with light at $\lambda = 436$ nm. Photolysis was stopped, when the optical density of the solution in the region of the long-wave absorption maximum approximately halved. Then 5 % water was added into the solution, which led to complete destruction of the complexes of dye **4b** and photoadduct **9b**, and then the mixture was irradiated with light at $\lambda = 436$ nm, until the photo steady state was established. This state is caused only by the reversible *trans—cis*-photoisomerization of the dye, since free CSD does not undergo the PCA reaction. Moreover, the reverse reaction of photodissociation of the cycloadduct, which does not absorb light with $\lambda = 436$ nm, also does not proceed under these conditions. Optical density of the obtained solution at 440 nm (D_t) was measured. Then an equal amount of water was added into the initial solution of the complex, and it was irradiated until the photo steady state of *trans—cis*-photoisomerization was established; optical density at 440 nm (D_0) was measured. The consumption of the dye in PCA ΔC in the first solution was found from the relationship $\Delta C = C_L(D_0 - D_t)/D_0$. The Φ value was determined using the optical density D of the complex at 436 nm, average of those prior to and after irradiation, and the average rate of dye consumption $\Delta C/\Delta t$. The Φ value was calculated from the formula: $\Phi = (\Delta C/\Delta t) \cdot E$, where $E = 1 \cdot 10^3 \cdot N_A^{-1} \cdot (1 - 10^{-D}) \cdot d^{-1}$ (I is the light intensity (cm$^{-2} \cdot$ s^{-1}), d is the cell thickness, N_A is the Avogadro number).

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

2-Methyl-1-(3-sulfopropyl)quinolinium betaine (5a). A mixture of 2-methylquinoline (**7a**) (2.8 mL, 0.02 mol) and γ-propanesultone (**8**) (2.9 mL, 0.03 mol) in 10 mL of benzene was boiled for 20 h. The precipitate was filtered off, washed

with hot benzene and acetone, and recrystallized from ethanol to give 1.31 g (20 %) of betaine **5a**, m.p. 278 °C (*cf.* Ref. 14). ^{1}H NMR (DMSO-d_6, 400 MHz), δ: 2.22 (m, 2 H, CH_2); 2.75 (m, 2 H, $CH_2SO_3^-$); 3.13 (s, 3 H, CH_3); 5.17 (m, 2 H, CH_2N); 7.96 and 8.19 (2 m, 2 H, H(C-6) and H(C-7)); 8.07 (m, 1 H, H(C-3), $J_{H(3),H(4)}$ = 8.5 Hz); 8.37 (dd, 1 H, H(C-5), $J_{H(5),H(6)}$ = 8.5 Hz); 8.78 (d, 1 H, H(C-8), $J_{H(8),H(7)}$ = 8.9 Hz); 9.05 (d, 1 H, H(C-4), $J_{H(4),H(3)}$ = 8.5 Hz). Found (%): C, 58.58; H, 5.50; N, 5.63. $C_{13}H_{15}NO_3S$. Calculated (%): C, 58.85; H, 5.70; N, 5.28.

4-Methyl-1-(3-sulfopropyl)quinolinium betaine (5b). This compound was obtained similarly to **5a** in 75 % yield, m.p. 334 °C. ^{1}H NMR (DMSO-d_6, 400 MHz), δ: 2.30 (m, 2 H, CH_2); 2.58 (m, 2 H, $CH_2SO_3^-$); 3.02 (s, 3 H, CH_3); 5.20 (m, 2 H, CH_2N); 8.03 (m, 1 H, H(C-3)); 8.06 and 8.25 (2 m, 2 H, H(C-6) and H(C-7)); 8.54 and 8.71 (2 d, 2 H, H(C-5) and H(C-8)); 9.38 (d, 1 H, H(C-2)). Found (%): C, 58.45; H, 5.74; N, 5.20. $C_{13}H_{15}NO_3S$. Calculated (%): C, 58.85; H, 5.70; N, 5.28.

2-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-16-yl)ethenyl]-1-(3-sulfopropyl)quinolinium betaine (4a). A mixture of 2-methyl-1-(3-sulfopropyl)-quinolinium betaine (**5a**) (0.15 g, 0.57 mmol) and 4-formylbenzo-15-crown-5 (**6**) (0.16 g, 0.54 mmol) was dissolved in 5 mL of anhydrous EtOH, and 1.5 mL of pyridine was added. The reaction mixture was boiled for 20 h and concentrated *in vacuo*. The residue was treated with hot benzene to remove impurities and recrystallized successively from MeOH and MeCN to give 0.13 g (41 %) of **4a**, m.p. 348 °C. ^{1}H NMR (MeCN-d_3, 400 MHz), δ: 2.52 (m, 2 H, CH_2); 2.96 (m, 2 H, $CH_2SO_3^-$); 3.72 (m, 8 H, γ, γ′, δ, δ′-CH_2O); 3.90 (m, 4 H, β, β′-CH_2O); 4.26 (m, 2 H, α-CH_2O); 4.50 (m, 2 H, α′-CH_2O); 5.41 (m, 2 H, CH_2N); 7.06 (d, 1 H, benzocrown H(C-5), $J_{H(5),H(6)}$ = 8.3 Hz); 7.49 (dd, 1 H, benzocrown H(C-6), $J_{H(6),(5)}$ = 8.3 Hz, $J_{H(6),H(2)}$ = 1.9 Hz); 7.89 (m, 1 H, quinoline H(C-6)); 8.00 (d, 1 H, CH=CH, $^3J_{trans}$ = 15.6 Hz); 8.12 (d, 1 H, benzocrown H(C-2), $J_{H(2),H(6)}$ = 1.9 Hz); 8.14 (m, 1 H, quinoline H(C-7)); 8.21 (dd, 1 H, quinoline H(C-5), $J_{H(5),H(6)}$ = 7.0 Hz); 8.27 (d, 1 H, CH=CH, $^3J_{trans}$ = 15.6 Hz); 8.34 (m, 1 H, quinoline H(C-3), $J_{H(3),H(4)}$ = 9.0 Hz); 8.50 (m, 1 H, quinoline H(C-8), $J_{H(8),H(7)}$ = 9.0 Hz); 8.74 (m, 1 H, quinoline H(C-4), $J_{H(4),H(3)}$ = 9.0 Hz). Found (%): C, 58.04; H, 6.49; N, 2.39. $C_{28}H_{33}NO_8S \cdot 2H_2O$. Calculated (%): C, 58.02; H, 6.43; N, 2.42.

4-[2-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-16-yl)ethenyl]-1-(3-sulfopropyl)quinolinium betaine (4b). A mixture of 4-methyl-1-(3-sulfopropyl)-quinolinium betaine **5b** (0.086 g, 0.32 mmol) and 4-formylbenzo-15-crown-5 (**6**) (0.1 g, 0.34 mmol) was dissolved in 3 mL of anhydrous EtOH, 1 mL of pyridine was added, and the mixture was boiled for 20 h. The target compound was isolated similarly to **4a**, the yield of **4b** was 0.020 g (12 %), m.p. 258—260 °C. ^{1}H NMR (MeCN-d_3, 400 MHz), δ: 2.50 (m, 2 H, CH_2); 2.74 (m, 2 H, $CH_2SO_3^-$); 3.72 (m, 8 H, γ, γ′, δ, δ′-CH_2O); 3.91 (m, 4 H, β, β′-CH_2O); 4.25 (m, 2 H, α-CH_2O); 4.31 (m, 2 H, α′-CH_2O); 5.27 (m, 2 H, CH_2N); 7.08 (d, 1 H, benzocrown H(C-5), $J_{H(5),H(6)}$ = 8.3 Hz); 7.43 (dd, 1 H, benzocrown H(C-6), $J_{H(6),H(5)}$ = 8.3 Hz, $J_{H(6),H(2)}$ = 2.0 Hz); 7.51 (d, 1 H, benzocrown H(C-2), $J_{H(2),H(6)}$ = 2.0 Hz); 7.88 (d, 1 H, CH=CH, $^3J_{trans}$ = 15.8 Hz); 7.96 (d, 1 H, CH=CH, $^3J_{trans}$ = 15.8 Hz); 8.00 (m, 1 H, quinoline H(C-6)); 8.19 (d, 1 H, quinoline H(C-3), $J_{H(3),H(2)}$ = 6.6 Hz); 8.23 (m, 1 H, quinoline H(C-7)); 8.65 (d, 1 H, quinoline H(C-8), $J_{H(8),H(7)}$ = 8.9 Hz); 8.80 (dd, 1 H, quinoline H(C-5), $J_{H(5),H(6)}$ = 8.6 Hz, $J_{H(5),H(7)}$ = 0.9 Hz); 9.18 (d, 1 H, quinoline H(C-2), $J_{H(2),H(3)}$ = 6.6 Hz). Found (%): C, 61.43; H, 6.08; N, 2.50. $C_{28}H_{33}NO_8S$. Calculated (%): C, 61.86; H, 6.12; N, 2.58.

1,*cis*-3-Di[1-(3-sulfopropyl)quinolinium-2-yl]-*trans*-2-*trans*-4-di(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-16-yl)cyclobutane dibetaine (9a). A solution of CSD **4a** (0.01 mmol) and $Mg(ClO_4)_2$ (0.0125 mmol) in dry MeCN (5 mL) was irradiated with light of a DRSh-250 mercury lamp at λ = 405 nm for several hours. When dye **4a** was wholly consumed (the reaction was monitored by spectrophotometry), MeCN was evaporated *in vacuo*. ^{1}H NMR (MeCN-d_3—D_2O (10 %), 400 MHz) δ: 2.07 (m, 4 H, 2 CH_2); 2.73 (m, 4 H, 2 $CH_2SO_3^-$); 3.53 and 3.56 (both m, 16 H, 2 γ,γ′, δ,δ′-CH_2O); 3.71 (m, 8 H, 2 β,β′-CH_2O); 3.99 (m, 4 H, 2 α-CH_2O); 4.07 (m, 4 H, 2 α′-CH_2O); 4.31 (br.t, 2 H, H(C-2), cyclobutane H(C-4)); 4.70 (br. m, 4 H, 2 CH_2N); 4.88 (t, 2 H, H(C-1), cyclobutane H(C-3), $^3J_{H(1),H(2)} = {}^3J_{H(1),H(4)} = {}^3J_{H(3),H(2)} = {}^3J_{H(3),H(4)}$ = 9.85 Hz); 6.90 (d, 2 H, benzocrown 2 H(C-5), $J_{H(5),H(6)}$ = 8.3 Hz); 7.19 (d, 2 H, benzocrown 2 H(C-2), $J_{H(2),H(6)}$ = 1.9 Hz); 7.23 (dd, 2 H, benzocrown 2 H(C-6), $J_{H(6),H(5)}$ = 8.3 Hz, $J_{H(6),H(2)}$ = 1.9 Hz); 7.87 (m, 2 H, quinoline 2 H(C-6)); 8.11 (m, 2 H, quinoline 2 H(C-7)); 8.24 (dd, 2 H, quinoline 2 H(C-5), $J_{H(5),H(6)}$ = 8.2 Hz, $J_{H(5),H(7)}$ = 1.3 Hz); 8.32 (m, 2 H, quinoline 2 H(C-8), $J_{H(8),H(7)}$ = 9.1 Hz); 8.45 (d, 2 H, quinoline 2 H(C-3), $J_{H(3),H(4)}$ = 8.8 Hz); 9.03 (d, 2 H, quinoline 2 H(C-4), $J_{H(4),H(3)}$ = 8.8 Hz).

1,*trans*-3-Di[1-(3-sulfopropyl)quinolinium-4-yl]-*trans*-2-*cis*-4-di(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecin-16-yl)cyclobutane dibetaine (9b). A solution of CSD **4b** (0.005 mmol) and $Mg(ClO_4)_2$ (0.01 mmol) in dry MeCN (50 mL) was irradiated with light of a DRSh-250 mercury lamp at λ = 405 nm for several hours. When dye **4b** was wholly consumed (the reaction was monitored by spectrophotometry), MeCN was evaporated *in vacuo*. ^{1}H NMR (MeCN-d_3-D_2O (10 %), 400 MHz), δ: 2.35 (m, 4 H, 2 CH_2); 2.75 (m, 4 H, 2 $CH_2SO_3^-$); 3.55—3.75 (both m, 24 H, 2 β,β′, γ,γ′, δ,δ′-CH_2O); 3.85 (m, 8 H, 2 α, α′-CH_2O); 5.31 (m, 2 H, H(C-2), cyclobutane H(C-4), $^3J_{H(2),H(3)} = {}^3J_{H(1),H(4)}$ = 7.61 ± 0.01 Hz, $^3J_{H(1),H(2)} = {}^3J_{H(3),H(4)}$ = 10.29 ± 0.01 Hz, $^4J_{H(2),H(4)}$ = 0.32 ± 0.02 Hz); 5.10 (br.t, 4 H, 2 CH_2N); 5.42 (m, 2 H, H(C-1), cyclobutane H(C-3), $^4J_{H(1),H(3)}$ = 0.49 ± 0.02 Hz); 6.56 (d, 2 H, benzocrown 2 H(C-5), $J_{H(5),H(6)}$ = 8.4 Hz); 6.81 (d, 2 H, benzocrown 2 H(C-2), $J_{H(2),H(6)}$ = 1.7 Hz); 6.82 (m, 2 H, benzocrown 2 H(C-6), $J_{H(6),H(5)}$ = 8.4 Hz, $J_{H(6),H(2)}$ = 1.7 Hz); 7.95 (m, 2 H, quinoline 2 H(C-6)); 8.13 (m, 2 H, quinoline 2 H(C-7)); 8.26 (d, 2 H, quinoline 2 H(C-3), $J_{H(3),H(4)}$ = 6.3 Hz); 8.36 (m, 2 H, quinoline 2 H(C-8), $J_{H(8),H(7)}$ = 9.0 Hz); 8.57 (d,

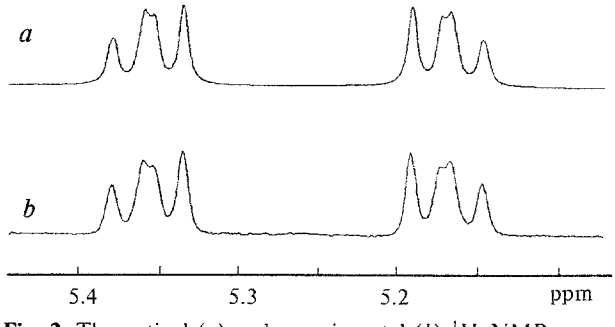


Fig. 2. Theoretical (*a*) and experimental (*b*) ^{1}H NMR spectra (Bruker AMX-400, 400.13 MHz, D_2O, 321 K) of cyclobutane protons of **9b**.

2 H, quinoline 2 H(C-5), $J_{H(5),H(6)}$ = 8.5 Hz); 9.20 (d, 2 H, quinoline 2 H(C-2), $J_{H(2),H(3)}$ = 6.3 Hz). Spin-spin coupling constants of the protons of the benzocrown moiety and cyclobutane were taken from analysis of the spectrum of **9b** in D_2O due to the strong coherence of the H(C-2) and H(C-6) protons. Cyclobutane protons were also analyzed in the spectrum recorded in D_2O due to the higher signal/noise ratio and lower coherence of these protons. Analysis of the cyclobutane subspectrum (Fig. 2) was carried out using the CALM iteration program. The CALM program is a PC-adapted version of the UEAITR program.[15] The root-mean-square deviation of the calculation was 0.027 Hz.

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