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Edited by

V. Balzani and L. De Cola

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PHOTOCHEMISTRY OF CROWN ETHER STYRYL DYES

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ABSTRACT. The structure of crown ether styryl dyes representing a novel class of dyes is considered. Data on absorption and fluorescence spectra as well as photoisomerization and complexation of photochromic 15-crown-5-ethers are analyzed. The results are exhibited concerning dimerization of the complexes incorporating trans- and cis-isomers of the compounds obtained and stereospecificity of photoinduced cycloaddition of the latter with formation of cyclobutane derivatives.

1. Introduction

Arylethylenes are a classical object of photochemistry. The products of their photolysis are: cis- and trans- isomers, condensed aromatic compounds and cyclobutane derivatives, each resulting in the course of photoisomerization, photocyclization and photocycloaddition, respectively [1-3].

One can imagine two basically different ways of the reaction control. The first one implies photochemical reactions in molecular organized microsystems, which influence the reaction course either incorporating one or many molecules into the matrix reaction cavity or building out of the reactants the following organized systems: glassy matrix, crystal, polylayers of Langmuir-Blodgett, micelle, host-guest complex [4]. Influence of supramolecular organization of arylethylenes on their photochemical transformations in organized and disorganized systems was thoroughly studied by us [5]. The second way of arylethylenes phototransformation control can be based on the principles of molecular self-organization [6]. Spontaneous molecular self-organization occurs when the molecules capable of forming supramolecular structures wanted are obtained. The control over the process of self-organization on the molecular level, being of a considerable interest in terms of development and creation of the molecular system, becomes an object of scientific researches. As for the formation of supramolecular complexes in the course of photostructural and photoconformational changes in the recipient molecules, it is of special interest being based on the most promising method of molecular system control i.e. on light control.

Heretofore this approach has not found application in arylethylene photochemistry due to similarity of physical and chemical properties of trans- and cis- isomeric derivatives of ethylene studied [7]. A possibility that molecules

will be constructed whose photoisomers differ by their reactivity would mean new prospects for the chemical control. A considerable achievement in creating such systems would be a directed synthesis of arylenes where a change of molecule geometrical configuration under irradiation could lead to significant change of such parameters as, for instance, complexation constant. Such aryene derivatives can be of a considerable interest to supra-molecular photochemistry.

2. Presentation of the molecules.

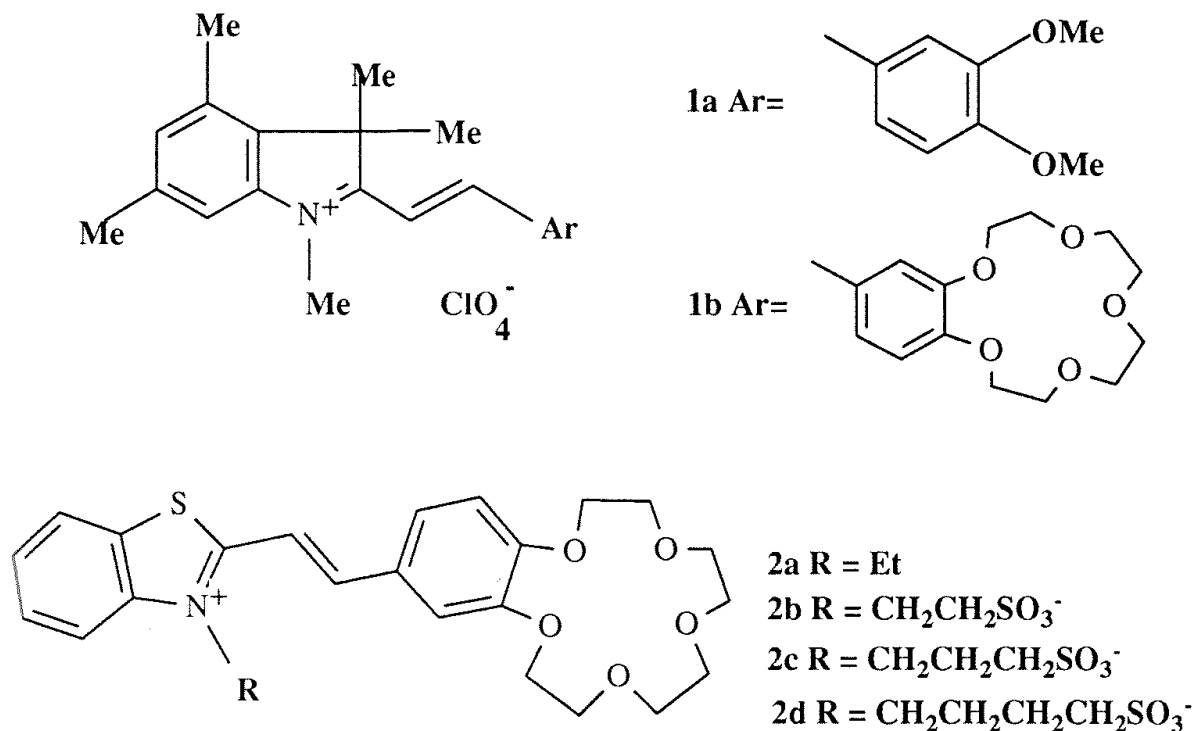
At present there are intensive investigations on macroheterocyclic compounds which can serve as a basis for the construction of multifunctional compositions, possessing an ability to selectively complexate ions or neutral molecules according to host-guest type [8,9]. In this connection the photoactive compounds which can be constructed on the basis of styryl dyes containing macroheterocyclic fragment and possessing an ability to complexate metal cations are of interest.

We have supposed that bifunctional aryene derivatives which are crown ether styryl dyes comprising two structural fragments represented by dye and crown-ether residue, will serve as the efficient photochromic systems and photosensitive ionophores. On the other hand, ionophores containing a crown-ether cycle and anion group in a spatially accessible position are known to be more efficient receptors of cations of alkaline earth metals [10]. We could also expect that the synthesis of crown ether styryl dyes "covered" in *cis*-form by anion groups would allow us to obtain chromogenic crown ether capable of "taking off" and "putting on" its "anion cap" under photoirradiation, which in its turn provides an opportunity to achieve photocontrol of alkaline earth metal cations binding.

We have performed a synthesis of indolenine styryl dyes 1a,b [11,12] and styryl dyes of benzothiazole series 2a-d [13,14]. Compound 1b contains a fragment of crown ether, and perchlorate 2-[2-(3,4-dimethoxyphenyl)ethenyl]indolinium (1a) has in a benzene cycle two methoxy groups which reproduce in general terms electron-donating effect of a crown ether substituent on the dye conjugated double bonds. However, in contrast to crown ether styryl dye 1b, compound 1a should not be noticeably capable of complexation with ions of alkaline and alkaline earth metals.

Polyether macrocycle 15-crown-5 acting as pentadentate ligand at complexation with metal ions is built into compounds 2a-d. However, in contrast to cation dye 2a, compounds 2b - d are betaines containing sulfogroup which can form under certain conditions a bond with metal cation, thus supplementing its coordination sphere. Consideration of molecular models of the promising dyes from this series has shown that sulfopropyl and sulfobutyl groups are likely to be long enough as to form an additional coordination bond with a metal cation in *cis*-form of a dye.

According to the H-NMR data all styryl dyes obtained exist in a *trans*-form. This



conclusion can be made on the basis of a high constant of spin-spin interaction $^3J_{\text{trans}} = 15,6-16,7$ Hz for olefinic protons of the dyes obtained. A performed X-ray analysis of monocrystals showed a molecule of crown ether styryl dye 2a being flat in a crystal lattice which is, evidently, attributed to a tight conjugation between orbitals of benzothiazole fragment, ethylene bond, carbon atoms of benzene cycle and some oxygen atoms of benzocrown ether [15].

The obtained data also allow the evaluation of conjugation chain length which spans a chain of bonds between nitrogen atom and oxygen atom, the latter being in para position to C=C bond. Since this oxygen atom participates in the electron pair conjugation, a considerable distortion of three-dimensional macrocycle structure occurs making the unpaired electrons of the rest oxygen atoms orientate to the exterior of the macrocycle cavity. All this indicates that before complexation crown ethers need preorganization by a series of conformational rearrangements.

The molecules of a crown ether styryl dye have been discovered to be arranged in monocrystal in pairs according to "head-to-tail" type so as to make ethylene bonds be situated one above the other. By analogy, the existence of dye molecules in dimeric form could be suggested for the solutions too. Later on we have discovered the susceptibility of crown ether styryl dyes to the formation of dimer in solutions [16].

3. Absorption and fluorescence spectra

Figure 1a and 2b show absorption and fluorescence spectra of the solution of

trans 1b in water and the solution of trans-2a in acetonitrile, respectively. The absorption spectra of corresponding cis-isomers are represented in Figure 1a and 2b too. The quantum yields of fluorescence are exhibited in Table 1. A long-wave absorption band of trans-1a and trans-1b has a significant hypsochromic shift at an increase of solvent polarity. The band maximum of trans-1b is at $\lambda=466$ nm ($\epsilon=4.1 \times 10^4$ l/mol \times cm) in chloroform and at $\lambda=432$ nm ($\epsilon=3.9 \times 10^4$ l/mol \times cm) in water.

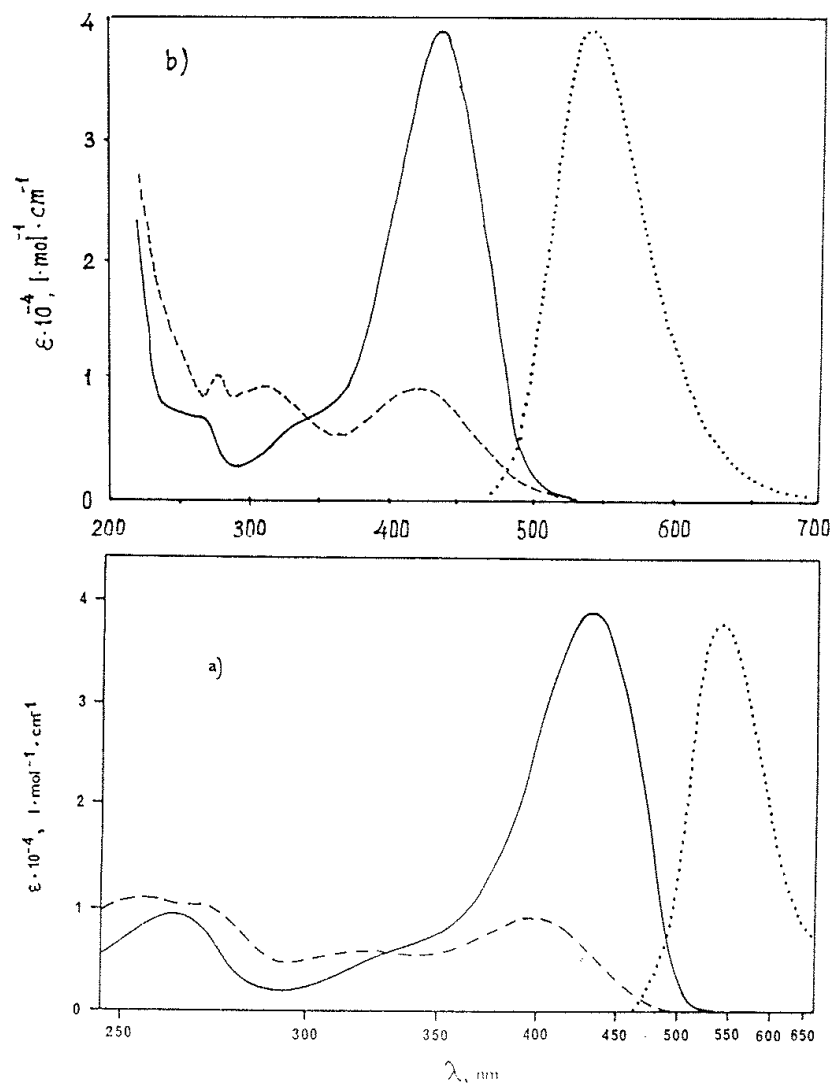


Figure 1. a) Absorption (—) and fluorescence (···) spectra of trans-1b and the calculated absorption spectrum of cis-1b (- -) in water at $T=295K$. b) Absorption (—) and fluorescence (···) spectra of trans-2c and the calculated absorption spectrum of cis-2c (- -) in acetonitrile at $T=295K$

In order to analyze the character of the absorption spectra we have simulated on a computer both the conformational changes and dye 2b electronic absorption spectrum shift. The calculation of conformation was performed by the MMX method using the program PCMODEL, and the calculations of the electronic

absorption spectra were performed by CNDO/S method accounting for the conformational interaction (CI) [17].

According to our estimations trans-2b possesses flat configuration and exhibits only one long-wave electron transition which is in good agreement with the experimentally observed spectrum. It is mostly attributed about 90% to the configuration corresponding to electron transition from upper completed molecular orbit to lower uncompleted one. The second electron transition being close to the first one has relatively low intensity thus being seen as a shoulder against a long-wave absorption band.

Good agreement with the experiment is observed for both, energy and intensity of the electron transitions. Long-wave electron transition in cis- and trans isomers has the same nature and the character of their parameters change occurring at the disturbance of flat symmetry of trans- and cis-isomers are alike. At the same angle of inclination of the fragments the positions of long-wave absorption band is practically the same for both 2b isomers but their intensities differ.

4. Photoisomerization

Under the irradiation of trans-isomer solutions with light in the range of a long-wave absorption band the intensity of the latter decreases with a simultaneous rise of the absorption in the short-wave range which lasts till a photostationary state is achieved (Figure 1).

In all cases isobestic points are observed. These spectral changes are, apparently, explained by the reversible trans-cis-photoisomerization occurring in solution [12]. When the irradiation ceases in the moderate polarity solvents chloroform, acetone quick dark recovery of the spectra proceeds. It is, apparently, connected with the process of thermal cis-trans isomerization. In aqueous solutions the cis-1a,b are stable enough to allow the evaluation of the spectra of individual cis-isomers and their molar absorbance ϵ by Fisher method [18]. Knowing ϵ_c and ϵ_t a standard method was used to evaluate the quantum yield of trans-cis (ϕ_{tc}) and cis-trans (ϕ_{ct}) photoisomerization. The obtained values of fluorescence and photoisomerization quantum yields are given in Table 1 (The error of ϕ_{tc} and ϕ_{ct} measurements is about 20% and that of ν is about 40 %).

TABLE 1 Photochemical data for 1a,b and 2c at T=298K

Dye	ϕ_{tc}	ϕ_{ct}	ϕ_{fl}
11a (water)	0.47	0.51	0.0015
11b (water)	0.49	0.50	0.0020
12c (acetonitrile)	0.40	0.49	0.06

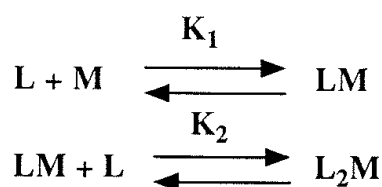
We studied quick stages of structural dynamics of crown ether styryl dyes by the method of picosecond fluorescence spectroscopy. It was found that the observed dependence of fluorescence lifetime on the solvent viscosity could be described by the barrier model of the trans-cis isomerization occurring in the existed singlet electron state [19].

5. Complexation of trans-2a-d with cations of alkaline and alkaline earth metals.

In the acetonitrile solution a compound 2c has in the absorption spectrum an intensive long-wave band with a maximum at $\lambda=435$ nm. On the addition of alkaline Na, K and alkaline-earth metals Mg, Ca, Ba into the solution of perchlorates a hypsochromic shift of the long-wave band is observed [13]. With the concentration of perchlorate $C_M \geq 10^{-3}$ M the absorption band maximum is at $\lambda=392$ nm ($\epsilon_{\max}=3.69 \cdot 10^4$ l/mol \times cm), at $\lambda=396$ nm ($\epsilon_{\max}=3.62 \cdot 10^4$ l/mol \times cm) and at $\lambda=407$ nm ($\epsilon_{\max}=3.66 \cdot 10^4$ l/mol \times cm) in case of Mg^{2+} , Ca^{2+} and Ba^{2+} , respectively. Similar spectral changes were earlier observed when studying complexation of metal ions with the crown ethers not containing styryl chromogene [20]. Thus we attribute the observed spectral changes to the complexation.

From the absorption spectra of the solutions at the constant initial concentration of the ligand $C_0=2.05 \cdot 10^{-5}$ M and different concentration of the cation, a degree of the ligand transformation into the complex form with metal ions was determined by formula $\alpha = (D_0 - D)/(D_0 - D)$, where D_0 is an absorption of the initial ligand solution at the fixed wavelength, D is an absorption of the solution upon complete complexation, D is an absorption of the solution at the different values of the cation concentration.

In the experiments on 2c complexation with Ba^{2+} ions the expenditure of the ligand at low degrees of transformation exceeded the concentration of the cation nearly two times. Thus, for the given compound the following scheme of the formation of the 2L:1M complex can be proposed:



where M is a metal cation, L is a ligand molecule. The following equation corresponds to the scheme given above:

$$\frac{C_M}{\alpha} = \frac{1 + C_0 K_1 (1 - \alpha) + C_0^2 K_1 K_2 (1 - \alpha)^2}{K_1 (1 - \alpha) (1 + 2C_0 K_2 (1 - \alpha))} \quad (1)$$

The experimental dependencies of the ligand concentration decrease $\alpha C_0 = C_0 - [L]$ on the total concentration of Mg^{2+} , Ca^{2+} and Ba^{2+} in the solutions are presented in Figure 2 by dots.

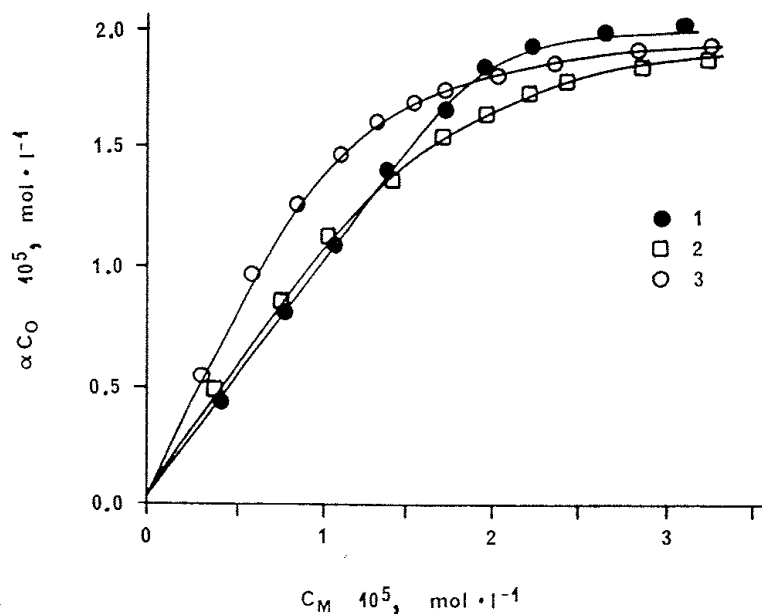


Figure 2. Experimental dependencies of the necessary amount of ligand 2c for the total concentration of Mg^{2+} (1), Ca^{2+} (2) and Ba^{2+} (3).

The solid lines represent the theoretical dependencies corresponding to the equation (1) with constants $K_1 = 4 \times 10^6$ l/mol and $K_2 = 0$ for Mg^{2+} ; 7×10^5 l/mol and 2×10^5 l/mol for Ca^{2+} and 6×10^5 l/mol and 1.5×10^5 l/mol for Ba^{2+} . A good agreement of the experimental data with the results of the calculation confirms the validity of the chosen scheme complexation. Besides, the decrease in value K_1 , in the order of $Mg^{2+} > Ca^{2+} \cong Ba^{2+}$ correlates with the value of the long wave absorption band shift in the spectra of the complexes. The increase of value K_1 in the $Mg^{2+} < Ca^{2+} < Ba^{2+}$ order corresponds to the idea that the cations of large diameter tend to form complexes at the ratio of 2:1 with ethers which have small size cavities [21]. With a Mg^{2+} cation such a complex is apparently not formed.

We performed a comparative analysis of the complexation ability of 2b-d compounds differing solely by the length of sulfo-alkyl substituent. Spectral characteristics of both free trans-2b-d and their complexes with Mg^{2+} differ insignificantly. In this case in order to reduce an error associated with the styryl dye sorption occurring from a solution to the cell walls, the inner surface of the latter was modified with trimethylchlorosilane. Except for this step, the method of estimation of the complexation constants was the same as the procedure mentioned above.

The constants of complexation of trans-2b-d with Mg^{2+} (K_1) obtained at $C_0 = 4.2 \times 10^{-6}$ M have the following values:

compound	2b	2c	2d
K_1 , l/mol	7×10^4	1×10^4	4×10^4

It is evident that an increase in number of methylene groups from 2 to 3 in sulfoalkyl N-substituent leads to a sharp increase of complexation constant. Further growth of their number up to 4 causes almost no changes [14].

6. Photoinduced formation of intramolecular coordination bond in 2b-d complexes with Mg^{2+} , Ca^{2+} and Ba^{2+} cations.

Compound 2c, like a crown-ether indolenine styryl dye 1b, can be subjected to a reversible photochemical reaction of trans-cis isomerization around the central double C=C bond. The absorption spectra of cis-2c in acetonitrile was calculated by means of Fisher method [18] using the spectra of trans-isomer and photostationary states obtained from the irradiation of a 2b solution with light at 365 nm and 436 nm.

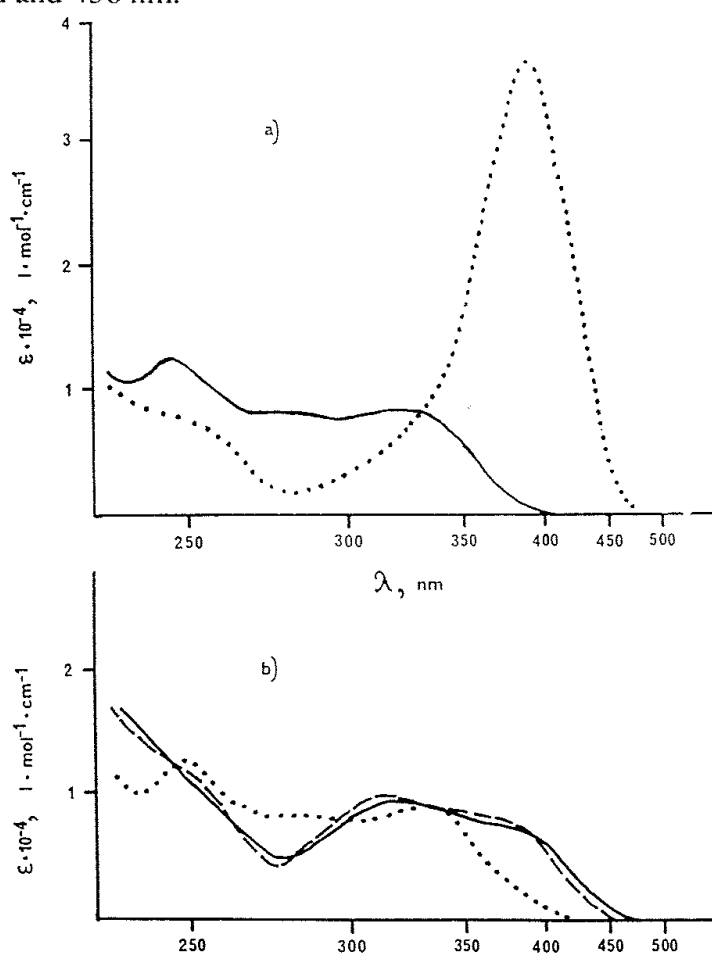
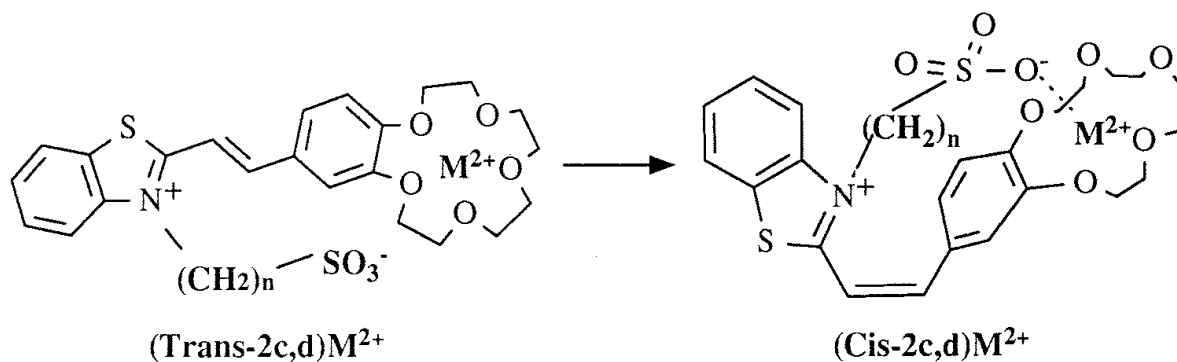


Figure 3. a) Absorption spectra of complexes of trans-2c (····) and cis-2c (—) with Mg^{2+} at $[Mg(ClO_4)_2] = 1 \times 10^{-3} M$. b) Absorption spectra of complexes of cis-2c with Mg^{2+} at $[Mg(ClO_4)_2] = 3 \times 10^{-3} M$ (····), $0.5 M$ (—) and a cis-2a and Mg^{2+} complex at $[Mg(ClO_4)_2] = 3 \times 10^{-3} M$ (-·-).

In Figure 3 trans- and cis-isomer absorption spectra of 2b are presented. The distance between the maxima of the long wave absorption bands of these isomers is only 15 nm which prevents complete transformation of trans-isomer into a cis-form through photoisomerization. Similar situation is characteristic for the majority of photochromic compounds [7]. Another situation is observed in the case of trans-2b complexation with cations of alkaline earth metals when the concentration of the latter is 10^{-3} M. The irradiation of the solutions with light at $\lambda=436$ nm leads to a photostationary state including more than 99% of cis-isomer. The absorption spectra of the cis-isomer complexes have a long-wave maximum at $\lambda=321$ nm ($\epsilon = 8.96 \times 10^3$ l/mol \times cm), at $\lambda=325$ nm ($\epsilon = 9.51 \times 10^3$ l/mol \times cm) and at $\lambda=338$ nm ($\epsilon = 8.05 \times 10^3$ l/mol \times cm) for Mg^{2+} , Ca^{2+} and Ba^{2+} , respectively. Figure 3a shows as an example the absorption spectra of cis- and trans-isomer of the complexes 2c with Mg^{2+} .

A strong hypsochromic shift by 70 nm of the cis-isomer complexes spectra in respect to the spectra of trans-isomers can be apparently explained by the formation in a cis-form of a coordination bond between a sulfo-group and a metal cation, located in a crown-cavity.



In fact, according to our calculations by MMX method [17] while complexing with alkaline earth metal cation it is energetically advantageous for the cis-2c molecule to coil (calculated values for $\tau_1=90^\circ$ and for $\tau_2=45^\circ$) and to form a coordination bond between a sulfo-group and a metal. Accordingly a conjugated chromophoric system undergoes full destruction and, as a result, long-wave absorption band not only shifts to a short-wave region but also absolutely loses its intensity. It occurs at any value of relative electric permittivity $\epsilon=\infty$ at the complete shielding of the cation electric field. Thus, in the experimentally observed spectrum it is the second absorption band of the molecule which corresponds to a long-wave absorption band. This circumstance accounts for the pronounced shift of a long-wave band in cis-2c electronic absorption spectrum observed at complexation. While comparing calculated values with various electric permittivity one can see the cation electric field influencing neither position nor intensity of the second absorption band of cis-2c. Thus, it can be concluded that the observed effect is due solely to the conformational change of cis-2c at complexation.

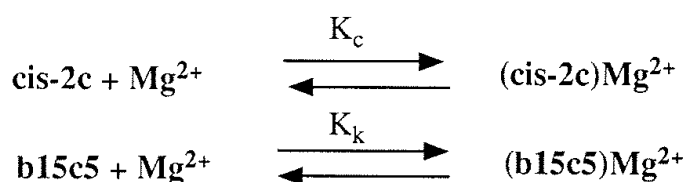
With an increase in the concentration of magnesium perchlorate in a cis-isomer solution of the 2c complex with Mg^{2+} ($C_M > 0.01$ M) the absorption in a

long-wave region of the spectrum gradually increases and at $C_M > 0.2$ M the spectrum takes an entirely different shape. The change of the spectrum shape is attributed probably to the destruction of intramolecular coordination bond due to the association of SO_3^- group with an additional cation of Mg^{2+} .

Figure 3b shows the absorption spectra of a cis-2c complex with Mg^{2+} at concentrations of the $\text{Mg}(\text{ClO}_4)_2$ equal to 3×10^{-3} M and 0.5 M, as well as of a cis-2a complex with Mg^{2+} at concentration $[\text{Mg}(\text{ClO}_4)_2] = 3 \times 10^{-3}$ M. In a compound 2a an ethyl group instead of a sulfopropyl group is present, therefore the formation of an intramolecular coordination bond is impossible. The fact that the spectrum of the (cis-2a) Mg^{2+} at $C_M = 3 \times 10^{-3}$ M and the spectrum of the (cis-2c) Mg^{2+} at $C_M = 0.5$ M practically coincide, confirms the assumption that the destruction of the intramolecular bond in (cis-2c) Mg^{2+} at high concentrations of $\text{Mg}(\text{ClO}_4)_2$ occurs.

The presence of an additional coordination bond in cis-isomer complexes of bethaines of chromogenic crown ethers allows the suggestion of their higher stability in comparison with trans-isomer complexes. On the other hand, of interest is the modification of sulfoalkyl N-substituent of crown-ether bethaine styryl dyes by means of varying the number of methylene groups between a nitrogen atom of heteroaromatic residue and SO_3^- group. The stability of such chelate complexes should probably depend on the degree of steric tension in macrocycle resulting in cis-form due to the formation of the coordination bond and incorporating an ion of the metal. A decrease in the number of methylene groups will presumably lower the stability.

Constant of complexation of cis-2c with Mg^{2+} was estimated using the competitive reaction method [14]. The cis-isomer of the complex was formed by irradiating with light at $\lambda = 436$ nm the solution of trans-2c and $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile with concentration $C = 4.2 \times 10^{-6}$ M and $C = 1.0 \times 10^{-5}$ M, respectively. Then benzo-15-crown-5 (b15c5) was added to the solution and the degree of cis-2c complexation (α) was estimated by the absorption at $\lambda = 421$ nm (the maximum of long-wave absorption band of cis-2c) [13]. The process of complexation in the presence of competitor can be represented as follows:



The scheme can be expressed by the following equation:

$$C_k = (1 + (K_c/K_k)(1-\alpha)/\alpha) \times (C_m - \alpha C_0 - \alpha/((1-\alpha)K_c)) \quad (2)$$

where C_k , C_M and C_0 is the total concentration of (b15c5), $\text{Mg}(\text{ClO}_4)_2$ and 2c respectively.

When $1/K_c \ll C_M = 1 \times 10^{-5}$ M the experimental dependence of the degree of cis-2 complexation on (b15c5) concentration

$C_k \times 10^3 M$	0	0.37	1.11	1.84
	1	0.72	0.51	0.39

corresponds to the equation (2) at $K_c/K_k=140$. Using the spectrophotometric titration we estimated $K_k > 1 \times 10^7$ the small molar absorptance of (b15c5) prohibits the exact measurements, then $K_c > 1.4 \times 10^9$ l/mol. The fact that K_c considerably exceeds more than two orders the corresponding constant for trans-isomer see above confirms the afore made conclusion that an intramolecular coordination bond is formed in the complexes of cis-2c with cations of alkaline earth metals.

At photoisomerization of (trans-2d) Mg^{2+} at $C_0 = 10^{-6} - 10^{-4}$ M, as in the case with (trans-2c) Mg^{2+} an intramolecular cis-isomer complex with short-wave absorption spectrum is formed. The constant of complexation of cis-2d with Mg^{2+} , also estimated by the competitive reaction method, is eight times greater for cis-2c isomer. It is probably attributed to the fact that the larger the cycle the easier it satisfies the attempts of cis-2d to form an intramolecular coordination bond between SO_3^- group and the metal cation.

As for complexes of 2b with Mg^{2+} no experimental conditions provided the considerable hypsochromic shift in the absorption spectrum at trans-cis-photoisomerization. Moreover (cis-2b) Mg^{2+} spectrum calculated by Fisher method practically coincides with the corresponding absorption spectrum of 2a. The sulfoethyl chain is probably too short to form intramolecular complex. Thus, the shorter is the sulfoalkyl N-substituent the weaker becomes the coordination bond in cis-isomer complexes and in the case of sulfoethyl derivative it is not formed at all.

7. Dimerization of trans- and cis-2c,d.

As we have shown above an intramolecular coordination bond in the complexes of cis-2c with alkaline-earth-metal cations breaks at a considerable excess of cations $C_M \geq 0.1$ M and a "closed" complex turns into an "open" form with longer-wave absorption spectrum. It turned out that the similar transition occurs when concentration of cis-2c complex increases under the lack of excessive metal. At $C_0 \geq 10^{-2}$ M cis-isomer complex is mostly in the "open" form. This effect is probably attributed to the dimerization of the complexes by "head-to-tail" type. intramolecular coordination bond breaks and corresponding intramolecular bonds form [16].

At the dilution of cis-isomer complex solution up to $C_0 < 10^{-4}$ M the slow transition of an "open" form into a "closed" one occurs.

These process is easily observed by the absorption spectra Figure 4. The kinetics of the transition which was followed by measuring the absorption of the solution at $\lambda = 393$ nm are of the first order. The life time of an "open" form of (cis-2c) Mg^{2+} does not depend on the dilution degree of the solution within the concentration range from 10^{-5} to 10^{-4} M at the constant concentration of an excessive Mg^{2+} (1×10^{-4} M), and equals 550 sec at $T = 298$ K.

The addition of $Mg(ClO_4)_2$ to the solution with low concentration of free cis-2c ($C_0 < 10^{-4}$ M) causes almost immediate formation of a "closed" form of a

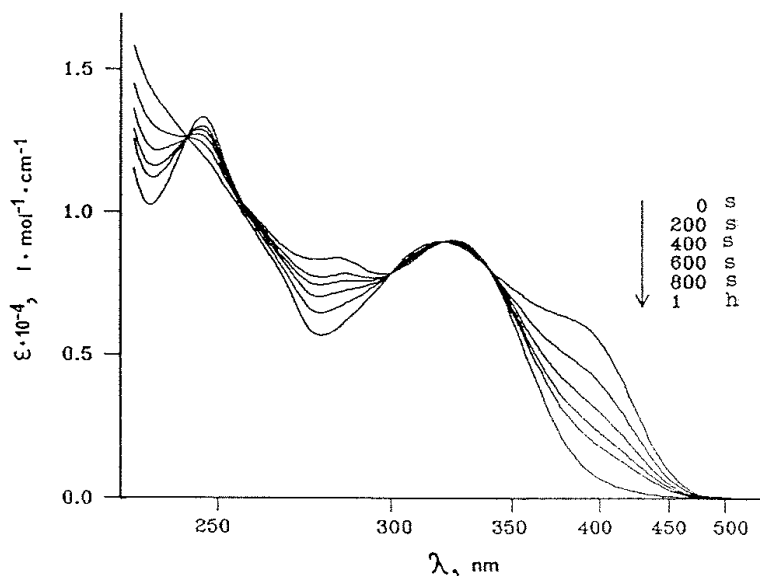


Figure 4. Absorption spectra of $(cis-2c)Mg^{2+}$ measured at different moments after dilution (in 10^3 times) of initial solution (2.2×10^{-2})

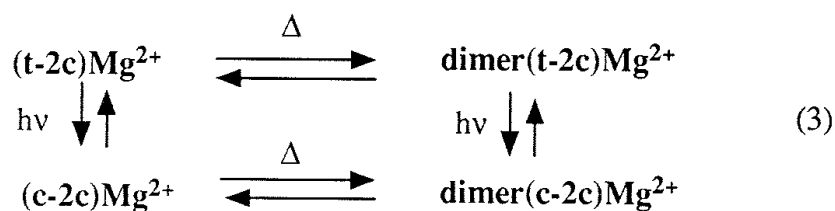
$(cis-2c)Mg^{2+}$ complex. Consequently, according to our assumption the rate of the transition of a $(cis-2c)Mg^{2+}$ "open" form to a "closed" one at the dilution of a solution is limited by the rate of the dimer dissociation, and the lifetime of an "open" form corresponds to the life time of dimers.

After a short-time irradiation of a diluted solution of $(trans-2c)Mg^{2+}$ ($5 \times 10^{-6} M \leq C_0 \leq 1 \times 10^{-4} M$, $C_M = 1.2 \times 10^{-4} M$) its absorption spectrum undergoes slow changes at dark. The character of these changes makes it reasonable to conclude that the transition of an "open" form of $(cis-2c)Mg^{2+}$ into a "closed" form occurs, the duration of the transition being of the same order as the afore given lifetime of $(cis-2c)Mg^{2+}$ dimers.

Basing on these data we assume that in the course of $(trans-2c)Mg^{2+}$ photoisomerization in the diluted solution an "open" form of $(cis-2c)Mg^{2+}$ is produced in the form of dimers. Such a situation is possible solely when the $(trans-2c)Mg^{2+}$ complex at $C_0 > 5 \times 10^{-6} M$ is at least partially dimerized, and in the course of photoisomerization of dimers the intermolecular coordination bond is retained.

As the quantum yield of cis-trans-isomerization of $2cMg^{2+}$, estimated at $C_0 = 1.6 \times 10^{-5} M$ and at $C_m = 1.2 \times 10^{-4} M$ is high ($\phi_{tc} = 0.46$) and the dissociation rate of $2cMg^{2+}$ dimers is low, the irradiation of the solution with high intensive light ($I_0 \approx 10^{16} \text{ cm}^{-2} \text{ sec}^{-1}$) at $\lambda = 436 \text{ nm}$ provokes the establishment of cis-trans-photostationary state, including $(cis-2c)Mg^{2+}$ dimers which absorb light of the given wave length. The process of dimers dissociation with the formation of $(cis-2c)Mg^{2+}$ "closed" form not absorbing light at $\lambda = 436 \text{ nm}$) gradually changes cis-isomer content in the mixture up to the full transition of a trans-isomer into a cis-form.

The processes occurring in the solution of $2cMg^{2+}$ at concentration $< 10 M$ under the influence of light at $\lambda = 436 \text{ nm}$ can be represented by the following scheme:



The picture changes when the solution of $2cMg^{2+}$ is irradiated with light at $\lambda=365$ nm which a "closed" form of $(cis-2c)Mg^{2+}$ can absorb. Proceeding with a high quantum yield $\phi_{ct}=0.58$ the reaction of cis-trans-isomerization of a $(cis-2c)Mg^{2+}$ "closed" form leads to the closure of the cycle in this scheme.

A comparison of 2c,d complexes differing solely by the length of sulfoalkyl substituent reveals, as far as their ability to form dimers is concerned, that they are almost similar.

Thus, we can conclude that the formation of the complexes of 2c,d with Mg^{2+} cations in acetonitrile solution leads to the association of the 2c,d complexes in dimers.

8. Photochemical 1,2-cycloaddition of 2c,d.

It is known that the association of the molecules with double C=C bond in the solution can attribute to an increase in the quantum yield of photocycloaddition and influence its stereoselectivity. In our case it is reasonable to suggest that from $(cis-2c)Mg^{2+}$ dimers the cyclodimers are photosynthesized. In fact in the solution of $2cMg^{2+}$ complex at concentration 1×10^{-2} M under the long-term influence of light at $\lambda \geq 365$ nm a new photoproduct is formed. Its absorption spectrum is represented in Figure 5.

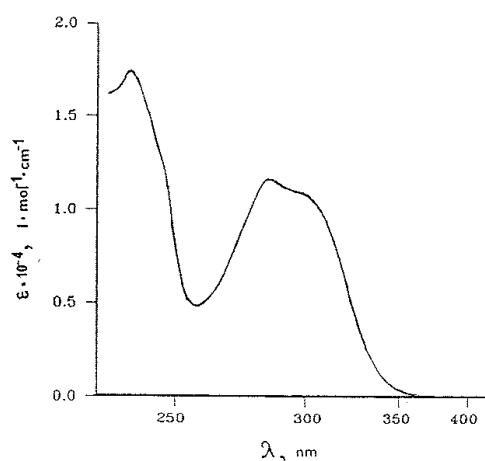
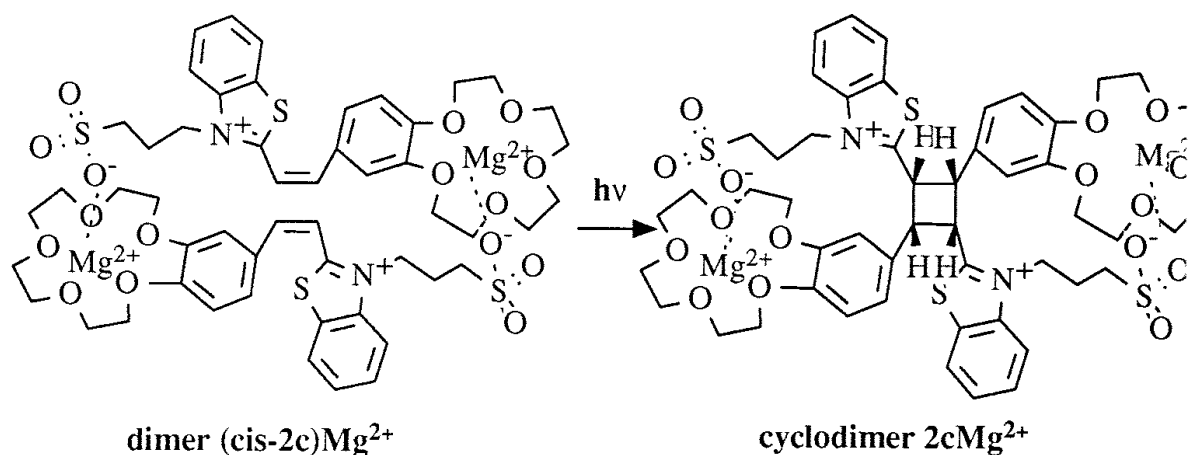


Figure 5. Absorption spectra of $(cyclodimer-2c)Mg^{2+}$ solution ($6 \times 10^{-3} M$) after photolysis ($IR365$ nm)

As in the solution irradiated with light both *cis*- and *trans*-isomers of a $2cMg^{2+}$ are present, the formation of various isomers of cyclobutane derivative is probable. The NMR 1H and ^{13}C data, however, show undoubtedly that in the course of photolysis a single-type isomer is formed. It is obvious that it can be produced solely from two *cis*- $2c$ molecules in the course of cycloaddition by "head-to-tail" type. Thus, the existence of photocycloaddition and its high stereoselectivity give further evidence for the production of (*cis*- $2c$) Mg^{2+} dimers which form the intermolecular coordination bonds in acetonitrile solution under the high concentrations of dimers.

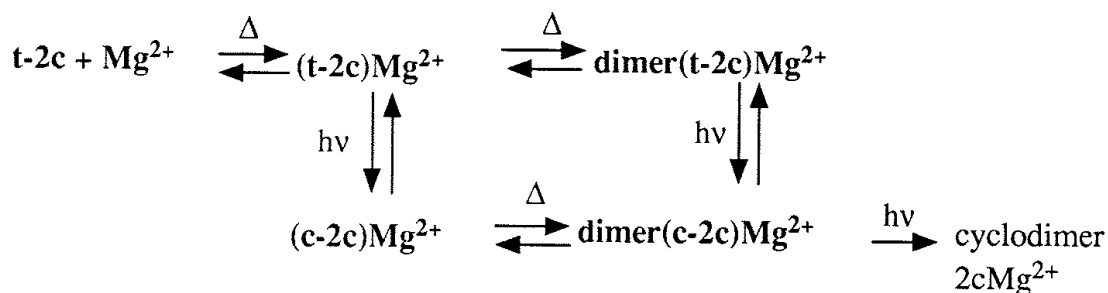


In the solution under the influence of constant irradiation the concentration of (*cis*- $2c$) Mg^{2+} dimers reaches some stationary level. Owing to this effect the reaction of photocycloaddition can achieve a grade of reactivity more than 90% even at concentrations of $2cMg^{2+}$ 10^{-5} M. The dependence of quantum yield of photo-cycloaddition ϕ_d on $2cMg^{2+}$ concentration estimated at constant intensity of light at $\lambda=365$ nm, $I_0=3.7 \times 10^{15}$ $cm^{-2} \times sec^{-1}$, looked as follows:

C_0, M	5×10^{-6}	2.4×10^{-5}	4.6×10^{-5}	2.1×10^{-4}	2.0×10^{-3}
ϕ_d	0.0022	0.0043	0.0052	0.0051	0.0055

A decrease in $2cMg^{2+}$ concentration from 2×10^{-3} M to 5×10^{-5} M pays practically no effect on the quantum yield of photocycloaddition. This fact as well as the structure of cyclodimers allow us to conclude that it is constructed solely from (*cis*- $2c$) Mg^{2+} dimers. A quantum yield within a following range of concentrations: 5×10^{-5} M - 5×10^{-6} M becomes 2.5 times lower which can be explained by a decrease in the degree of (*trans*- $2c$) Mg^{2+} dimerization and accordingly by a decrease in the degree of (*cis*- $2c$) Mg^{2+} dimerization at photostationary state.

Using the data obtained we can represent the general scheme of the processes of $2c$ dimerization and $2c$ photocycloaddition proceeding in acetonitrile solution under the influence of light at $\lambda=365$ nm as follows:



Thus the formation of dimers allows us to perform the reaction of photocycloaddition with high stereoselectivity and within a broad range of concentrations.

9. Conclusion

Spontaneous molecular self-organization is based on the molecules obtained capable of forming of themselves a desired supramolecular architecture. The studies on photochemical transformations of crown ether styryl dyes representing a novel class of bifunctional dyes and chosen as an example allow us to demonstrate for the first time two step molecular self-organization. The first step of the process includes self-organization of dye molecules into dimers in the course of complexation. The second step comprises photoinduced pre-organization of dye complexes (trans-cis-photoisomerization) serving as the basis for the formation of cis-form dimers, and followed by the process of photocycloaddition is completed with the formation of cyclobutane derivatives.

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