Crown ether styryl dyes 22.* Synthesis and complexation of the *cis*-isomers of photochromic aza-15-crown-5 ethers

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New crown ether-containing styryl dyes of the benzothiazole series containing an aza-15-crown-5-ether moiety were synthesized. The *trans--cis*-photoisomerization of these dyes and their analogs was studied; the effect of metal cations on the kinetics of dark *cistrans*-isomerization was elucidated. The stability constants of the complexes of the *cis*isomers of these dyes with $Ca(ClO_4)_2$ were estimated. The dramatic increase (by more than three orders of magnitude) in the stability of the complexes on passing from a cationic dye to a betaine was attributed to the formation of an intramolecular bond in the *cis*-complexes between the sulfo group of the *N*-substituent and the metal cation located in the cavity of the azacrown-ether moiety.

Key words: crown ether-containing styryl dyes, synthesis, photoisomerization, complexation, anion-"capped" complexes.

Up to now, most attention has been devoted to crown-containing photoswitchable systems based on azobenzene derivatives² in which the N=N double bond, able to undergo reversible photoinduced *trans-cis-* and thermal *cis-trans*-isomerization, served as the functional group (the antenna). However, the advantages and potentialities of crown compounds with one C=C double bond (photo- and thermally switchable functional group) have not yet been used in full measure.

It was found^{3,4} and, later, confirmed by theoretical calculations⁵ that, among the compounds that we obtained, crown-containing styryl dyes (CSD) with a terminal sulfo group are the most promising. This made it possible to synthesize for the first time the simplest derivatives of photo- and thermochromic CSD, capable of "putting on" and taking off" their anionic "cap" during irradiation, and thus to achieve photochemical control over binding of metal cations.⁶



* For Part 21, see Ref. 1.



n = 3 (a), 4 (b)

The anion-"capped" complexes $(cis-1a,b) \cdot Mg^{2+}$ were prepared by irradiating solutions of the complexes of *trans*-1a,b with Mg²⁺ with light of a mercury lamp with $\lambda = 436 \text{ nm}^{3,4}$ (Scheme 1).

Synthesis of CSD able to undergo molecular photoswitching in a longer-wavelength region of the

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Scheme 1

spectrum is of principal importance. The introduction of an electron-donating N atom having a lone electron pair (LEP) into the *para*-position with respect to the C=C bond of the chromophore of a CSD makes it possible to obtain a photochromic transition in the region of 500-600 nm. In this work, using photochromic dyes of the benzothiazole series (2a-c) as examples, we studied the effect of the N atom in the crown-ether moiety and the effect of the nature of the metal cation on photoinduced and dark isomerization and on the formation of anion-"capped" complexes.

The perchlorate of dye 2a was synthesized in 66% yield by condensation of quaternary salt 3a with N-(4-formylphenyl)aza-15-crown-5 ether (4) in EtOH in the presence of pyridine. 3-Ethyl-2-methylbenzo-thiazolium perchlorate (3a) was obtained by adding an excess of perchloric acid to an ethanolic solution of 3-ethyl-2-methylbenzothiazolium iodide (5). N-(4-Formylphenyl)aza-15-crown-5 ether (4) was prepared by a known procedure⁷ (Scheme 2).



CSD 2b was prepared in 82% yield similarly to 2a by the condensation of betaine 3b with N-(4-formylphenyl)aza-15-crown-5 ether (4) in the presence of pyridine. The starting betaine 3b was synthesized by heating 2-methylbenzothiazole (6) with γ -sultone (7) without a solvent at 120 °C; the yield of the product was markedly higher than the yield that we reported previously.⁸ Dye 2c, which, unlike 2b, contains no crownether fragment, was obtained in a yield of 48% by refluxing betaine 3b and para-dimethylaminobenzaldehyde in Ac₂O (Scheme 3).

The structures of compounds 2a-c were confirmed by ¹H NMR spectroscopy (see Experimental). The data of elemental analysis correspond to the proposed structures. According to the spin-spin coupling constant for



olefinic protons, ${}^{3}J_{rrans} = 15.2 - 15.5$ Hz (see Ref. 10), the resulting dyes **2a**-c have the *trans*-configuration.

We studied the formation of complexes of *trans*-2a-c with Ca^{2+} ions in anhydrous MeCN using the methods of electronic spectroscopy. The results were presented in the previous communication.¹⁰ It was found that in the case of complexation of *trans*-2a with Ca^{2+} , the dependences of the absorption and fluorescence spectra of the dye on the concentration of the metal cation added (C_M) can be adequately described in terms of only one equilibrium (Scheme 4).

Scheme 4



The spectral variations for *trans*-2b are more complex. It was found¹⁰ that the addition of a small quantity of Ca^{2+} ions results in aggregation of the dye molecules (this is manifested as splitting of the long-wavelength absorption band and quenching of fluorescence, which are typical of aggregates of many dyes). The occurrence of cation-induced aggregation was explained¹⁰ by the formation of $(trans-2b)_n \cdot Ca^{2+}$ complexes (n = 2 to 4)in which the metal cation does not interact with the crown-ether moiety but is bound only to the sulfo group of the dye molecule. As C_M increases, the degree of aggregation of *trans-2b* first increases and then the equilibrium shifts toward A-LCa, CaA-L, and CaA-LCa complexes, where A-L is a *trans-2b* molecule (A is the sulfo group and L is the azacrown-ether moiety).

It was shown¹⁰ that the aggregation of *trans*-2b (as well as *trans*-2c) molecules can be induced not only by Ca^{2+} ions but by small amounts of other doubly-charged cations added, for example, Mg^{2+} , Ba^{2+} , or Zn^{2+} . However, the singly-charged Na⁺ ion does not cause aggregation of these dyes.

Trans-cis-isomerization of 2a-c and complexation of cis-isomers

When solutions of *trans*-2a-c are exposed to visible light, spectral changes typical of *trans*--*cis*-isomerization occur. The *cis*-isomers formed in this reaction are unstable and are converted in the dark into the corresponding *trans*-isomers. The rate constants of the dark *cis*--*trans*-isomerization (Table 1) are more than three orders of magnitude higher than those for CSD 1a,b studied previously ($k_{c-t} = 2 \cdot 10^{-5} \text{ s}^{-1}$ for 1a, see Ref. 6). This is due to the fact that the degree of conjugation in the chromophoric fragments of *cis*-2a-c is higher than that for *cis*-1a,b, because the former compounds contain a nitrogen atom with a LEP in the *para*-position with respect to the C=C bond. This results, apparently, in a substantial decrease in the barrier to *cis*--*trans*-isomerization.

When Ca(ClO₄)₂ with $C_{\rm M} = 0.05$ mol L⁻¹ is added to a solution of **2a**, the rate constant of dark *cis-trans*isomerization decreases to $6.4 \cdot 10^{-4}$ s⁻¹ (by a factor of more than 50). This suggests that a fairly strong coordination bond is formed between the metal cation and the N atom of the azacrown-ether fragment in (*cis*-**2a**) \cdot Ca²⁺, and this decreases the extent to which the LEP of the N atom is involved in the conjugation with the chromophore.

Figure 1 presents the dependence of the rate constant of the dark *cis*—*trans*-isomerization (k_{c-t}) on C_M for 2a and Ca²⁺. For all samples, the isomerization kinetics, as followed by the variation of the optical



Fig. 1. Experimental and theoretical (Eq. (2)) dependences of the rate constant of dark *cis*—*trans*-isomerization of CSD 2a in MeCN ($C_{\rm L} = 1.0 \cdot 10^{-5}$ mol L⁻¹) on the concentration of Ca²⁺ ions at a constant concentration of ClO₄⁻ ($C_{\rm A} = 0.01$ mol L⁻¹).

density of the solution at 522 nm, corresponded exactly to a first-order equation. The resulting dependence was analyzed within the framework of the following scheme of dark transformations of cis-2a:

Scheme 5

Since the formation and dissociation of complexes are fast reactions compared to dark isomerization, the observed rate constant of the dark *cis*—*trans*-isomerization (k_{c-t}^{obs}), can be presented by the following expression provided that $C_{\rm M} \gg C_{\rm L}$ (this condition was satisfied over the whole experimental range of $C_{\rm M}$).

Table 1. Stability constants of the complexes of *trans*- and *cis*-CSD **2a**,**b** with Ca²⁺ ions and rate constants of the dark *cis*-trans-isomerization of **2a**-c in MeCN at $T = 20\pm 2$ °C

Dye	$\log K$ (complex with Ca ²⁺)		$k_{c-t} \cdot 10^2$	$k_{c-t}^{obs} - 10^2/s^{-1}$					
	trans-isomer	cis-isomer	/s ⁻¹	Na ⁺	Ba ²⁺	Ca ²⁺	Mg ²⁺	Zn ²⁺	+
2 a	2.4±0.1 (Ref. 1)	2.85±0.1	3.6						
2Ь		>6.3	2.5	2.6	0.21	0.03	0.45	3.6	
2c			10	14	35	56	59	50	

Note: k_{c-1} are the rate constants for free dyes; k_{c-1}^{obs} are the observed rate constants at $C_L = 1 \cdot 10^{-5} \text{ mol } L^{-1}$ in the presence of Na, Zn, and alkaline earth metal perchlorates $C_M = 1 \cdot 10^{-3} \text{ mol } L^{-1}$.

The data obtained at $C_{\rm M} = 0.05$ mol L⁻¹ (see above) indicate that $k'_{c,t}k_{c-t}^{-1} < 50$. Therefore, in the range of $C_{\rm M}$ in which $K \cdot C_{\rm M} < 5$, the following approximate equation can be used instead of Eq. (1):

$$k_{c-1}^{obs} \approx k_{c-1}(1 + KC_{\rm M})^{-1}.$$
 (2)

It can be seen from Fig. 1 that the experimental dependence of k_{c-r}^{obs} on $C_{\rm M}$ is closely approximated (nonlinear least-squares method) by the theoretical curve corresponding to Eq. (2). The stability constant of the complex of *cis*-2a with Ca²⁺ found using this approximation is presented in Table 1.

It follows from Table 1 that when *trans*-2a is converted into the *cis*-form, the stability of the complex increases approximately 2.5-fold. This is apparently due to the fact that the electron-withdrawing effect of the positively charged benzothiazole residue on the binding of metal cations becomes weaker. In fact, it is known that in *cis*-alkenes, the effects of substituents are less efficiently transferred through the C=C bond than in the corresponding *trans*-isomers.

Betaine *trans*-2b, like cationic dye *trans*-2a, isomerizes on exposure to visible light. The resulting *cis*-2b is also unstable and is converted in the dark into the *trans*isomer; the rate constant for this transformation differs only slightly from k_{c-t} for *cis*-2a (see Table 1).

The addition of Ca^{2+} ions to a dilute solution of 2b $(C_{\rm L} = 1 \cdot 10^{-5} \text{ mol } \text{L}^{-1})$ also results in a decrease in the rate of the dark isomerization. This effect, unlike that in the case of 2a, is manifested even at $C_{\rm M}/C_{\rm L} \leq 1$; however, the time dependence of the optical density of the solution cannot be described adequately by a simple exponent; one reason for this is the fact that the absorption spectrum of the resulting trans-isomer depends on the concentration.¹⁰ The retardation of the dark isomerization indicates that cis-2b is less prone to aggregation than the corresponding trans-isomer, and that it forms, at least in dilute solutions, complexes in which the Ca²⁺ ion is located in the crown-ether cavity. Otherwise, it could hardly be expected that the metal cation would exert a substantial effect on the electronic structure of the chromophore.

When the C_M/C_L ratio is increased to 1.5 and the proportion of *cis*-2b is not larger than 20% of the total concentration of the dye, the plot for the dark variation of the optical density of the solution is multiexponential. The observed rate constant for *cis*-*trans*-isomerization is $9.0 \cdot 10^{-4} \text{ s}^{-1}$. By substituting the resulting k_{c-1}^{obs} value and the corresponding k_{c-1} value from Table 1 as well as $C_M = 1.5 \cdot 10^{-5} \text{ mol } L^{-1}$ in formula (2), one can estimate the lower limit for the stability constant of the complex of *cis*-2b with Ca²⁺ (see Table 1).

It can be seen from Table 1 that on going from the cationic dye to the betaine, stability of the complexes formed by the *cis*-isomer increases by more than three orders of magnitude. This can apparently be explained by

the fact that in complexes of *cis*-2b, an intramolecular coordination bond is formed between the Ca^{2+} ion located in the crown-ether cavity and the sulfo group at the *N*-substituent. Previously,^{3,4} we found that a bond of this type is formed in the complexes of *cis*-1a,b with Mg²⁺.

When a solution of 2b containing Ca²⁺ ions is irradiated with light with $\lambda = 546$ nm under conditions in which the degree of aggregation of the trans-isomer is low ($C_L = 1 \cdot 10^{-5}$ mol L^{-1} , $C_M/C_L = 100$, see Ref. 10), a *trans-cis*-photosteady state is established; as can be seen from Fig. 2, the equilibrium in this state is markedly shifted toward the cis-isomer (>97%). The spectrum of $(cis-2b) \cdot Ca^{2+}$ exhibits a medium-intensity band with a maximum at 350-360 nm, and the residual absorption in the long-wavelength region of the spectrum is extremely low. The very large hypsochromic shift, equal to 170 nm, of the spectrum of (cis-2b) · Ca²⁺ with respect to the spectrum of (trans-2b) · Ca²⁺, can, apparently, be explained, as in the case of dyes la,b, by the formation of anion-"capped" complexes in which the molecule of the dye acquires a twisted conformation with marked disruption of the conjugation in the chromophore.4

When a solution of 2b is irradiated under conditions in which the *trans*-isomer is mostly aggregated ($C_{\rm L} = 6 \cdot 10^{-4}$ mol L⁻¹, $C_{\rm M}/C_{\rm L} = 0.25$, see Ref. 10), the equilibrium in the *trans*-cis-photosteady state is, conversely, shifted substantially toward the *trans*-isomer. Evidently, this indicates that the *trans*-isomer does not isomerize in the aggregated state. Deactivation of the excited state through an internal conversion is a characteristic feature of the behavior of aggregates of many dyes.¹¹



Fig. 2. Absorption spectra of CSD 2b in MeCN ($C_L = 1.0 \cdot 10^{-5} \text{ mol } L^{-1}$) in the presence of Ca(ClO₄)₂ at $C_M/C_L = 100$; *trans*-isomer (1), *trans*-cis-photosteady state formed on exposure to light with a wavelength of 546 nm and an intensity of ~1 · 10¹⁶ cm⁻² s⁻¹.



M = Ca, Ba, Mg

Table 1 presents the observed rate constants for the dark *cis*—*trans*-isomerization of 2b,c at $C_{\rm L} = 1 \cdot 10^{-5}$ mol L⁻¹ in the presence of Na, Zn, Mg, Ca, and Ba perchlorates with $C_{\rm M} = 1 \cdot 10^{-3}$ mol L⁻¹ (under these conditions, aggregation of the dyes can be neglected¹⁰).

It can be seen that all the metal cations without exception accelerate the dark cis-trans-isomerization of dye 2c. The smaller the diameter of the cation and the higher its charge, the more pronounced this effect. The increase in the rate constant of dark isomerization is obviously due to the interaction of the metal cation with the sulfo group at the N-substituent, which exerts a certain effect on the electronic structure of the chromophore. This is indicated, for example, by the fact that the addition of doubly-charged metal cations to a solution of *trans*-2c results in a small (in the case of Mg^{2+} , up to 2 nm) bathochromic shift of the long-wavelength absorption band and in an increase in the extinction coefficient. It can be suggested that the interaction between the metal cation and the sulfo group leads to the decomposition of the intramolecular ion pair formed between the negatively charged sulfo group and the positively charged N atom of the benzothiazolium residue; this, in turn, results in more efficient delocalization of this positive charge over the conjugation chain of the chromophore and, consequently, in a decrease in the activation barrier to cis-trans-isomerization.

In the case of dye 2b, Na⁺ and Zn²⁺ ions also accelerate dark *cis—trans*-isomerization. Evidently, the ability of the aza-15-crown-5-ether moiety in *cis*-2b to bind these cations is very low, and they react only with the sulfo group of the *N*-substituent.

At the same time, it can be seen from Table 1 that alkaline earth metal cations exert a substantial inhibitory effect on the cis—trans-isomerization of 2b; this indicates that these cations interact with the azacrown-ether moiety in cis-2b and that anion-"capped" complexes are formed. The greatest effect is observed in the case of Ca^{2+} ions, which are known¹² to form the most stable complexes with aza-15-crown-5 ethers of the alkaline earth metal cations.

Thus, we synthesized styryl dyes containing an aza-15-crown-5-ether moiety; this made it possible to discover and to study the ion-selective reaction yielding photochromic anion-"capped" complexes, characterized by great hypsochromic shifts of the long-wavelength absorption bands upon *trans-cis*-isomerization, which is not typical of photochromic systems.

Experimental

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

Electronic absorption spectra were measured on a Specord-M40 spectrophotometer. The kinetics of dark *cis*—*trans*-isomerization was monitored based on the variation of the optical density of the solution at a particular wavelength (for lifetimes of the *cis*-isomer $\tau > 20$ s, a Specord-M40 spectrophotometer was used, while for $\tau < 20$ s, the measurements were carried out using a setup described previously¹³). Solutions of the dyes were irradiated with light from a DRSh-250 mercury lamp with a wavelength of 546 nm and an intensity of $\sim 1 \cdot 10^{16}$ cm⁻² s⁻¹. The experiments were carried out at ~ 20 °C in quartz cells of length d = 1 cm. In the case of concentrate solutions of dyes, a cell with d = 100 mm was used. The internal surfaces of all the cells were modified with hydrophobic groups.¹⁴

The stability constants of the complexes of *cis*-2a.b with Ca^{2+} ions in MeCN were estimated from the dependence of the rate constant of the dark *cis*-*trans*-isomerization on the concentration of added metal cation (for more details, see the text of the paper). To exclude the interaction of complexes with perchlorate ions from consideration, ¹⁴ the overall concentration of ClO_4^- in solutions was maintained constant ($C_A = 0.01 \text{ mol } L^{-1}$) by means of Et_4NClO_4 used as the supporting electrolyte (as was done in the case of *trans*-2a.b, see Ref. 10). The ionic strength of solutions of *cis*-2a varied over a very narrow range, from 0.01 to 0.015 mol L^{-1} , and in the case of *cis*-2b, it amounted to 0.01 mol L^{-1} . The resulting stability constants are effective values and correspond to the equation

$$K = [LM]^{\bullet}([L][M]^{\bullet})^{-1},$$

where $[LM]^* = [LM] + [LMA]$, $[M]^* = [M] + [MA]$, L is the dye, M is the metal cation, and A is perchlorate anion. Since under the experimental conditions, the $[ClO_4^-]$ value varied only slightly and was close to the overall constant concentration C_A in solution,

$$K = K_{LM}(1 + K_{LMA}C_A)(1 + K_{MA}C_A)^{-1},$$

where $K_{LM} = [LM]([L][M])^{-1}$, $K_{LMA} = [LMA]([LM][A])^{-1}$, and $K_{MA} = [MA]([M][A])^{-1}$ (for more details, see Refs. 10 and 14). Acctonitrile and Mg, Ca, and Ba perchlorates were dehydrated by known procedures.¹⁴ The Na and Zn perchlorates and Et_4NClO_4 were dried *in vacuo* at 230, 110, and 40 °C, respectively.

3-Ethyl-2-methylbenzothiazolium perchlorate (3a). 3-Ethyl-2-methylbenzothiazolium iodide (5) (0.314 g, 1.03 mmol) was dissolved in hot MeOH, and 56% HClO₄ (0.55 mL) was added. Three hours later the precipitate was filtered off, washed with cold MeOH, and dried. The yield of 3a was 0.25 g (88%), m.p. 177-179 °C. Found (%): C, 43.02; H, 4.47; N, 4.95. $C_{10}H_{12}CINO_4S$. Calculated (%): C, 43.32; H, 4.37; N, 5.05.

2-Methyl-3-(3-sulfopropyl)benzothiazolium (3b). A mixture of 2-methylbenzothiazole (6) (2 g, 1.71 mL, 13.4 mmol) and 1,3-propanesultone (7) (2.128 g, 1.53 mL, 17.4 mmol) was heated for 13 h at 120 °C. Then the reaction mixture was refluxed with Me₂CO, and the solid product was filtered off and recrystallized from MeOH. The yield of betaine 3b was 1.85 g (51%), m.p. 276-278 °C (cf. Ref. 8).

trans-3-Ethyl-2-{2-[4-(4,7,10,13-tetraoxa-1-azacyclopentadecyl)phenyl]vinyl]benzothiazolium perchlorate (2a). A mixture of 3-ethyl-2-methylbenzothiazolium perchlorate (3a) (0.25 g, 0.9 mmol) and N-(4-formylphenyl)aza-15-crown-5 ether (4) (0.32 g, 1 mmol) was dissolved in 10 mL of anhydrous EtOH, and pyridine (0.15 mL) was added. The reaction mixture was refluxed for 8 h and concentrated in vacuo. The crude product was refluxed with hexane, and the residue was recrystallized from MeOH. The yield of 2a was 0.35 g (66%), m.p. 237-239 °C. ¹H NMR (MeCN-d₃, 400 MHz), δ: 1.58 (t, 3 H, Me, J = 7.3 Hz); 3.60 (br.s, 4 H, δ-CH₂O); 3.65 (m, 8 H, γ,γ '-CH₂O); 3.74 (m, 4 H, α,α '-CH₂N); 3.82 (m, 4 H, β , β '-CH₂O); 4.71 (q, 2 H, <u>CH₂Me</u>, J = 7.3 Hz); 6.92 (m, 2 H, H(C-3'), H(C-5')); 7.30 (d, 1 H, H(C-a), ${}^{3}J_{mars} = 15.2$ Hz); 7.70 (m, 1 H, H(C-6), $J_{H(6),H(7)} = 8.1$ Hz); 7.79 (m, 2 H, H(C-2'), H(C-6')); 7.81 (m, 1 H, H(C-5), $J_{H(5),H(4)} = 8.5 \text{ Hz}$; 7.94 (d, 1 H, H(C-4), $J_{H(4),H(5)} =$ $J_{H(5),H(4)} = 0.5 H_{2}$, $J_{J} = 0.5 H_{2}$, $J_{J} = 0.5 H_{2}$, $J_{H(4),H(5)} = 0.1 H_{2}$. Found (%): C, 54.93; H, 6.00; N, 4.64. $C_{27}H_{35}CIN_2O_8S \cdot 0.5 H_2O$. Calculated (%): C, 54.81; H, 6.14; N, 4.74.

trans-2-{2-[4-(4,7,10,13-Tetraoxa-1-azacyclopentadecyl)phenyl]vinyl}-3-(3-sulfopropyl)benzothiazolium (2b) was prepared from betaine 3b and N-(4-formylphenyl)azal5-crown-5 ether (4) similarly to 2a. Yield 82%, m.p. 230-231 °C. ¹H NMR (DMSO-d₆, 400 MHz), δ : 2.07 (m, 2 H, CH₂); 2.66 (m, 2 H, CH₂SO₃⁻); 3.61 (br.s. 4 H, δ -CH₂O); 3.66 (m, 8 H, γ,γ' -CH₂O); 3.80 (m, 8 H, α,α' -CH₂N, β,β' -CH₂O); 4.91 (m, 2 H, N<u>CH₂CH₂CH₂); 6.94 (m, 2 H, H(C-3'), H(C-5')); 7.77, 7.87 (2 m, 2 H, H(C-6) and H(C-5), J = 8.1 Hz, J = 8.6 Hz); 7.84 (d, 1 H, <u>CH=CH</u>, ³ $J_{rrans} =$ 15.2 Hz); 8.04 (m, 2 H, H(C-2'), H(C-6')); 8.16 (d, 1 H, CH=<u>CH</u>, ³ $J_{rrans} =$ 15.2 Hz); 8.30, 8.38 (2 d, 1 H, H(C-7) and H(C-4), J = 8.1 Hz, J = 8.6 Hz). Found (%): C, 54.15; H, 6.32; N, 4.27. C₂₈H₃₆N₂O₇S₂ · 2.5 H₂O. Calculated (%): C, 54.09; H, 6.65; N, 4.51.</u>

trans-2-[2-(4-Dimethylaminophenyl)vinyl]-3-(3-sulfopropyl)benzothiazolium (2c). A mixture of betaine 3b (0.24 g, 0.88 mmol) and para-dimethylaminobenzaldehyde (4) (0.16 g, 1.07 mmol) in 5 mL of Ac₂O was refluxed for 6 h. Product 2c was precipitated from the reaction mixture with Et₂O. The precipitate was filtered off, washed with hot MeCN, and recrystallized from MeOH. Yield 0.178 g (48%), m.p. 187--189 °C. ¹H NMR (DMSO-d₆, 400 MHz), δ : 2.32 (m, 2 H, CH₂); 2.77 (m, 2 H, CH₂SO₃⁻); 3.22 (s, 6 H, NMe₂); 5.09 (m, 2 H, NCH₂); 6.95 (d, 2 H, H(C-3'), H(C-5')); 7.76, 7.87 (2 m, 2 H, H(C-6) and H(C-5)); 7.99 (d, 1 H, <u>CH</u>=CH, ³J_{trans} = 15.5 Hz); 8.06 (d, 2 H, H(C-2'), H(C-6')); 8.14 (d, 1 H, CH=<u>CH</u>, ³J_{trans} = 15.5 Hz); 8.32, 8.35 (2 d, 1 H, H(C-7) and H(C-4)). Found (%): C, 57.22; H, 5.29. C₂₀H₂₂N₂O₃S₂ · H₂O. Calculated (%): C, 57.13; H, 5.76.

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