

Diammonium cation-induced self-assembly into a pseudocyclic complex leading to the stereospecific [2 + 2]-photocycloaddition of a crown-containing bis(styryl) dye

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A new bis(styryl) dye of the pyridine series containing two 18-crown-6 ether fragments forms a pseudocyclic complex with the 1,3-diammoniumpropane dication, which undergoes [2 + 2]-photocycloaddition affording a single cyclobutane isomer.

Macrocyclic ligands containing photochromic fragments are of interest as potential materials for information recording and storage systems and as optical molecular sensors and photo-switched molecular devices.^{1–6} The relationship between complexation and photochromic reaction is the most interesting subject of investigations in this field. An example of photochromic macrocyclic ligands is provided by crown-containing unsaturated compounds, for example, stilbenes, styryl and butadienyl dyes, which are capable of selective binding of metal and ammonium cations at the crown-ether fragment and can undergo reversible structural changes during *E–Z* photoisomerization and [2 + 2]-photocycloaddition (PCA).^{3,7–9}

Recently, we reported the synthesis of a photochromic bis-(18-crown-6) ether composed of two crown-containing styryl dyes connected by a *para*-xylyl spacer.¹⁰ This dye can form pseudocyclic complexes with diammoniumalkane cations. The photochemistry of this dye is limited to *E–Z* photoisomerization because intramolecular PCA is impossible for steric reasons.

Here, we present the synthesis and the results of a preliminary study of the complexation and photochromic properties of a new 18-crown-6-containing bis(styryl) dye **2** with a *meta*-xylyl spacer between the two styryl chromophores (Scheme 1).

Dye **2** was prepared in a moderate yield by quaternization of 18-crown-6-containing 1-pyridyl-2-phenylethylene [(*E*)-**1**, ref. 10] with 1,3-bis(bromomethyl)benzene followed by anion exchange with perchloric acid.[†] Dye **2** was characterised by elemental analysis and ¹H NMR spectroscopy, including COSY spectra. According to ¹H NMR data, both styryl moieties of **2** have *E*-configuration (³*J*_{H_aH_b} 15.9 Hz).

The *E,E*-isomer of dye **2** in acetonitrile exhibits an intense long-wavelength absorption band (LAB) with a maximum at 410.5 nm (Figure 1, curve 1). Long-term irradiation of a solution of (*E,E*)-**2** with visible light resulted in a slight decrease in the LAB intensity and gave rise to signals typical of *cis*-CH=CH (two doublets, 6.69 and 7.18 ppm, ³*J*_{H_aH_b} 12.1 Hz) in the ¹H NMR

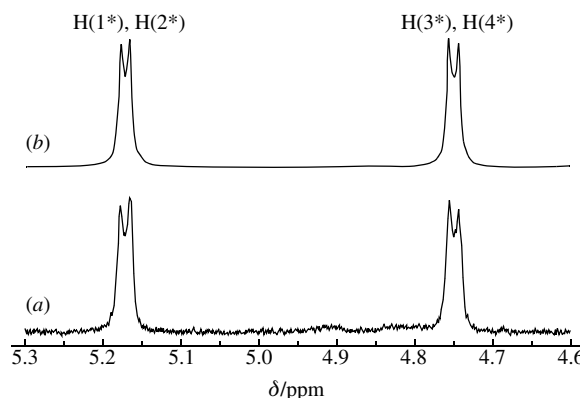


Figure 2 (a) ¹H NMR spectrum of the cyclobutane protons of *rctt*-3 ([²H₆]DMSO, 25 °C) and (b) its best fit to an AA'BB' spin system.

spectra, which is indicative of reversible *E–Z* photoisomerization of the dye. According to NMR, the *E–* to *Z*-isomer ratio was about 9:1 per styryl fragment. No other photoproducts, apart from the *Z*-isomers of the dye, were detected.

The addition of 1,3-diammoniumpropane diperchlorate to a solution of (*E,E*)-**2** induced a hypsochromic shift of the LAB ($\Delta\lambda_{\text{max}} = 27$ nm, Figure 1, curve 2). Analysis of the ¹H NMR titration[‡] data shows that bis(crown) ether **2** and the H₃N⁺-(CH₂)₃N⁺H₃ cation form a 1:1 complex (log *K* > 5) in CD₃CN. The complex has probably a pseudocyclic structure due to the ditopic interaction between the components (Scheme 2). The formation of the pseudocyclic complex implies close proximity

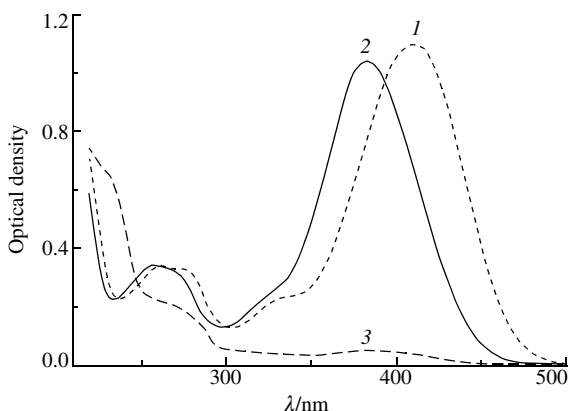
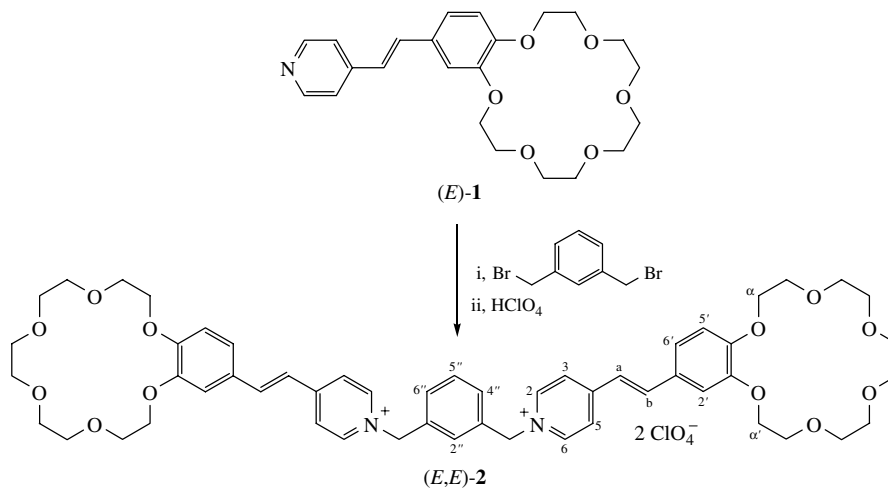


Figure 1 UV/VIS spectra of (*E,E*)-**2** (1.6×10^{-5} M, 1 cm cell) in MeCN (1) in the absence of diammonium salt and (2) in the presence of H₃N⁺(CH₂)₃N⁺H₃·2ClO₄[−] at a concentration of 1×10^{-3} M. Curve 3 is the spectrum of the solution containing the diammonium salt after extended photolysis with visible light.

[†] 4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)ethenyl]-1-[4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)ethenyl]pyridinium-1-yl]methylbenzylpyridinium diperchlorate [(*E,E*)-**2**]. A solution of 4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-1-ethenyl]pyridine [(*E*)-**1**] (100 mg, 0.24 mmol) and 1,3-bis(bromomethyl)benzene (29 mg, 0.11 mmol) (Aldrich) in anhydrous ethanol (15 ml) was refluxed for 25 h and then cooled to 5 °C. The precipitate formed was filtered off, washed with cold ethanol (2 × 3 ml) and then with benzene (3 ml) and dried in air to give the yellow dibromide of the dye (55 mg, 0.05 mmol). The dibromide salt was dissolved in a minimum quantity of hot anhydrous ethanol, and 70% aq. HClO₄ (18 μl, 0.20 mmol) was added. After cooling to −10 °C, the precipitate formed was filtered off, washed with cold ethanol (2 × 3 ml) and dried in air to give dye (*E,E*)-**2** as a yellow powder (33 mg, overall yield of 27%). mp > 221 °C (decomp.). ¹H NMR (Bruker DRX500, [²H₆]DMSO, 25 °C) δ: 3.53 (s, 8H, 4CH₂O), 3.56 (m, 8H, 4CH₂O), 3.62 (m, 8H, 4CH₂O), 3.79 (m, 8H, 4CH₂O), 4.16 (m, 8H, 4CH₂OAr), 5.73 (s, 4H, 2CH₂N), 7.07 [d, 2H, 2H(5'), *J* 8.2 Hz], 7.27 [br. d, 2H, 2H(6'), *J* 8.2 Hz], 7.38 [br. s, 2H, 2H(2')], 7.41 (d, 2H, 2H_a, *J* 15.9 Hz), 7.53 [m, 3H, H(4''), H(5''), H(6'')], 7.58 [br. s, 1H, H(2'')], 7.95 (d, 2H, 2H_b, *J* 15.9 Hz), 8.17 [d, 4H, 2H(3), 2H(5), *J* 6.7 Hz], 8.94 [d, 4H, 2H(2), 2H(6), *J* 6.7 Hz]. Found (%): C, 56.04; H, 5.81; N, 2.30. Calc. for C₅₄H₆₆Cl₂N₂O₂₀·1.5H₂O (1161.03) (%): C, 55.86; H, 5.99; N, 2.41.

[‡] CD₃CN solution, 30 °C; the concentration of (*E,E*)-**2** was maintained at 2×10^{-3} M, and the concentration of 1,3-diammoniumpropane diperchlorate was varied from 0 to 6×10^{-3} M.



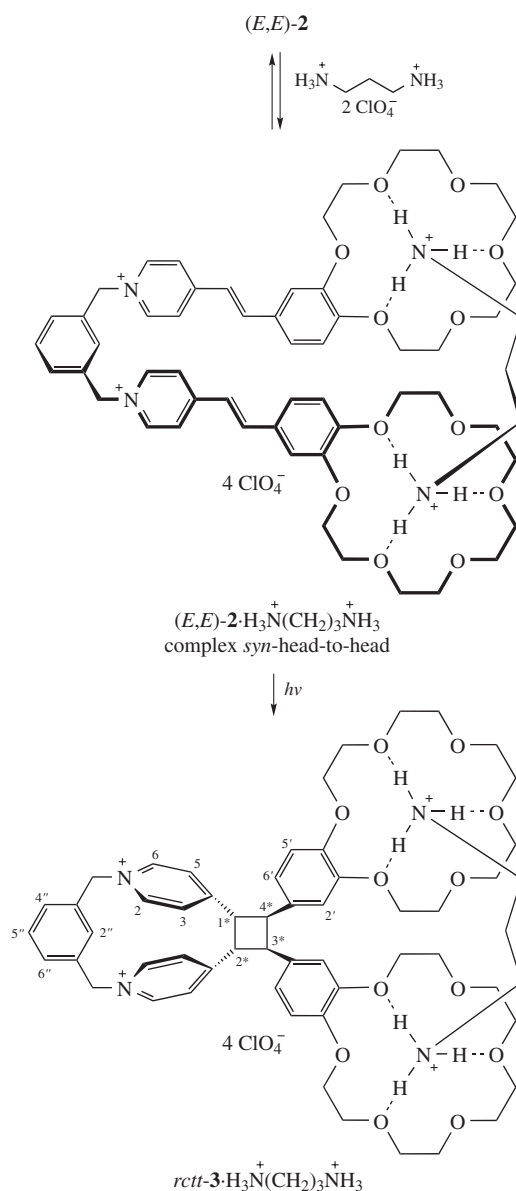
Scheme 1

between the styryl fragments of the dye, as the $\text{H}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{H}_3$ cation is rather short. This proximity is manifested in the ^1H NMR spectra as an upfield shift of the signals of some aromatic and ethylene protons of the dye ($\Delta\delta_{\text{H}}$ up to 0.55 ppm), because they get in the shielding regions of the conjugated fragments. The existence of ditopic interaction in $(E,E)\text{-2} \cdot \text{H}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{H}_3$ is additionally confirmed by the fact that the stability constant of this complex is much higher than typical stability constants of complexes formed by ammonium cations with mono-18-crown-6 ethers ($\log K \leq 4$).⁹

On long-term photolysis of the $(E,E)\text{-2} \cdot \text{H}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{H}_3$ complex with visible light, the absorption at about 400 nm disappeared almost entirely (Figure 1, curve 3). Analysis of the ^1H NMR spectra of the photolysis products shows that the dye underwent stereospecific PCA in the pseudocyclic complex to give a single isomer of a cyclobutane derivative⁸ (compound **3**, Scheme 2). The spectrum of the cyclobutane protons of **3** was found to fit well to an AA'BB' spin system¹¹ with the vicinal coupling constants $^3J_{\text{H}(1^*),\text{H}(4^*)} = ^3J_{\text{H}(2^*),\text{H}(3^*)} = 6.2$ Hz and $^3J_{\text{H}(1^*),\text{H}(2^*)} = ^3J_{\text{H}(3^*),\text{H}(4^*)} = 4.7$ Hz (Figure 2). A similar cyclobutane sub-spectrum has been reported previously for one of the two cycloadducts formed upon photolysis of the barium complex of a 15-crown-5-containing bis(styryl) benzothiazole dye.¹² By analogy, the *rc*tt type structure was assigned to cyclobutane isomer **3**. This structure could result from concerted cycloaddition of two *syn*-head-to-head styryl residues of $(E,E)\text{-2}$. The stereospecificity of PCA in the complex $(E,E)\text{-2} \cdot \text{H}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{H}_3$ is apparently due to the rigid structure of the *meta*-xylyl spacer and the small length of the diammonium cation, which minimise the number of conformations of the pseudocyclic complex with an orientation of the C=C bonds favourable for cycloaddition.

In the case of dye $(E,E)\text{-2}$, two pairs of pyridine protons, H(2) and H(6), H(3) and H(5), are responsible for averaged

signals, one for each pair [Figure 3(a)], due to fast conformational transitions. In the case of cycloadduct *rc*tt-**3**, each proton gives rise to a separate signal [Figure 3(b)] because the presence of a 15-membered ring annelated to the cyclobutane ring hampers the rotation of pyridine rings. Analysis of the NOESY spectrum of *rc*tt-**3** has shown that the H(3) protons are located close to



Scheme 2

⁸ 3,4-Di-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-9,17-diazoniapentacyclo[15.2.2.2^{6,9}.1^{11,15}.0^{2,5}]-tetracos-1(19),6,8,11,13,15(24),17,20,22-nonaene diperchlorate (*rc*tt-**3**). A solution of dye $(E,E)\text{-2}$ (6.4 mg, 5.6 μmol) and 1,3-diammonium-propane diperchlorate⁹ (3.1 mg, 11.2 μmol) in acetonitrile (10 ml) placed in a thin-walled glass flask was irradiated with light of a 60 W incandescent lamp (70 h; distance from the light source, 15 cm) and then evaporated *in vacuo*. According to ^1H NMR data, the residue consisted of initial dye **2** and photoadduct *rc*tt-**3** in a ratio of 1:8.6. ^1H NMR (Bruker DRX500, [$^2\text{H}_6$]DMSO, 25 °C) δ : 3.53 (s, 8H, 4CH₂O), 3.55 (m, 8H, 4CH₂O), 3.59 (m, 8H, 4CH₂O), 3.71 (m, 8H, 4CH₂O), 3.97 and 4.00 (2m, 8H, 4CH₂OAr), 4.75 [m, 2H, H(3*), H(4*)], 5.17 [m, 2H, H(1*), H(2*)], 5.88 and 5.92 (2d, 4H, 2CHH'N, 2CHH'N, J 17.3 Hz, J 17.3 Hz), 6.83 [m, 7H, 2H(2'), 2H(5'), 2H(6'), H(2'')], 7.51 [br. d, 2H, H(4''), H(6''), J 7.6 Hz], 7.59 [t, 1H, H(5''), J 7.6 Hz], 7.98 [br. d, 2H, 2H(3), J 6.6 Hz], 8.21 [br. d, 2H, 2H(5), J 6.4 Hz], 8.75 [d, 2H, 2H(2), J 6.6 Hz], 8.91 [d, 2H, 2H(6), J 6.4 Hz].

¹¹ Fitting was performed using the CALM iterative program (a PC version of UELTR¹¹).

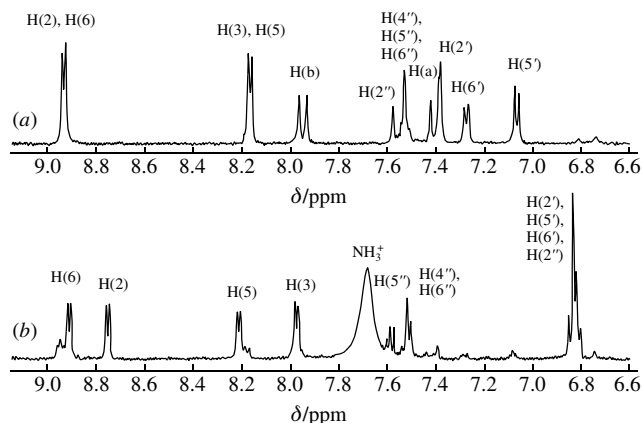


Figure 3 ^1H NMR spectra of (a) (E,E) -**2** and (b) a mixture of *rctt*-**3** and $\text{H}_3\text{N}^+(\text{CH}_2)_3\text{N}^+\text{H}_3 \cdot 2\text{ClO}_4^-$ (aromatic region, $[\text{D}_6]\text{DMSO}$, 25 °C). The minor signals in the lowermost spectrum are attributed to unreacted dye **2**.

the cyclobutane protons, $\text{H}(1^*)$ and $\text{H}(2^*)$, and the $\text{H}(5)$ protons, to $\text{H}(3^*)$ and $\text{H}(4^*)$, i.e., the photocycloadduct has the spatial structure shown in Scheme 2.

To elucidate the possible influence of the length of the polymethylene chain in the diammoniumalkane cation on the photochemical properties of pseudocyclic complexes of dye (E,E) -**2**, we used 1,12-diammoniumdodecane diperchlorate. We found that the complex (E,E) -**2**· $\text{H}_3\text{N}^+(\text{CH}_2)_{12}\text{N}^+\text{H}_3$ ($\Delta\lambda_{\text{max}} = 19.5$ nm) does not undergo PCA upon long-term photolysis with visible light. The photolysis products were a mixture of the *E*- and *Z*-isomers of dye complexes. The lack of PCA in (E,E) -**2**· $\text{H}_3\text{N}^+(\text{CH}_2)_{12}\text{N}^+\text{H}_3$ is apparently due to steric factors, in particular, to the relatively large average distance between the styryl fragments.

Thus, diammoniumalkane salts can pre-organise dye (E,E) -**2** toward stereospecific intramolecular PCA. The feasibility of this photoreaction depends on the length of a polymethylene chain in the diammonium salt. The results demonstrate the possibility of using styryl dyes of this type in information recording and storage systems and as optical molecular sensors for diammonium salts.

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