Available online at www.sciencedirect.com
SCIENCE DIRECT®
Mendeleev Commun., 2007, **17**, 264–267

Mendeleev Communications

New cation-‘capped’ complex of the *Z*-isomer of a crown-containing styryl dye bearing a long *N*-ammonioalkyl substituent

Artem I. Vedernikov, Dmitry V. Kondratuk, Natalia A. Lobova, Tatyana M. Valova, Valery A. Barachevskii, Mikhail V. Alfimov and Sergei P. Gromov*

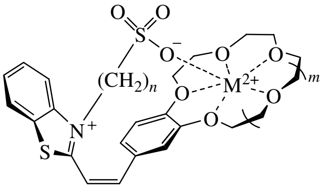
Photochemistry Center, Russian Academy of Sciences, 119421 Moscow, Russian Federation. Fax: +7 495 936 1255; e-mail: gromov@photonics.ru

DOI: 10.1016/j.mencom.2007.09.005

Two new styryl dyes of the benzothiazole series containing a 18-crown-6 moiety and an *N*-ammoniohexyl or *N*-ethyl substituent were synthesised. In acetonitrile, the dye bearing the ammoniohexyl linker forms a stable dimeric complex in the *E*-form and an intramolecular cation-‘capped’ complex in the *Z*-form due to ‘host–guest’ hydrogen bonding.

Photosensitive crown-containing compounds are promising for the creation of photoswitchable molecular devices and data recording and storage systems.[1–3] Previously, attention has been focused on the photoswitchable crown-containing systems based on azobenzene derivatives in which switching is attained through *E*–*Z* photoisomerisation of the N=N double bond.[1,4,5] However, azobenzene derivatives suffer from drawbacks, *e.g.*, poorly pronounced photochromic properties due to the π→π* electron transition apart from the *n*→π* transition and the lack of fluorescence. The photochromism of carbon unsaturated compounds is more pronounced; they readily fluoresce and are more easily synthesised than azo compounds. However, the potential of using *E*–*Z*–photoisomerisation of crown-containing unsaturated compound has not been fully implemented.

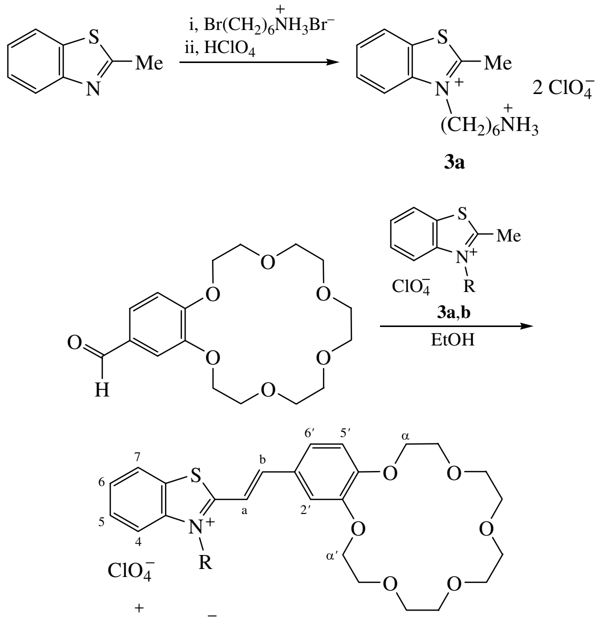
Previously,[6–8] we studied crown-containing styryl dyes having an *N*-sulfonatoalkyl substituent in the heterocyclic fragment (for example, **1**), in which photoisomerisation of the ethylene bond in the presence of alkaline earth metal cations resulted in the formation of stable anion-‘capped’ complexes and a substantial change in the spectral characteristics of complexes (*Z*)-**1**·M^{2+} compared with the complexes formed by the *E*-isomers [the hypsochromic shift of the long-wavelength absorption band (LAB) peak reached 90 nm].



(Z)-**1**·M^{2+}
$n = 3, 4; m = 1, 2$

For these systems, the presence of a metal cation was obligatory; systems in which the sulfonate group of the N-substituent is replaced by the ammonium group are free from this drawback. Thus, the presence of an ammonioalkyl substituent in the crown-containing azobenzene resulted in the formation of relatively stable cation-‘capped’ complexes in the *Z*-form.[4] We suggested that the introduction of a long *N*-ammonioalkyl substituent into the styryl dye structure would also allow one to obtain, upon *E*→*Z* isomerisation, stable cation-‘capped’ complexes possessing substantial spectral differences from the corresponding *E*-isomers.

Here, we report the synthesis of new 18-crown-6-based styryl dye **2a** containing an *N*-ammoniohexyl substituent and model dye **2b** having the same structure of the chromoionophore fragment as **2a** but devoid of the functional group in the N-substituent. The complexation of dyes **2a**,**b** with ethylammonium ions and their photochemical behaviour were studied.



a R = $(CH_2)_6\overset{+}{N}H_3ClO_4^-$ (*E*)-**2a**,**b**
b R = Et

Scheme 1

Dyes **2a**,**b** were prepared by the condensation of quaternary salts of 2-methylbenzothiazolium **3a** and **3b**[9] with 4′-formylbenzo-18-crown-6 ether. Salt **3a** was synthesised by the quaternization of 2-methylbenzothiazole with bromohexylammonium bromide[10] followed by treatment with concentrated perchloric acid (Scheme 1).[†] Dyes **2a**,**b** are *E*-configured at the ethylene bond, as indicated by the spin–spin coupling constant $^3J_{H^a,H^b}$ 15.8–15.9 Hz.

The solutions of dyes **2a** and **2b** in MeCN exhibit LABs at 428 and 431 nm, respectively (Figure 1, curves *1* and *2*).[‡] The addition of a 100-fold excess of $EtNH_3ClO_4$ to solutions of **2a**,**b** induces hypsochromic shifts of the LABs of the dyes by 12 and 14 nm, respectively, which attest to the formation of complexes of the ethylammonium ion with their crown-ether moieties. The intensity of the long-wavelength absorption of free **2a** is somewhat lower than that of **2b**, while their spectra in the presence of $EtNH_3ClO_4$ almost coincide. This is indicative of a weak intermolecular interaction of chromophore fragments in free **2a**, probably, due to the formation of dimer [(*E*)-**2a**]$_2$ through hydrogen bonding between the ammonium group of one dye molecule and the crown-ether moiety of a second molecule (Scheme 2).

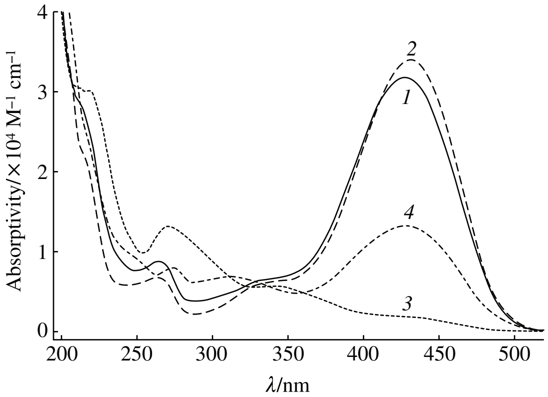
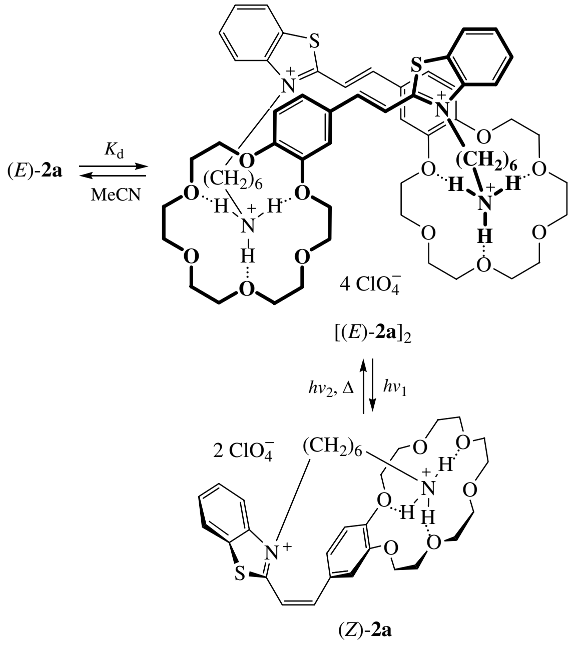


Figure 1 Absorption spectra of (*1*) (*E*)-**2a** and (*2*) (*E*)-**2b** (2×10^{-5} M, MeCN, 1 cm cell, room temperature) and photostationary state of (*3*) **2a** and (*4*) **2b** (irradiation with light at 436 nm).



Scheme 2

The ^{1}H NMR spectra of dyes (*E*)-**2a**,**b** in a solution in [$^2H_3$]MeCN exhibited considerable upfield shifts of the signals of the H^4, $H^{5'}$, $H^{6'}$ aromatic protons, the H^b ethylene proton, and the CH_2N-group protons of dye **2a** with respect to these signals of **2b** [Figure 2(*a*),(*b*)]. In dimer [(*E*)-**2a**]$_2$, these protons fall, apparently, into the shielding area of the conjugated fragment of the neighbouring molecule; the most probable structure of the dimeric complex complying with this spectral behaviour is shown in Scheme 2. The other aromatic protons and the CH_2O-group protons of dye **2a** show downfield shifts with respect to **2b**, which evidently reflect the electron-withdrawing influence of the ammonium group bound by the crown-ether moiety in the dimer complex. The downfield shift of all types of protons was also observed upon the addition of excess $EtNH_3ClO_4$ to model dye **2b**.

The stability of complexes (*E*)-**2a**,**b** was quantitatively determined by ^{1}H NMR titration.[§] First, the stability constant of the complex formed by **2b** with $EtNH_3^+$ was measured in terms of the equation

$$(E)\text{-}\mathbf{2b} + \mathrm{EtNH_3^+} \xrightleftharpoons{K} (E)\text{-}\mathbf{2b}\cdot\mathrm{EtNH_3^+}. \tag{1}$$

[†] *3-(6-Ammoniohexyl)-2-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)ethenyl]-1,3-benzothiazol-3-ium diperchlorate* (*E*)-**2a**. A mixture of **3a** (200 mg, 0.45 mmol), 4′-formylbenzo-18-crown-6 ether (167 mg, 0.49 mmol) and abs. EtOH (6 ml) was heated at 80 °C (oil bath) for 120 h. After cooling, the precipitate was filtered off, washed with CH_2Cl_2 (2×5 ml) and abs. EtOH (5 ml) and dissolved in MeCN, and the solution was filtered and then evaporated *in vacuo*. The residue was washed with abs. EtOH (5 ml) and dried in air to give **2a** (226 mg, yield 63%) as a dark orange powder; mp 243–246 °C (decomp.). ^{1}H NMR (Bruker DRX500, [$^2H_6$]DMSO, 25 °C) δ: 1.35 (m, 2H, $CH_2CH_2CH_2NH_3$), 1.42 (m, 2H, $CH_2CH_2CH_2N$), 1.47 (m, 2H, $CH_2CH_2NH_3$), 1.84 (m, 2H, CH_2CH_2N), 2.72 (m, 2H, CH_2NH_3), 3.54 (s, 4H, $2CH_2O$), 3.57 (m, 4H, $2CH_2O$), 3.64 (m, 4H, $2CH_2O$), 3.80 (m, 2H, CH_2CH_2OAr), 3.83 (m, 2H, CH_2CH_2OAr), 4.23 (m, 4H, $2CH_2OAr$), 4.93 (m, 2H, CH_2N), 7.16 (d, 1H, $H^{5'}$, *J* 8.6 Hz), 7.55 (br. s, 3H, NH_3), 7.66 (s, 1H, $H^{2'}$), 7.67 (dd, 1H, $H^{6'}$, *J* 8.6 Hz, *J* 1.8 Hz), 7.79 (m, 1H, H^6), 7.85 (d, 1H, H^a, *J* 15.9 Hz), 7.86 (m, 1H, H^5), 8.19 (d, 1H, H^b, *J* 15.9 Hz), 8.26 (d, 1H, H^4, *J* 8.6 Hz), 8.43 (d, 1H, H^7, *J* 8.2 Hz). Found (%): C, 46.31; H, 5.54; N, 3.72. Calc. for $C_{31}H_{44}Cl_2N_2O_{14}S\cdot 1.5H_2O$ (798.68) (%): C, 46.62; H, 5.93; N, 3.51.

*2-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)ethenyl]-3-ethyl-1,3-benzothiazol-3-ium perchlorate* (*E*)-**2b**. A mixture of 3-ethyl-2-methylbenzothiazolium perchlorate **3b**[8] (47 mg, 0.17 mmol), 4′-formylbenzo-18-crown-6 ether (64 mg, 0.19 mmol), pyridine (0.46 ml) and abs. EtOH (10 ml) was heated at 80 °C for 30 h. After cooling to –10 °C, the precipitate formed was filtered off, washed with cold abs. EtOH (2×2 ml) and dried in air to give **2b** as an orange powder (73 mg, 72% yield); mp 194–196 °C. ^{1}H NMR (Bruker DRX500, [$^2H_6$]DMSO, 30 °C) δ: 1.49 (t, 3H, Me, *J* 7.1 Hz), 3.54 (s, 4H, $2CH_2O$), 3.58 (m, 4H, $2CH_2O$), 3.64 (m, 4H, $2CH_2O$), 3.80 (m, 2H, CH_2CH_2OAr), 3.84 (m, 2H, CH_2CH_2OAr), 4.23 (m, 4H, $2CH_2OAr$), 4.95 (q, 2H, CH_2N, *J* 7.1 Hz), 7.14 (d, 1H, $H^{5'}$, *J* 8.4 Hz), 7.65 (br. d, 1H, $H^{6'}$, *J* 8.4 Hz), 7.68 (br. s, 1H, $H^{2'}$), 7.78 (m, 1H, H^6), 7.84 (d, 1H, H^a, *J* 15.8 Hz), 7.87 (m, 1H, H^5), 8.16 (d, 1H, H^b, *J* 15.8 Hz), 8.26 (d, 1H, H^4, *J* 8.5 Hz), 8.41 (d, 1H, H^7, *J* 8.0 Hz). Found (%): C, 54.09; H, 5.76; N, 2.31. Calc. for $C_{27}H_{34}ClNO_{10}S$ (600.08) (%): C, 54.04; H, 5.71; N, 2.33.

3-(6-Ammoniohexyl)-2-methyl-1,3-benzothiazol-3-ium diperchlorate **3a**. A mixture of 6-bromohexylammonium bromide[9] (0.88 g, 3.4 mmol) and 2-methylbenzothiazole (1.0 g, 6.7 mmol) was heated at 160 °C (oil bath) for 18 h. After cooling, the resulting coloured mass was washed gradually with benzene (15 ml), acetone (15 ml), and hot chloroform (3×10 ml). The insoluble substance (0.99 g) was dissolved in a minimum quantity of abs. EtOH with heating, and 70% aq. $HClO_4$ (0.5 ml, 5.8 mmol) was added to the solution followed by evaporation *in vacuo*. The solid residue was dissolved in MeOH (~5 ml), and Et_2O (~40 ml) was added to the solution. The precipitate formed was filtered off, washed with Et_2O and dried in air to give **3a** as a yellowish powder (0.93 g, 61% yield); mp 133–135 °C. ^{1}H NMR (Bruker DRX500, [$^2H_6$]DMSO, 25 °C) δ: 1.37 (m, 2H, $CH_2CH_2CH_2NH_3$), 1.45 (m, 2H, $CH_2CH_2CH_2N$), 1.53 (m, 2H, $CH_2CH_2NH_3$), 1.84 (m, 2H, CH_2CH_2N), 2.78 (m, 2H, CH_2NH_3), 3.21 (s, 3H, Me), 4.70 (m, 2H, CH_2N), 7.61 (br. s, 3H, NH_3), 7.81 (m, 1H, H^6), 7.90 (m, 1H, H^5), 8.33 (d, 1H, H^4, *J* 8.6 Hz), 8.45 (d, 1H, H^7, *J* 8.2 Hz). Found (%): C, 37.65; H, 4.89; N, 6.48. Calc. for $C_{14}H_{22}Cl_2N_2O_8S$ (449.30) (%): C, 37.42; H, 4.94; N, 6.24.

[‡] Absorption spectra of (*E*)-**2a**, (*E*)-**2b** (2×10^{-5} M) and a mixture of (*E*)-**2b** (2×10^{-5} M) and $EtNH_3^+ClO_4^-$ (2×10^{-3} M) were recorded on a Cary 50 Bio spectrophotometer (Varian) in the range 200–600 nm with an increment of 1 nm (MeCN, 1 cm cell, room temperature).

[§] ^{1}H NMR titration was performed on a Bruker DRX500 instrument in [$^2H_3$]MeCN at 30 °C. The concentration of (*E*)-**2a**,**b** was 5×10^{-3} M, and the concentration of $EtNH_3^+$ ions was varied from 0 to 1.5×10^{-2} M in the **2b**/$EtNH_3ClO_4$ system or from 0 to 0.25 M in the **2a**/$EtNH_3ClO_4$ system. The stability constants were determined by changes in the positions of signals for the protons of **2a**,**b** *vs.* varied concentration of $EtNH_3ClO_4$. The $\Delta\delta_H$ values were measured with an accuracy of 0.001 ppm. The HYPNMR program[11] was used for the calculations.

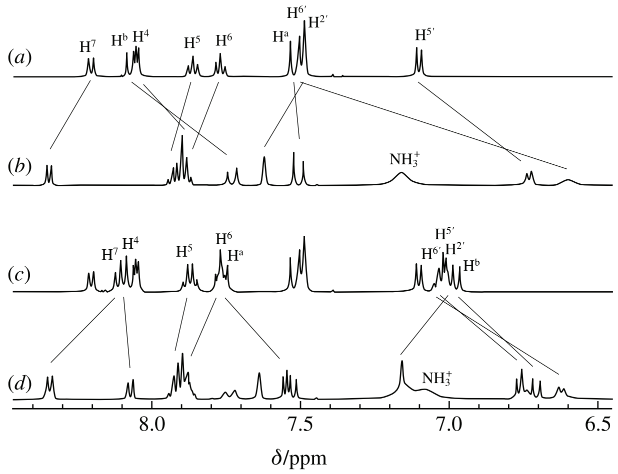


Figure 2 ^{1}H NMR spectra of (*a*) (*E*)-**2b**, (*b*) (*E*)-**2a** and mixtures of (*c*) (*E*)/(*Z*)-**2b** and (*d*) (*E*)/(*Z*)-**2a** (aromatic region, [^{2}H$_3$]MeCN, 5×10^{-3} M, 30 °C). In spectra (*c*) and (*d*), the assignments were made only for the *Z*-isomer proton signals.

The resulting constant, $\lg K = 3.50\pm0.05$ is typical of the complexes of benzo-18-crown-6 derivatives with alkylammonium ions.[12] The stability constant of the dimeric complex (K_d) was estimated by competitive NMR titration in the **2a**/EtNH$_3$ClO$_4$ system taking into account simultaneously the two equilibria

$$(E)\text{-}\mathbf{2a} + \mathrm{EtNH_3^+} \overset{K}{\rightleftharpoons} (E)\text{-}\mathbf{2a}\cdot\mathrm{EtNH_3^+}; \qquad (2)$$

$$2(E)\text{-}\mathbf{2a} \overset{K_d}{\rightleftharpoons} [(E)\text{-}\mathbf{2a}]_2. \qquad (3)$$

with a fixed value of K. The equilibrium constant of (2) cannot be determined by NMR; therefore, it was taken equal to the equilibrium constant of (1) with the assumption that the stability of complexes with EtNH$_3^+$ does not depend on the structure of the N-substituent in the dye. The stability constant of the dimeric complex found in this way was high: $\lg K_d = 6.1\pm0.1$; this means that, at concentrations of **2a** equal to 1×10^{-5}, 1×10^{-4} and 1×10^{-3} M in MeCN, the dimeric complex incorporates 82, 94 and 98% dye, respectively.

Exposure of solutions of (*E*)-**2a**,**b** to visible light[¶] decreased the LAB intensity due to reversible *E*–*Z* isomerisation, this decrease being considerably more pronounced for **2a** than for the photostationary state of model **2b** (Figure 1, curves *3* and *4*). This is apparently due to the substantial shift of the LAB of (*Z*)-**2a** to shorter wavelengths [~85 nm with respect to (*E*)-**2a**]. Previously, we observed analogous effects[6,7] when investigating the formation of anion-‘capped’ metallocomplexes by dyes (*Z*)-**1**. This similarity of spectral patterns indicates that the cation-‘capped’ complex incorporates the *Z*-isomer of dye **2a**, in which the coplanarity of the chromophore fragment is strongly disrupted due to the intramolecular coordination of the terminal ammonium group to the crown-ether moiety (Scheme 2).

The formation of *Z*-isomers of dyes **2a**,**b** upon irradiation of their solutions in [^{2}H$_3$]MeCN was detected by ^{1}H NMR spectroscopy.[††] For both dyes, a second set of proton signals was observed for all types of protons; the typical value $^3J_{\mathrm{H^a,H^b}}$ 11.6–12.0 Hz for the new isomers confirmed the *Z*-configuration of the ethylene bonds [Figure 2(*c*),(*d*)]. The signals of the H^b ethylene protons and the protons of the benzocrown-ether fragments in *Z*-isomers shift upfield relative to the corresponding signals of *E*-isomers, which is due to the disruption of conjugation in the *Z*-form caused by a twisting of the chromophore fragment and, correspondingly, a decrease in the electron-withdrawing effect of the benzothiazolium residue. Unlike (*Z*)-**2b**, in the case of (*Z*)-**2a**, the signals of the benzocrown-ether protons H$^{5'}$ and H$^{6'}$ occur in a higher field than the signal of H$^{2'}$, while the signals of all methylene groups of the N-substituent are markedly shifted upfield (to 0.33 ppm) with respect to those of (*E*)-**2b**. This spectral behaviour of (*Z*)-**2a** points to the predominant shielding of the H$^{5'}$ and H$^{6'}$ protons by the benzothiazole residue and the arrangement of the ammoniohexyl spacer above the conjugated system of the benzocrown-ether fragment. Scheme 2 shows the most probable structure of the cation-‘capped’ complex of the *Z*-isomer of dye **2a** corresponding to the above spectral features.

One more piece of evidence for the formation of a rather stable cation-‘capped’ complex in the case of (*Z*)-**2a** was obtained by comparing kinetic features of the *E*→*Z* photoisomerisation and the subsequent dark *Z*→*E* relaxation of dyes **2a**,**b**.[¶] Exposure of model dye (*E*)-**2b** in MeCN to light (436 nm) both in the absence and in the presence of excess EtNH$_3$ClO$_4$ resulted in a photostationary-state equilibrium established over < 15 s (Figure 3, curves *1* and *2*). For dye (*E*)-**2a**, the decrease in the long-wavelength absorption intensity required a much longer time of ~90 s (Figure 3, curve *3*). This is apparently due to relatively slow dissociation of mixed complexes [(*Z*)-**2a**]·[(*E*)-**2a**] formed initially from [(*E*)-**2a**]$_2$ and dimeric complexes [(*Z*)-**2a**]$_2$, which are expected to have spectral characteristics similar to those of (*Z*)-**2b**. Similar effects have been observed previously[13] in the evolution of the LAB intensity for irradiated solutions of metallocomplexes of dyes **1**. After irradiation was terminated, solutions of **2b** restore rapidly the initial absorption intensity (Figure 3, curves *1* and *2*); this attests to efficient thermal *Z*→*E* isomerisation, which depends little on binding of the crown-ether moiety to the ethylammonium ion. The relaxation of the LAB intensity for **2a** (Figure 3, curve *3*) occurs much more slowly than that for **2b**, which confirms the presence of additional stabilization of dye (*Z*)-**2a** owing to the formation of the cation-‘capped’ complex.

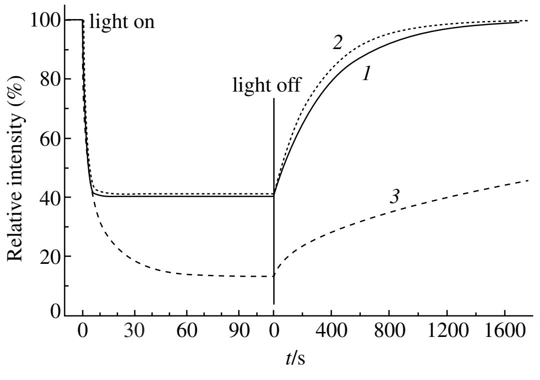


Figure 3 Kinetics of the photoinduced *E*→*Z* and subsequent thermal *Z*→*E* isomerisation of **2b** (*1*) in the absence and in the presence of (*2*) EtNH$_3$ClO$_4$ (2×10^{-3} M) and (*3*) **2a** ($C_{\mathbf{2a,b}}$ = 2×10^{-5} M, MeCN, 1 cm cell, room temperature, monitoring at the maximum of the LAB). Excitation with light at 436 nm.

[¶] Irradiation of a solution of (*E*)-**2a**,**b** (2×10^{-5} M) and a solution of a mixture of (*E*)-**2b** (2×10^{-5} M) and EtNH$_3$ClO$_4$ (2×10^{-3} M) (MeCN, 1 cm cell, room temperature) was performed with a Hamamatsu L8444 light source (Hg-Xe lamp at a minimum power, monochromatic light with λ = 436 nm). For studying the *E*→*Z* isomerisation, the change of absorption intensity at the maximum of the LAB was monitored with an increment of 0.1 s. After the photostationary state was attained (110 s), the irradiation was switched off and the intensity relaxation of the LAB was monitored for 30 min with an increment of 1 s.

[††] A solution of (*E*)-**2a**,**b** (5×10^{-3} M, [^{2}H$_3$]MeCN) in a standard NMR tube was irradiated with light from an incandescent lamp (60 W, distance from the light source of ~10 cm) for 2 h and then ^{1}H NMR spectrum was immediately recorded.

Thus, we synthesised a 18-crown-6-based styryl dye containing a long *N*-ammonioalkyl substituent. In MeCN, the dye *E*-isomers are self-assembled to give stable dimeric complexes upon intermolecular coordination of the terminal ammonium group of the N-substituent to the crown-ether moiety through hydrogen bonding. A cation-'capped' complex of the *Z*-isomer of styryl dye, characterised by a pronounced hypsochromic shift with respect to the *E*-isomer owing to the intramolecular binding of the ammonium group to the crown-ether moiety was synthesised for the first time. Dyes with this structure can be used in the design of optical data recording systems, light-controlled molecular devices and machines.

This work was supported by the Russian Foundation for Basic Research and the Russian Academy of Sciences.

References

1 *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001.

2 V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines: A Journey into the Nano World*, Wiley-VCH, Weinheim, 2003.

3 S. P. Gromov, *Rossiiskie Nanotekhnologii*, 2006, **1**, 29 (in Russian).

4 S. Shinkai, M. Ishihara, K. Ueda and O. Manabe, *J. Chem. Soc., Perkin Trans. 2*, 1985, 511.

5 S. Shinkai, T. Yoshida, O. Manabe and F. Fuchita, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1431.

6 S. P. Gromov and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 641 (*Russ. Chem. Bull.*, 1997, **46**, 611).

7 M. V. Alfimov, S. P. Gromov and I. K. Lednev, *Chem. Phys. Lett.*, 1991, **185**, 455.

8 S. P. Gromov, E. N. Ushakov, O. A. Fedorova, I. I. Baskin, A. V. Buevich, E. N. Andryukhina, M. V. Alfimov, D. Johnels, U. G. Edlund, J. K. Whitesell and M. A. Fox, *J. Org. Chem.*, 2003, **68**, 6115.

9 S. P. Gromov, E. N. Ushakov, O. A. Fedorova, V. A. Soldatenkova and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1192 (*Russ. Chem. Bull.*, 1997, **46**, 1143).

10 W. Bardsley and J. Ashford, *Biochem. J.*, 1970, **122**, 557.

11 C. Frassineti, S. Ghelli, P. Gans, A. Sabatini, M. S. Moruzzi and A. Vacca, *Anal. Biochem.*, 1995, **231**, 374.

12 R. M. Izatt, K. Pawlak, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721.

13 E. N. Ushakov, O. B. Stanislavsky, S. P. Gromov, O. A. Fedorova and M. V. Alfimov, *Dokl. Akad. Nauk*, 1992, **323**, 702 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1992, **323**, 164].

Received: 9th April 2007; Com. 07/2907