Photochromic crown ethers

1. Formation of ion pairs, *trans—cis*-isomerization, and metal ion binding in a nonpolar medium

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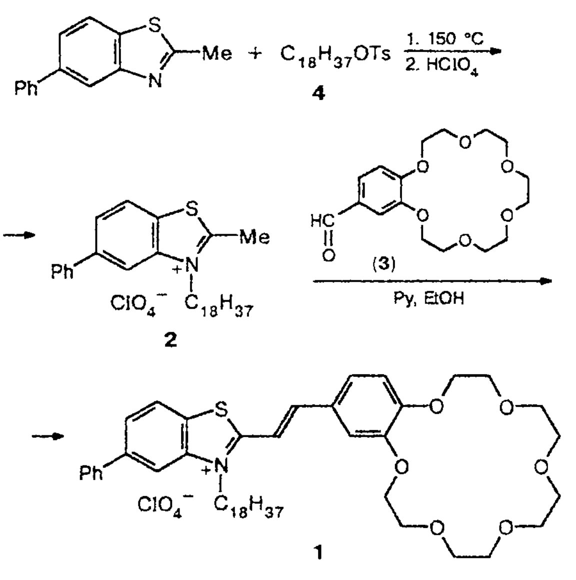
An amphiphilic crown-containing styryl dye (**1**) was synthesized, and the effects of irradiation, temperature, and alkali and alkali-earth metal ions on the conductivity and optical spectra of its solutions in dioctyl phthalate were studied. Compound **1** in the *trans*-form almost completely exists as ion pairs (IP). Irradiation at a long-wavelength absorption maximum (λ_{max}) results in a reversible increase in the conductivity and, hence, a degree of dissociation of IP (α); these parameters decrease when complexes with metal ions are formed. The relaxation times for the photoinduced conductivity coincide with a decrease in the extinction within experimental error in the 20—60 °C temperature range. The photoinduced increase in α is caused by *trans—cis*-isomerization and an increase in steric hindrances for the interaction of the ClO_4^- anion with the N^+ atom of benzothiazolium in the *cis*-form of **1**. The activation energies for the dark *cis—trans*-relaxation, absolute α values, and thermodynamic parameters of dissociation of IP in the *trans*-form, as well as the α values in a photostationary mixture of *cis—trans*-isomers, were estimated. The decrease in α after binding with metal ions is likely caused by the redistribution of the positive charge to benzothiazolium through the conjugated system of **1**. Correlations between the decrease in conductivity (decrease in α) and the hypsochromic shift $\Delta\lambda_{max}$ after the formation of complexes between **1** and metal ions were observed.

Key words: crown ethers, styrene dyes, ion pairs, *cis—trans*-isomerization, electroconductivity, photochromism.

Photochromic crown ethers (PCE) are a new class of compounds containing an aromatic heterocycle and a crown ether (CE) conjugated through the ethylene bond.[1] Under irradiation with visible light, PCE undergo reversible *trans—cis*-isomerization resulting in changes in the electronic absorption spectra and the affinity of the CE fragment for metal ions.[2,3] Due to these properties, PCE are promising photocontrolled ionophores in lipid membranes and other nonpolar media.

The photochemical properties of PCE and their formation of complexes with metal ions have previously been studied[2,3] in strongly polar solvents only. Since PCE are, as a rule, cations or zwitter ions, the formation of ion pairs (IP) can exert a substantial effect on their ability to transport ions and on processes of *trans—cis*-isomerization and complex formation in a nonpolar medium (membrane). In the present work, the correlation between these properties was studied. For this purpose, the absorption spectra and conductivity of solutions of the amphiphilic crown ether in the dark and under irradiation were studied. The experiments were carried out in the viscous nonpolar solvent dioctyl phthalate, which is widely used for the preparation of ion-exchange liquid and polymeric membranes.

Scheme 1



For the studies in a nonpolar medium (membrane), PCE (**1**) containing hydrophobic substituents (Ph in

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position 5 and the $C_{18}H_{37}$ group in position 3) was synthesized. *trans*-Isomer **1** is formed when quaternary salt **2** and the formyl derivative of CE **3** are condensed in the presence of pyridine as the catalyst (Scheme 1).

Experimental

^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer (frequency 400.13 MHz) at 300 K. Chemical shifts were measured with an accuracy of 0.01 ppm, and SSC constants were measured with an accuracy of 0.1 Hz.

The structure of the compounds synthesized for the first time was proved by ^1H NMR and confirmed by the elemental analysis data.

4′-Formylbenzo-18-crown-6 (3) was obtained by the formylation of benzo-18-crown-6 under conditions of the Duff reaction[4] in 53% yield, m.p. 157 °C (*cf.* Ref. 5).

2-Methyl-3-octadecyl-5-phenylbenzothiazolium perchlorate (2) was obtained by the previously described procedure.[5] A mixture of octadecyl alcohol (2.7 g, 0.01 mol) and tosyl chloride (1.9 g, 0.01 mol) was dissolved in dichloromethane (20 mL), and triethylamine (1 g, 0.9 mL, 0.001 mol) was added dropwise. The solution was stored at −20 °C for 1 day and washed with water to remove the triethylammonium salt. The solvent was distilled off on a rotary evaporator, and the residue was chromatographed on alumina using ether as the eluent. The yield of octadecyl *p*-toluenesulfonate (**4**) was 3.85 g (91%) with m.p. 88 °C (*cf.* Ref. 6).

Ester **4** (1 g, 2.5 mmol) was fused with 2-methyl-5-phenylbenzothiazole (0.56 g, 2.5 mmol) at 150 °C for 3 h. The product was recrystallized from benzene, dried, dissolved in ethanol, and conc. $HClO_4$ (1.5 mL) was added to the hot solution. Benzothiazolium salt **2** precipitated after cooling and was filtered off and dried. The yield was 0.88 g (65%), m.p. 154 °C. ^1H NMR ($CDCl_3$), δ: 0.98 (m, 3 H, Me); 1.36—1.45 (m, 30 H, 15 CH_2); 1.42 (m, 2 H, CH_2); 2.02 (m, 2 H, CH_2); 3.14 (s, 3 H, CH_3); 4.49 (t, 2 H, CH_2N); 7.62—7.70 (m, 4 H, C_6H_5 of benzothiazole); 7.85—7.89 (m, 3 H, C_6H_5 of benzothiazole); 8.97 (s, 1 H, H-4 of benzothiazole). Found (%): C, 66.17; H, 8.53; N, 2.29. $C_{32}H_{48}NO_4S$. Calculated (%): C, 66.47; H, 8.37; N, 2.42.

2-[2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-hexaoxabenzocyclooctadecin-18-yl)ethenyl]-3-octadecyl-5-phenylbenzothiazolium perchlorate (1). Quaternary salt **2** (0.25 g, 0.43 mmol), the formyl derivative of crown ether (CE) **3** (0.15 g, 0.44 mmol), Py (0.5 mL), and abs. ethanol (5 mL) were mixed in a flask with a reflux condenser. The mixture was refluxed for 10 h, ethanol and pyridine were distilled off, and the residue was twice treated with hot hexane to remove unconsumed CE and recrystallized from methanol. The yield of **1** was 0.1 g (27%), m.p. 185 °C. ^1H NMR ($(CD_3)_2CO$), δ: 0.88 (m, 3 H, Me); 1.29 (m, 28 H, 14 CH_2); 1.42 (m, 2 H, CH_2); 1.60 (m, 2 H, CH_2); 2.17 (m, 2 H, CH_2); 3.63 (m, 4 H, ε,ε′-CH_2O); 3.66 (m, 4 H, δ,δ′-CH_2O); 3.73 (m, 4 H, γ,γ′-CH_2O); 3.92 (m, 4 H, β′,β′-CH_2O); 4.29 (m, 4 H, α,α′-CH_2O); 5.19 (t, 2 H, CH_2N); 7.16 (d, 1 H, H-5 of benzocrown ether), 7.45—7.62 (m, 4 H, H-6 of benzocrown ether, C_6H_5); 7.67 (s, 1 H, H-2 of benzocrown ether); 7.85 (d, 2 H, C_6H_5); 7.97 (d, 1 H, H_a, J_{trans} = 15.9 Hz); 8.11 (d, 1 H, H-6 of benzothiazole); 8.29 (d, 1 H, H_b, J_{trans} = 15.9 Hz); 8.44 (d, 1 H, H-7 of benzothiazole); 8.49 (s, 1 H, H-4 of benzothiazole).

Na, K, Mg, Ca, and Ba perchlorates (chemically pure grade) were used. Dioctyl phthalate (DOP) (pure grade) was triply distilled *in vacuo* until a constant value of the refractive index was achieved: n_D^{20} = 1.4860.

The viscosity of DOP was measured on a Hoeppler viscosimeter with thermostatting.

Absorption spectra were recorded on a UV-3100 instrument (Shimadzu) in cells with quartz inserts of different thickness, and the optical path length was varied from 1 to $5 \cdot 10^{-2}$ cm, which made it possible to study solutions in the 10^{-5}—10^{-3} mol L^{-1} concentration range.

The conductivity of solutions of **1** was measured on a home-made bridge-type instrument using a 232-V nanovoltmeter as a zero-device. The a.c. frequency was varied in the 5—10^4 Hz range. The sensitivity of the instrument was $5 \cdot 10^{-12}$ Ohm^{-1} cm^{-1} with an accuracy of 0.5% in the 10^{-10}—10^{-5} Ohm^{-1} cm^{-1} range. The measurements were carried out in a thermostatted cell with a distance between electrodes of 0.7 mm. A conducting glass 3 mm in diameter with a coated layer of tin dioxide was one of the electrodes. A nontransparent platinum film applied onto a quartz support served as the second electrode.

Reactions with alkali (Na, K) and alkali-earth (Mg, Ca, Ba) metal ions were studied by the addition of perchlorates of these metals (concentration 10 mmol L^{-1}) in isopropanol to a solution of **1** in DOP followed by the removal of isopropanol on a rotary evaporator.

KGM (90 W) and DKSSh-200 lamps were used as light sources. Light irradiation during optical and electrical measurements was carried out through SZS-8 and interference (with a transmission maximum at 432 nm) light filters under maximally similar conditions of irradiation. In some kinetic experiments, an IFK-120 flash lamp with a pulse energy of 20 J and pulse durations of 5 ms was also used. The light intensity incident on the sample was measured by a bolometer. For measurements with KGM and DKSSh-200, light intensity was 9.4 and 45 W cm^{-2}, respectively.

Results and Discussion

Formation of ion pairs and trans-cis isomerization. The dependence of the dark specific conductivity of solutions of **1** in DOP on the concentration of **1** (*c*) in the range of 0 to 0.5 mmol L^{-1} is described satisfactorily by the equation (Fig. 1):

$$\sigma_D = \sigma_D{}^0 + B_D c^{1/2}, \qquad (1)$$

where $\sigma_D{}^0 \approx 4.7 \cdot 10^{-11}$ Ohm^{-1} cm^{-1} at 25 °C is the conductivity of DOP in the absence of **1**,

$$B_D = (11.6 \pm 0.4) \cdot 10^{-10}\ Ohm^{-1}\ cm^{-1}\ mmol^{-1/2}\ L^{1/2}.$$

The replacement of ClO_4^- with the larger anions tetraphenyl borate (TPB^-) and picrate (PC^-) by the addition of the corresponding sodium salts to the aqueous phase (the experiments were carried out on nitrocellulose membranes saturated with DOP) increases σ_D by 6 and 3 times, respectively, which is substantially greater than the increase produced by both salts in the absence of **1** (20—30%).

The conductivity of solutions of **1** in DOP increases when they are irradiated with visible light for 1 min; in the dark it decreases again to the initial value. The

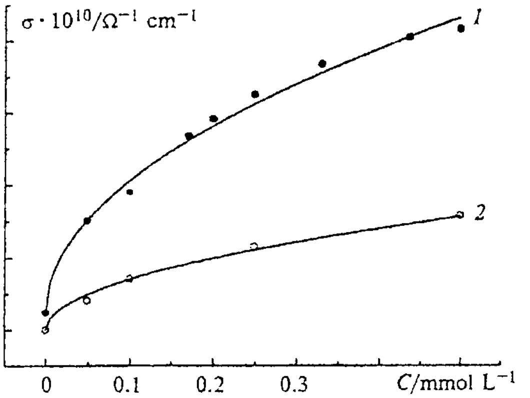

Fig. 1. Concentration dependences of the dark conductivity (*1*) and photoconductivity (*2*) of solutions of crown ether **1** in dioctyl phthalate. Dots indicate experimental values. Solid lines show simulation by Eq. (1) using the nonlinear least-squares method.

kinetics of the decrease in photoconductivity (σ_P) at 20 °C cannot be satisfactorily described by one exponent; however, using the nonlinear least-squares method, it can be approximated by a sum of two exponents with good accuracy (Fig. 2). Because at other temperatures the number of points on the kinetic curves was insufficient to perform an analogous expansion, the half-times of conversion ($t_{1/2}$) were used in further discussion to characterize the relaxation kinetics of σ_P.

Similarly to σ_D, the concentration dependence of σ_P is satisfactorily described by Eq. (1) (Fig. 1) with the value of $B_P = (4.4\pm0.1)\cdot10^{-10}$ Ohm^{-1} cm^{-1} mmol$^{-1/2}$ L$^{1/2}$ for a light intensity of 45 W cm^{-2}. The $\sigma_P/(\sigma_D - \sigma_D{}^0)$ ratio is 35—40% when the concentration of **1** is equal to 0.1 mmol L^{-1}.

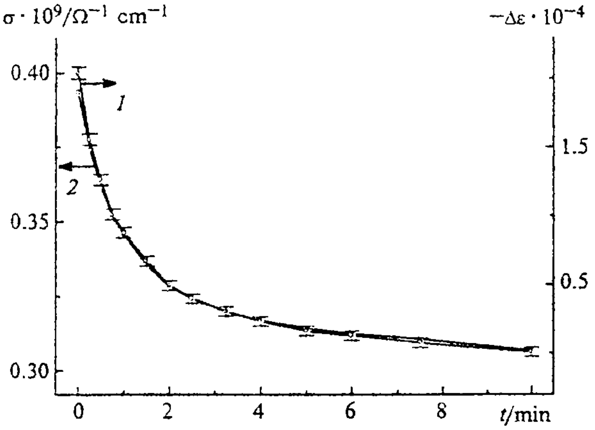

Fig. 2. Kinetics of the dark relaxation of extinction in the band at λ = 440 nm (*1*) and of the conductivity (*2*) of solutions of **1** in dioctyl phthalate after irradiation in the same absorption band. Irradiation was carried out with a DKSSh-200 lamp through SZS-8 and interference light filters with a transmission maximum at 432 nm. The concentration of **1** is 0.1 mmol L^{-1}, temperature 20 °C. Dots indicate experimental values. Solid lines present simulation by a sum of two exponents $A_1\exp(-t/t_1) + A_2\exp(-t/t_2)$ using the nonlinear least-squares method. The characteristic decay times t_1 and t_2 are equal to 0.64±0.05 and 3.44±0.5 min, respectively. The contribution of the fast exponent is 55±9%.

The photoinduced changes in the absorption spectrum of **1** are presented in Fig. 3. The main effect, as for other PCE in polar media,[1—3] is a decrease in the extinction of the absorption band with a maximum at 440 nm (ε_{440}). Like those for conductivity, at short irradiation times (1 min), the changes in extinction are reversible and are repeated with subsequent irradiation. It is important to note that the relaxation kinetics of σ_P and ε_{440} coincide within experimental error (Fig. 2) when the light intensity and spectral composition are maximally similar in both experiments. Similar values of $t_{1/2}$ for σ_P and ε_{440} are observed in the 20—60 °C range, where $t_{1/2}$ changes by more than an order of magnitude. The temperature dependences of $t_{1/2}$ for σ_P and $\Delta\varepsilon_{440}$ as well as those of the dark conductivity of solutions of **1** and the viscosity of DOP (η) are exponential. The activation energy of the conductivity $E(\sigma_D)$ and viscosity $E(\eta)$, the relaxation half-times of photoconductivity $E(t_{\sigma P})$, and extinction (*cis—trans*-isomerization) $E(t_\varepsilon)$, as well as the thermodynamic parameters of association of the ion pairs $\mathbf{1}^+ClO_4^-$ at 20 °C (ΔG_d, ΔH_d/kcal mol^{-1}; ΔS_d/cal mol^{-1} deg^{-1}; K_d/L mol^{-1}) are presented below.

$E(\sigma_D)$	$E(\eta)$	$E(t_{\sigma P})$	$E(t_\varepsilon)$	$K_d\cdot10^9$	ΔG_d	ΔH_d	ΔS_d
10.8±0.1	8.7±0.7	11.6±0.6	10.9±0.9	2.7±0.1	11.8	4.2	27.3

The quantum yield of isomerization of **1** (β) was determined for small degrees of *trans—cis*-conversion: $\Delta\varepsilon_{440} \approx 9\%$. Since for the maximum intensity and maximum irradiation dose, the ε_{440} value decreases from $3.4\cdot10^4$ to $1.4\cdot10^4$, for the *cis*-form, $\varepsilon_{440} \le 1.4\cdot10^4$. (According to the published data,[3] for the analog of **1** containing no phenyl substituent, $\varepsilon_{440}{}^{cis} \approx 0.25\varepsilon_{440}{}^{trans}$).

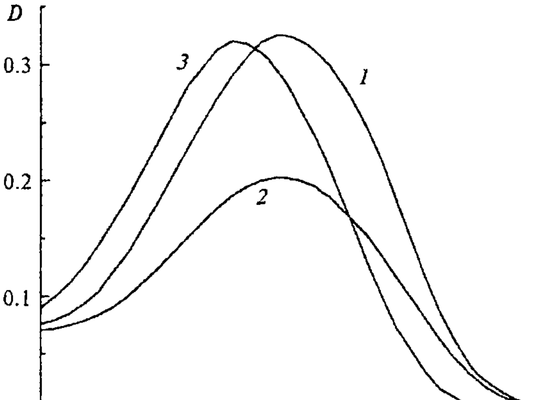

Fig. 3. Absorption spectra of a solution of **1** in dioctyl phthalate: initial (*1*), after irradiation in the band at 432 nm for 1 min (*2*), during interaction with Ca^{2+} ions (*3*). The concentration of **1** and CaClO$_4$ is 0.1 mmol L^{-1}. The optical path length is 0.1 cm.

Thus, for $\Delta\varepsilon_{440} \approx 9\%$, the degree of *trans—cis*-conversion was not greater than 15%, and the contribution of the *cis*-form to the $\Delta\varepsilon_{440}$ value did not exceed 7% of the indicated value, *i.e.*, the main changes in ε are caused by a change in the content of the *trans*-form. The value of β, which was determined taking into account nonuniform irradiation over the cell thickness (d = 0.5 mm, $\varepsilon_{440} = 3.4 \cdot 10^4$), is equal to 0.3. In analogous measurements of the quantum yield of σ_P, the effect of light reflection from the platinum electrode was additionally taken into account. This gives $\sigma_P = 0.35 \cdot 10^{-10}$ Ohm^{-1} cm^{-1} for a flux of $2 \cdot 10^{15}$ photon s^{-1} on a cell in the spectral range determined by the transmission width of the interference light filter (12 nm).

For both anions, TPB^- and PC^-, $\sigma_P/(\sigma_D - \sigma_D{}^0) \approx$ 30%.

Interaction with metal ions. The formation of complexes of **1** with metal ions in DOP solutions in the dark, as in polar media,[1–3] results in a hypsochromic shift ($\Delta\lambda_{max}$) and a decrease in the extinction of the long-wavelength band (in the absence of ions, λ_{max} = 440 nm). When salts are added, σ_D does not increase, but decreases, and correlations (different for mono- and divalent metal ions) are observed between $\Delta\sigma_D$ and $\Delta\lambda_{max}$ (Fig. 4).

Visual light irradiation results in an increase in the conductivity of the complexes, but to a lower extent than for free **1** (Table 1). The increase in s and its decrease in the dark at the concentration of **1** of 0.1 mmol L^{-1} and irradiation time of 1 min are reversible. The relaxation times $t_{1/2}$ of σ_P and ε_{440} are close to each other and to the $t_{1/2}$ times for free **1**.

An increase in the conductivity due to **1** is caused by free ions that exist in the organic phase along with electrically neutral IP $1^+ClO_4^-$. This can be seen, in particular, from the experiments on the replacement of counterions. There is 3—6-fold increase in σ_D when ClO_4^- is replaced by more bulky TPB^- or PC^- caused by the fact that the degree of dissociation of the 1^+TPB^- or 1^+PC^- IP is higher than that of the $1^+ClO_4^-$ ion pair.

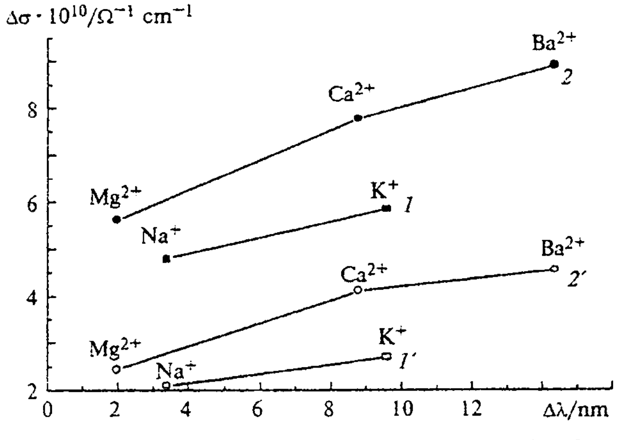

Fig. 4. Correlations between the short-wavelength shift of the absorption band maximum of **1** ($\Delta\lambda_{max}$) and the decrease in dark conductivity (*1*, *2*) and photoconductivity (*1'*, *2'*) of solutions of **1** due to formation of complexes with alkali (*1*, *1'*) and alkali-earth (*2*, *2'*) metal ions.

Table 1. Effect of binding of cations with **1** on the position of the long-wavelength absorption maximum (λ_{max}), dark conductivity (σ_D), σ_P/σ_D ratio, and degree of dissociation of IP in the *trans*-form (α_D) and in the photostationary *cis—trans*-mixture (α_P). The concentration of **1** in dioctyl phthalate is 1 mmol L^{-1}

Cation	λ_{max} /nm	$\sigma_D \cdot 10^{-10}$ /Ohm^{-1} cm^{-1}	σ_P/σ_D	$\alpha_D \cdot 10^{-3}$	$\alpha_P \cdot 10^{-3}$
—	440.4	11.9	0.419	1.76	2.50
Na^+	437	7.1	0.408	1.05	1.48
K^+	430.8	6.05	0.380	0.89	1.23
Mg^{++}	438.4	6.28	0.406	0.93	1.31
Ca^{++}	431.6	4.13	0.216	0.61	0.74
Ba^{++}	426	3.01	0.146	0.25	0.52

Along with the formation of IP, in a nonpolar medium the aggregation of molecules **1**, similar to that of other dyes, is also possible.[7] This aggregation can affect the σ_P value due to a decrease in the mobility and a change in the degree of dissociation of IP, it can also change the kinetics and affect the value of photoinduced changes in the conductivity and extinction.* In this work, the main experiments were carried out for comparatively low concentrations of **1**, and in the discussion of the results presented above, in the first approximation we neglect the effect of aggregation. The arguments in favor of this approximation are the concentration dependences of the dark conductivity and photoconductivity, which can be satisfactorily described by the $c^{1/2}$ law (see Fig. 1) in the 0.05—0.5 mmol L^{-1} range. This dependence can be derived from a simple model of dissociation of IP:

$$K_d = \frac{[1^+]\cdot[ClO_4^-]}{[1^+ClO_4^-]}\,, \tag{2}$$

$$\sigma_D - \sigma_D{}^0 = 10^{-3}(\Lambda_1[1^+] + \Lambda_{ClO_4^-}[ClO_4^-]),$$

where $[1^+]$ and $[ClO_4^-]$ are the molar concentrations of free ions. According to Eq. (2), $[\mathbf{1}^+]$, $[ClO_4^-] \approx c^{1/2}K_d{}^{1/2}$; $c \approx c_0$ is the concentration of **1**; and Λ_1 and $\Lambda_{ClO_4^-}$ are the equivalent conductivities of ions, Ohm^{-1} g-equiv^{-1} cm^2.

The concentration of free ions and the degree of dissociation (α) of the $1^+ClO_4^-$ pair can be estimated from the σ_D values with the assumption that the mobility of the ions in the electric field satisfies the Stokes—Einstein law. In terms of this theory, the $\Lambda_1/\Lambda_{ClO_4^-}$ ratio

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* The next publication of this series will be devoted to aggregation effects.

is equal to the ratio of friction coefficients of ions, which, in turn, are determined by their effective radii and Perrin's nonsphericity factor;[8] in addition, the following relation holds[9]

$$\Lambda\eta = \mathrm{const.} \qquad (3)$$

The ClO_4^- anion is spherical with a radius of ≅3 Å. The average radius of **1** (r_{eff}^0) corresponding to a sphere of the same volume as for a molecular ellipsoid, and the ratio of the semiaxes, a/b for this ellipsoid were estimated by calculating the conformation of **1** by the molecular mechanics method (PC MODEL program). The calculations showed that the a/b ratio depends substantially on the conformation of the $C_{18}H_{37}$ radical; however, the r_{eff} values calculated with account for Perrin's factor (F): $r_{\mathrm{eff}} = F \cdot r_{\mathrm{eff}}^0$, differ slightly for different conformations. For example, for one of the two conformations with maximally different a/b ratio, the a and b values are equal to 13.5 and 6 Å, respectively; $r_{\mathrm{eff}}^0 \approx 7.9$ Å, and taking into account the F factor, $r_{\mathrm{eff}} \approx 10$ Å. For the second conformation, $a \approx 10.6$ Å, $b \approx 11.1$ Å, and $r_{\mathrm{eff}} \approx 10.8$ Å. Thus, $\Lambda_{\mathbf{1}}/\Lambda_{ClO_4^-} \cong 0.3$ for both conformations. The $\Lambda_{ClO_4^-}$ values are equal to 70.9 and 33.8 Ohm^1 g-equiv^{-1} cm^2 at 25 °C in methanol and ethanol, respectively.[10] The viscosity of DOP measured at 22 °C is equal to 65 cP. Equation (3) gives the 0.51—0.53 Ohm^{-1} g-equiv^{-1} cm^2 range for $\Lambda_{ClO_4^-}$ in DOP. Based on this estimate, one obtains for $c_0 = 0.1$ mmol L^{-1} $[\mathbf{1}^+]$, $[ClO_4^-] \approx (5.2\pm0.1)\cdot10^{-7}$ mol L^{-1}. This corresponds to $\alpha \cong 5.2\cdot10^{-3}$, *i.e.*, almost all molecules of **1** in a DOP solution exist as IP. The dissociation constant of IP is related to the degree of dissociation by the correlation $K_d = \alpha^2 c_0$; the values of K_d at 20 °C are given above.

Similar estimates of the degree of dissociation of IP were obtained for **1** with the concentration of 1 mmol L^{-1} and for complexes of **1** with metal ions (see Table 1).

The similar $t_{1/2}$ values for ε_{440} and σ_P and the similar activation energies, $E(t_{\sigma P})$ and $E(t_\varepsilon)$, show that the photoconductivity is caused by the *trans—cis*-isomerization of **1**. The nature of this effect is of considerable interest. Since the contribution of $\mathbf{1}^+$ to the σ_P value is relatively small (≅30%) and the change in the mobility of $\mathbf{1}^+$ due to the change in its geometrical size that occurs with the *trans—cis*-transition is also small (according to the calculation, Perrin's factor changes by no more than 3—5%), the value of σ_P is due not to the change in the mobility, but to the change in the concentration of ions, *i.e.*, to an increase in the degree of dissociation of IP.

The transition to the *cis*-form is accompanied by a change in the electron and charge density distribution, in particular, by an increase in the positive charge on the N atom of benzothiazolium with which the ClO_4^- anion interacts in IP due to partial distortion of the conjugation between benzothiazolium and the crown ether. This should result in an enhancement of the interaction between the ClO_4^- anion and the N^+ atom and, hence, a decrease in α. The experimentally observed increase in α shows that this effect is not predominant. It is likely that the increase in α during *trans—cis*-isomerization is caused by conformational changes in the dye molecule and in the packing of the bulky hydrocarbon substituent, due to which the distance from the ClO_4^- ion to the N^+ atom in the *cis*-form increases. It is noteworthy that although the absolute values of α are not high, the relative change in α during *trans—cis*-isomerization is considerable. For example, $\sigma_P/\sigma_D \approx 30$—40% when the intensity is equal to 10^{15} photon cm^{-2} s^{-1}. Since during irradiation compound **1** is a photostationary mixture of *cis*- and *trans*-forms, 30—40% is a lower estimate for the increase in α in the *cis*-form.

The temperature dependences of $\Lambda_{\mathbf{1}}$ and $\Lambda_{ClO_4^-}$ in the Stokes—Einstein model are determined by the temperature dependence of the viscosity (η). Since the $\sigma_D-\sigma_D^0$ value is equal to the product of $\Lambda_{\mathbf{1}}$ and $\Lambda_{ClO_4^-}$ times the concentrations of these ions (Eq. (2)), the difference between the activation energies of the σ_D and η values is equal to the activation energy of the formation of the $\mathbf{1}^+$ and ClO_4^- ions, *i.e.*, it is half the value of the dissociation enthalpy of the $\mathbf{1}^+ClO_4^-$ IP in the *trans*-form ($[\mathbf{1}^+],[ClO_4^-] \sim K_d^{1/2}$).*

The free energy (ΔG_d) and entropy (ΔS_d) of dissociation of IP were also determined from the K_d value using the standard thermodynamic correlations. The obtained values* show that the main contribution to the stabilization (ionization) of IP is caused by changes in entropy.

It can be seen that the activation energy of *cis—trans*-relaxation is somewhat greater than the activation energy of viscosity. It can be assumed that the *cis—trans*-isomerization includes two stages, one of which is independent of the viscosity and is characterized by a low activation energy; the rate of the second stage is limited by the viscosity in accordance with the Kramers diffusion theory.[11]

The effect of IP on *cis—trans*-isomerization, the lifetimes of triplet states, and electron transfer are known for cyanine dyes.[12,13] As can be seen from the results obtained, for PCE the transition from polar to nonpolar solvents, which is accompanied by the formation of IP, does not change, at least qualitatively, the spectral manifestation of *cis—trans*-isomerization. In this work, the opposite effect was observed: *trans—cis*-isomerization had an effect on the dissociation of IP. As far as we know, this effect has not previously been described. The nature of this effect is likely due to the reversible changes in the conformation and the spatial molecular packing that occur during isomerization.

The decrease in σ_D caused by binding of the metal ions means that the newly formed IP (metallocomplex crown ether—ClO_4^-) is not dissociated; moreover, the insertion of a metal ion in the CE decreases the degree

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* The ΔH_d, ΔS_d, and ΔG_d values thus obtained are presented on page 1241.

of dissociation ($\Delta\alpha < 0$) of the $1^+ClO_4^-$ IP in another part of the molecule.

Unlike *trans—cis*-isomerization, the binding of a metal ion with a CE fragment likely does not change the conformation or molecular packing near the N^+ atom of benzothiazolium. On the other hand, it is known that for PCE and its metal complexes, the long-wavelength transition corresponds to the transfer of charge between the withdrawing (benzothiazolium) and donating (CE) regions. The binding of a metal ion by CE changes the effective charge on this fragment, which results in a hypsochromic shift of λ_{max} and the redistribution of positive charge through the conjugated system to benzothiazolium.[14] Thus, $\Delta\lambda_{max}$ reflects the change in the electron (charge) distribution in **1** during complex formation. Therefore, based on the sign of $\Delta\alpha$ (unlike the sign of $\Delta\alpha$ during *trans—cis*-isomerization and the observed correlation between $\Delta\sigma_D$ and $\Delta\lambda_{max}$ (Fig. 4)), we can conclude that the decrease in the degree of dissociation for the initial IP $1^+ClO_4^-$ after binding with a metal ion is caused by changes in the charge distribution rather than changes in the conformation, namely, by the transfer of positive charge from the CE to the N^+ atom through the conjugated system of the dye, which results in an increase in the Coulomb attraction in the IP. The relations between λ_{max} and the charge on the N^+ differ for mono- and divalent cations, which results in different correlation dependences for alkali and alkali-earth metals (Fig. 4).

Thus, in this work, the amphiphilic photochromic crown ether (**1**) was synthesized for the first time; its *cis—trans*-isomerization, formation of ion pairs, and formation of complexes with alkali and alkali-earth metal ions were studied in a nonpolar medium with irradiation and in the dark. It was established that the degree of dissociation of IP α depends in different ways on *trans—cis*-isomerization and on complex formation, *i.e.*, these effects have opposite signs and occur *via* different mechanisms. The increase in α during *trans—cis*-isomerization is likely caused by an increase in steric hindrances to the interaction of the ClO_4^- anion with the N^+ atom of benzothiazolium, and the decrease in α caused by the formation of complexes with metal ions is due to the redistribution of positive charge from the crown ether fragment to the N^+ atom.

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