Photosensitive molecular tweezers

3.* Synthesis and homoditopic complex formation of a bisstyryl dye containing two crown-ether fragments with diammonium salts

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A new molecular tweezers, *viz.*, bisstyryl dye containing two 18-crown-6-ether moieties and one *p*-phenylenedimethylene spacer group, was synthesized. Complex formation of this dye and a model monostyryl dye with ions $EtNH_3^+$ and $NH_3^+(CH_2)_nNH_3^+$ ($n = 2$—6) in MeCN was studied using spectrophotometry and ^1H NMR spectroscopy. The homoditopic bisstyryl dye and diammonium salts form strong supramolecular complexes with pseudocyclic structure.

Key words: crown-ether-containing styryl dyes; molecular tweezers; complexation; diammonium salts.

The ability for self-organization at the molecular level (spontaneous assembling) in solution with a selective formation of supramolecular structures and the presence of photosensitive moieties are prerequisite for the creation of optical molecular sensors.[2—6] Among weak interatomic interactions, which play the major role in molecular self-assembling involving organic substrates, a hydrogen bond is important.[7] Design of molecular sensors capable of recognizing substituted ammonium ions are of special interest.[8] Crown ethers bind primary ammonium ions through three hydrogen bonds with the NH_3^+ groups.[9] Diammonium ions compose a significant group of ammonium ions, and many of them are natural compounds. The use of the two identical diaza-18-crown-6-ether moieties within macrotri- and macrotetracyclic structures capable of binding NH_3^+ groups made it possible to prepare homoditopic receptors that form molecular cryptates due to bonds with the terminal ammonium groups of the substrate.[10,11] However, if the receptors contain no photosensitive fragments, they cannot be used as optical molecular sensors.

Bisstyryl dye **1**, in which two chromogens are covalently linked by a short trimethylene chain, has attracted our attention, because this dye was preorganized to form photosensitive sandwich-like complexes with al-

kaline-earth metal cations with large ion radii due to the cooperative effect of two crown-ether fragments.[12]


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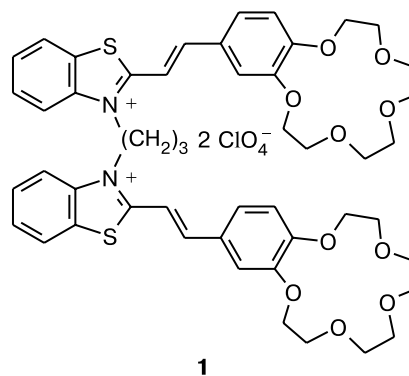
The use of a conformationally rigid *p*-phenylenedimethylene spacer instead of the short polymethylene chain in the crown-containing bisstyryl dyes is one of the promising approaches to the creation of optical molecular sensors for rather large diammonium cations.

In the present work, we report the synthesis of a crown-containing bisstyryl dye of the pyridine series (**2a**) and the study of complex formation of this ditopic dye with several oligomethylenediammonium salts by spectrophotometry and ^1H NMR spectroscopy.

Dye **2a** (in the form of dibromide) was synthesized in high yield (86%) by quaternization of pyridylvinylbenzo-

* For Part 2, see Ref. 1.

Scheme 1
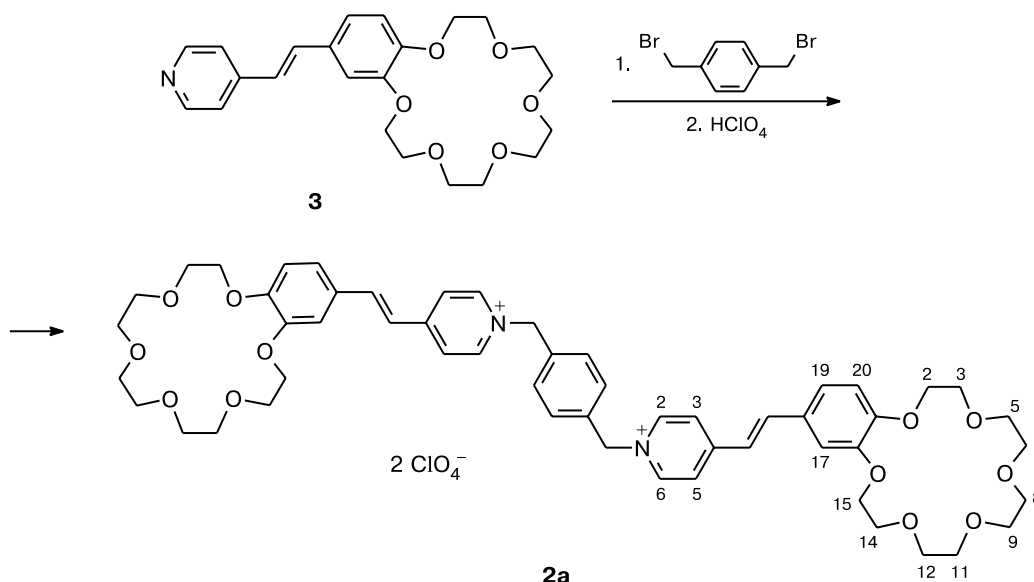
18-crown-6 **3** with α,α´-dibromo-*p*-xylene in anhydrous EtOH (Scheme 1). Bromide anions were replaced by perchlorate anions by treatment with concentrated perchloric acid. Perchlorate of the target dye was prepared as the *E,E*-isomer ($^3J_{CH=CH}$ = 16.2 Hz) in an overall yield of 76%.

When studying the complex formation of biscrown ether **2a**, we chose crown-containing monostyryl dye **2b** as a reference compound, because its chromogen was completely identical to chromogens of dye **2a**. Dye **2b** was prepared by a two-step synthesis according to a known procedure.[13]
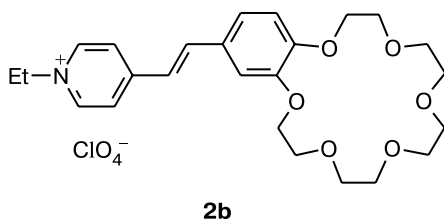
Diammonium salts $NH_3^+(CH_2)_nNH_3^+$ $2ClO_4^-$ (**4a—e**, *n* = 2—6, respectively) and ethylammonium perchlorate were synthesized by treatment of the corresponding α,ω-diaminoalkanes and ethylamine with concentrated perchloric acid.

The stability constants of complexes of dyes **2a** and **2b** with the ions $EtNH_3^+$ and $NH_3^+(CH_2)_nNH_3^+$ in MeCN were determined spectrophotometrically. Compounds **2a** and **2b** exhibit an intense absorption band in the visible spectral region (λ_{max} = 409.5 nm, ε_{max} = $6.8 \cdot 10^4$ mol^{-1} L cm^{-1} for **2a**; λ_{max} = 399 nm, ε_{max} = $3.5 \cdot 10^4$ mol^{-1} L cm^{-1} for **2b**). When ethylammonium perchlorate or diammonium salts **4a—e** were added to solutions of **2a**

or **2b**, this band underwent a substantial hypsochromic shift, indicating complex formation between the ammonium ion and the crown-ether fragment of the dye. The absorption spectra of solutions **2b** and **2a** in MeCN at different concentrations of the dication $NH_3^+(CH_2)_2NH_3^+$ are shown in Figs 1 and 2, respectively.

To analyze the concentration dependences of the absorption spectra, we used the parametrized matrix modeling (PMM) method[1] for the calculation of the corresponding theoretical spectra in the framework of the assumed complexation model and a set of experimental spectra. Then the standard deviation σ_D between the experimental and theoretical spectra is minimized by varying the equilibrium constants. The validity criterion of the
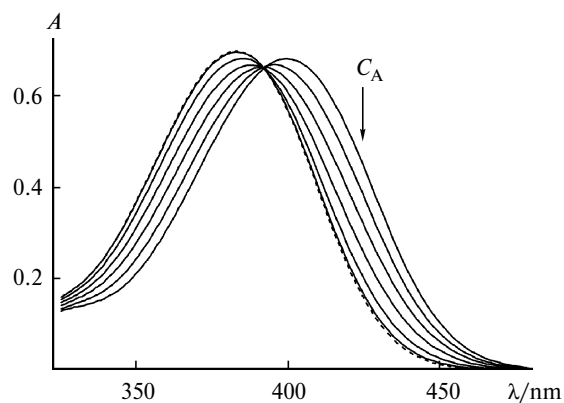

Fig. 1. Absorption spectrum of a solution of **2b** in MeCN ($1.95 \cdot 10^{-5}$ mol L^{-1}) at different concentrations of the ions $NH_3^+(CH_2)_2NH_3^+$ (C_A, interval of changes from 0 to $3 \cdot 10^{-3}$ mol L^{-1}); dotted line is the spectrum of the complex **2b**·$NH_3^+(CH_2)_2NH_3^+$ (calculated by the PMM method).
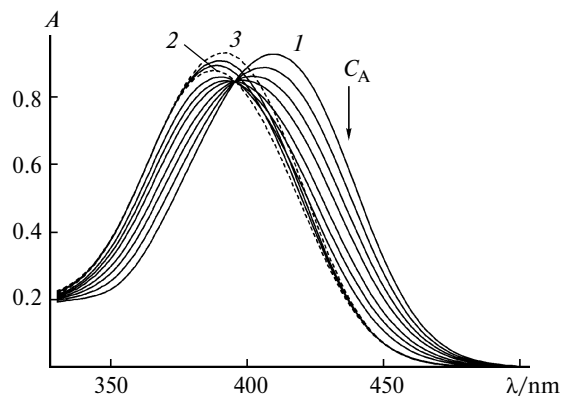
Fig. 2. Absorption spectrum of a solution of **2a** in MeCN ($1.36 \cdot 10^{-5}$ mol L^{-1}) at different concentrations of the ions NH$_3^+$(CH$_2$)$_2$NH$_3^+$ (C_A, interval of changes from 0 to $1 \cdot 10^{-2}$ mol L^{-1}): spectrum of **2a** in the absence of ammonium ions (*1*) and the spectra of the complexes **2a** · NH$_3^+$(CH$_2$)$_2$NH$_3^+$ (*2*) and **2a** · {NH$_3^+$(CH$_2$)$_2$NH$_3^+$}$_2$ (*3*) (calculated by the PMM method).

assumed reaction model is the σ_D at the minimum. The equilibrium constants and absorption spectra of complexes with different compositions result from these calculations.

For the systems **2b** · EtNH$_3^+$ClO$_4^-$ and **2b** · **4a—c**, the concentration dependences of the absorption spectra were found to agree with the model including the only equilibrium (1). At the same time, for the systems **2a** · EtNH$_3^+$ClO$_4^-$ and **2a** · **4a—e**, good correspondence is provided by a model including two equilibria (1 and 2):

$$L + A \underset{K_1}{\overset{}{\rightleftharpoons}} LA, \tag{1}$$

$$LA + A \underset{K_2}{\overset{}{\rightleftharpoons}} LA_2, \tag{2}$$

where L is the dye, A is the mono- or diammonium ion, and K_1 and K_2 are the stability constants of the complexes 1 : 1 (LA) and 1 : 2 (LA$_2$), respectively.

The stability constants K_1 and K_2 and the standard deviation σ_D obtained by the PMM method are presented in Table 1. In all cases, σ_D is much lower than 0.002 (in absorbance units), which indicates that the complexation models[1] assumed for dyes **2a** and **2b** are valid. The $\Delta\lambda_{max}$ and $\Delta\varepsilon_{max}$ values for the complexes of dyes **2a** and **2b** are listed in Table 2.

In the studied concentration region, model dye **2b** and the cation EtNH$_3^+$ or dications NH$_3^+$(CH$_2$)$_n$NH$_3^+$ (n = 2—4) form only 1 : 1 complexes (Scheme 2), whose absorption spectra are shifted to the short-wavelength region in relation to the spectrum of the dye by 15—16 nm. The stability constant of the complex **2b** · NH$_3^+$(CH$_2$)$_2$NH$_3^+$ is almost threefold higher than the corresponding constant of the complex **2b** · EtNH$_3^+$. This is, probably, caused by a higher density of the positive charge on the ammonium groups in the dication NH$_3^+$(CH$_2$)$_2$NH$_3^+$ as compared to that of EtNH$_3^+$ due

Table 1. Stability constants of the complexes of dyes **2a,b** with the ions EtNH$_3^+$ and NH$_3^+$(CH$_2$)$_n$NH$_3^+$ (n = 2—6) in MeCN at room temperature

System	$\log K_1$	$\log K_2$	σ_D [a]
2b · EtNH$_3^+$ClO$_4^-$	3.56 (3.57 [b])		0.0009
2b · **4a**	4.02		0.0015
2b · **4b**	3.97		0.0011
2b · **4c**	3.85		0.0009
2a · EtNH$_3^+$ClO$_4^-$	3.81	3.12 (3.06 [b])	0.0010
2a · **4a**	5.53	2.20	0.0013
2a · **4b**	5.92 (>5 [b])	2.02	0.0013
2a · **4c**	5.60	2.06	0.0011
2a · **4d**	5.56	2.07	0.0011
2a · **4e**	5.55	2.05	0.0011

[a] Standard deviation (in absorbance units) for absorption spectra modeling by the PMM method.
[b] ^{1}H NMR titration, MeCN-d$_3$, 30 °C.

Table 2. Spectrophotometric data for dyes **2a,b** and their complexes with the ions EtNH$_3^+$ and NH$_3^+$(CH$_2$)$_n$NH$_3^+$ (n = 2—6) in MeCN at room temperature[a]

| System	$\Delta\lambda_{max}$ /nm		$\Delta\varepsilon_{max} \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	
	1 : 1	1 : 2	1 : 1	1 : 2
2b · EtNH$_3^+$ClO$_4^-$	15		−0.05	
2b · **4a**	16		−0.08	
2b · **4b**	15		−0.05	
2b · **4c**	15		−0.05	
2a · EtNH$_3^+$ClO$_4^-$	9.5	16	0.18	−0.25
2a · **4a**	22	18	0.36	−0.01
2a · **4b**	22.5	19.5	0.36	−0.18
2a · **4c**	22	18.5	0.41	−0.19
2a · **4d**	22	18.5	0.41	−0.18
2a · **4e**	21.5	17.5	0.38	−0.09

[a] $\Delta\lambda_{max} = \lambda_{max}$(dye) − λ_{max}(complex), $\Delta\varepsilon_{max} = \varepsilon_{max}$(dye) − ε_{max}(complex); the λ_{max} and ε_{max} values for the complexes of dye **2a** in the framework of the PMM method.

to the mutual electron-acceptor influence of these groups through the systems of σ-bonds. This effect becomes weaker as the polymethylene chain in the dication elongates, decreasing the stability constant of the complex.

Bisstyryl dye **2a** can form 1 : 1 and 1 : 2 complexes with the ion EtNH$_3^+$ or dications NH$_3^+$(CH$_2$)$_n$NH$_3^+$ (n = 2—6) (Scheme 3). The stability constants K_1 of complexes **2a** · **4a—e** are much higher than that of the complex **2a** · EtNH$_3^+$. To the contrary, the stability constants K_2 of complexes **2a** · **4a—e** are much lower than the corresponding constant for the complex **2a** · EtNH$_3^+$. Note that the K_1 values of complexes **2a** · **4a—c** are almost two orders of magnitude higher than the corresponding constants for model systems **2b** · **4a—c**. These

Scheme 2

2b

2b · RNH₃⁺
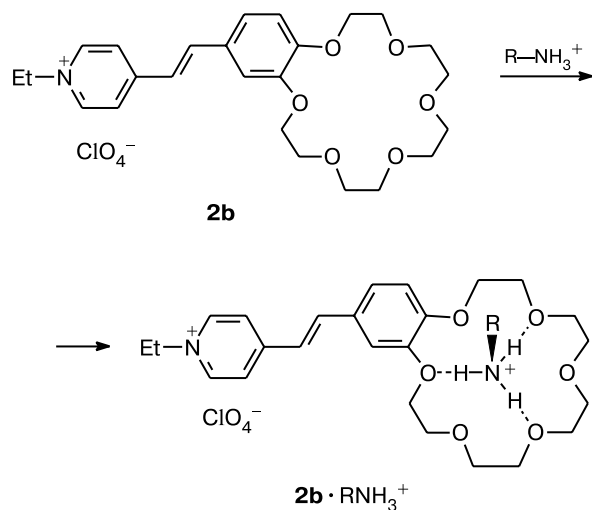
$R = Et, (CH_2)_nNH_3^+$

results indicate a two-center interaction between the dication $NH_3^+(CH_2)_nNH_3^+$ and dye in complexes $2a \cdot NH_3^+(CH_2)_nNH_3^+$ (Scheme 3).

The spectra of complexes $2a \cdot NH_3^+(CH_2)_nNH_3^+$ are characterized by a stronger hypsochromic shift of the absorption band ($\Delta\lambda_{max} = 21—23$ nm) as compared to those of the 1 : 2 complexes, *i.e.*, $2a \cdot [NH_3^+(CH_2)_nNH_3^+]_2$ ($\Delta\lambda_{max} = 18—20$ nm), and complexes of model dye $2b$ ($\Delta\lambda_{max} = 15—16$ nm). This additionally favors the pseudo-cyclic structure of the complexes $2a \cdot NH_3^+(CH_2)_nNH_3^+$.

The stability constant of the complex $2a \cdot NH_3^+(CH_2)_nNH_3^+$ depends weakly on the poly-methylene chain length in the dication with $n = 2—6$. However, it should be mentioned that the plot of K_1 *vs. n* for dye $2a$ has a maximum at $n = 3$. At the same time, for the complexes $2b \cdot NH_3^+(CH_2)_nNH_3^+$, K_1 decreases monotonically with an increase in n from 2 to 4. The presence of the maximum in the plot of K_1 *vs. n* for dye $2a$ is caused, most likely, by a sharp decrease in steric strains in the pseudocyclic complexes on going from $n = 2$ to $n = 3$.

Additional arguments in favor of the pseudocyclic structure of the complexes $2a \cdot NH_3^+(CH_2)_nNH_3^+$ were obtained by studying the complex formation of dyes $2a$ and $2b$ in a solution of MeCN-d₃ by ^1H NMR spectroscopy. The addition of ethylammonium perchlorate or

Scheme 3

2a

2 EtNH₃⁺

$NH_3^+(CH_2)_nNH_3^+$

$NH_3^+(CH_2)_nNH_3^+$

2a · NH₃⁺(CH₂)ₙNH₃⁺

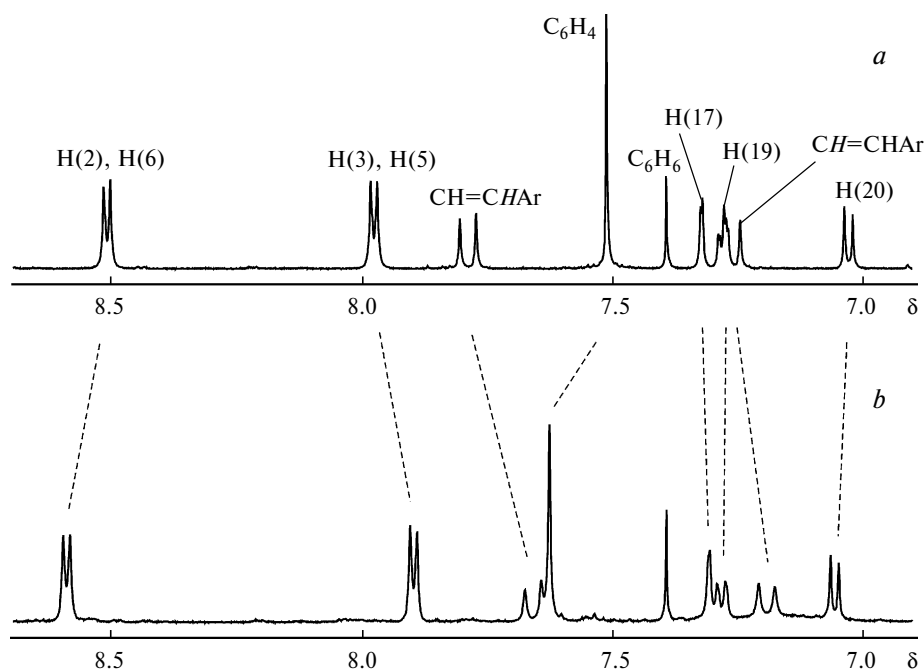**2a · (RNH₃⁺)₂**
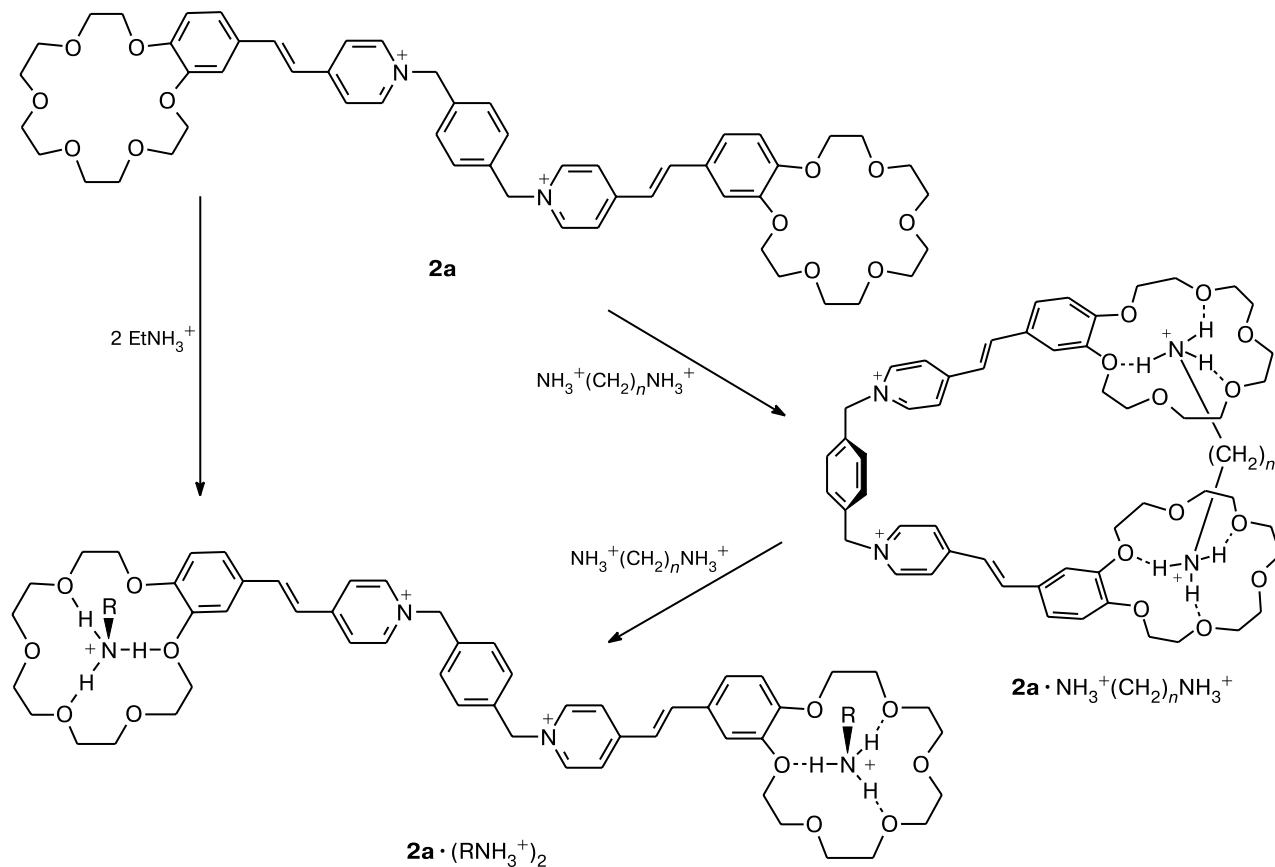
$R = Et, (CH_2)_nNH_3^+$

Fig. 3. Fragments of the ^1H NMR spectra (MeCN-d$_3$, 30 °C, $c_L = 2 \cdot 10^{-3}$ mol L^{-1}, region of signals of aromatic protons) of dye **2a** (*a*) and a mixture of **2a** and salt **4b** in a ratio of 1 : 1 (*b*).

salt **4b** to solutions of **2a** or **2b** induces the downfield shift of signals of the CH$_2$O groups of the dye ($\Delta\delta_H$ to 0.15) due to the interaction of the crown-ether fragment of the dye with the ammonium cation. In the systems **2a,b** · · EtNH$_3^+$ClO$_4^-$, complex formation also induces a slight downfield shift of all signals of the aromatic and ethylenic protons.

Signals of aromatic protons in the ^1H NMR spectra observed upon the complex formation of bisstyryl dye **2a** with dication NH$_3^+$(CH$_2$)$_3$NH$_3^+$ (**4b**) shift to an opposite direction. The signals of the aromatic protons of dye **2a** in MeCN-d$_3$ before and after the addition of **4b** in a ratio of 1 : 1 are shown in Fig. 3. It is seen that complex formation results in an upfield shift of some signals of protons of the central parts of the styryl moieties. This fact indicates the formation of the 1 : 1 pseudocyclic complex in which two relatively planar conjugated fragments are brought together in space due to the interaction of the dication NH$_3^+$(CH$_2$)$_3$NH$_3^+$ simultaneously with the two fragments of the dye. This approach allows one styryl fragment to get into the region of shielding of another fragment, which results in the upfield shift of protons of these fragments.

The changes in chemical shifts ($\Delta\delta_H$) of some protons in **2a** at different concentrations of the added salt **4b** (c_{4b}/c_{2a}) are shown in Fig. 4. For $c_{4b}/c_{2a} < 1$, the plots of $\Delta\delta_H$ *vs.* c_{4b}/c_{2a} are virtually linear. In the region $c_{4b}/c_{2a} \approx 1$, the derivative of the $\Delta\delta_H$ function of c_{4b}/c_{2a} changes its sign. This shape of the curves agrees well with the complexation model including two equilibria, (1) and (2), which was used to interpret spectrophotometric data. The
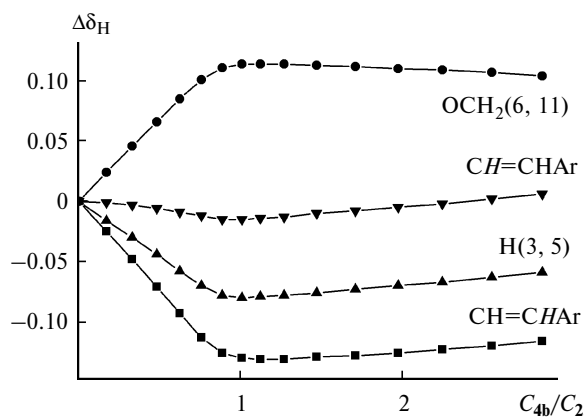

Fig. 4. Changes in the chemical shifts of protons in dye **2a** in MeCN-d$_3$ at different relative concentrations of the added salt **4b**, $\Delta\delta_H = \delta_H$ (in the presence of **4b**) $-\delta_H$ (without **4b**).

stability constant K_1 cannot exactly be estimated because of the almost linear character of the plots of $\Delta\delta_H$ *vs.* c_{4b}/c_{2a} at $c_{4b}/c_{2a} < 1$. However, the lower estimate of this constant ($\log K_1 > 5$) agrees with the results of spectrophotometric measurements.

In the case of the systems **2a,b** · EtNH$_3^+$ClO$_4^-$, all signals in the ^1H NMR spectra of the dyes shift monotonically with an increase in the concentration of the added ammonium salt. The character of the $\Delta\delta_H$ plots *vs.* c_A/c_L indicates the simple complexation model for the system **2b** · EtNH$_3^+$ClO$_4^-$ (equilibrium 1) and assumes two equilibria (1) and (2) for the system

2a · EtNH$_3^+$ClO$_4^-$. The stability constants of the corresponding complexes (Table 1) were calculated using the HYPNMR program[14] by the plots of $\Delta\delta_H$ of protons in **2a,b** *vs.* relative concentration of EtNH$_3^+$ClO$_4^-$. It should be mentioned that the estimates of K_1 for the complex **2b · EtNH$_3^+$** and K_2 for the complex **2a · (EtNH$_3^+$)$_2$**, which were made by H^1 NMR spectroscopy and spectrophotometry, virtually coincide. The K_1 value for the complex **2a · EtNH$_3^+$** obtained from the data of ^{1}H NMR titration is threefold higher than the value of this constant obtained by spectrophotometric titration. This distinction is caused, most likely, by a low accuracy of estimation of changes in chemical shifts of the protons in **2a** upon the formation of the 1 : 1 complex ($\Delta\delta_H < 0.07$).

Thus, we synthesized a new bisstyryl dye with the molecular tweezers structure. The regularities of its complex formation with mono- and diammonium compounds were established. The 1 : 1 complexes formed by this dye with the diammonium salts were shown to be pseudocyclic and to be much more thermodynamically stable than the monoammonium salt complexes. The stability constant of the pseudocyclic complex depends weakly on the polymethylene spacer length in the diammonium salt. The results obtained demonstrate that the crown-containing bisstyryl dyes can be used as selective optical molecular sensors with respect to diammonium ions.

Experimental

^{1}H NMR spectra were recorded on a Bruker DRX500 spectrometer (500.13 MHz) using DMSO-d$_6$ (2.50 ppm) or MeCN-d$_3$ (1.96 ppm) as the internal standard. Chemical shifts (δ_H) were measured with an accuracy of 0.01 ppm, and the accuracy of measuring coupling constants was 0.1 Hz. Absorption spectra were measured on a Specord-M40 spectrophotometer in a range of 330—600 nm with an increment of 80 cm^{-1}. Melting points were measured on a Mel-Temp II instrument. The course of the reactions was monitored by TLC on DC-Alufolien Kieselgel 60 F$_{254}$ plates (Merck). Elemental analyses were carried out at the Microanalytical Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow).

α,α´-Dibromo-*p*-xylene, linear α,ω-diaminoalkanes with the hydrocarbon chain length C$_2$—C$_6$, 70% perchloric acid, anhydrous ethanol, MeCN (spectral purity, >200 nm), MeCN-d$_3$, and DMSO-d$_6$ (Aldrich, Merck) were used.

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-({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-pyridiniumyl}methyl)benzyl]pyridinium diperchlorate (2a). A solution of pyridylvinylbenzocrown ether **3**[13] (166 mg, 0.40 mmol) and α,α´-dibromo-*p*-xylene (48 mg, 0.18 mmol) in anhydrous EtOH (5 mL) was refluxed for 36 h and then cooled to −10 °C. The precipitate was filtered off, washed with cold anhydrous EtOH, and dried *in vacuo* with heating. The resulting dye in the form of dibromide (170 mg) was dissolved in a minimum amount of hot anhydrous EtOH, and 70% perchloric acid (54 µL, 0.62 mmol) was added. The mixture was cooled to −10 °C, and the precipitate was filtered off, washed with cold anhydrous ethanol, and dried *in vacuo* with heating. Dye **2a** (134 mg, 76%) was obtained as an orange powder, m.p. 257—259 °C (with decomp.). ^{1}H NMR (DMSO-d$_6$, 60 °C) δ: 3.51 (s, 8 H, 2 8-CH$_2$O, 2 9-CH$_2$O); 3.56 (m, 8 H, 2 6-CH$_2$O, 2 11-CH$_2$O); 3.62 (m, 8 H, 2 5-CH$_2$O, 2 12-CH$_2$O); 3.79 (m, 8 H, 2 3-CH$_2$O, 2 14-CH$_2$O); 4.16 (m, 8 H, 4 2-C$\underline{H}_2$OAr); 5.70 (s, 4 H, 2 CH$_2$N); 7.08 (d, 2 H, 2 H(20), $J = 8.4$ Hz); 7.30 (dd, 2 H, 2 H(19), $J = 8.4$ Hz, $J = 1.8$ Hz); 7.38 (d, 2 H, 2 C$\underline{H}$=CHAr, $J = 16.2$ Hz); 7.39 (d, 2 H, 2 H(17), $J = 1.8$ Hz); 7.59 (s, 4 H, C$_6$H$_4$); 7.92 (d, 2 H, 2 CH=C$\underline{H}$Ar, $J = 16.2$ Hz); 8.16 (d, 4 H, 2 H(3), 2 H(5), $J = 6.7$ Hz); 8.96 (d, 4 H, 2 H(2), 2 H(6), $J = 6.8$ Hz). Found (%): C, 55.84; H, 5.87; N, 2.29. C$_{54}$H$_{66}$Cl$_2$N$_2$O$_{20}$·2 H$_2$O. Calculated (%): C, 55.43; H, 6.03; N, 2.39.

Synthesis of NH$_3^+$(CH$_2$)$_n$NH$_3^+$ 2ClO$_4^-$ (4a—e) (general procedure). 70% Perchloric acid (2.1 mL, 24 mmol) was added to a solution of diamine H$_2$N(CH$_2$)$_n$NH$_2$ (10 mmol) in anhydrous EtOH (10 mL), and the solvent was thoroughly evaporated *in vacuo*. The residue was dissolved in anhydrous EtOH (5 mL), and Et$_2$O (40 mL) was added. The precipitate was filtered off, washed with Et$_2$O (2×10 mL), and dried in air. The target salts were obtained as white crystalline powders in 92—98% yields.

1,2-Diammonioethane diperchlorate (4a). M.p. 280—281 °C (with decomp.). Found (%): C, 8.80; H, 3.91. C$_2$H$_{10}$Cl$_2$N$_2$O$_8$· ·0.5 H$_2$O. Calculated (%): C, 8.90; H, 4.11.

1,3-Diammoniopropane diperchlorate (4b). M.p. 269—271 °C (with decomp.). Found (%): C, 13.18; H, 4.42; N, 10.02. C$_3$H$_{12}$Cl$_2$N$_2$O$_8$. Calculated (%): C, 13.10; H, 4.40; N, 10.19.

1,4-Diammoniobutane diperchlorate (4c). M.p. 267—270 °C (with decomp.). Found (%): C, 16.77; H, 4.81; N, 9.75. C$_4$H$_{14}$Cl$_2$N$_2$O$_8$. Calculated (%): C, 16.62; H, 4.88; N, 9.69.

1,5-Diammoniopentane diperchlorate (4d). M.p. 220—224 °C. Found (%): C, 19.97; H, 5.41; N, 9.24. C$_5$H$_{16}$Cl$_2$N$_2$O$_8$. Calculated (%): C, 19.81; H, 5.32; N, 9.24.

1,6-Diammoniohexane diperchlorate (4e). M.p. 246—249 °C (with decomp.). Found (%): C, 22.79; H, 5.65; N, 8.77. C$_6$H$_{18}$Cl$_2$N$_2$O$_8$. Calculated (%): C, 22.72; H, 5.72; N, 8.83.

Study of complex formation. *Spectrophotometry*. The solvent was MeCN, which was purified from specific admixtures by distillation in the presence of one of the salts **4d,e** and then dried by distillation from CaH$_2$. The composition and thermodynamic stability of the complexes were determined from the dependence of the absorption spectrum of a solution of the dye in MeCN on the overall concentration (c_A) of the EtNH$_3^+$ or NH$_3^+$(CH$_2$)$_n$NH$_3^+$ ($n = 2$—6) ions. The c_A value was varied in the range from 0 to 0.01 mol L^{-1}, while the overall dye concentration (c_L) remained unchanged, being ~2.0·10^{-5} mol L^{-1} for **2b** or ~1.3·10^{-5} mol L^{-1} for **2a**. The overall concentration of the ClO$_4^-$ counterions (0.02 mol L^{-1}) in all experiments was maintained by addition of tetrabutylammonium perchlorate. In daylight, dyes **2a,b** underwent photochemical *trans-cis*-isomerization. Therefore, all procedures with solutions of the dyes were carried out in dark room with the red light. The PMM method[1] was used for experimental data processing.

^{1}H NMR spectroscopy. The solvent was MeCN-d$_3$. The composition and stability constants of the complexes of **2a,b** with the salts EtNH$_3^+$ClO$_4^-$ and NH$_3^+$(CH$_2$)$_3$NH$_3^+$ 2 ClO$_4^-$ were determined by analysis of changes in the positions of signals for the protons of the dye at different concentrations of the added am-

monium salt. The ammonium salt concentration varied in the interval from 0 to 0.015 mol L^{-1}; in this case, the overall dye concentration remained unchanged, being about $5 \cdot 10^{-3}$ mol L^{-1} for **2b** or about $2 \cdot 10^{-3}$ mol L^{-1} for **2a**. The $\Delta\delta_H$ value was measured with the accuracy of 0.001 ppm. The stability constants of the complexes were calculated using the HYPNMR program.[14]

References

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