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Effect of arrangement of the styryl fragment on the optical properties and complexation of mono- and bis(styryl)-substituted *N*-methylpyridinium perchlorates containing benzo-15-crown-5 ether moieties

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Using ^{1}H NMR spectroscopy and steady-state and time-resolved electronic spectroscopy, the optical properties of mono- and bis(styryl)pyridinium perchlorates and their complexes with Mg^{2+}, Ba^{2+} cations were studied. The stability constants of the complexes were determined using spectrophotometric titration. The formation of inclusion complexes for Mg^{2+} and sandwich type complexes for Ba^{2+} results in fluorescence enhancement and increases the lifetimes of the excited states of the initial bis-styryl ligands. The variation of position of the styryl fragment in the pyridinium aromatic ring gives rise to photochromic crown ethers with different optical and photophysical characteristics and is also an easy route to bis(crown-ethers) of symmetrical and unsymmetrical structure.

Key words: bis(crown ether), styryl dyes, benzo-15-crown-5 ether, complex formation, *E—Z* photoisomerization.

The ability of photochromic crown ethers to recognize metal cations of various nature and neutral molecules is widely used to design molecular optical sensors promising for analytical chemistry, biochemistry, and medicine, materials for ion selective electrodes, nonlinear optical devices and switches.[1—6] The recognition of metal cations and neutral molecules is based on their interaction with ionophoric fragments of photochromic molecules accompanied by a change in their photophysical and electrochemical properties.[7] It is known[8,9] that bis(crown ethers) have a number of advantages over monocrown-containing analogs: they are able to form both intermolecular and intramolecular sandwich type complexes with larger metal cations. Upon complexation, bis(crown ethers) can be aligned to form head-to-head sandwich type species and then extended supramolecular assemblies forming nanoparticles and nanostructures.

The photosensitive bis(crown ethers) reported in the literature[8,9] are diverse in structure. Some known bis(crown ethers) incorporate fragments of azobenzenes, naphthalenes, acridines, squaraine dyes, porphyrins, polyruthenium complexes, and dithienoethylenes. Bis(crown ethers) based on bis-styryl dyes have now been prepared and studied. These compounds are formed by coupling of two crown-containing styryl dyes through a spacer.[10,11] Bis-styryl crown dyes based on benzobisthiazole[12,13] and crown bis(styryl)benzenes[14—20] have also been described and studied.

This communication presents the results of the synthesis and studies of the complexing ability of a number of mono- and bis(benzo-15-crown-5) dyes based on mono- and bis(styryl)pyridinium salts. Note that the crown bis-styryl dyes reported in the literature were assembled in a molecule either through a spacer or by annulation through a benzene ring. Crown bis-styryl dyes where the styryl fragments are substituents in the same pyridinium nucleus have not yet been synthesized and studied. We varied the mutual arrangement of the styryl fragments in the pyridine molecule in order to analyze the optical properties of

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compounds and the complexation involving both crown ether fragments.

Experimental

The reactions were monitored by TLC on DC-Alufolien Kieselgel 60 F_{254} plates. Column chromatography was carried out on alumina.

Melting points (uncorrected) were measured on a Mel-temp II device. ^{1}H NMR spectra were measured on a Bruker DRX-500 spectrometer (500.13 MHz). The chemical shifts were determined to an accuracy of 0.01 ppm and the spin-spin coupling constants, to an accuracy of 0.1 Hz. Electrospray ionization mass spectra (2 kV) were run on a JEOL AccuTOF JMS-T100LC mass spectrometer.

Acetonitrile for spectroscopy (Aldrich, water content <0.005%) was used as received. Solutions of ligands **1—4** were prepared under red light. Electronic absorption spectra were recorded on a Varian-Cary spectrophotometer and fluorescence spectra were measured on a FluoroLog (Jobin Yvon) spectrofluorimeter at 20±1 °C. The fluorescence quantum yields for the ligands and complexes (φ_{fl}) were determined for air-saturated acetonitrile solutions at 20±1 °C with respect to 9,10-diphenylanthracene in cyclohexane ($\varphi_{fl} = 0.9$). The quantum yields were calculated using corrected fluorescence spectra. The complexation of compounds **1—4** with magnesium and barium perchlorates was studied by spectrophotometric titration at 20±1 °C while varying the concentration of the corresponding perchlorate at a constant ligand concentration. The complexation constants and absorption spectra of complexes based on the data of electronic spectra of solutions were calculated by SPECFIT Global Analysis System software. The procedure of measurement of time resolved fluorescence spectra was reported previously.[21]

Photochemical transformations were induced by irradiation of acetonitrile solutions of compounds **1—4** with a mercury lamp (DRK-120, 120 W). Particular lines of the mercury lamp spectrum were isolated by glass filters from the standard set of color optical glasses (UFS-2 + ZhS-3, UFS-6 + BS-7, PS-13 + ZhS-10, and PS-7 + SZS-21 + ZhS-18 for the lines with λ = 313, 365, 405, and 546 nm, respectively). The photoprocesses were studied with stirring in a 1-cm thick quartz cell with a fluoroplastic plug, the radiation intensity was $5.233 \cdot 10^{-6}$ Einstein s^{-1} L^{-1} (for λ = 365 nm). For Fischer calculation of the spectra of the *cis*-isomers of dyes **1** and **2**, the solutions were irradiated at λ = 313 and 365 nm until the photostationary states were attained.

Synthesis of compounds 1—4 (general procedure). A mixture of dimethylpyridinium tosylate (or trimethylpyridinium tosylate for the synthesis of compounds **3**, **4**) (0.32 mmol), 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecyne-15-carbaldehyde (0.32 mmol or 0.64 mmol for the synthesis of **3**, **4**), pyrrolidine (0.1 mL), and dry Bu^{n}OH (3 mL) was refluxed for 30 min on an oil bath. The reaction mixture was concentrated and the residue was washed with hot benzene. Then the residue was dissolved in MeOH and 70% $HClO_4$ (0.32 mmol) was added dropwise. The precipitate was filtered off and washed with Et_2O.

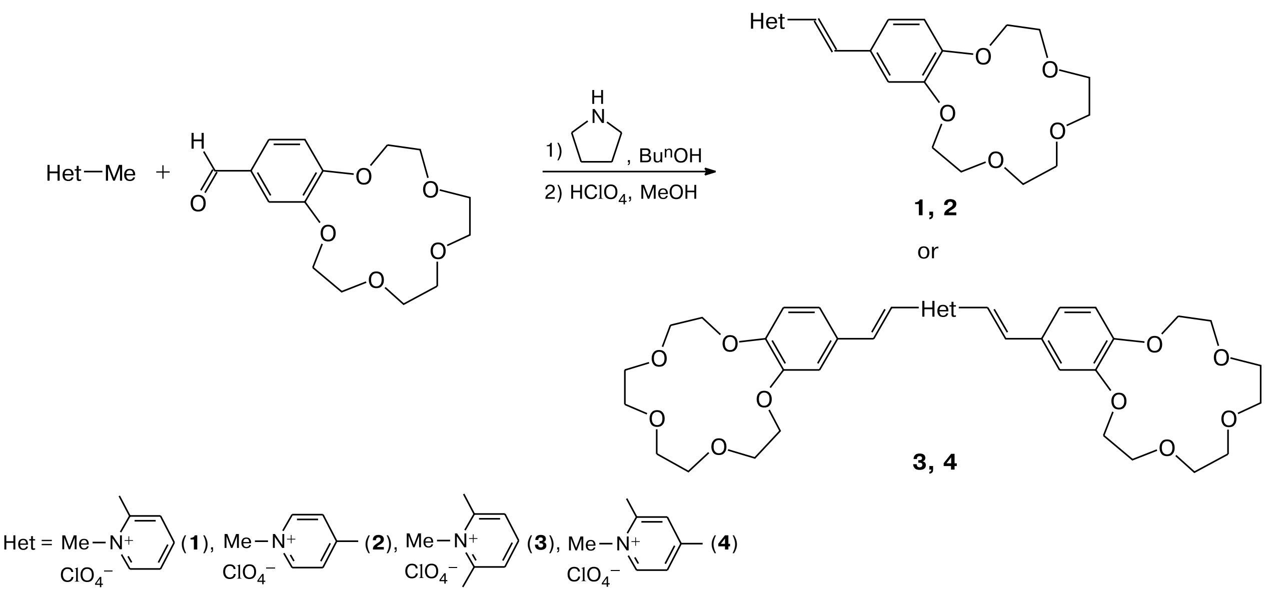
1-Methyl-2-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecyn-15-yl)vinyl]pyridinium perchlorate (1). Yield 0.090 g (58%), m.p. 146 °C. Found (%): C, 52.49; H, 5.87; N, 2.89. $C_{22}H_{28}ClNO_9 \cdot H_2O$. Calculated (%): C, 52.44; H, 6.00; N, 2.78. ^{1}H NMR (CD_3CN, 30 °C), δ: 3.62 (s, 8 H, H(5), H(6), H(8), H(9)); 3.80 (m, 4 H, H(3), H(11)); 4.14 (m, 4 H, H(2), H(12)); 4.34 (s, 3 H, NMe); 7.06 (d, 1 H, H(17), ^3J = 8.3 Hz); 7.37 (dd, 1 H, H(16), ^3J = 8.3 Hz, ^4J = 1.4 Hz); 7.43 (d, 1 H, H_b, $^3J_{trans}$ = 16.0 Hz); 7.49 (d, 1 H, H(14), ^4J = 1.4 Hz); 7.83 (dd, 1 H, H(5′), ^3J = 6.0 Hz, ^3J = 6.3 Hz); 7.86 (d, 1 H, H_a, $^3J_{trans}$ = 16.0 Hz); 8.43 (m, 2 H, H(3′), H(4′)); 8.83 (d, 1 H, H(6′), ^3J = 6.3 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 47.17 (NMe); 69.43 (C(3), C(11)); 69.88 (C(2), C(12)); 70.78 (C(5), C(9)); 71.50 (C(6), C(8)); 113.21 (C(14)); 113.99 (C(17)); 115.23 (C_b); 125.54 (C(16)); 125.87 (C(3′)); 129.63 (C(19)); 145.00 (C_a); 145.25 (C(4′), C(5′)); 145.33 (C(18)); 146.44 (C(6′)); 148.25 (C(15)); 152.93 (C(2′)). ESI MS (solution in MeCN), *m/z*: 386.2 $[M]^+$.

1-Methyl-4-[(*E*)-2-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecyn-15-yl)vinyl]pyridinium perchlorate (2). Yield 0.108 g (70%), m.p. 245 °C. Found (%): C, 49.85; H, 6.13; N, 2.79. $C_{22}H_{28}ClNO_9 \cdot 2.5H_2O$. Calculated (%): C, 49.77; H, 6.26; N, 2.64. ^{1}H NMR (CD_3CN, 30 °C), δ: 3.62 (s, 8 H, H(5), H(6), H(8), H(9)); 3.80 (m, 4 H, H(3), H(11)); 4.14 (m, 4 H, H(2), H(12)); 4.21 (s, 3 H, NMe); 7.03 (d, 1 H, H(17), ^3J = 8.6 Hz); 7.27 (dd, 1 H, H(16), ^3J = 8.6 Hz, ^4J = 1.5 Hz); 7.37 (d, 1 H, H_a, $^3J_{trans}$ = 16.2 Hz); 7.38 (d, 1 H, H(14), ^4J = 1.5 Hz); 7.89 (d, 1 H, H_b, $^3J_{trans}$ = 16.2 Hz); 8.10 (d, 2 H, H(3′), H(5′), ^3J = 6.8 Hz); 8.74 (d, 2 H, H(2′), H(6′)). ^{13}C NMR (100 MHz, CD_3CN), δ: 47.95 (NMe); 69.21 (C(3), C(11)); 69.66 (C(2), C(12)); 70.50 (C(5), C(9)); 71.27 (C(6), C(8)); 112.64 (C(14)); 113.92 (C(17)); 121.38 (C_b); 124.16 (C(16)); 124.44 (C(3′)); 129.10 (C(19)); 142.26 (C_a); 145.33 (C(18)); 149.91 (C(3′), C(5′)); 152.32 (C(4′)); 154.69 (C(2′), C(6′)). MS ESI (solution in MeCN), *m/z*: 386.2 $[M]^+$.

1-Methyl-2,6-bis[(*E*)-2′′-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecyn-15-yl)vinyl]pyridinium perchlorate (3). Yield 0.162 g (65%), m.p. 152 °C. Found (%): C, 57.40; H, 6.20; N, 1.85. $C_{38}H_{48}ClNO_{14} \cdot H_2O$. Calculated (%): C, 57.32; H, 6.33; N, 1.76. ^{1}H NMR (CD_3CN, 30 °C), δ: 3.62 (s, 8 H, H(5), H(6), H(8), H(9)); 3.80 (m, 4 H, H(3), H(11)); 4.14 (m, 4 H, H(2), H(12)); 4.27 (s, 3 H, NMe); 7.05 (d, 2 H, H(17), H(17′), ^3J = 8.3 Hz); 7.37 (d, 2 H, H(16), H(16′), ^3J = 8.3 Hz); 7.50 (s, 2 H, H(14), H(14′)); 7.51 (d, 2 H, H_b, $H_{b'}$, $^3J_{trans}$ = 15.7 Hz); 7.67 (d, 2 H, H_a, $H_{a'}$, $^3J_{trans}$ = 15.7 Hz); 8.18 (d, 2 H, H(3″), H(5″), ^3J = 8.1 Hz); 8.36 (dd, 1 H, H(4″), ^3J = 8.1 Hz). ^{13}C NMR (100 MHz, CD_3CN), δ: 49.56 (NMe); 69.64 (C(3), C(3′), C(11), C(11′)); 69.86 (C(2), C(2′), C(12), C(12′)); 70.59 (C(5), C(5′), C(9), C(9′)); 71.41 (C(6), C(6′), C(8), C(8′)); 113.14 (C(14), C(14′)); 114.05 (C(17), C(17′)); 117.18 (C_b, $C_{b'}$); 124.27 (C(3′), C(5′)); 124.61 (C(16), C(16′)); 129.03 (C(19), C(19′)); 143.80 (C_a, $C_{a'}$); 143.88 (C(4″)); 150.12 (C(18), C(18′)); 152.49 (C(15), C(15′)); 155.14 (C(2″), C(6″)). ESI MS (solution in MeCN), *m/z*: 678.3 $[M]^+$.

1-Methyl-2,4-bis[(*E*)-2′′-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecyn-15-yl)vinyl]pyridinium perchlorate (4). Yield 0.169 g (68%), m.p. 206 °C. Found (%): C, 58.51; H, 6.40; N, 1.99. $C_{38}H_{48}ClNO_{14}$. Calculated (%): C, 58.65; H, 6.22; N, 1.80. ^{1}H NMR (CD_3CN, 30 °C), δ: 3.62 (s, 8 H, H(5), H(6), H(8), H(9)); 3.80 (m, 4 H, H(3), H(11)); 4.14 (m, 4 H, H(2), H(12)); 4.24 (s, 3 H, NMe); 7.05 (d, 1 H, H(17), ^3J = 8.2 Hz); 7.07 (d, 1 H, H(17′), ^3J = 8.2 Hz); 7.27 (dd, 1 H, H(16), ^3J = 8.2 Hz, ^4J = 1.6 Hz); 7.31 (d, 1 H,

Scheme 1

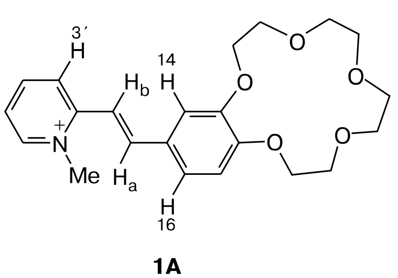


H$_{b'}$, $^3J_{trans}$ = 16.4 Hz); 7.36 (d, 1 H, H(14), ^4J = 1.6 Hz); 7.38 (dd, 1 H, H(16´), ^3J = 8.4 Hz, ^4J = 1.6 Hz); 7.41 (d, 1 H, H$_b$, $^3J_{trans}$ = 15.8 Hz); 7.49 (d, 1 H, H(14´), ^4J = 1.6 Hz); 7.86 (d, 1 H, H$_a$, $^3J_{trans}$ = 15.8 Hz); 7.89 (dd, 1 H, H(5″), ^3J = 5.8 Hz, ^4J = 1.3 Hz); 7.95 (d, 1 H, H$_{a'}$, $^3J_{trans}$ = 16.4 Hz); 8.46 (d, 1 H, H(3″), ^4J = 1.3 Hz); 8.69 (d, 1 H, H(6″), ^3J = 5.8 Hz). ^{13}C NMR (100 MHz, CD$_3$CN), δ: 46.07 (NMe); 69.31 (C(3), C(3´), C(11), C(11´)); 69.80 (C(5), C(5´), C(9), C(9´)); 70.58 (C(2), C(2´), C(12), C(12´)); 71.48 (C(6), C(6´), C(8), C(8´)); 112.57 (C(14)); 112.98 (C(14´)); 113.97 (C(17), C(17´)); 115.48 (C$_b$); 121.32 (C(3″)); 121.34 (C(5″)); 121.80 (C$_{b'}$); 124.18 (C(16)); 124.81 (C(16´)); 128.95 (C(19)); 129.39 (C(19´)); 141.27 (C$_a$); 143.98 (C$_{a'}$); 145.64 (C(6″)); 150.12 (C(18), C(18´)); 152.18 (C(15)); 152.62 (C(15´)); 153.47 (C(2″)); 153.67 (C(2″)). ESI MS (solution in MeCN), *m/z*: 678.3 [M]$^+$.

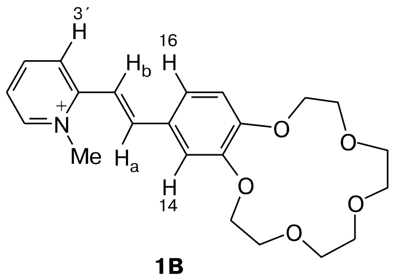
Results and Discussion

Synthesis and structure of compounds 1—4. Using a known method,[21] we synthesized mono- and bis(styryl)-substituted *N*-methylpyridinium perchlorates **1—4** containing a benzo-15-crown-5 ether moiety (Scheme 1).

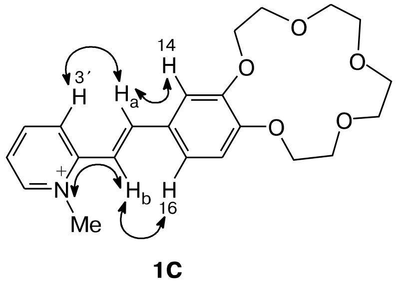
The structures of compounds **1—4** were proved by ^{1}H and ^{13}C NMR spectroscopy and ESI mass spectrometry and confirmed by elemental analysis. The fact that



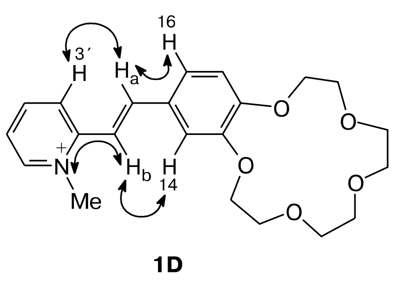
1A



1B



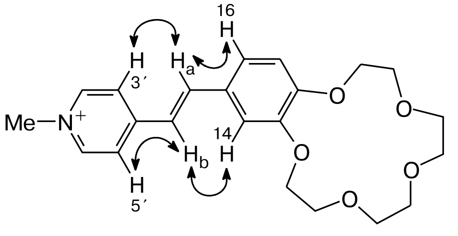
1C



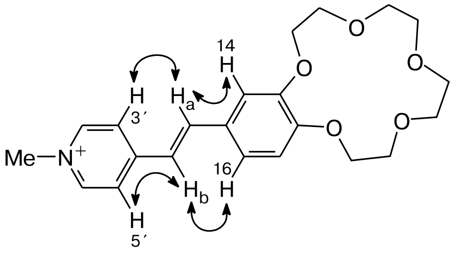
1D

compounds **1—4** exist as *E* isomers follows from the data of ^{1}H NMR spectra (the spin-spin coupling constants for the vinylene protons ^3J_E = 16.0 (**1**), 16.2 (**2**), 15.7 (**3**), 15.8, and 16.4 Hz (**4**)). The conformations of compounds **1—4** were determined using the NOESY experiment (the significant NOE factors in the structures of these compounds are marked by arrows). Styryl dye **1** can be conceived as existing simultaneously as four conformers **A—D**. The 2D NMR data indicate that in a MeCN-d$_3$ solution, compound **1** exists as a mixture of conformers **C** and **D**, as the NOESY spectra of this compound exhibit intense cross-peaks for coupled proton for these conformers.

Monostyryl dye **2** also exists in solution as a mixture of two conformers **A** (*syn*) and **C** (*anti*).



2A



2C

A more complex composition of conformers can be expected for bis-styryl dyes **3** and **4**. The 2D NMR spectrum of compound **3** was found to exhibit coupling of the NMe group only with the double bond protons H—C$_b$ and H—C$_{b'}$ of two styryl fragments, namely, the H—C$_{b'}$↔H—C(14′), H—C$_b$↔H—C(14), and also H—C$_a$↔H—C(3″) and H—C$_a$↔H—C(16), H—C$_{a'}$↔H—C(5″) and H—C$_{a'}$↔H—C(16′) coupling. This set of cross-peaks indicates that for compound **3** in a MeCN-d$_3$ solution, the predominant species is the highly symmetrical conformer shown below.

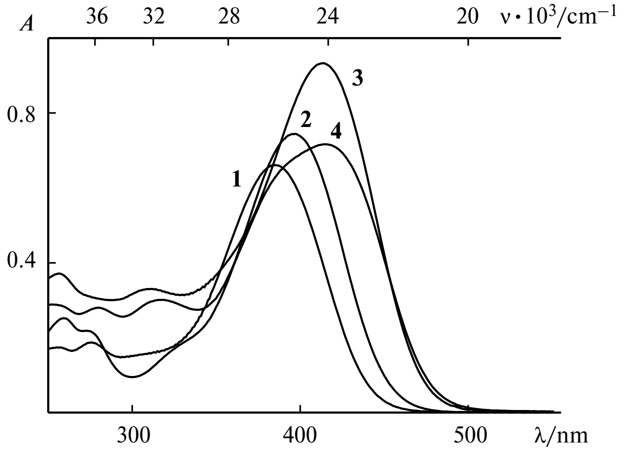
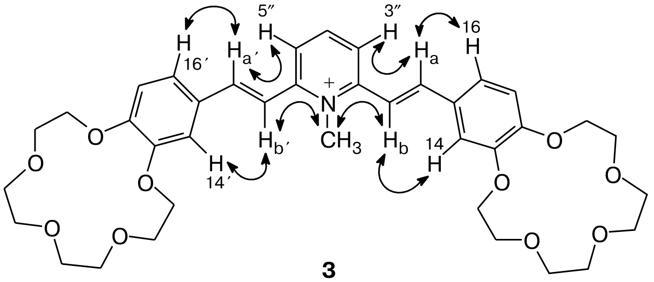


Fig. 1. Absorption spectra of dyes **1—4** (C = 2.5•10^{-5} mol L^{-1}, MeCN, 293 K).



3

For compound **4**, ^{1}H NMR spectroscopy data do not provide unambiguous conclusion about the composition of conformers in solution; the differences between the chemical shifts for analogous pairs of protons (H—C(2′) and H—C(2″), H—C(14), and H—C(14′), H—C(16) and H—C(16′), H—C(17), and H—C(17′), H—C$_a$ and H—C$_{a'}$, and H—C$_b$ and H—C$_{b'}$) of two styryl fragments are due to the unsymmetric structure of molecule **4**.

Optical characteristics of ligands 1—4. The electronic absorption spectra of dyes **1—4** are shown in Fig. 1 and the fluorescence spectra are in Fig. 2. The key spectral characteristics of dyes **1—4** are presented in Table 1. The positions of the long-wavelength absorption bands (LAB) and fluorescence bands (FB) of styrylpyridinium salts and also the band widths and shapes depend essentially on the position of substituents (*ortho*- or *para*-substitution). The *para*-substituted styrylpyridinium salts have a more extended system of conjugation than the *ortho*-isomers, resulting in a pronounced shift of the LAB maximum for the *para*-derivatives to lower energies. Previously,[22,23] it was found that in the absorption spectra of bis-styryls and bis-carbocyanines containing two conjugated chromophores in one molecule, the absorption band of the parent dye splits into two new bands located at shorter and longer wavelengths. In the case of ligands **3** and **4**,

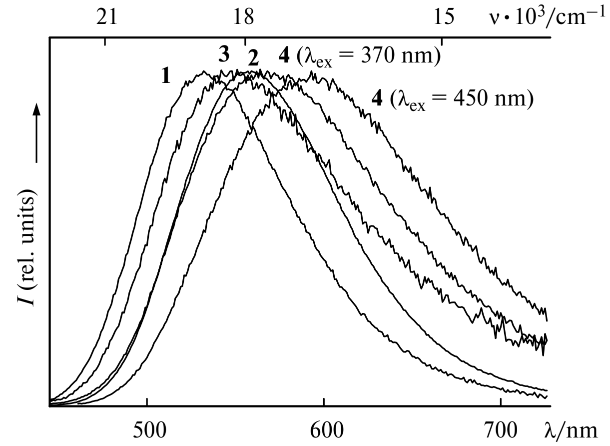


Fig. 2. Fluorescence spectra of dyes **1—4** (MeCN, 293 K).

noticeable splitting of the LAB is observed only for ligand **4**, which has identical substituents in both the *ortho-* and *para*-positions of the pyridinium ring. The splitting of the LAB can be attributed to the presence of two nonequivalent internal charge transfer excited states in the donor—acceptor—donor sysem.

It should also be noted that the LAB of bis(styryl)pyridinium salts **3** and **4** are shifted bathochromically with respect to the LAB of mono(styryl) analogs **1** and **2**. This may be interpreted in terms of adiabatic interaction of two charge transfer excited states. A similar behavior was found previously[23] for mono- and bis-styryl dyes devoid of crown ether moieties.

Table 1. Data of electronic absorption spectra and logarithms of the stability constants (log*K*) of the complexes of dyes **1—4** with magnesium and barium perchlorates (MeCN, 293 K)

Compound	$\varepsilon_{trans} \cdot 10^4$ /L mol^{-1} cm^{-1}	λ_{max}/nm ($\Delta\lambda$*/nm)	log*K*
1	2.64	385	—
$[(\mathbf{1})(Mg^{2+})]$	3.25	351 (34)	$\log K_{11} = 4.02 \pm 0.03$
$[(\mathbf{1})(Ba^{2+})]$	2.80	356 (29)	$\log K_{11} = 3.94 \pm 0.02$
2	2.98	395	—
$[(\mathbf{2})(Mg^{2+})]$	3.21	360 (35)	$\log K_{11} = 4.52 \pm 0.02$
$[(\mathbf{2})(Ba^{2+})]$	3.20	363 (32)	$\log K_{11} = 4.04 \pm 0.04$
3	3.73	414	—
$[(\mathbf{3})(Mg^{2+})]$	3.41	405 (9)	$\log K_{11} = 4.8 \pm 0.2$
$[(\mathbf{3})(Mg^{2+})_2]$	3.75	378 (36)	$\log K_{12} = 7.9 \pm 0.2$
$[(\mathbf{3})_2(Ba^{2+})_2]$	7.39	392 (22)	$\log K_{22} = 15.5 \pm 0.2$
$[(\mathbf{3})(Ba^{2+})_2]$	3.61	390 (24)	$\log K_{12} = 9.9 \pm 0.2$
$[(\mathbf{4})(Mg^{2+})]$	2.55	370 sh, 412 (8)	$\log K_{11} = 5.0 \pm 0.1$
$[(\mathbf{4})(Mg^{2+})_2]$	3.08	364 sh, 380 (40)	$\log K_{12} = 8.4 \pm 0.1$
$[(\mathbf{4})_2(Ba^{2+})_2]$	5.34	361 sh, 390 (30)	$\log K_{22} = 17.7 \pm 0.3$
$[(\mathbf{4})(Ba^{2+})_2]$	2.65	365 sh, 394 (26)	$\log K_{12} = 10.4 \pm 0.3$

* $\Delta\lambda = (\lambda_{max})_L - (\lambda_{max})_{compl}$.

The fluorescence quantum yields (φ_{fl}) of dyes **1—4** increase in the sequence **3** < **1** < **4** < **2**, the φ_{fl} value for symmetrical 2,6-substituted bis(styryl)pyridinium **3** is 5 times lower than that for its 2,4-substituted isomer **4**, while φ_{fl} of 2-substituted styrylpyridinium **1** is 6 times lower than that for 4-substituted derivative **2**. It was found during the studies that φ_{fl} of bis(styryl)pyridinium **4** depends essentially on the excitation wavelength.

Fluorescence kinetics of ligands 1—4. Of all compounds studied in this work, only for the monosubstituted salt of styrylpyridinium **1**, can the curve of fluorescence decay in highly polar aprotic acetonitrile solvent be described by a monoexponential kinetic equation (Table 2). In the case of mono- and bis-styryl dyes **2—4**, the decay curve can only be described by biexponential kinetic equations. The lifetime of the excited state of 2-mono(styryl)-*N*-methylpyridinium salt **1** is lower than for 4-mono(styryl) analog **2**. The same behavior is typical of bis(styryl)pyridinium salts **3** and **4**: the lifetimes of the fast and slow components of 2,6-bis(styryl)pyridinium **3** are much shorter than those for isomeric 2,4-bis(styryl)pyridinium **4**. Note also that measurements of fluorescence decay curves for compound **4** showed a dependence of the relative amplitudes of the fast and slow components not only on the excitation wavelength but also on the wavelength of emission observation.

Photochemistry. Previously, we showed[24] that irradiation of acetonitrile solutions of styryl dyes induces a reversible photochemical *E—Z* isomerization. Thus on irradiation of dyes **1** and **2** at 405 nm, the absorption near the long-wavelength band decreases with a simultaneous increase in the absorption in the short-wavelength part of the spectrum until a photostationary state is attained. The subsequent irradiation of the obtained solution at 365 nm induces the reverse changes in the absorption spectra up to transition to a new photostationary state. A clear-cut isosbestic point is observed and a linear dependence between the absorbances at two different wavelengths holds; this is typical of *E—Z* photoisomerization. The absorption spectra of *cis*-isomers of monostyryl dyes **1** and **2** (Fig. 3) were calculated from the corresponding spectra of *trans*-isomers and photostationary states obtained on exposure to light at λ = 365 and 405 nm.[25]

Previously,[12,13] we demonstrated that irradiation of a crown benzobisthiazole induces reversible photochemical *E—Z* isomerization and photocycloaddition. Unlike crown benzobisthiazole, bis-styryl dyes **3** and **4** irradiated at 313, 365, 405, and 436 nm do not show changes in the absorption spectra.

The photoexcitation of molecules constructed according to the donor-acceptor mechanism is known[26—28] to lead to photoinduced charge transfer. For styryl dyes **1** and **2**, *E—Z* photoisomerization is the main channel of radiationless deactivation of the excited state, which is consistent with low fluorescence quantum yields observed

Table 2. Fluorescence characteristics of dyes **1**—**4** and their complexes (MeCN, 295 K)

Compound	λ^{fl}_{max}/nm ($\Delta\lambda^{fl}$/nm)*	φ_{fl}	Lifetime	
			τ_1^{fl}/ps	τ_2^{fl}/ns
1	532	0.016	147	—
[(**1**)(Mg^{2+})]	457 (75)	0.002	6	—
[(**1**)(Ba^{2+})]	491 (41)	0.004	16, 37	—
2	559	0.095	67	0.570
[(**2**)(Mg^{2+})]	482 (77)	0.011	37	—
[(**2**)(Ba^{2+})]	530 (29)	0.060	120	0.30
3	548	0.004	34, 145	—
[(**3**)(Mg^{2+})]	530 (18)	0.006	—	—
[(**3**)(Mg^{2+})$_2$]	490 (58)	0.037	199	—
[(**3**)$_2$(Ba^{2+})$_2$]	547 (1)	0.114	108	1.46, 6.19
4	568 [λ_{ex} = 370 nm]	0.02	—	—
4	593 [λ_{ex} = 450 nm]	0.015	135	0.50
[(**4**)(Mg^{2+})]	536 [λ_{ex} = 360 nm]	0.02	57	—
[(**4**)(Mg^{2+})]	557 [λ_{ex} = 420 nm]	0.016	340	1.07
[(**4**)(Mg^{2+})$_2$]	511 [λ_{ex} = 350 nm]	0.09	480	1.07
[(**4**)(Mg^{2+})$_2$]	515 [λ_{ex} = 410 nm]	0.08	—	—
[(**4**)$_2$(Ba^{2+})$_2$]	554 [λ_{ex} = 360 nm]	0.13	750	3.3
[(**4**)$_2$(Ba^{2+})$_2$]	551]λ_{ex} = 430 nm]	0.14	—	—

* See the Footnote to Table 1.

for these compounds. Apparently, relaxation of the excited state of ligands **3** and **4** follows a different mechanism and gives rise to a radiationless twist-state, which can be deactivated without the formation of *Z*-isomers.

Complexation. The addition of Mg^{2+} and Ba^{2+} perchlorates to solutions of compounds **1**—**4** in acetonitrile causes hypsochromic shifts of the LAB upon complex formation involving the crown-ether moiety of the molecule (see Table 1). The stability constants of complexes **1**—**4** with metal cations were calculated using the spectrophotometric titration data and the SPECFIT program.[29] The constants thus obtained are summarized in Table 1. The calculations took into account a number of pathways to the complexes (Scheme 2); however, not more than two equations were used simultaneously for processing of titration data in each particular case.

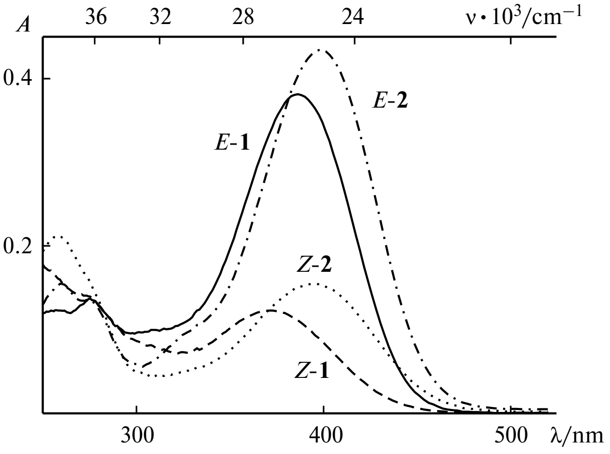


Fig. 3. Absorption spectra of *E*-isomers of dyes **1** and **2** ($C = 1.5 \cdot 10^{-5}$ mol L^{-1}) and spectra of *Z*-isomers of dyes **1** and **2** calculated by the Fischer method.

Scheme 2

$$L + M^{n+} \underset{}{\overset{K_{11}}{\rightleftharpoons}} LM$$

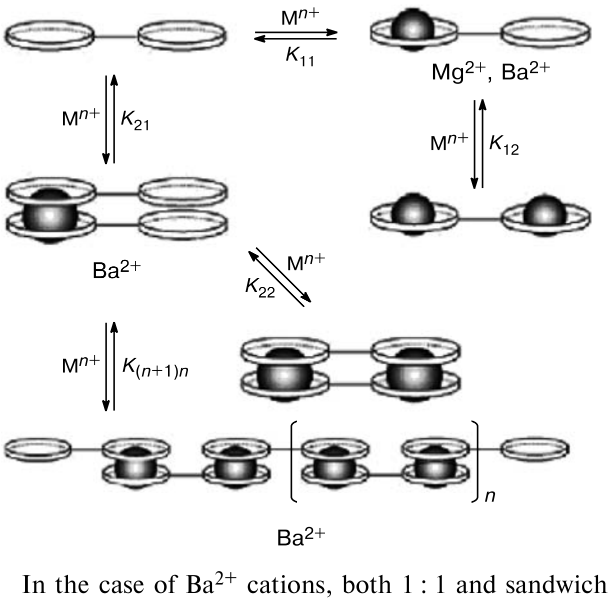
$$L + 2\,M \overset{K_{12}}{\rightleftharpoons} LM_2$$

$$2\,L + M \overset{K_{21}}{\rightleftharpoons} L_2M$$

$$2\,L + 2\,M \overset{K_{22}}{\rightleftharpoons} L_2M_2$$

Mono(crown ether) ligands **1** and **2** form complexes [(L)(Mg^{2+})] with Mg^{2+} cations. The stability constants of complexes formed by 2-monocrown-styrylpyridinium **1** are lower than those for 4-substituted analog **2** (see Table 1). Bis(crown ether) ligands **3** and **4** form two sorts of complexes with Mg^{2+} cations, [(L)(Mg^{2+})] and [(L)(Mg^{2+})$_2$] (Scheme 3, Table 1). The stability constants of the Mg^{2+} complexes of bis(crown ethers) **3** and **4** formed with participation of one crown ether moiety are higher than these values for the complexes of mono(crown ethers) **1**, **2**. The involvement of the second crown ether moiety of bis(crown ethers) **3**, **4** in complexation gives complexes [(L)(Mg^{2+})$_2$]; the addition of the second magnesium cation is less efficient than that of the first one, whereas the stepwise complexation constant ($\log\beta = \log K_{12} - \log K_{11}$) is lower than the stability constant $\log K_{11}$ for the corresponding ligand **3** or **4**. This effect is attributable to difficulty of addition of the second magnesium cation to the formed triply charged cation $[(L)(Mg)]^{3+}$ due to the Coulomb repulsion. Spectrophotometric titration of bis(crown ether)-containing ligand **4** gives rise to an isosbestic point at an early stage; this, however, disappears on further addition of magnesium salt, which is accompanied by appearance of an isosbestic point at a different wavelength. The calculation of the solution composition during titration showed that for complexation constants of ligand **4** with magnesium cations (see Table 1) and ligand concentration of $2.4 \cdot 10^{-5}$ mol L^{-1}, if 63% of the initial ligand is incorporated in 1 : 1 complex, only 5% of the ligand form 1 : 2 complex. After addition of a small amount of Mg^{2+} cations during titration of ligand **4**, the shoulder at 395 nm corresponding to the charge transfer electron transition from the crown ether located in position 2 of the pyridinium ring to the acceptor disappears and a band with a maximum at 364 nm appears. At a large amount of Mg^{2+} added, the LAB maximum of ligand **4** at 420 nm, which is due to the charge transfer electron transition from the crown ether located in position 4 of the pyridinium ring to the acceptor, shifts hypsochromically to 380 nm (see Fig. 4).

Scheme 3



In the case of Ba^{2+} cations, both 1 : 1 and sandwich type complexes can be formed with ligands containing a benzo-15-crown-5 ether fragment.[9] The complexes [(L)Ba] were found for ligands **1** and **2**. Complexes with more diverse structures may be expected of ligands **3** and **4** with two crown ether moieties (see Scheme 3). Note that the formation of sandwich type intramolecular complexes is unlikely for ligands **3** and **4** for geometric reasons. Due to the complexity of this system, it is impossible to determine the complexation constants for all complexes of ligands **3** and **4** with Ba^{2+} cations from the spectrophotometric titration data. However, we attempted to describe the ligand **3**(**4**)—Ba^{2+} cation system taking into account only the formation of 2 : 2 and 1 : 2 complexes and this led to a satisfactory result (see Table 1). The 2 : 2 and 1 : 2 complexes were chosen because the latter is likely to predominate in the presence of an excess of Ba^{2+} cations and the possibility of formation of sandwich type complexes is consistent with the observed sharp increase in the lifetimes of barium complexes.

It can be seen from the results (see Table 1) that the involvement of two crown ether moieties of molecule **3**, **4** into complexation results in complexes with more diverse structures and in stronger metal cation binding.

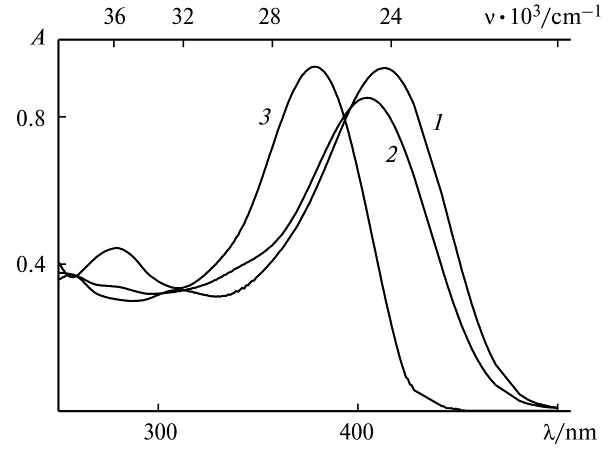


Fig. 4. Simulated absorption spectra of dyes **3** ($C_L = 2.5 \cdot 10^{-5}$ mol L^{-1}) (*1*) and its complexes $[(\mathbf{3})(Mg^{2+})]$ (*2*) and $[(\mathbf{3})(Mg^{2+})_2]$ (*3*).

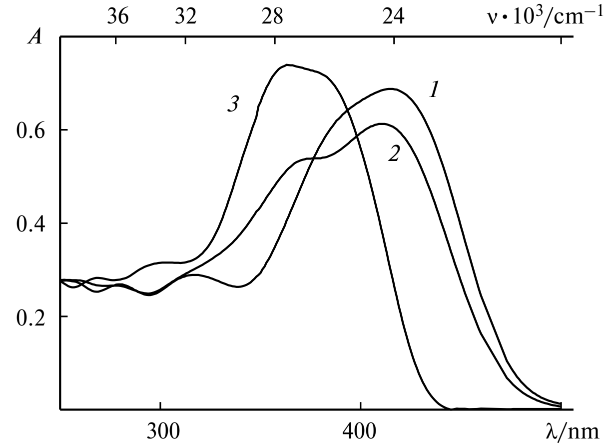


Fig. 5. Simulated absorption spectra of dyes **4** ($C_L = 2.4 \cdot 10^{-5}$ mol L^{-1}) (*1*) and its complexes $[(\mathbf{4})(Mg^{2+})]$ (*2*) and $[(\mathbf{4})(Mg^{2+})_2]$ (*3*).

Fluorescence of complexes 1—4. Proceeding from the obtained stability constants (see Table 1), solutions of complexes with particular predominant compositions were prepared. The fluorescence spectra of complexes of dyes **1—4** are shifted hypsofluorically relative to the fluorescence spectra of free ligands.

Complexes of dye **4** show a dependence of emission characteristics on the excitation wavelength. For complexes of monocrown ligands **1**, **2**, fluorescence quenching with respect to the initial ligands was found. This is rather typical of crown styryl dyes and was also noted previously.[28,30,31] The formation of sandwich type complex $[(L)_2(Ba^{2+})_2]$ and Mg^{2+} complexes $[(L)(Mg^{2+})_2]$ in the case of bis-styryl dyes **3**, **4** is accompanied by an increase in the fluorescence quantum yield; φ_{fl} of the complexes $[(\mathbf{3})(Mg^{2+})_2]$ and $[(\mathbf{4})(Mg^{2+})_2]$ increases 9.25- and 4.5-fold with respect to φ_{fl} of the initial ligands, while φ_{fl} of the sandwich complexes $[(\mathbf{3})_2(Ba^{2+})_2]$, $[(\mathbf{4})_2(Ba^{2+})_2]$ increases 28.5- and 6.5-fold. In the latter case, stacking of the chromophore fragments and interaction between them in the excited state are possible, which gives rise to long-lived states characterized by high fluorescence yields.[12] In the case of monostyryl dyes **1** and **2**, no stacks are formed in the sandwich complex, because free likely charged heterocyclic ends of molecules are *anti*-arranged relative to each other. The lifetime of the excited state and the fluorescence quantum yield of this complex would be similar to those for inclusive complexes with magnesium perchlorate cations.

The fluorescence lifetimes of ligands **1—4** change essentially upon complexation. The fluorescence decay curves of complexes of compound **1** can be described by biexponential kinetic equations with appearance of shorter-lived components compared to the initial ligand **1** (see Table 2). As noted above, for the complex formed by ligand **2** with Ba^{2+}cation, fluorescence quenching is typical but the fluorescence decay curve of this complex can be described by biexponential kinetic equations with appearance of longer-lived components compared to the initial ligand **2**. Apparently, a decrease in the fluorescence quantum yields and lifetimes of compounds **1** and **2** complexed with metal cations is due to an increase in the rate of radiationless *E—Z* photoisomerization. Analysis of the fluorescence decay curves for the complexes $[(L)(Mg^{2+})_2]$ and $[(L)_2(Ba^{2+})_2]$ for ligands **3** and **4** has shown that in accordance with the observed increase in φ_{fl} of the complexes, the complexation of these ligands is also accompanied by the appearance of long-lived components (see Table 2) in the range from 400 ps to 6 ns. Since the rotation of fragments of the molecule accompanied by the formation of twist states in the complexes of bis-styryl dyes with metal cations is hampered, emission becomes a key channel of excited state relaxation.

Thus, we synthesized for the first time crown mono- and bis-styryl dyes in which two styryl residues are substituents in one pyridinium ring and studied them by NMR, optical, and emission (steady-state and time-resolved) spectroscopy. Optical studies showed that the electronic interaction between two styryl fragments is apparently rather weak. Bis-styryl dyes synthesized in this work are distinguished by high complexation constants with barium cations due to sandwich binding and by considerable fluorescence enhancement and increase in the excited state lifetime, which have not been observed previously for bis-styryl dyes. The variation of the position of the styryl substituents in the pyridinium aromatic ring leads to photochromic crown ethers with different optical and photophysical characteristics and represents a facile method for the design of symmetric and unsymmetric bis(crown ethers).

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