Synthesis, structure and complexation of biscrown-containing 1,4-distyrylbenzenes*

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An improved method for the synthesis of two symmetric biscrown-containing and one model tetramethoxy-substituted 1,4-distyrylbenzenes was suggested. The structures of compounds were established by ¹H and ¹³C NMR spectroscopy and X-ray diffraction analysis. Spectrophotometric and fluorescent titration were used to determine spectral properties, stoichiometry, and stability of complexes of biscrown-containing 1,4-distyrylbenzenes with alkali and alkaline-earth metal cations. The stability of the complexes was found to depend on the metal cation size and charge, as well as on the size of the crown ether fragment. The electrochemical oxidation and reduction potentials of the biscrown-containing 1,4-distyrylbenzenes and the model compound in solution were determined and their basic differences from the corresponding characteristics of biscrown-containing stilbenes were identified.

Key words: distyrylbenzenes, crown ethers, complexes, stoichiometry of complexes, electronic spectroscopy, NMR spectroscopy, X-ray diffraction analysis, electrochemistry.

In the last years, the supramolecular direction in organic chemistry became one of the most intensively developing areas.¹ Supramolecular systems frequently are composed of complex and scarcely available organic compounds, the synthesis of which in many cases becomes the subject of separate studies. Apart from that, in supramolecular chemistry it is important to predict properties of compounds in supramolecular systems and develop directed methods for their self-assembly.

One of the promising types of photoactive molecules for the research of supramolecular self-organization became crown-containing compounds²⁻⁷ with N=N, C=N, and C=C double bonds in the structure. The interest to the studies of such compounds is caused by their ability to self-assembly to supramolecules and supramolecular ensembles resulting from the complexation with metal and ammonium ions and related to this considerable changes in their spectral characteristics, as well as by a possibility of changing their structure and properties upon irradiation. The most typical photochemical processes taking place in the indicated supramolecular systems which proceed with considerable changes in the properties are the *trans/cis*-photoisomerization and [2+2] photocycloaddition reactions.⁸⁻¹⁴

We have shown that biscrown-containing stilbenes **1a**,**b** and a number of bis-ammonium-alkyl derivatives of viologen or its analogs, as well as cyanine dyes, formed unusual bi- and trimolecular complexes through hydrogen bonding, ^{15,16} in which an effective intermolecular charge trans-

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^{*} Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 85th birthday.



fer was observed due to the spatial preorganization of donor and acceptor parts of the molecule.^{17,18} Such supramolecular systems are characterized by high stability, which allows one to regard them as convenient models in the studies of photoinduced intermolecular electron transfer¹⁹ and effecting [2+2] photocycloaddition reaction,²⁰ as well as promising objects with rich electrochemical behavior.²¹

1,4-Distyrylbenzenes due to the long conjugated fragment possess higher quantum yields of fluorescence as compared to stilbenes.^{22,23} The presence of two C=C double bonds in the structure of 1,4-distyrylbenzenes also leads to the appearance of additional possibilities for molecular photoswitching.^{24–26} This and a number of other properties made 1,4-distyrylbenzenes attractive objects to be used for the development of photoactive materials: organic light-emitting diodes, materials for solar cells, nonlinear optical materials, chemical sensors.^{27–32}

There are known derivatives of biscrown-containing 1,4-distyrylbenzenes 2a,b containing substituents at the double bonds and in the central benzene fragment,^{33,34} however, they were not studied as deeply as biscrowncontaining stilbenes **1a**,**b**, though they could exhibit no less interesting photochemical behavior and pronounced ability to complexation. Therefore, a high potential of biscrown-containing 1,4-distyrylbenzenes as structural blocks in the construction of complex supramolecular ensembles has not been fully exhausted, that, not in the least, was caused by relative difficulty of their preparation and the presence of substituents at the double bonds or in the central benzene ring. Therefore, the purpose of the present work is the development of a convenient method for the synthesis of symmetric 1,4-distyrylbenzenes, having unsubstituted ethylene groups and the central benzene ring,

which contains two 15(18)-crown-5(6)-ether fragments; studies of their structural specific features, complexation, and electrochemical properties, as well as a possibility of their use for the development of photoactive materials.

Results and Discussion

Synthesis of compounds. The first representative of biscrown-containing 1,4-distyrylbenzenes, namely, bis(15crown-5)-1,4-distyrylbenzene (2a), was obtained earlier³⁵ by Wittig-Horner condensation of bisphosphonate 3 with 4'-formylbenzo-15-crown-5 ether (4a) upon treatment with 85% aqueous solution of KOH in refluxing benzene in 53% yield. One of the disadvantages of this approach, which we identified during reproduction of the procedure, was a necessity of additional purification of compound 2a by recrystallization from dioxane, that led to a considerable decrease in the yield. Using the data given in the work,35 we developed an original procedure based on the use of DMF as the solvent. The advantage of DMF consists in the fact that the starting compounds and the side reaction products are readily soluble in it, while the target 1,4-distyrylbenzenes are poorly soluble, therefore, their isolation considerably simplifies, especially after addition of water to the reaction mixture.

Initially, we studied the applicability of this method for the synthesis of the model compound, namely, tetramethoxy-1,4-distyrylbenzene (5), the methoxy groups of which generally reproduce the electron-donating character of crown ether fragments. It was found that the reaction of bisphosphonate 3 with veratric aldehyde (6) upon treatment with NaH in DMF led to the formation of compound 5 in 91% yield (Scheme 1). Scheme 1





The optimized procedure was extended to 4'-formylbenzo-15(18)-crown-5(6) ethers **4a,b**. However, in this case the reaction proceeded somewhat differently from the reaction with the model compound **5**: the precipitated product required additional purification and after recrystallization from dioxane the yields of the products considerably decreased, to 51% (**2a**) and 26% (**2b**). This can be possibly explained by the Cannizzaro reaction of aldehydes **4a,b** proceeding due to the presence of NaOH impurity in NaH. Therefore, in the next step we replaced the base with Bu^tONa, which was obtained *in situ* calculated as 2.1 mol. equiv. per one methylene group of bisphosphonate **3**. This allowed us to obtain biscrown-containing 1,4-distyrylbenzenes **2a,b** in 73 and 63% yields, respectively (Scheme 2).

According to the ¹H NMR spectroscopy data, 1,4-distyrylbenzenes **5** and **2a,b** were isolated as *E,E*-isomers, that follows from the large spin-spin coupling constant values for olefinic protons (${}^{3}J_{\text{HC}=\text{CH}} = 16.3 \text{ Hz}$). A comparison of the melting point and the color of compound **2a** (285–289 °C, bright yellow crystals) with the literature data³⁵ (272 °C, colorless crystals) indicates that the authors of this publication, apparently, worked with not pure enough compound.

To sum up, the use of available bisphosphonate 3 and formyl derivatives of benzocrown ethers 4a,b as the starting compounds, feasibility of the synthesis and high yields

of final products make the suggested method of obtaining of compounds **2a**,**b** more convenient as compared to those reported in the literature, while the purity and the structure of product **2a** more reliable.

X-ray diffraction study. Molecular structure of tetramethoxy-1,4-distyrylbenzene (5) in the frontal and the lateral projections are shown in Fig. 1, selected bond distances and bond angles are given in Table 1.

Molecule **5** has a centrosymmetric structure (the center of symmetry matches the center of the central benzene ring), a *trans*-configuration of the ethylene fragments, a propeller-like structure of the 1,4-distyrylbenzene conjugation system and exists in the crystal in the *anti*,*anti*conformation (see discussion of the NMR spectroscopy data and results of quantum chemical calculations).

The dimethoxyphenyl residues in molecule **5** are rotated to the opposite sides relative to the plane of the central benzene ring by $23.3(2)^\circ$. Such a structure is mainly adopted due to the twisting of the molecule around the C(5)–C(7) bond, the torsion angle C(6)–C(5)–C(7)–C(8) is 167.9(2)° (the atom numbering scheme is shown in Fig. 1). In molecule **5**, the double bonds of the ethylene bridges are greatly localized (see Table 1). Thus, the ethylene bond lengths C(7)=C(8) and C(7')=C(8') are equal to 1.345(3) Å. The C–C single bonds conjugated with the double bonds, C(7)–C(5) (C(7')–C(5')) and C(8)–C(9) (C(8')–C(9')), have the length of 1.459(3) and 1.454(3) Å, respectively.





Fig. 1. Molecular structure of tetramethoxy-1,4-distyrylbenzene 5 in the frontal (a) and the lateral projections (b). The mean-square thermal deviations of atoms are given with 50% probability. The numbers of atoms in the side projection are given for the centrosymmetric half of the molecule.

Note. Figures 1 and 2 are available in full color on the web page of the journal (http://www.linkspringer.com).

 Table 1. Some geometric parameters of structure 5

Parameter	Value
Bond length	d∕Å
C(7)=C(8), C(7')=C(8')	1.345(3)
C(7)-C(5), C(7')-C(5')	1.459(3)
C(8)-C(9), C(8')-C(9')	1.454(3)
C(1)-C(6), C(1')-C(6')	1.375(3)
C(2)-C(1), C(2')-C(1')	1.408(3)
C(6)-C(5), C(6')-C(5')	1.411(3)
C(3)-C(4), C(3')-C(4')	1.386(3)
C(2)-C(3), C(2')-C(3')	1.384(3)
C(4)-C(5), C(4')-C(5')	1.391(3)
C(11)–C(10′)	1.377(3)
C(10) - C(11')	1.377(3)
C(9)-C(10)	1.407(3)
C(9)–C(11)	1.404(3)
Angle	ω/ deg
C(6) - C(5) - C(7) - C(8)	167.9(2)
O(2) - C(2) - C(1)	115.27(19)
O(1) - C(1) - C(2)	114.72(18)
O(2) - C(2) - C(3)	125.40(19)
O(1) - C(1) - C(6)	125.57(19)
C(12) - O(1) - C(1) - C(6)	-6.1(3)
C(13) - O(2) - C(2) - C(3)	5.9(3)

C(4)C(5) bonds are actually equivalent. The distribution of the bonds in the central benzene ring bears a pronounced quinonoid character, which is indicated by the noticeably shorter bonds C(11)-C(10') and C(10)-C(11') as compared to the rest of them. This confirms the existence of a long chain of conjugation in 1,4-distyrylbenzene 5 involving the central benzene fragment.

The methoxy groups in compound 5 are located almost in the plane of the benzene rings. In molecule 5, a slight deformation of the bond angles at the atoms C(2) and C(1) of the benzene ring is observed. This deformation is reflected in the fact that the angles O(2)C(2)C(1) and O(1)C(1)C(2) are noticeably decreased to ~115°, while the external angles O(2)C(2)C(3) and O(1)C(1)C(6), conversely, are increased to ~125°. Such a kind of deformation contradicts to the idea on the steric repulsion of the oxygen atoms O(2) and O(1), the distance between which in compound 5 (2.56 Å) is less than the sum of their van der Waals radii (~ 2.8 Å), and is usually explained by the conjugation of the lone pairs of electrons (LPE) on *p*-orbitals of the atoms O(2) and O(1) with the benzene ring. Such a conjugation is also favored by the conformation of the fragment $MeOC_{Ar}C_{Ar}$, at which the indicated torsion angle is close to 0° or 180° . In molecule 5, these torsion angles are small $(5.9^{\circ} \text{ and } -6.1^{\circ})$.

Since we suppose that the crystal packing strongly influences the molecular geometry of tetramethoxy-1,4distyrylbenzene **5** and electron effects in it, it is interesting to consider it in more details.

The three layers of the crystal packing of **5** are shown in Fig. 2. Here, the stack-like layout of the molecules in the neighboring layers is absent. The molecules in the crys-



Fig. 2. A fragment of the crystal packing of tetramethoxy-1,4-distyrylbenzene 5.

tal are packed in the columns with the T-shaped mutual arrangement. The neighboring columns contact with each other through the methoxy groups. The shortest contacts between the columns are effected through the methyl groups: the distances C(12)...C(13) are equal to 3.962(3) Å.

The fact of the formation in the crystal of hydrophilic regions by the methoxy groups of the neighboring molecules is of special interest. It is possible that this is the tendency to form such vast hydrophilic regions which prevents the formation of the stack-like packing motif, somewhat more typical of the conjugated organic systems.

NMR spectroscopy. NMR spectroscopy provides a possibility to determine a fine structure of organic molecules and their ensembles in solutions.³⁶ A comparison of NMR data with the structure of compounds known from crystallographic analysis of is carried out not very often because of impossibility to obtain high-quality crystals for the whole series. In the case of biscrown-containing 1,4-distyrylbenzenes, it is especially important to find their conformational behavior in solutions, that is related to the determination of the structure of supramolecular systems on their basis. In this connection, we studied structural characteristics of 1,4-distyrylbenzenes **2a,b** and **5**, using different techniques of NMR spectroscopy.

In the crystal state, tetramethoxy-1,4-distyrylbenzene **5** exists as a symmetric *anti,anti,anti*-conformer (see Fig. 1), that is apparently substantiated by the requirements for the most dense packing of the molecules. Upon dissolution, a rapid conformational equilibrium can be established between symmetric *anti,anti,anti-*, *anti,syn,anti-*, *syn,anti,syn-*, *syn,syn,syn-* and nonsymmetric *syn,anti,anti-*, *syn,anti-*forms (Fig. 3) similarly to the earlier studied crown-containing styryl dyes and biscrown-containing stilbenes.^{12,37} In this case, we considered only conformations of terminal fragments of distyrylbenzenes, since *anti-* and *syn-*orientation of two double bonds relative to

the central benzene ring are indistinguishable by NMR spectroscopy. The NOESY spectra, unfortunately, do not provide a possibility to evaluate the contribution of each conformer of compounds 2a,b and 5 to the equilibrium due to the strong interaction of protons of the ethylene fragments with both the protons of the types H(4) and H(6) in all the conformers (the atom numbering system differing from the IUPAC rules is shown in Fig. 3). Apart from that, the signals for the protons H(4) and H(6) overlap with the signal of one of the ethylene protons (H(7)), as a result it is impossible to identify individual crosspeaks from the NOESY spectrum.

An indirect indication in favor of predominance in solution of syn,(syn/anti), syn-conformers follows from the comparison of positions of two benzene protons H(4) and H(6), which are in *ortho*-position to the ethylene substituent. The protons of the H(6) type are also in the *ortho*-position to the strong donor alkoxy substituent and, actually, should appear in the higher fields as compared to H(4). However, quite the opposite picture is observed, *i.e.*, the signals for the H(6) atom in the ¹H NMR spectra of all the studied distyrylbenzenes were found in the lower fields as compared to the signals for H(4) atom (approximately by 0.02–0.04 ppm). Such a situation is possible in the case when predominantly the H(6) type protons get into the deshielding area of the ethylene fragment and, consequently, more compact syn,(syn/anti), syn-forms of 1,4-distyrylbenzenes 2a.b and 5 predominate in the equilibrium mixture. The signals for the protons of the CH₂O groups of the crown ether fragments in compounds 2a,b consistently shift toward higher fields as they become more remote from the benzene ring. The NOESY spectra showed that among the CH₂OAr (MeOAr) groups, the most downfield signals belong to the protons of the $CH_2O(1)$ (MeO(1) in compound 5) groups, which, apparently, as the aromatic protons H(6), experience a deshielding influence of the C=Cbond in the syn,(syn/anti), syn-conformers of 2a, b and 5.



Fig. 3. Possible conformers of distyrylbenzenes 2a,b and 5 and their stability relative to the most favorable *syn,syn,syn-conformer* (for compound 5). Molar fractions of conformers (in %) were obtained from the results of quantum chemical calculations at room temperature.

Compounds **2a,b** and **5** were studied by ¹³C NMR spectroscopy in solutions of CD_2Cl_2 . The positions of the signals for analogous ¹³C nuclei of 1,4-distyrylbenzenes **2a,b** are virtually the same, that indicates their similar conformational composition and, probably, the absence of considerable strains in the macrocyclic fragments. In tetramethoxy-1,4-distyrylbenzene **5**, the positions of most carbon signals of the 1,4-distyrylbenzene core differ little from the analogous signals in 1,4-distyrylbenzenes **2a,b**. An exception are the signals for C(3) and C(6) atoms, which are shifted upfield by 0.45–1.12 ppm. Apparently, the methyl groups instead of alkoxyethyl ones at O(2) and O(1) increase the electron-donating character of the latter, that is reflected in the δ_C of the carbon atoms at *ortho*-positions to them.

Quantum chemical calculations. In order to find out the most favorable conformation of the conjugated fragment in 1,4-distyrylbenzenes of the studied type, we carried out density functional (DFT) quantum chemical calculations of conformers for their parent representative, that is, (E,E)-tetramethoxy-1,4-distyrylbenzene (5), and distyrylbenzene 2a. The choice of distyrylbenzene 5 is substantiated by the absence of flexible macrocyclic fragments in it. The latter, having many local minima on the potential

energy surface close to the global one, can make the computational results inaccurate. For *anti*,*anti*,*anti*-5, this method demonstrated a good agreement of the bond distances and bond angles calculated in the gas phase with the X-ray diffraction data (the maximum difference for bond lengths was 0.015 Å and the maximum difference for angles was 0.7°). A small difference in the calculated and X-ray diffraction data was found for the angles between the planes of the ethylene bond and the benzene rings (10 and 12°), as well as for the torsion angles $COC_{Ar}C_{Ar}$ (6°). This difference is apparently due to the influence of the crystal field on the structure of compound 5.

For tetramethoxy-1,4-distyrylbenzene **5**, we calculated the energies of conformers shown in Fig. 3, as well as their molar fractions at room temperature. The calculations show that the energies of transoid and cisoid (with respect to the central divinylbenzene fragment) forms of molecule **5** differ only by $0.07 \text{ kcal mol}^{-1}$, therefore, these conformers are present in the equilibrium mixture in approximately equal amounts. The *syn*,(*syn/anti*),*syn*-forms were found to be the most stable, the *anti*,(*syn/anti*),*anti*-forms the least stable. Nonetheless, the total amount of the latter conformers was found to be 11% (the solvent effects not taken into account), that is not negligible.

Similar calculations for compound **2a** gave the same fraction of *anti*,(*syn/anti*),*anti*-conformers in the mixture.

We calculated chemical shifts in the ¹H NMR spectra for all the conformers. The calculations showed that chemical shifts for the protons H(4) and H(6) in the pairs of svn,(svn/anti),svn- or anti,(svn/anti),anti conformers are almost the same, however, their difference in the pairs (syn/anti), syn, (syn/anti) or (syn/anti), anti, (syn/anti) is quite noticeable. For compound 5, the calculated chemical shifts for H(4) in the conformers with syn- and antiorientation of the dimethoxystyryl fragment are 6.88 and 7.56 ppm, respectively, while those for H(6) are 7.27 and 6.64 ppm. For the H(7) signal, the chemical shift is 7.29 ppm, for H(8) it is 7.07 and 7.20 ppm. Taking into account the molar fractions of conformers, the average chemical shifts for H(4) and H(6) are 7.04 and 7.12 ppm, while for H(7)and H(8) they are 7.29 and 7.10 ppm, respectively, that is in good agreement with the experiment. Similar calculations for compound 2a gave 7.02 and 7.10 ppm for H(4) and H(6) and 7.27 and 7.09 ppm for H(7) and H(8), respectively.

Electronic spectroscopy. The spectral characteristics of tetramethoxy-containing and biscrown-containing distyrylbenzenes are given in Table 2. A mixture of MeCN–CH₂Cl₂ (10:1, v/v) was used as the solvent for recording absorption and fluorescence spectra, since our preliminary studies showed that in pure MeCN compound **2a** is virtually insoluble.

1,4-Distyrylbenzenes **2a,b** and **5** absorb light stronger and in the longer wavelength region of the spectrum $(\lambda_{max} \text{ at } 370-372 \text{ nm})$ as compared to the related stilbenes $(\lambda_{max} \text{ at } \sim 335 \text{ nm})$,²⁰ that, obviously, is due to the longer chromophore moiety and the efficient conjugation in it for the first group of compounds.



As an example, Fig. 4 shows absorption and fluorescence spectra of tetramethoxy-1,4-distyrylbenzene (5) and tetramethoxystilbene (7). The fluorescence maximum of compound 5 ($\lambda_{max}^{fl} = 439$ nm) is bathochromically shifted relative to the maximum of stilbene 7 ($\lambda_{max}^{fl} = 385$ nm), that indicates the presence of conjugation over all the long chromophore in the first case. The fluorescence was excited using the light with a 339-nm wavelength, at which the extinctions of these two compounds are the same. From Fig. 4, it is seen that the fluorescence of compound 5 is much better, that also indicates more efficient conjugation in the long chromophore of distyrylbenzene as compared to stilbene. A similar spectral behavior characterizes also the studied pairs of biscrown-containing distyrylbenzenes and stilbenes.



Fig. 4. Absorption (1, 2) and fluorescence spectra (3, 4) of compounds 5 (1, 3) and 7 (2, 4) (absorption at $C = 1 \cdot 10^{-5}$ mol L⁻¹, fluorescence at $C = 1 \cdot 10^{-6}$ mol L⁻¹, MeCN–CH₂Cl₂(10:1, v/v), ~20 °C, $\lambda_{ex} = 339$ nm).

We also studied complexation properties of biscrowncontaining distyrylbenzenes 2a and 2b. The stability constants of their complexes with alkali and alkaline-earth metal perchlorates were determined by spectrophotometric and fluorescent titration. The concentration dependences of absorption and fluorescence spectra were analyzed using the HypSpec program,³⁸ in which the corresponding theoretical spectra and stability constants of the complexes were calculated based on a suggested complexation model and a set of experimental spectra.

It was found that in the studied range of concentrations for biscrown-containing distyrylbenzenes from $5 \cdot 10^{-7} - 2 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ to $8.8 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$ for $\text{M}^{m+}(\text{ClO}_4^{-})_m$ (to $1.8 \cdot 10^{-2} \text{ mol } \text{L}^{-1}$ in the case of LiClO_4 and bis(18-crown-6)-containing distyrylbenzene), for the systems bis(15-crown-5)distyrylbenzene/Li⁺(Na⁺, Cs⁺, Mg²⁺, Ca²⁺) and bis(18-crown-6)distyrylbenzene/Li⁺(Na⁺, K⁺, Cs⁺, Ba²⁺), the concentration dependences of absorption and fluorescence spectra agree with the model which includes equilibria (1) and (2). For the system bis(15-crown-5)distyrylbenzene/K⁺(Sr²⁺, Ba²⁺), the best agreement was found for the model including three equilibria (1), (2), and (3).

$$L + M^{m+} \stackrel{K_{1:1}}{\longleftarrow} L \cdot M^{m+}, \qquad (1)$$

$$\mathbf{L} \cdot \mathbf{M}^{m+} + \mathbf{M}^{m+} \stackrel{K_{1:2}}{\longleftrightarrow} \mathbf{L} \cdot (\mathbf{M}^{m+})_2, \tag{2}$$

$$2 L + 2 M^{m+} \stackrel{K_{2:2}}{=} (L)_2 \cdot (M^{m+})_2, \qquad (3)$$

where L is distyrylbenzene, $K_{1:1}$ (L mol⁻¹), $K_{1:2}$ (L mol⁻¹), and $K_{2:2}$ (L³ mol⁻³) are the stability constants of complexes with the composition 1 : 1 (L · M^{*m*+}), 1 : 2 (L · (M^{*m*+})₂), and 2 : 2 ((L)₂ · (M^{*m*+})₂), respectively.

The spectral characteristics of complexes and their stability constants $K_{1:1}$, $K_{1:2}$, and $K_{2:2}$ are given in Table 2.

Compound	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{max}/L \text{ mol}^{-1} \text{ cm}^{-1}$	$\Delta \lambda_{\max}^{\ b}$	$\lambda_{max}{}^{fl}\!/nm$	$\Delta\lambda_{\max}^{\ \ \text{fl}\ b}$	$\log K_{1:1}^{c}$	$\log K_{1:2}^{c}$	$\log K_{2:2}^{c}$
5	370	71500	_	439	_	_	_	_
2a	371	56400	_	442	_	_	_	_
2a • Li ⁺	370	62000	-1	_	_	5.02	_	_
$2\mathbf{a} \cdot (\mathrm{Li}^+)_2$	367	60000	-4	_	_	_	4.00	_
$2a \cdot Na^+$	370	58000	-1	_	_	5.07	_	_
$2a \cdot (Na^+)_2$	366	58600	-5	_	_	—	3.89	_
$2\mathbf{a} \cdot \mathbf{K}^+$	370	59900	-1	_	_	6.06	_	_
$2a \cdot (K^+)_2$	362	60000	-9	_	_	_	4.61	_
$(2a)_2 \cdot (K^+)_2$	371	66400	0	_	_	—	—	~16.5
$2\mathbf{a} \cdot \mathbf{C} \mathbf{s}^+$	371	58700	0	_	_	6.34	_	_
$2\mathbf{a} \cdot (\mathbf{Cs}^+)_2$	371	61000	0	_	_	—	5.16	_
$2a \cdot Mg^{2+}$	370	58800	-1	_	_	5.84	—	_
$2a \cdot (Mg^{2+})_2$	363	61300	-8	_	_	_	5.18	_
$2\mathbf{a} \cdot \mathbf{C} \mathbf{a}^{2+}$	370	56300	-1	441	-1	4.98 (>7 ^d)	—	_
$2\mathbf{a} \cdot (\mathbf{Ca}^{2+})_2$	363	57600	-8	449	7	_	5.02 (6.00 ^d)	—
$2a \cdot Sr^{2+}$	353	51500	-18	_	_	>6.5		_
$2a \cdot (Sr^{2+})_2$	355	55900	-16	_	_	_	6.42	_
$(2a)_2 \cdot (Sr^{2+})_2$	357	55700 ^e	-14	_	_	_	_	~19.4
$2\mathbf{a} \cdot \mathbf{B} \mathbf{a}^{2+}$	356	52200	-15	~442	~0	>6.5	_	_
$2a \cdot (Ba^{2+})_2$	355	56200	-16	~463	~21	_	4.96	_
$(2a)_2 \cdot (Ba^{2+})_2$	354	58200 ^e	-17	~442	~0	—	_	~19.8
2b	372	58400		440	—	—	—	—
2b • Li ⁺	369	59600	-3	_	_	2.42	—	_
$2\mathbf{b} \cdot (\mathrm{Li}^+)_2$	368	65300	-4	—	—	—	1.23	—
2b ⋅ Na ⁺	371	59400	-1	—	—	5.87	—	—
$2\mathbf{b} \cdot (\mathrm{Na}^+)_2$	369	60200	-3	_	_	—	4.59	_
2b ⋅ K ⁺	371	59000	-1	440	0	>6.2 (5.97 ^d)	—	_
$2\mathbf{b} \cdot (\mathbf{K}^+)_2$	369	60500	-3	434	-6		4.86 (4.68 ^d)	—
2b • Cs ⁺	371	59400	-1	_	_	5.92	_	_
$2\mathbf{b} \cdot (\mathbf{Cs}^+)_2$	369	63300	-3	_	_	_	3.44	_
2b • Ba ²⁺	370	57800	-2	~440	~0	>6.5	_	_
$2\mathbf{b} \cdot (\mathbf{B}\mathbf{a}^{2+})_2$	366	60800	-6	<429	<-11	_	6.35	_

Table 2.	Spectral characteristics of	compounds 2a	b and 5 and stabilit	v constants of their com	plexes with M^{m+1}	$(ClO_4^{-})_m^a$
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^a Spectrophotometric titration, MeCN-CH₂Cl₂ (10 : 1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C.

 ${}^{b} \Delta \lambda_{\max} = \lambda_{\max}(\operatorname{complex}) - \lambda_{\max}(\operatorname{free distyrylbenzene}).$ ${}^{c} K_{1:1} = [L \cdot M^{m+}]/([L] \cdot [M^{m+}]) (L \operatorname{mol}^{-1}), K_{1:2} = [L \cdot (M^{m+})_2]/([L \cdot M^{m+}] \cdot [M^{m+}]) (L \operatorname{mol}^{-1}), K_{2:2} = [(L)_2 \cdot (M^{m+})_2]/([L]^2 \cdot [M^{m+}]^2) (L^3 \operatorname{mol}^{-3}), \text{ where } L \text{ is the distyrylbenzene; the error of determination of stability constant lies within ±30\%.}$

^d Fluorescent titration, MeCN–CH₂Cl₂ (10:1, v/v), 0.01 M Et₄NClO₄, ~20 °C. The fluorescence was excited by the light with the wavelength at which the free biscrown-containing distyrylbenzene and its complexes have the closest values of extinction (from the spectrophotometry data).

^e Recalculated per one distyrylbenzene molecule.

Figure 5 shows the absorption spectrum of bis(15crown-5)-containing distyrylbenzene 2a and the calculated absorption spectra of complexes $2a \cdot \text{NaClO}_4$ and $2a \cdot (NaClO_4)_2$. For complex with the composition $1(2a): 2(Na^+)$, the long wavelength absorption maximum is hypsochromically shifted ($\Delta\lambda_{max} = -5$ nm), while its extinction slightly increases. This is a typical spectral behavior of the donor-acceptor chromoionophoric compounds when the donor part is involved in bonding with a metal cation. The absorption of a light quantum transfers the compound to the excited state with intramolecular transfer of electron density from the donor part (the benzocrown ether fragment) to the acceptor one (the central benzene ring). The ion-dipole interaction of the oxygen atoms of the crown ether fragment bonded with the benzene ring with the positively charged metal ion weakens the degree of their conjugation with the chromophore, that results in the increase in the energy of electron transfer



Fig. 5. Absorption spectrum of compound **2a** (*1*) and calculated absorption spectra of complexes **2a** \cdot NaClO₄ (*2*) and **2a** \cdot \cdot (NaClO₄)₂ (*3*) (MeCN-CH₂Cl₂ (10 : 1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C).

involving the indicated oxygen atoms. The studied distyrylbenzenes are rather of a "donor—acceptor—donor" chromophore type, but, apparently, the formation of complexes of the composition $1(2a) : 1(Na^+)$ has little effect on the electronic properties of the system at its bonding with the second sodium cation. That means that the studied type of chromoionophore can be approximately regarded as a combination of two chromoionophores of the "donor—acceptor" type.

From Fig. 5, it is seen that the formation of the 1(2a): $1(Na^+)$ complex leads to very small changes in the absorption spectrum ($\Delta\lambda_{max}$ is only -1 nm). Such a spectral behavior is generally typical of all the studied systems distyrylbenzene—metal cation with the formation of complexes of the composition 1 : 1 and 1 : 2. It should be noted that a small difference of the spectra of free compounds **2a,b** and their 1 : 1 complexes considerably complicates the determination of the corresponding stability constants of the complexes and in a number of cases significantly decreases the accuracy of their measurement.

The formation of complexes $1(2\mathbf{a},\mathbf{b}): 2(\mathbf{M}^{m+})$ in all the cases is characterized by a strong hypsochromic shift

of the long wavelength absorption maximum ($\Delta\lambda_{max}$) as compared to the corresponding complexes of the composition 1 : 1 (see Table 2). The alkaline-earth metal cations cause stronger shifts ($\Delta\lambda_{max}$ up to -8 nm) as compared to the alkali metal cations ($\Delta\lambda_{max}$ up to -5 nm). No doubt, this is related to the stronger electron-accepting influence of the doubly charged cation in the complex with the crown ether fragment as compared to the singly charged cation.

In all the cases, the stability of 1:1 complexes is higher than the stability of 1:2 complexes (by 0.6 orders of magnitude and higher) that, undoubtedly, is explained by the lower favorability of binding of the second metal cation with the 1:1 complex because of the Coulomb repulsion of two cations and the weakening of electron-donating ability of the oxygen atoms bonded to the benzene ring in the free crown ether fragment of the 1:1 complex because of the electron-withdrawing effect of the first metal cation bonded to the complex at the other end of the chromophore.

The stability of 1:1 complexes of bis(15-crown-5)containing compound **2a** increases in the order of alkali and alkaline-earth metal cations as the size of cation increases. This is an unusual behavior for the benzo-15crown-5-ether derivatives, which more frequently³⁹ demonstrate the opposite dependence on the size of metal cation explained by the decrease in the charge density on the cation and, consequently, by the decrease in its electron-withdrawing effect upon bonding with the crown ether fragment when the metal cation size increases.

Apart from that, the character of the spectral changes in the systems $2a/K^+(Sr^{2+}, Ba^{2+})$ at the increase in the ratio $C_M{}^{m+}/C_{2a}$ considerably differs from that of the systems involving other metal cations. This indicates the presence of other types of absorbing components in the reaction mixture. It was found that the satisfactory results were obtained when making allowance for the formation of complexes with the composition $2(2a) : 2(M^{m+})$, which have, apparently, the structure of double sandwich additionally stabilized by the stacking-interactions of the conjugated fragments (Fig. 6).



Fig. 6. The structure of bissandwich complex of the composition $2(2a) : 2(M^{m+})$.

The formation of the sandwich structures is typical property of crown ethers with the size of the macroheterocycle considerably smaller than the diameter of the metal cation.^{20,40} For 15-crown-5 derivatives, this condition is met in the case of K^+ , Cs^+ , Sr^{2+} , Ba^{2+} ions; for 18-crown-6 derivatives, in the case of Cs^+ ion. However, the more complicated composition of absorbing components present in the mixture with insignificant difference in the spectra of the complexes and high stability of complexes of all types make the measurement of the corresponding stability constants even more difficult. Apart from that, it should be taken into account that biscrown-containing distyryl-benzenes can exist as six conformers differing in the mutual direction of the ethylene bonds and crown ether moieties (see Fig. 3).

The barrier for the interconversion of conformers should be relatively low (about 5–6 kcal mol⁻¹),³⁷ therefore, they all coexist in the equilibrium in solution at room temperature (see above). The bissandwich complexes of the composition $2(2a) : 2(M^{m+})$ can be formed from two the same or different conformers of distyrylbenzene with the parallel or crossed arrangement of the ethylene bonds. The number of mutual combinations is rather large, and such bissandwich complexes can possess different spectral properties. This introduces an additional error in the determination of the stability constants, which, naturally, are averaged over all the structures of the composition 2 : 2 present in the solution.

For example, Fig. 7 shows the calculated absorption spectra of complexes $2\mathbf{a} \cdot \text{Ba}(\text{ClO}_4)_2$, $2\mathbf{a} \cdot (\text{Ba}(\text{ClO}_4)_2)_2$, and $(2\mathbf{a})_2 \cdot (\text{Ba}(\text{ClO}_4)_2)_2$. It is seen that the formation of any of the complexes leads to a considerable hypsochromic shift of the long wavelength absorption maximum $(\Delta \lambda_{\text{max}} = -(15-17) \text{ nm})$, but the spectra of the complexes differ little between each other in the values of their extinction coefficient. The complexes of compound $2\mathbf{a}$ with



Fig. 7. Absorption spectrum of compound **2a** (1) and calculated absorption spectra of complexes $2\mathbf{a} \cdot \text{Ba}(\text{ClO}_4)_2$ (2), $2\mathbf{a} \cdot (\text{Ba}(\text{ClO}_4)_2)_2$ (3), and $(2\mathbf{a})_2 \cdot (\text{Ba}(\text{ClO}_4)_2)_2$ (4) (recalculated per one molecule of **2a**) (MeCN-CH₂Cl₂(10:1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C).

Sr(ClO₄)₂ demonstrated similar spectral characteristics. In these cases, attempted determination of stability constants of the 1 : 1 complexes were unsuccessful because of their too large values, which were higher than the upper limit of applicability of the spectrophotometric titration method (log $K_{1:1} > 6.2$ [L mol⁻¹]). Therefore, the stability constants of the 2 : 2 complexes (see above equilibrium (3)) can be also evaluated only approximately on the level of log $K_{2:2} = 19.5$ [L³ mol⁻³].

In the case of the system $2a/K^+$, the spectral changes $(\Delta\lambda_{\max} \text{ up to } -9 \text{ nm})$ also indicate the presence of the bissandwich complexes. The stability of the 2 : 2 complex is estimated at $\log K_{2:2} = 16.5 \text{ } [\pi^3 \text{ mol}^{-3}]$, that is logically lower than the stability of similar complexes of the doubly charged strontium and barium cations.

For the system $2a/Cs^+$, we failed to evaluate even approximately the stability of possible 2 : 2 complexes because of the small spectral changes in the course of the spectrophotometric titration. Probably, the interaction of two chromophores in the structures of the type shown in Fig. 6 is very weak because of their considerable remoteness in space due to the large size of the cesium cation. At the same time, the minimal charge density on the Cs⁺ ion among all the cations studied, obviously, leads to a weak influence of complexation on the chromoionopore of the donor-acceptor type. The use of only two equilibria ((1) and (2)) gives a too high value of the stability constant for the 1 : 1 complex (see Table 2), that indirectly indicates the presence of other equilibria.

The changes in the stability of complexes of bis(18crown-6)-containing distyrylbenzene **2b** in the series of alkali metal cations have a traditional pattern. The least stable complexes are formed with Li⁺ because of the mismatch of the 18-crown-6 cavity size and the diameter of this cation, which is the smallest in the series of metals studied. At the same time, the highest stability was found for complexes with K⁺ ions, the size of which, according to the multitude of literature data,⁴¹ fits the most the cavity size of the 18-crown-6 derivatives. As in the case of the system **2a**/Cs⁺, the system **2b**/Cs⁺ was also found to have too high value of the stability constant of the 1 : 1 complex, that can indicate also the presence of the bissandwich complexes of the composition 2 : 2. However, we did not obtain the spectrophotometric evidence of this.

We also attempted to study the complexation of biscrown-containing distyrylbenzenes **2a** and **2b** with metal cations by fluorescent titration. This method allows one to more accurately measure high stability constants of complexes (the upper threshold of the method applicability is $\log K_{1:1}$ up to 7 [L mol⁻¹]) provided that the fluorescent properties of the starting compound and its complexes considerably differ.

Figure 8, *a* shows the fluorescence spectrum of bis(15crown-5)-containing distyrylbenzene **2a** and the calculated fluorescence spectra of the complexes $2\mathbf{a} \cdot \text{Ca}(\text{ClO}_4)_2$





Fig. 8. (*a*) Fluorescence spectrum of compound **2a** (*1*) ($C_{2a} = 1.40 \cdot 10^{-6} \text{ mol } L^{-1}$) and calculated fluorescence spectra of complexes **2a** · Ca(ClO₄)₂ (*2*) and **2a** · (Ca(ClO₄)₂)₂ (*3*). (*b*) The changes in the fluorescence intensity for compound **2a** at the 442 nm wavelength depending on the C_{Ca}/C_{2a} ratio. Conditions: MeCN—CH₂Cl₂ (10 : 1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C, $\lambda_{ex} = 367$ nm.

and $2a \cdot (Ca(ClO_4)_2)_2$. The fluorescence spectra of the free ligand and the 1:1 complex were found to be virtually identical. This is clearly seen from Fig. 8, b, in which we show the changes in the fluorescence intensity of compound 2a at the 442 nm wavelength depending on the ratio of concentrations C_{Ca}/C_{2a} . In the region where $C_{\text{Ca}}/C_{2a} < 1$, the fluorescence does not virtually change, while in the region where $C_{Ca}/C_{2a} > 1$, it slightly decays. This is accompanied by a bathochromic shift of the fluorescence maximum by 7 nm. This allowed us to evaluate only approximately the $\log K_{1:1} > 7$ [L mol⁻¹]. Provided this condition, the second constant is calculated easily: $\log K_{1,2} =$ = 6.00 [L mol⁻¹]. The spectrophotometric and fluorescent titration data in the system $2a/Ca^{2+}$ greatly differ and, therefore, additional studies are necessary. However, the general principle when the stability of the 1:1 complexes is higher than that of the corresponding 1 : 2 complexes is held.

It was interesting to check the applicability of fluorescent titration to the systems in which the equilibrium (3), *i.e.*, the formation of bissandwich complexes, was knowingly observed. This was exemplified on the system $2a/Ba^{2+}$. Figure 9 shows the evolution of the fluorescence spectrum of compound 2a depending on the concentration of added Ba(ClO₄)₂ and the changes of the fluorescence intensity at the 442 nm wavelength depending on the ratio of C_{Ba}/C_{2a} .

In this case again, the fluorescence spectrum intensity initially changed very little, virtually linearly, while then at $C_{\text{Ba}}/C_{2a} > 2$ a strong decay and a bathochromic shift of the fluorescence maximum to 21 nm were observed. Thus, it turned out that the fluorescent properties of free 2a and its 1:1 and 2:2 complexes almost do not differ. This circumstance did not allow us to quantitatively characterize stability of complexes in this system.

Attempted determination of stability constants for 1 : 1 and 1 : 2 complexes of bis(18-crown-6)-containing distyrylbenzene **2b** with Ba(ClO₄) by fluorescent titration was also unsuccessful. Figure 10 shows the changes in the fluorescence spectrum of compound **2b** depending on the concentration of added Ba(ClO₄)₂ and the changes of the fluorescence intensity at the 440 nm wavelength depending on the ratio of C_{Ba}/C_{2b} . It is clearly seen that in this



Fig. 9. (*a*) The changes in the fluorescence spectrum of compound **2a** ($C_{2a} = 4.39 \cdot 10^{-7} \text{ mol L}^{-1}$) depending on the concentration of added Ba(ClO₄)₂ (C_{Ba} was varied from 0 to $3.08 \cdot 10^{-6} \text{ mol L}^{-1}$). (*b*) The changes in the fluorescence intensity for compound **2a** at the 442 nm wavelength depending on the C_{Ba}/C_{2a} ratio. Conditions: MeCN-CH₂Cl₂ (10:1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C, $\lambda_{ex} = 363$ nm.



Fig. 10. (a) The changes in the fluorescence spectrum of compound **2b** ($C_{2b} = 5.26 \cdot 10^{-7} \text{ mol } \text{L}^{-1}$) depending on the concentration of added Ba(ClO₄)₂ (C_{Ba} was varied from 0 to $3.08 \cdot 10^{-6} \text{ mol } \text{L}^{-1}$). (b) The changes in the fluorescence intensity for compound **2b** at the 440 nm wavelength depending on the C_{Ba}/C_{2b} ratio. Conditions: MeCN-CH₂Cl₂ (10:1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C, $\lambda_{ex} = 370 \text{ nm}$.

system as well, as the ratio of C_{Ba}/C_{2b} increases the fluorescence initially almost does not change and only at $C_{Ba}/C_{2b} > 3$ it begins to slightly enhance, while its maximum shifts hypsochromically to -11 nm. This distinguishes the bis(18-crown-6)-containing distyrylbenzene from the bis(15-crown-5)-containing analog, for which the formation of the 1 : 2 complexes led to the decay of fluorescence and the bathochromic shift. These differences require further studies.

Finally, fluorescent titration was successfully applied to the system $2b/KClO_4$. Figure 11 shows the calculated fluorescence spectra of complexes $2b \cdot KClO_4$ and $2b \cdot (KClO_4)_2$ and the changes in the fluorescence intensity at the 434 nm wavelength depending on the ratio of C_K/C_{2b} . Like in all the preceding cases, at the beginning of titration only insignificant spectral changes were observed and only at the ratio of $C_K/C_{2b} > 3$ the tendency to fluorescence enhancement and its hypsochromic shift became noticeable (see Table 2). The presence of only two equilibria in this system, as well as relatively low values of stability constants of 1 : 1 and 1 : 2 complexes allowed us to determine them with high accuracy and calculate the



Fig. 11. (*a*) Fluorescence spectrum of compound **2b** (*1*) ($C_{2b} = 1.08 \cdot 10^{-6} \text{ mol } L^{-1}$) and calculated fluorescence spectra of complexes **2b** · KClO₄ (*2*) and **2b** · (KClO₄)₂ (*3*). (*b*) The changes in the fluorescence intensity for compound **2b** at the 434 nm wavelength depending on the $C_{\rm K}/C_{2b}$ ratio. Conditions: MeCN–CH₂Cl₂ (10 : 1, v/v), 0.01 *M* Et₄NClO₄, ~20 °C, $\lambda_{\rm ex} = 373$ nm.

corresponding fluorescence spectra. A comparison of the data of spectrophotometric and fluorescent titration in this case showed fairly good agreement of the constant values (for the fluorescent titration, both constants were lower by approximately 0.2 logarithmic units).

Cyclic voltammetry. Distyrylbenzenes **2a,b** and **5** and stilbenes **1b** and **7** earlier studied in MeCN,²¹ as well as biscrown-containing stilbene **1a**, were studied by cyclic voltammetry (CVA) in a MeCN–DMF solvent mixture (3:1, v/v) on a glassy carbon (GC) and gold (Au) electrodes in the presence of 0.1 *M* solution of Bu₄NClO₄ as a supporting electrolyte. The electrochemical oxidation and reduction potentials measured relative to Ag/AgCl/KCl (aqueous, sat.) are given in Table 3.

The electrochemical study of distyrylbenzenes **2a**,**b** was carried out for comparison of their redox potential values with the values for the model distyrylbenzene **5** and structurally close analogs, namely, stilbenes **1a**,**b** and a model compound **7**, in order to evaluate the influence of the elongation of the conjugated system on electrochemical potentials. The cyclic voltamperograms (CVA-curves) were obtained for the solutions of the substrates in mixed solvents because of very low solubility of distyrylbenzenes

Compound	E _{red}	E _{ox}	Compound	E _{red}	E _{ox}
		/			V
5	-2.06	1.06	1 a	-2.37	1.08
	-2.30 (prepeak)	1.18 (prepeak)			1.19
	-2.36	1.33			1.37
2a	-2.05	1.07			1.63
	-2.35	1.30	1b	-2.38	1.09
2b	-2.06	1.06			1.21
	-2.35	1.31			1.58
7	-2.35	1.07 (rev.)			1.77
		1.36			
		1.59			

Table 3. Electrochemical potentials (Ag/AgCl/KCl (aqueous, sat.)) for compounds **1a**,**b**, **2a**,**b**, **5**, and **7** in MeCN–DMF (3:1, v/v) in the presence of 0.1 *M* Bu₄NClO₄ on GC electrode

in MeCN. Increasing amount of a polar solvent had a beneficial effect on the resolution of voltamperograms. Potentials were measured on Au and GC elec-

trodes. A GC electrode has a wider range of measurements, while an Au electrode allows one to obtain higher resolution (Fig. 12).



Fig. 12. CVA-curves for compounds 5 (a, c) and 2a (b, d) on Au (a, b) and GC electrodes (c, d) in MeCN–DMF (3 : 1, v/v).

The values of first redox potentials of distyrylbenzenes under study virtually do not differ. This is explained by the fact that in biscrown-containing distyrylbenzenes 2a,b the oxygen atoms unconjugated with the benzene ring are not involved in the oxidation and reduction process, $2^{1,42}$ while the rest of the molecule is structurally close to tetramethoxy derivative 5. The primary process of oxidation in distyrylbenzenes is largely localized on the dialkoxybenzene fragment of the molecules, while the reduction process is localized on the system of the conjugated double bonds, including the phenylene ring.²¹

A similar localization of primary anodic processes is also characteristic of biscrown-containing stilbenes 1a,b and the model tetramethoxystilbene 7 studied under analogous conditions. This is indicated by the very close oxidation potentials of test distyrylbenzenes and stilbenes. However, in the cathodic region the behavior of two families was dramatically different. Distyrylbenzenes underwent reduction at the lower values of cathodic potentials (by ~300 mV) than the corresponding stilbenes. Distyrylbenzenes have a phenylene ring in their structure, which is a conducting spacer between two styryl moieties, that leads to a considerable elongation of the conjugation chain and, as it is known,^{43,44} to facilitation of the reduction process. This is explained by a possibility of better delocalization of charge in the distyrylbenzene radical anions generated in the first step.

The cation-binding properties of the ditopic ligands were studied by cyclic voltammetry using titration of a well soluble in MeCN biscrown-containing stilbene 1a with sodium perchlorate as an example. The electrochemical response to the presence of Na⁺ ions was studied varying their concentration from 0 to 16 equiv. per 1 equiv. of the ligand. Since, as it was indicated above, the oxidation processes are predominantly localized on the dialkoxybenzene fragment and the same fragment is involved in the complexation, it is naturally that more significant electrochemical response to the presence of Na⁺ was observed in the anodic region. As the concentration of $NaClO_4$ increased, the intensity of the free ligand peaks decreased and the intensity of a new peak responsible for the oxidation of the complex increased. When the ratio of ligandsalt reached 1:8, the peaks of the free ligand completely disappeared, while further addition of the salt did not change the CVA-curve (Fig. 13).

The shift to the anodic region of the first oxidation potential on going from a free ligand to the complex was 160 mV, that indicated the formation of a stable complex (Table 4). In the cathodic region, the first reduction peak of the complex is shifted to the anodic side only by 60 mV. Thus, compound **1a** is a receptor possessing an electrochemical response to the complexation process.

It should be noted that electrochemically determined values of complexation constants are several order of magnitude lower than the values obtained by other methods,



Fig. 13. CVA-curves for mixtures of compound **1a** ($C_{1a} = 4 \cdot 10^{-4} \text{ mol } \text{L}^{-1}$) and NaClO₄ in the ratios of 1 : 0 (solid line) and 1 : 8 (dashed line) on GC electrode in MeCN.

including spectrophotometric.²¹ Therefore, to reach a complete binding of the ligand, an excessive concentration of the salt is required.

In conclusion, we developed an improved method for the synthesis of symmetric biscrown-containing and model tetramethoxy-substituted 1,4-distyrylbenzenes from available formyl benzocrown derivatives in high yields. Conformational analysis of (E,E)-1,4-distyrylbenzenes by X-ray diffraction and NMR spectroscopy revealed their structural specific features in the crystalline state and in solution. Quantum chemical calculations were used to confirm the higher favorability of syn,(syn/anti),syn-conformation of the conjugated fragment of 1,4-distyrylbenzenes having four alkoxy substituents. Spectrophotometric and fluorescent titration were used to determine stability

Table 4. Electrochemical potentials (Ag/AgCl/KCl (aqueous, sat.)) for stilbene **1a** and its complex with NaClO₄ in MeCN in the presence of 0.1 M Bu₄NClO₄ on a GC electrode

Compound	$E_{\rm red}/V$	$\Delta E_{\rm red}^{*}$ /mV	$E_{\rm ox}/{\rm V}$	$\Delta E_{\rm ox}^{**}$ /mV
1a	-2.23 -2.41	_	1.01 1.22	_
1a : Na ⁺ (1 : 8)		60	1.33 1.17	
	-2.39	—	—	—

* The shift of the reduction potential for complex of stilbene **1a** with NaClO₄ relative to that of free stilbene **1a**. ** The shift of the oxidation potential of complex of stilbene **1a** with NaClO₄ relative to that of free

Vedernikov et al.

of complexes of biscrown-containing distyrylbenzenes with alkali and alkaline-earth metal ions. In the case of ions with large ionic radii, the formation of unusual bissandwich complexes of 2 : 2 stoichiometry was observed. It was found that the presence of a long system of conjugation leads to a considerable facilitation of the process of electrochemical reduction of distyrylbenzenes as compared to stilbenes. The structure and properties, as well as the specific features of complexation of biscrown-containing 1,4-distyrylbenzenes, can be used in the design of photoactive supramolecular systems on their basis.

Experimental

Equipment. Melting points (uncorrected) were measured in capillary tubes on an IA9300 heating stage. Elemental analysis was carried out on a Vario Micro Cube CHN-analyzer at the Department of Chemistry of the M. V. Lomonosov Moscow State University. The samples for elemental analysis were dried in vacuo at 80 °C. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 spectrometer (500.13 and 125.76 MHz, respectively) in CD₂Cl₂ using residual signals of the solvent as a reference ($\delta_{\rm H}$ 5.30, $\delta_{\rm C}$ 54.00). Chemical shifts and spin-spin coupling constants were measured with the accuracy to 0.01 ppm and 0.1 Hz, respectively. 2D COSY and NOESY spectra and heteronuclear correlation spectra (HSQC and HMBC) were used for the assignment of signals of protons and ¹³C nuclei. 2D experiments were carried out using standard parameters included in the Bruker software package. The time of mixing in the NOESY experiment was 300 µs, the HMBC experiments were optimized for the constant $J_{\rm H,C} = 8$ Hz.

MALDI-TOF mass spectra were recorded on Bruker Daltonics Ultraflex and Bruker Daltonics Ultraflex II instruments equipped with nitrogen laser and a time-of-flight mass-analyzer. The samples were deposited on support made of polished steel using 1,8,9-trihydroxyanthracene as a matrix and poly(ethylene glycols) PEG-200, 300, 400, 600, 1000, and 1500 as internal standards. The spectra were recorded in the positive ion mode, which were extracted from the ionization region by accelerating potential of 20 kV. The resulting spectrum was a sum of 300 spectra obtained in different points of the sample. The spectra were processed using the Bruker DataAnalysis, Version 1.6g program (Bruker Daltonik GmbH, 1999). From the cluster of isotope peaks of molecular ion, we selected a peak corresponding to the monoisotopic mass. The GC/MS spectra were recorded on a Thermo TSQ8000 triple quadrupole mass-spectrometer, a Trace-1310 chromatograph, ionization energy 70 eV.

Electronic absorption spectra were measured on a Cary 4000 spectrophotometer (Agilent) using quartz cells with the optical pathlength l = 10 mm. All cells had well-ground stoppers.

Stationary fluorescence spectra were recorded on a RF-5301PC spectrofluorimeter (Shimadzu) using quartz cells with the optical pathlength l = 10 mm.

Electrochemical studies were carried out on a IPC-Pro M potentiostat. The measurements were performed in a cell using a three-electrode scheme. Glassy carbon (GC) (d = 2 mm) and gold (Au) (d = 2 mm) disks serve as working electrodes, Ag/AgCl/KCl (aqueous, sat.) was a reference electrode, platinum plate served as an auxiliary electrode.

Materials. Li, Na, K, Cs, Mg, Ca, Sr, and Ba perchlorates (Aldrich) were dried in vacuo at 200 °C. MeCN (high purity-0 grade, the content of water <0.03% (v/v), Kriokhrom) and CH₂Cl₂ (HPLC grade, Aldrich) were used for the studies by electronic spectroscopy. For electrochemical studies, DMF (reagent grade) was stirred with anhydrous K_2CO_3 (20 g L⁻¹) for 4 days at 20 °C, decanted from the solid phase, and then purified sequentially by reflux and vacuum distillation over calcium hydride and anhydrous copper sulfate (10 g L^{-1}). MeCN (Acros Organics, extra dry) was distilled over CaH₂ before use. The purified solvents were stored over molecular sieves 4 Å. DMF used in the synthesis was dried by distillation over CaH₂. Et₄NClO₄ (Aldrich), Bu₄NClO₄ (≥99.0%, Fluka), veratric aldehyde (Aldrich) were used without additional purification. Stilbenes 1a,b and 7 were obtained according to the procedure described earlier.³⁷ 4'-Formylbenzo-15(18)-crown-5(6)-ethers 4a,b were synthesized according to the known procedures (see Refs 45-48). Tetraethyl [1,4-phenylenedi(methylene)]bis-(phosphonate) (3) was obtained according to the described procedure.49

15,15⁻-{1,4-Phenylenebis[(E)-ethen-2,1-diyl]}bis-2,3,5,6, 8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (2a). Metallic Na (27 mg, 1.17 mmol) and an excess of anhydrous tert-butanol were placed into a three-neck flask (15 mL) equipped with a reflux condenser. The reaction mixture was refluxed with stirring under argon until complete dissolution. Excessive tert-butanol was evaporated in vacuo. A solution of bisphosphonate 3 (106 mg, 0.28 mmol) in DMF (0.4 mL) was added to the residue at -10 °C, the reaction mixture was stirred for 45 min, followed by a dropwise addition of a solution of 4'-formylbenzo-15-crown-5-ether (4a) (165 mg, 0.56 mmol) in DMF (0.4 mL) at -10 °C. After raising temperature to ambient, the reaction mixture was stirred for 75 h, then quenched with water (5 mL). A precipitate formed was collected by filtration and washed with water (3 mL) to obtain compound 2a (135 mg, 73%) as bright yellow fine crystals, m.p. 285-289 °C (cf. Ref. 35: 272 °C). $R_f 0.49$ (benzene-EtOAc (1:5, v/v) with addition of 2-3 drops of pyrrolidine, DC-Alufolien Aluminiumoxide 60 F₂₅₄ neutral, Merck). Found (%): C, 68.81; H, 6.87. C₃₈H₄₆O₁₀. Calculated (%): C, 68.86; H, 7.00. ¹H NMR (CD₂Cl₂, 27 °C), δ: 3.64-3.72 (m, 16 H, 5,5',6,6',8,8',9,9'-CH₂O); 3.82-3.89 (m, 8 H, 3,3',11,11'-CH₂O); 4.10 (m, 4 H, 2,2'-CH₂O); 4.15 $(m, 4 H, 12, 12'-CH_2O); 6.84 (d, 2 H, H(17), H(17'), {}^{3}J = 8.3 Hz);$ 6.96 (d, 2 H, 2 C₆H₄C<u>H</u>=CH, ${}^{3}J_{trans} = 16.3$ Hz); 7.02–7.08 $(m, 6 H, 2 C_6 H_4 CH = CH, H(14), H(14'), H(16), H(16')); 7.49$ (s, 4 H, C₆H₄). ¹³C NMR (CD₂Cl₂, 30 °C), δ: 68.12, 68.23 (2,2',12,12'-CH₂O); 68.73 (3,3',11,11'-CH₂O); 69.55, 70.14 (5,5',6,6',8,8',9,9'-CH₂O); 110.72 (C(14), C(14')); 113.04 (C(17), C(17')); 119.66 (C(16), C(16')); 125.72 (2 C₆H₄<u>C</u>H=CH); 125.92 (<u>C</u>₆H₄); 127.48 (2 C₆H₄CH=<u>C</u>H); 130.22 (C(15), C(15')); 136.04 (C(1), C(4)); 147.31, 148.60 (C(13a), C(13a'), C(17a), C(17a')). UV $(C = 1 \cdot 10^{-5} \text{ mol } L^{-1}, C(17a'))$ MeCN-CH₂Cl₂ (10:1, v/v)), λ/nm (ε): 371 (56400). Fluorescence ($C = 1.4 \cdot 10^{-6} \text{ mol } L^{-1}$, MeCN-CH₂Cl₂ (10 : 1, v/v)): $\lambda^{\text{ex}} = 367 \text{ nm}, \lambda^{\text{fl}}_{\text{max}} = 442 \text{ nm}. \text{ MALDI MS}, m/z: 662.0 \text{ [M]}^+$ (calculated m/z = 662.31 for $[C_{38}H_{46}O_{10}]^+$), 685.0 $[M + Na]^+$, $701.0 [M + K]^+$.

18,18⁻-{1,4-Phenylenebis[(*E*)-ethen-2,1-diyl]}bis-2,3,5,6, 8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine (2b). Metallic Na (27 mg, 1.17 mmol) and an excess of anhydrous *tert*-butanol were placed into a three-neck flask (15 mL) equipped with a reflux condenser. The reaction mixture was refluxed with stirring under argon until complete dissolution. Excessive tert-butanol was evaporated in vacuo. A solution of bisphosphonate 3 (56 mg, 0.15 mmol) in DMF (0.3 mL) was added to the residue at -10 °C, the reaction mixture was stirred for 45 min, followed by a dropwise addition of a solution of a solution of 4'-formylbenzo-18-crown-6-ether (4b) (100 mg, 0.30 mmol) in DMF (0.3 mL) (0.3 mL) at -10 °C. After raising temperature to ambient, the reaction mixture was stirred for 75 h, then quenched with water (5 mL). A precipitate formed was collected by filtration and washed with water (3 mL) to obtain compound 2b (71 mg, 63%) as bright yellow fine crystals, m.p. 243–245 °C. $R_f 0.32$ (benzene–EtOAc (1 : 5, v/v) with the addition of 2-3 drops of pyrrolidine, DC-Alufolien Aluminiumoxide 60 F₂₅₄ neutral, Merck). Found (%): C, 67.16; H, 7.15. C₄₂H₅₄O₁₂. Calculated (%): C, 67.18; H, 7.25. ¹H NMR (CD₂Cl₂, 27 °C), δ: 3.61 (s, 8 H, 8,8',9,9'-CH₂O); 3.62-3.72 (m, 16 H, 5,5',6,6',11,11',12,12'-CH₂O); 3.83–3.89 (m, 8 H, 3,3',14,14'-CH₂O); 4.13 (m, 4 H, 2,2'-CH₂O); 4.18 (m, 4 H, 15,15'-CH₂O); 6.85 (d, 2 H, H(20), H(20'), ${}^{3}J = 8.3$ Hz); 6.96 (d, 2 H, 2 C_6H_4CH =CH, ${}^3J_{trans}$ = 16.3 Hz); 7.02–7.09 (m, 6 H, 2 C₆H₄CH=C<u>H</u>, H(17), H(17[']), H(19), H(19['])); 7.47 (s, 4 H, C_6H_4). ¹³C NMR (CD₂Cl₂, 30 °C), δ : 67.98 (2,2',15,15'-CH₂O); 68.74, 68.78 (3,3',14,14'-CH₂O); 69.83, 69.95 (5,5',6,6',8,8', 9,9',11,11',12,12'-CH₂O); 110.26 (C(17), C(17')); 112.61 $(C(20), C(20')); 119.47 (C(19), C(19')); 125.65 (2 C_6 H_4 CH=CH);$ 125.91 (\underline{C}_6H_4); 127.50 (2 $C_6H_4CH=\underline{C}H$)); 130.04 (C(18), C(18')); 136.04 (C(1), C(4)); 148.23, 148.34 (C(16a), C(16a'), C(20a), C(20a')). UV ($C = 1 \cdot 10^{-5} \text{ mol } L^{-1}$, MeCN-CH₂Cl₂ (10:1, v/v), λ/nm (ϵ): 372 (58400). Fluorescence (C = = $1.1 \cdot 10^{-6} \text{ mol } L^{-1}$, MeCN-CH₂Cl₂ (10 : 1, v/v)): λ^{ex} = 373 nm, $\lambda^{\text{fl}}_{\text{max}}$ = 440 nm. MALDI MS, m/z: 750.19 [M]⁺ (calculated m/z = 750.36 for $[C_{42}H_{54}O_{12}]^+$, 773.17 [M + Na]⁺, 789.17 $[M + K]^+$.

1,1⁻-{1,4-Phenylenebis[(E)-ethen-2,1-diyl]}bis(3,4 dimethoxybenzene) (5). Sodium hydride (200 mg, 8.3 mmol; washed from mineral oil) and DMF (2 mL) were placed into a flask (25 mL) equipped with a reflux condenser under argon, followed by a dropwise addition of a solution of bisphosphonate 3 (410 mg, 1.08 mmol) in DMF (2 mL) at 0 °C. The mixture was allowed to stand for 30 min, then a solution of veratric aldehyde (6) (360 mg, 2.17 mmol) in DMF (2 mL) was added dropwise at a temperature kept below 10 °C. The temperature of the reaction mixture was raised to ambient, stored for 24 h, then heated for 2.5 h at 65 °C. Then, the reaction mixture was neutralized with 2N HCl to pH 7, a precipitate formed was collected by filtration, and washed with water to obtain compound 5 (397 mg, 91%) as bright yellow fine needle-like crystals, m.p. 266-268 °C (cf. Ref. 50: 272 °C; cf. Ref. 51: 266-267 °C; cf. Ref. 52: 265.8-266.1 °C). R_f 0.34 (hexane-EtOAc (3:1, v/v) with the addition of 2-3 drops of pyrrolidine, DC-Alufolien Aluminiumoxide 60 F₂₅₄ neutral, Merck). Found (%): C, 77.40; H, 6.85. C₂₆H₂₆O₄. Calculated (%): C, 77.59; H, 6.51. ¹H NMR (CD₂Cl₂, 27 °C), δ: 3.84 (s, 6 H, 4,4'-MeO); 3.88 (s, 6 H, 3,3'-MeO); 6.85-6.86 $(d, 2 H, H(5), H(5'), {}^{3}J = 7.4 Hz); 6.98 (d, 2 H, 2 C_{6}H_{4}CH = CH,$ ${}^{3}J_{trans} = 16.3 \text{ Hz}$; 7.04–7.08 (m, 6 H, 2 C₆H₄CH=C<u>H</u>, H(2), H(2'), H(6), H(6')); 7.48 (s, 4 H, C₆H₄). ¹³C NMR (CD₂Cl₂, 30 °C), δ: 56.39, 56.42 (4 MeO); 109.60 (C(2), C(2')); 112.16 (C(5), C(5')); 120.49 (C(6), C(6')); 126.79 (2 C₆H₄<u>C</u>H=CH); 127.14 (C(2), C(3), C(5), C(6), <u>C</u>₆H₄); 128.77 (2 C₆H₄CH=<u>C</u>H); 131.04 (C(1), C(1')); 137.27 (C(1), C(4), C₆H₄); 149.91 and

150.05 (C(3), C(3'), C(4), C(4')). UV ($C = 1 \cdot 10^{-5} \text{ mol } L^{-1}$, MeCN—CH₂Cl₂ (10 : 1, v/v)), λ /nm (ϵ): 370 (71500). Fluorescence ($C = 1 \cdot 10^{-6} \text{ mol } L^{-1}$, MeCN—CH₂Cl₂ (10 : 1, v/v)): $\lambda^{\text{ex}} = 344 \text{ nm}, \lambda^{\text{fl}}_{\text{max}} = 439 \text{ nm}.$ GC/MS MS (EI), m/z: 402.0 [M]⁺ (calculated m/z = 402.2 for [C₂₆H₂₆O₄]⁺), 441.0 [M + K]⁺, 479.0 [M + 2K]⁺.

X-ray diffraction experiment. Single crystals of compound **5** were obtained by slow saturation of a solution of the compound in dichloroethane with hexane vapors at ~ 20 °C.

Single crystal **5** was placed in a Bruker SMART APEX II diffractometer under the flow of cooled nitrogen and carried out measurements of crystallographic parameters and intensities of experimental reflections using Mo-*K* α radiation ($\lambda = 0.71073$ Å, graphite monochromator, ω -scan technique). The experimental data were processed using the SAINT program.⁵³ The structure was solved by direct method and refined by the least squares method in full-matrix anisotropic approximation with respect to F^2 for nonhydrogen atoms. Positions of hydrogen atoms were calculated geometrically and included in the refinement using a riding model.

All the calculations were carried out using the SHELXTL-Plus⁵⁴ and Olex-2⁵⁵ software packages. The crystallographic parameters and main characteristics of the X-ray diffraction exper-

 Table 5. Parameters of crystal 5 and conditions of X-ray diffraction experiment

Parameter	5
Molecular formula	C ₂₆ H ₂₆ O ₄
Molar mass/g mol ⁻¹	402.47
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.056(4)
b/Å	8.441(2)
c/Å	8.810(3)
β/deg	93.444(4)
$V/Å^3$	1043.4(5)
Ζ	2
$\rho_{calc}/g \text{ cm}^{-3}$	1.281
<i>F</i> (000)	428.0
$\mu(MoK_{\alpha})/mm^{-1}$	0.085
$2\theta_{\rm max}/{\rm deg}$	5.64-56.00
Crystal size/mm	$0.46 \times 0.44 \times 0.03$
T/K	150.0(2)
Type/range of scanning, θ/deg	ω/2.82-30.04
Ranges of reflection indices	$-19 \le h \le 19, -11 \le k \le 11,$
	$-12 \le l \le 12$
Number of measured reflections	11063
Number of independent reflections	3013
<i>R</i> (int)	0.0767
Number of reflections with $I \ge 2\sigma(I)$	1501
Refinement variables	138
<i>R</i> -factors on $I > 2\sigma(I)$	$R_1 = 0.0589,$
	$wR_2 = 0.1393$
on all reflections	$R_1 = 0.1419,$
	$wR_2 = 0.1826$
Reliability on F^2	0.915
Residual electron density, min/max/e Å ⁻³	-0.21/0.27

iment are given in Table 5. Atomic coordinates and other experimental data were deposited with the Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge CB21EZ, UK) (CCDC 1487427 (5)).

Quantum chemical calculations. The calculations were carried out with full geometry optimization of 1,4-distyrylbenzene **5** conformers by density functional theory with the Perdew—Burke—Ernzerhof (PBE) functional⁵⁶ and an original triple-zeta basis set (PBE/3z) using the PRIRODA program.^{57,58}

Chemical shifts of protons in the ¹H NMR spectra of were calculated using the PRIRODA program with the same functional and basis, using approximation of gauge-invariant atomic orbitals (GIAO).⁵⁹ This approach has been successfully used earlier in our work.⁶⁰

Molar fractions of conformers were calculated through their Boltzmann weights at room temperature

$$x_i = \frac{\exp(-\Delta G_i/kT)}{\sum_j \exp(-\Delta G_j/kT)},$$

where ΔG is the Gibb's free energy, k is the Boltzmann constant, T is the temperature. Vibrational and entropy contributions to the free energy for the conformers of the same molecule are virtually equal, therefore, the relative conformational energy ΔE obtained directly from the calculations can be used instead of ΔG .

Electronic spectroscopy methods. Absorption spectra in a mixture of MeCN-CH₂Cl₂ (10 : 1, v/v) were recorded in the 220-600 nm range with a 1-nm step at ~20 °C. The fluorescence spectra were measured in the 345-700 nm range with a 1-nm step at ~20 °C. Solutions of distyrylbenzenes were prepared in dark room under the red light, since the ambient light causes *trans/cis*-photoisomerization of the compounds.

During spectrophotometric titration the concentration of distyrylbenzene was maintained constant at ~1·10⁻⁵ mol L⁻¹, while the concentration of metal perchlorate was varied from 0 to $8.8 \cdot 10^{-5}$ mol L⁻¹ (to $1.8 \cdot 10^{-2}$ mol L⁻¹ in the case of complexation of LiClO₄ with bis(18-crown-6)-containing distyrylbenzene). During fluorescent titration the concentration of distyrylbenzene was maintained constant at ~5·10⁻⁷ mol L⁻¹ or 1·10⁻⁶ mol L⁻¹, while the concentration of metal perchlorate was varied from 0 to $1.3 \cdot 10^{-5}$ mol L⁻¹. The ionic strength of the solutions was maintained constant using Et₄NClO₄ with a concentration of 0.01 mol L⁻¹. Stoichiometric composition and stability constants of complexes were calculated using the HypSpec program from the Hyperquad package.³⁸

Electrochemical studies. A 0.1 *M* solution of Bu_4NClO_4 in a mixture of MeCN–DMF (3:1, v/v) or in MeCN was used as a supporting electrolyte. Potentials are given with correction for *iR*-compensation. The surface of working electrodes was polished with alumina powder with particle size less than 10 microns (Sigma–Aldrich). The concentration of the test compounds was varied within the $1 \cdot 10^{-4} - 1 \cdot 10^{-5}$ mol L⁻¹ range. In the CVA studies, the potential sweep speed was 200 mV s⁻¹. All the measurements were carried out under dry Ar, the samples were dissolved in preliminary deaerated (purged with argon) solvent.

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