

Synthesis, Structure, Spectral Properties, and Electrochemistry of Bis(crown ether) Containing 1,3-Distyrylbenzenes

V. N. Nuriev^a, O. V. Fedorov^b, A. A. Moiseeva^a, A. Ya. Freidzon^c, N. A. Kurchavov^c,
A. I. Vedernikov^c, A. V. Medved'ko^a, E. S. Pod'yacheva^a, S. Z. Vatsadze^a, and S. P. Gromov^{a,c*}

^a Lomonosov Moscow State University, Moscow, 119991 Russia

^b Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

^c Photochemistry Center of the Russian Academy of Sciences, ul. Novatorov 7A-1, Moscow, 119421 Russia

*e-mail: spgromov@mail.ru

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Abstract—The reaction of tetraethyl [1,3-phenylenedi(methylene)]bis(phosphonate) with formyl derivatives of benzocrown-ethers or formyl derivatives of *o*-dimethoxybenzene lead to high yield formation of the respectful bis(crown ether) containing 1,3-distyrylbenzenes or tetramethoxy-substituted 1,3-distyrenebenzenes. NMR spectra and quantum-chemical calculations showed the prevalence of unsymmetrical *syn/anti*, (*syn,anti*), *syn/anti*-conformations in 1,3-distyrylbenzenes. 1,3-Distyrylbenzenes absorb in shorter wavelength spectral region and have a weaker fluorescence than 1,4-distyrylbenzenes. The difficulty in the electrochemical reduction of 1,3-distyrylbenzenes comparing with 1,4-distyrylbenzenes is due to a less effective conjugation system in the *meta*-derivatives.

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Supramolecular chemistry is one of the most actively developing area of organic chemistry [1]. Components of supramolecular systems often are complex and difficultly accessible organic compounds, whose synthesis in many cases becomes a subject of individual research. On top of that the prediction of properties of compounds in supramolecular systems and development of purposeful methods of their self-assembly are important tasks in the supramolecular chemistry.

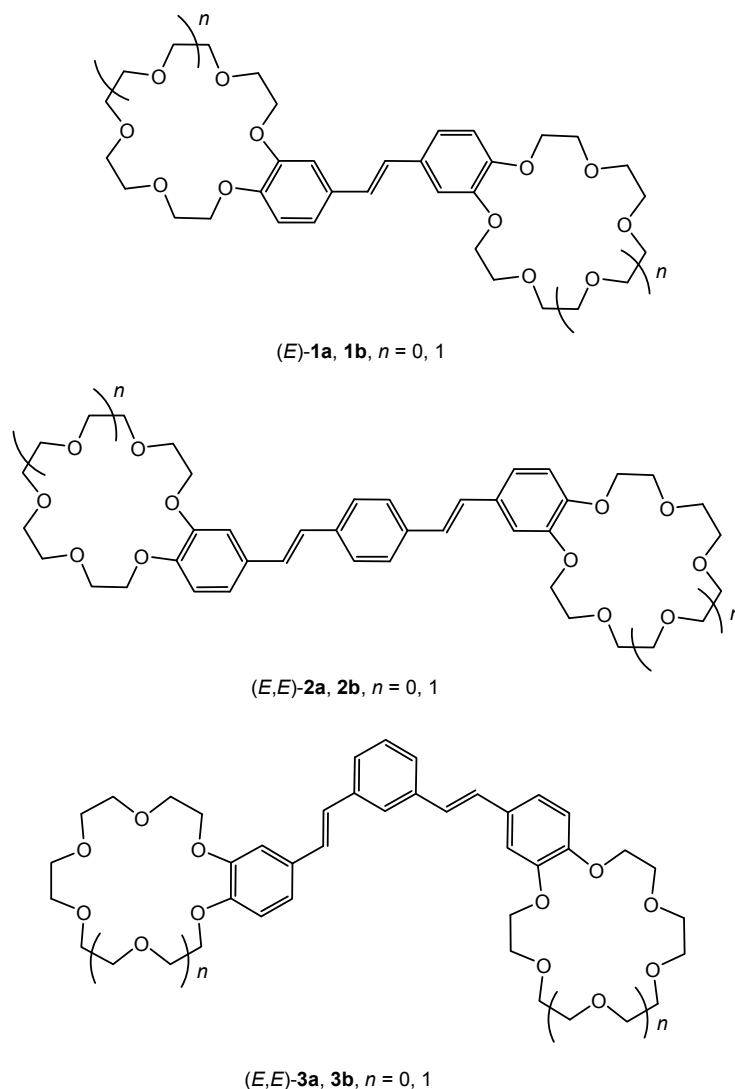
One of promising types of photoactive molecules for investigation of supramolecular self-assembly became crown-containing compounds [2–7], where the structure comprises double bonds N=N, C=N, and C=C. The ability to self-assembly into supermolecules and supramolecular ensembles as a result of complex formation with metal and ammonium ions leading to significant changes in spectral characteristics is the main property that attracts interest to investigation of such compounds; the capability of changing their structure and properties under radiation is also of particular interest. The most typical photochemical processes, occurring in the mentioned supramolecular systems and proceeding with significant changes in

properties, are reactions of *trans-cis*-photoisomerization and [2+2]-photocyclo-addition [8–14].

We proved that biscrown containing stilbenes **1** and a series of diammonium alkyl derivatives of viologen or its analogs, cyanine dyes, due to the formation of hydrogen bonds are giving unusual bi- and exotic trimolecular complexes [15, 16], where an effective intermolecular charge transfer is observed because of spatial prearrangement of donor and acceptor segments of molecules [17, 18]. High stability was discovered in such supramolecular systems that allows considering them also as convenient models for investigation of photo induced intermolecular electron transfer [19], of occurrence of [2+2]-photocycloaddition [20, 21] and promising objects with a rich electrochemical behavior [22].

1,4-Distyrylbenzenes possess higher quantum yields of fluorescence compared to stilbenes due to a prolonged conjugation chain [23, 24]. The presence in the structure of 1,4-distyrylbenzenes of two double bonds C=C results in the appearance of additional abilities for molecular photo switching [25–27]. This and a set of other properties recently made 1,4-distyrylbenzenes attractive objects for creation of

Scheme 1.



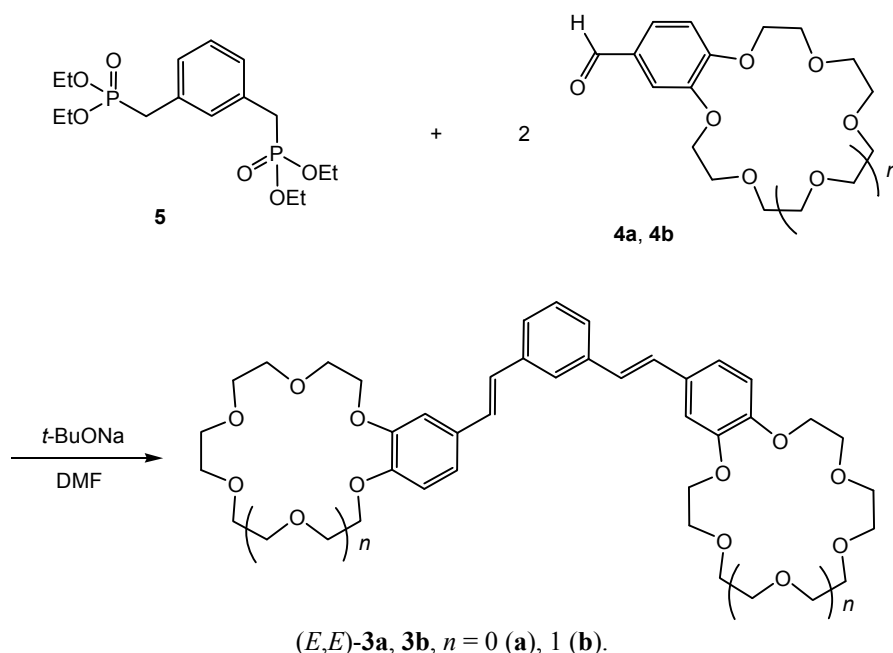
photoactive materials on their basis: organic light-emitting diodes, materials for solar batteries, nonlinear-optic materials, chemical sensors [28–33].

Previously we developed a method of a synthesis of biscrown containing 1,4-distyrylbenzenes **2** with various sizes of macrocycle [34, 35] and investigated their structure, spectral properties, complex formation, and electrochemistry. In particular, in case of metal cations with a large ionic radius formation of unusual bis-sandwich complexes of stoichiometry 2 : 2, promising for further investigations was discovered.

1,3-Distyrylbenzenes belong to scarcely studied type of compounds, their known functional derivatives, in general, always contain substituents in terminal and

central benzene fragments [36–40]. No published data exist on biscrown containing 1,3-distyrylbenzenes **3**, although no less rich photochemical behavior and significant capability to complex formation should be expected for them as compared with biscrown containing stilbenes **1** [41] and 1,4-distyrylbenzenes **2** [35] (Scheme 1). Correspondingly, the high potential of biscrown containing 1,3-distyrylbenzenes **3** as structural blocks in building complex supramolecular ensembles was not realized. Therefore we aimed in this study to develop a method of synthesis of symmetrical 1,3-distyrylbenzenes **3**, possessing unsubstituted ethylene groups and a central benzene ring, containing two 15(18)-crown-5(6)-ether fragments, to investigate their structure, spectral,

Scheme 2.



and electrochemical properties, a possibility of creation of photoactive supramolecular systems on their basis.

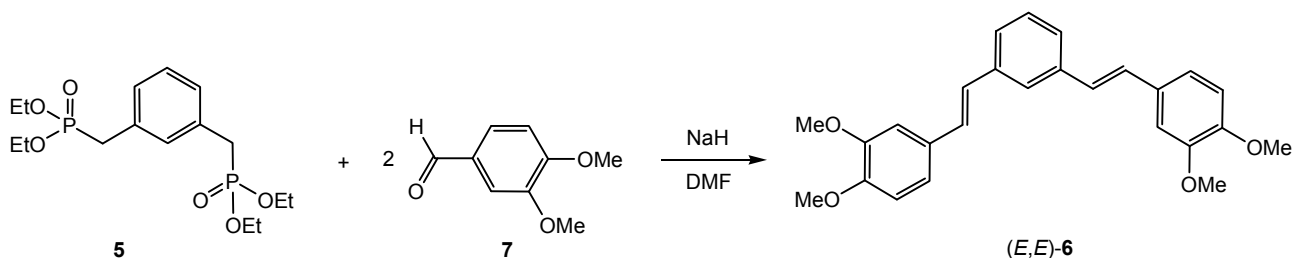
First representatives of biscrown containing distyrylbenzenes, bis(15-crown-5)- and bis(18-crown-6)-1,4-distyrylbenzenes **2a** and **2b**, recently synthesized by us via Horner–Wordsworth–Emmons reaction by condensation of tetraethyl [1,4-phenylenedi(methylene)]bis-(phosphonate) and 4'-formylbenzo-crown ethers **4a** and **4b** under the action of *t*-BuONa that was obtained *in situ*, taking 2.1 mol-equiv per one methylene group of bisphosphonate, in anhydrous DMF in yields 73 and 63% respectively [35]. Applying DMF is advantageous since initial compounds and side products are easily dissolved in it, while the target distyrylbenzenes are poorly soluble, so their isolation becomes significantly easier, especially at adding water to the reaction mixture.

The developed method was applied to tetraethyl [1,3-phenylenedi(methylene)]bis(phosphonate) **5** and 4'-formylbenzo-15(18)-crown-5(6)-ethers **4a** and **4b** to obtain biscrown containing 1,3-distyrylbenzenes **3a** and **3b** in 77 and 53% yields respectively (Scheme 2).

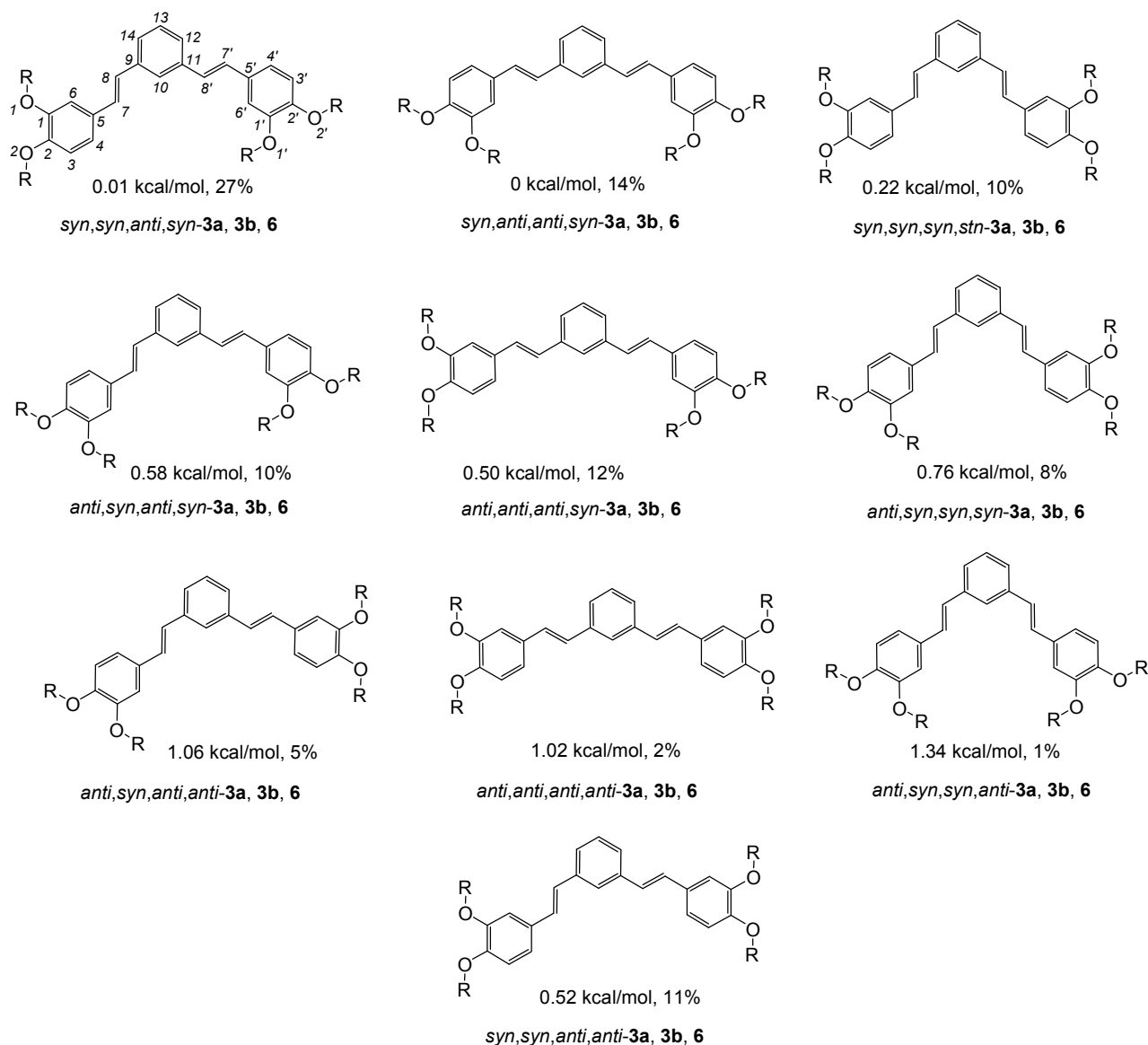
A model compound, tetramethoxy-1,3-distyrylbenzene **6**, where the methoxy groups repeat in general the electron-donor behavior of crown-ether fragments, was obtained similarly to tetramethoxy-1,4-distyrylbenzene **8** [35]. It was established that the reaction of tetraester **5** with veratric aldehyde **7** under the action of NaH in DMF results in the formation of substituted distyrylbenzene **6** in 32% yield (Scheme 3).

According to ^1H NMR data the obtained 1,3-distyrylbenzenes **3a**, **3b**, and **6** are *E,E*-isomers that follows from high spin-spin coupling values of olefin protons ($^3J_{\text{HC=CH}}$ 16.3 Hz).

Scheme 3.



Scheme 4.



Hence, the application of readily accessible bisphosphonate **5** and formyl derivatives of benzo crown ethers **4a** and **4b** as starting compounds, the simplicity of the synthesis and high yields of final products show that the developed method is convenient for the preparation of compounds **3a** and **3b**.

NMR spectroscopy is suitable to determine the fine structure of organic molecules and their ensembles in solutions [42]. The correlation of NMR data with the structure known from X-ray diffraction analysis is seldom possible due to difficulties for obtaining quality crystals for all series. In case of biscrown containing 1,3-distyrylbenzenes it is particularly

important to determine their conformational behavior in solutions that is connected to the prediction and the determination of the structure of supramolecular system on their basis. In this connection we carried out the investigation of structural characteristics of (*E,E*)-1,3-distyrylbenzenes **3a**, **3b**, and **6** applying diverse procedures of NMR spectroscopy.

In crystal state (*E,E*)-tetramethoxy-1,3-distyrylbenzene **6** is present like almost flat unsymmetrical *syn,syn,anti,anti*-conformer that is probably due to the demands of the most close-packed arrangement of molecules [43]. When going into solution a quick conformation equilibrium may be established between

Table 1. Chemical shifts of protons of compound **6** averaged in accordance with the molar fractions of conformers as compared with experimental data (in CD₂Cl₂).

Protons	δ , ppm	
	calculated	experiment
H ³ , H ^{3'}	6.76	6.86
H ⁴ , H ^{4'}	7.11	7.06
H ⁶ , H ^{6'}	7.13	7.10
H ⁸ , H ^{8'}	7.14	7.01
H ¹³	7.34	7.34
H ⁷ , H ^{7'}	7.39	7.11
H ¹² , H ¹⁴	7.43	7.38
H ¹⁰	7.71	7.63

symmetrical *anti,anti,anti,anti*-, *anti,syn,syn,anti*-, *syn,anti,anti,syn*-, *syn,syn,syn,syn*- and six unsymmetrical forms (Scheme 3) similarly to previously investigated biscrown containing stilbenes and 1,4-distyrylbenzenes [41, 35].

Therewith we consider only the conformation of terminal fragments of 1,3-distyrylbenzenes, since the *anti*- and *syn*-orientation of two double bonds with respect to the central benzene ring cannot be recognized by NMR spectroscopy methods. NOESY spectra, unfortunately, do not give a possibility to evaluate the contribution of every conformer of compounds **3a**, **3b**, and **6** in the equilibrium due to the strong coupling of protons of ethylene fragments with protons H⁴ and H⁶ in all conformers (enumeration of atoms differing from IUPAC rules is introduced in Scheme 4). More than that, the signals of protons H⁴ and H⁶ are overlapped with a signal of one of ethylene protons H⁷, as a result it is impossible to single out separate cross-peaks from NOESY spectrum.

An indirect evidence of the domination of *syn,(syn/anti,syn/anti),syn*-conformers in solution may be concluded from the comparison of signals positions of two benzene protons H⁴ and H⁶ that are in *ortho*-position to ethylene substituent. Protons H⁶ are located also in the *ortho*-position to a strong electron-donor alkoxy substituent and, principally, should appear upfield with respect to protons H⁴ in *para*-position. However in reality the opposite picture is observed, where signals of H⁶ in ¹H NMR spectra of investigated distyrylbenzenes are present in lower field comparing to signals of H⁴ (by ~0.03 ppm). Such situation is possible in case, when predominantly protons H⁶ occur in the range of deshielding effect of the ethylene

fragment and, evidently, in equilibrium mixture more compact *syn,(syn/anti,syn/anti),syn*-forms of 1,3-distyrylbenzenes **3a**, **3b**, and **6** prevail. Signals of CH₂O groups protons of crown ether fragments of compounds **3a** and **3b** shifted upfield the stronger the further this unit is from the benzene ring. According to NOESY spectral data, among CH₂OAr groups the more downfield are the signals of protons of C¹H₂O groups that evidently, like aromatic H⁶ protons, are subjected to deshielding effect of C=C bond in *syn*-, (*syn/anti*-, *syn/anti*-, *syn*-conformers **3a** and **3b**).

Compounds **3a**, **3b** and **6** were investigated with application of ¹³C NMR spectroscopy in CD₂Cl₂. Therewith the positions of signals of similar ¹³C nuclei of 1,3-distyrylbenzenes **3a** and **3b** have almost no differences between them that evidences their similar conformation structure and, probably, the lack of significant charges in macrocyclic fragments. In tetramethoxy-1,3-distyrylbenzene **6** the positions of most carbon signals of 1,3-distyrylbenzene structure has little differences from similar signals of 1,3-distyrylbenzenes **3a** and **3b**. The signals of atoms C³ and C⁶ that are shifted by 1.5–2.3 ppm into a high field form an exclusion. Evidently, methyl groups instead of alkoxyethyl at the atoms O² and O¹ are stronger electron-donor substituents that also is reflected in the values δ_C of carbon atoms in the *ortho*-position to them.

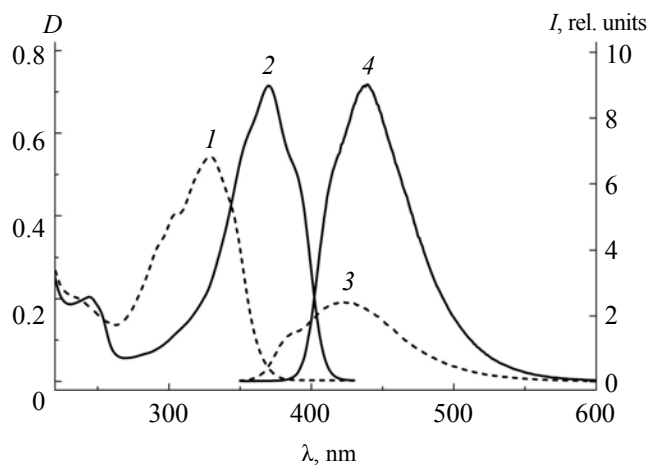
To determine the most feasible conformation of the conjugated fragment in the 1,3-distyrylbenzenes of the investigated type, we performed a quantum-chemical calculation of conformers of their simplest specimen, (*E,E*)-tetramethoxy-1,3-distyrylbenzene **6** and distyrylbenzene **3a** by the density functional theory method (DFT). The choice of distyrylbenzene **6** as an object was caused by the lack of macrocyclic fragments in it, since the conformations calculation of the latter often gave ambiguous results due to local minima on the potential energy surface located close to the global minimum. For *syn,syn,anti,anti*-conformer **6** the method demonstrated good correlation with X-ray diffraction analysis data [43] in lengths of chemical bonds calculated for vacuum (maximal difference 0.02 Å) and bond angles (maximal difference 1 deg).

For tetramethoxy-1,3-distyrylbenzene **6** energies of conformers shown on Scheme 3 and their molar fractions at room temperature were calculated. The calculation demonstrates that mixture all forms of compound **6** are present in the equilibrium. Although

the *syn,anti,anti,anti*-conformer possesses the lowest energy, in the equilibrium mixture prevails the unsymmetrical *syn,syn,anti,anti*-conformer due to its presence in two forms, connected by reflection in the plane perpendicular to the plane of the chromophore and passing through C¹⁰ and C¹³ atoms. In the same way all unsymmetrical conformers **6** are twice degenerate that considering their low relative energies results in the domination of unsymmetrical forms in the equilibrium mixture. Their total fraction is 53%. A similar calculation for compound **3a** gave approximately the same fraction of unsymmetrical forms in the mixture. The rotation of one dialkoxyphenyl residue by 180° with respect to the double bond from *syn*- into *anti*-conformation requires 0.5 kcal/mol, while the rotation of one styryl fragment by 180° with respect to the central benzene ring requires only 0.01 kcal/mol, therefore the presence of both *syn*-, and *anti*-conformers with respect to orientation of styryl fragments relative to the central benzene ring is expectable as well as their quick (by ¹H NMR time scale) exchange.

For all conformers the chemical shifts in ¹H NMR spectra were calculated (Table 1). Chemical shifts of protons H⁴, H^{4'}, and H⁶, H^{6'} differ by ~0.7 ppm depending on their location in *syn*- or *anti*-position with respect to double bonds (signal of proton, caught in the cone of deshielding by the double bond, is shifted downfield). However due to the quick exchange the positions of these signals are averaged. The difference of chemical shifts of protons H³, H^{3'} depending on *syn*- or *anti*-orientation of dialkoxy-phenyl rings with respect to the double bonds is only ~0.1 ppm. The position of signals of protons of double bonds H⁷, H^{7'} does not clearly depend either on the orientation of dialkoxy-phenyl residues, or the orientation of styryl fragments and only changes in the limits of ~0.15 ppm. Similarly behave protons of double bonds H⁸, H^{8'}, the position of their signals changes within ~0.2 ppm. The calculated positions of averaged signals of these protons however correlate with experimental data a little bit worse than the positions of signals of aromatic protons.

It is expectable that the positions of signals of protons H¹⁰, H¹²⁻¹⁴ of central ring would be sensitive to orientation of styryl fragments. Indeed, signals of protons H¹², H¹⁴ at the *anti*-orientation of styryl fragments are shifted downfield due to occurring of the double bonds in the cones of deshielding, and the differences of chemical shifts of protons H^{12,14} at *syn*- and *anti*-orientations of styryl fragments are ~0.6 ppm.



Absorption (1, 2) and fluorescence (3, 4) spectra of tetramethoxy containing distyrylbenzenes **6** (1, 3) and **8** (2, 4) (concentration of compounds at absorption 1×10^{-5} mol/L, at fluorescence 1×10^{-6} mol/L, MeCN-CH₂Cl₂, 10 : 1 v/v, room temperature). Fluorescence excitation with light of ν 344 nm.

And again due to the fast exchange the positions of these signals are averaged. As to proton H¹⁰, its chemical shift varies depending on *syn,syn*-, *syn,anti*- or *anti,anti*-orientations of styryl fragments with respect to the central benzene ring: these three groups of conformers give three groups of signals differing by ~0.7 ppm. The most downfield signal corresponds to *syn,syn*-, and the most upfield one, to *anti,anti*-conformer. The averaged signal of proton H¹⁰ turned to be the most downfield of all signals of investigated protons, in full correlation with experiment. The signal of proton H¹³ turned out to be practically insensitive to the orientation of styryl fragments (difference between positions of signal in different conformers <0.1 ppm). Similar results were obtained also for biscrown containing distyrylbenzene **3a**.

Good correlation of averaged chemical shifts obtained by quantum-chemically calculations with ¹H NMR experimental data evidences the adequacy of the chosen calculation method.

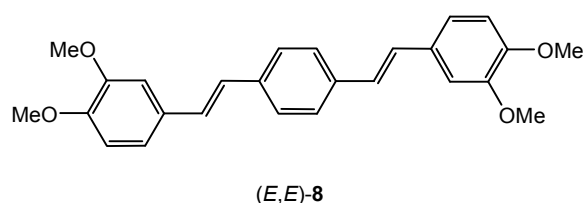
Table 2. UV and fluorescence spectra of compounds **3a**, **3b**, **6**, and **8**^a

Compound no.	λ_{\max} , nm	ϵ_{\max} , L mol ⁻¹ cm ⁻¹	λ_{fl} , nm ^b
3a	330	60500	426
3b	331	64500	425
6	329	54300	422
8	370	71500	439

^a MeCN-CH₂Cl₂, 10 : 1, room temperature.

^b Excitation wavelength 344 nm.

Scheme 5.



Spectral characteristics of tetramethoxy containing (**6**) and biscrown containing distyrylbenzenes **3a** and **3b** are listed in Table 2.

Distyrylbenzenes may be divided in two groups depending on the type of substitution in the central benzene ring. 1,3-Distyrylbenzenes absorb in shorter wavelength region of spectrum (λ_{max} 329–331 nm) comparing to 1,4-distyrylbenzenes (λ_{max} 370–372 nm) that is due to the effective π -conjugation by all chromophores at 1,4-disubstitution. In the 1,3-disubstituted benzenes the conjugation is significantly weakened or lacks at all, so their absorption spectra may be considered as approximate arithmetic sum of two independent stilbene fragments. In all cases longwave absorption bands have unsymmetrical shape, often with significant longwave shoulder that points to the existence of few energetically close electron transfers in their chromophore fragments.

For example on the figure and in Table 2 are demonstrated absorption and fluorescence spectra for isomeric compounds **6** and **8** (Scheme 5).

The maximum of fluorescence of 1,3-distyrylbenzene **6** ($\lambda_{\text{max}}^{\text{fl}}$ 22 nm) is shifted hypsochromically with respect to the maximum of 1,4-distyrylbenzene **8** ($\lambda_{\text{max}}^{\text{fl}}$ 439 nm) that points to the existence of π -

conjugation along all chromophore in the second case. To excite the fluorescence we used light of the wavelength 344 nm, at which the absorption of two isomers is equal. From the data of Table 2 it is evident that isomer with substitution type 1,3 in the central benzene ring possesses a significantly weaker fluorescence that also points to less effective conjugation in the chromophore of 1,3-distyrylbenzene comparing to its 1,4-isomer. Similar spectral behavior characterized pairs of isomers of biscrown containing distyrylbenzenes **3a**, **3b** and **2a**, **2b** [35].

1,3-Distyrylbenzenes **3a**, **3b**, and **6** and previously investigated 1,4-distyrylbenzenes **2a**, **2b**, and **8** [35] were examined by the method of cyclic voltammetry (CVA) in a mixture of solvents MeCN–DMF, 3 : 1, v/v, on glassy-carbon and golden electrodes in the presence of 0.1 M solution of Bu₄NClO₄ as background electrolyte. Potentials of electrochemical oxidation and reduction measured with respect to Ag/AgCl/KCl (aqueous, saturated) electrode are compiled in Table 3, figures of CVA-curves may be obtained from the authors by e-mail.

Electrochemical investigation of 1,3-distyrylbenzenes **3a** and **3b** was carried out in order to compare the values of their redox-potentials with the values of the model tetramethoxy-1,3-distyrylbenzene **6** and close structural analogs, 1,4-distyrylbenzenes **2a**, **2b**, and **8** aiming at the evaluation of the effect of prolongation of the conjugated system on electrochemical potentials. Cyclic voltammograms (CVA-curves) were obtained for solutions of substrates in a mixture of solvents due to the low solubility of distyrylbenzenes in MeCN. Increasing the content of a polar solvent acted beneficially on the resolution of the obtained voltammograms. Measuring of the potentials was performed on golden and glassy-carbon electrodes. The latter has wider range for measurements and is inert, while the first sometimes allows obtaining a higher resolution, but the possibility is not excluded of changing mechanism of redox processes due to another orientation of substrates on the surface of the working electrode.

Compared to the previously investigated 1,4-distyrylbenzenes **2a** and **2b** 1,3-distyrylbenzenes **3a** and **3b** are reduced at more cathodic (by 210–240 mV), and are oxidized at more anodic (by 220–230 mV) potentials. Evidently, the *meta*-substituted phenylene ring in compounds **3a** and **3b** is a less conductive spacer between two styryl residues, than *para*-

Table 3. Electrochemical potentials with respect to Ag/AgCl/KCl (aqueous, saturated) electrode of compounds **6**, **3a**, **3b**, **8**, **2a**, and **2b** in MeCN–DMF, 3 : 1, in the presence of 0.1 M solution of Bu₄NClO₄ on glassy-carbon electrode

Compound	E_{red} , B	E_{ox} , B
6	–2.29	1.19
3a	–2.27	1.28
3b	–2.29	1.28
8 [35]	–2.06	1.06
2a [35]	–2.05	1.07
2b [35]	–2.06	1.06

substituted phenylene ring in 1,4-distyrylbenzenes **2a** and **2b**. The disruption of conjugation in compounds **3a**, **3b**, and **6** results in shortening the conjugation chain and, consequently, to the growth in absolute values of first cathode and anode potentials connected with worse charge delocalization in cation and anion radicals [44–46] generated in the first stages of redox-processes.

Values of first cathode potentials for 1,3-distyrylbenzenes **3a** and **3b** had no difference from similar potential of model tetramethoxy-1,3-distyrylbenzene **6**, as well as potential values for previously investigated biscrown containing 1,4-distyrylbenzenes **2a** and **2b** and stilbenes **1a** and **1b** [35, 22] were not distinguished from those of respective model compounds. However the processes of primary oxidation of compounds **3a** and **3b** occur at more anodic potentials (by 90 mV), than for respective model tetramethoxy derivative **6**. Evidently, it is due to higher electron-donor properties of methyl groups in compound **6** compared to alkoxyethyl groups of compounds **3a** and **3b** providing better conjugation that results in easier oxidation of compound **6** [45, 46]. CVA-curves of 1,3-distyrylbenzenes **3a** and **3b** on golden electrode are significantly different from voltammetric curves obtained on a glassy-carbon electrode. Probably it is connected with a different orientation of molecules on golden electrode compared to glassy-carbon one and, consequently, with changes in the mechanism of redox-processes.

Hence a method of synthesis of symmetrical biscrown containing and model tetra-methoxy-substituted 1,3-distyrylbenzenes was developed, allowing their preparation from available formyl benzo crown ethers in high yields. The conformational analysis of (*E,E*)-1,3-distyrylbenzenes using the data of NMR and X-ray diffraction analysis revealed their structural features in solution. By using quantum-chemical calculations we confirmed more feasibility of *syn*,(*syn/anti*,*syn/anti*),*syn*-conformations of conjugated fragment of 1,3-distyrylbenzenes, possessing four alkoxy substituents, and the prevalence of unsymmetrical *syn/anti*,(*syn,anti*),*syn/anti*- conformations was revealed. By electronic spectroscopy we compared the spectral properties of 1,3- and 1,4-distyrylbenzenes. The presence of less effective conjugation system in 1,3-distyrylbenzenes compared to 1,4-distyrylbenzenes allows explaining a significant complication of process of their chemical reduction. The investigation of the structure and properties of biscrown containing 1,3-distyrylbenzenes may be used

in construction of photoactive supramolecular systems on their basis.

EXPERIMENTAL

^1H and ^{13}C spectra were obtained on a spectrometer Bruker DRX-500 (500.13 and 125.76 MHz respectively) in CD_2Cl_2 using residual protons and the carbon atoms of the solvent as internal references (δ_{H} 5.30, δ_{C} 53.60 ppm). To assign the signals 2D homonuclear ^1H – ^1H COSY and NOESY and heteronuclear ^1H – ^{13}C COSY (HSQC and HMBC) spectra were used. 2D experiments were performed applying standard parameters included in a software package of Bruker. NOESY mixing time was 300 μs , HMBC experiment was optimized for the constant $J_{\text{H,C}}$ 8 Hz. Chemical shifts were measured with the accuracy of 0.01 ppm, and coupling constants, with the accuracy of 0.1 Hz. Mass spectra MALDI-TOF were registered on instruments Bruker Daltonics Ultraflex and Bruker Daltonics Ultraflex II, equipped with nitrogen laser and time-of-flight mass analyzer. Samples were applied on a sublayer of polished steel using 1,8,9-trihydroxyanthracene as matrix and polyethylene glycols PEG-200, 300, 400, 600, 1000, 1500 as internal standards. Recording of spectra was performed in a positive ions mode which were extracted from the ionization chamber by accelerating voltage 20 kV. The resulting spectrum was a sum of 300 spectra obtained at different points of the sample. Processing of spectra was done using software of Bruker DataAnalysis, Version 1.6g (Bruker Daltonik GmbH, 1999). From the set of isotope peaks of molecular ion a peak was chosen that corresponded to monoisotopic mass. GC/MS spectra were obtained on a triple quadrupole mass-spectrometer Thermo TSQ8000, chromatograph Trace-1310, ionizing electrons energy 70 eV. Elemental analyses were carried out at the chemical facility of the Moscow State University on a CHN-analyzer Vario Micro Cube. Samples for elemental analysis were dried in a vacuum at 80°C. Melting points (uncorrected) were measured in capillaries on an apparatus IA9300. Electron absorption spectra were recorded on a spectrophotometer Cary 4000 (Agilent) using a quartz cell with the length of optical path 10 mm. All cells had fine ground plugs. Stationary fluorescence spectra were registered on a spectrofluorimeter RF-5301PC (Shimadzu), quartz cells with the length of optical path 10 mm. For electrochemical investigations potentiostat IPC-Pro M was used. Measurements were carried out in a cell by the three electrode scheme. Working electrodes were

glassy-carbon (d 2 mm) and golden (d 2 mm) discs, comparison electrode, Ag/AgCl/KCl (aqueous, saturated), additional electrode was platinum plate.

Electronic spectra were registered in MeCN of “specially pure-zero” grade (water content <0.03%, Kriokhrom) and CH_2Cl_2 (HPLC grade, Aldrich). For electrochemical investigations DMF of “chemically pure” grade was stirred with anhydrous K_2CO_3 (20 g/L) for 4 days at 20°C, decanted from the solid phase and purified in succession by boiling and a vacuum distillation on calcium hydride and anhydrous copper sulfate (10 g/L). MeCN (Acros Organics, extra dry) before use was distilled on CaH_2 . Purified solvents were kept above molecular sieves 4 Å. For the synthesis DMF was dried by distillation on CaH_2 . Bu_4NClO_4 and veratric aldehyde **7** (Aldrich) were used without additional purification. 1,4-Distyrylbenzenes **2a**, **2b**, and **8** were obtained by method [35]. 4'-Formylbenzo-15(18)-crown-5(6)-ethers **4a** and **4b** were synthesized by methods [47–50], tetraethyl[1,3-phenylenedi(methylene)]bis(phosphonate) **5**, by method [51].

Quantum-chemical calculations were performed with a full geometry optimization of conformers of 1,3-distyrylbenzene **6** by the method of density functional of Perdew–Burke–Ernzerhof (PBE) [52] and original three exponent basis set (PBE/3z) with application of software PRIRODA [53, 54]. Effect of the solvent is not considered because nonspecific solvation has almost no effect on the ratio of molar fractions of different conformers.

Chemical shifts of protons in ^1H NMR spectra were also calculated with software PRIRODA with the same basis and functional. An approach of calibration-invariant atomic orbitals (GIAO) [55] was applied. This approach we previously applied successfully in [56]. Chemical shifts of equilibrium mixture of conformers were calculated considering molar fractions of conformers and the number of chemically equivalent protons in them.

Molar fractions of conformers are calculated through their Boltzmann weights at room temperature: where ΔG_i is the free Gibbs energy, g_i is the multiplicity of i conformer (1 for symmetrical structures, 2 for unsymmetrical), k is Boltzmann constant, T is temperature. For conformers of the same molecule the vibrational and enthalpy contributions into the free energy are almost identical, therefore instead of ΔG_i the relative conformational energy ΔE_i obtained directly from calculation may be applied.

Methods of electronic spectroscopy. a mixture $\text{MeCN}-\text{CH}_2\text{Cl}_2$, 10 : 1, was used as a solvent for recording absorption and fluorescence spectra, because preliminary investigations demonstrated that in pure MeCN distyrylbenzenes were poorly soluble.

Absorption spectra of samples of concentration $1 \cdot 10^{-5}$ mol/L were recorded in a mixture $\text{MeCN}-\text{CH}_2\text{Cl}_2$, 10 : 1, at room temperature, fluorescence spectra were taken in the same mixture at the concentration $1 \cdot 10^{-6}$ mol/L at room temperature. Solutions of distyrylbenzenes were prepared in a dark room in a red light, because under ambient light compounds underwent *trans-cis*-photoisomerization.

Electrochemical properties. As background electrolyte 0.1 M solution of Bu_4NClO_4 in a mixture $\text{MeCN}-\text{DMF}$, 3 : 1 v/v, was used. Potentials are reported considering *iR*-compensation. The surface of working electrodes was polished with powder of aluminum oxide particles of the size less than 10 microns (Sigma Aldrich). The concentration of investigated compounds was varied in the range 1×10^{-4} – 1×10^{-5} mol/L. At investigation with CVA the rate of potential rise was 200 mV/s. All measurements were performed in a dry argon atmosphere, samples were dissolved in preliminary deaerated solvent.

1,3-Distyrylbenzenes (3a and 3b). General method. Into three-neck flask equipped with a reflux condenser was placed 26 mg (1.11 mmol) of metal Na, 5 mL of *t*-BuOH, and the reaction mixture was boiled while stirring in an argon flow until sodium fully dissolved. Excess of *t*-BuOH was distilled off in a vacuum. To the precipitate at cooling was added a solution of 98 mg (0.26 mmol) of ester **5** in 0.42 mL of DMF and the reaction mixture was stirred for 45 min. Then at cooling a solution of 0.52 mmol of crown ether **4a** and **4b** in 0.42 mL of DMF was added dropwise. The temperature of reaction mixture was raised to room temperature and it was stirred for 75 h. The workup is described below.

15,15'-{1,3-Phenylenebis[(*E*)-ethene-2,1-diyl]}-bis-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopenta-oxacyclopentadecine) or bis(15-crown-5)-1,3-distyrylbenzene (3a). To the reaction mixture 5 mL of water was added, the precipitate was filtered off, washed with 3 mL of water, dried in air. Yield 77%, fine light-brown crystals, mp 179–180°C. R_f 0.54 (benzene–EtOAc, 1 : 5, with addition of 2–3 drops of pyrrolidine, DC–Alufolien Aluminiumoxid 60 F₂₅₄

neutral, Merck). ^1H NMR spectrum (27°C), δ , ppm: 3.64–3.73 m (16H, $4\text{C}^{5,6,8,9}\text{H}_2\text{O}$, $4\text{C}^{5',6',8',9'}\text{H}_2\text{O}$), 3.82–3.89 m (8H, $2\text{C}^{3,11}\text{H}_2\text{O}$, $2\text{C}^{3',11'}\text{H}_2\text{O}$), 4.08–4.12 m (4H, $\text{C}^2\text{H}_2\text{O}$, $\text{C}^{2'}\text{H}_2\text{O}$), 4.12–4.17 m (4H, $\text{C}^{12}\text{H}_2\text{O}$, $\text{C}^{12'}\text{H}_2\text{O}$), 6.85 d (2H, $\text{H}^{17,17'}$, J 8.1 Hz), 6.99 d (2H, $2\text{CH}^2=\text{CH}$, J 16.3 Hz), 7.03–7.12 m (6H, $2\text{CH}=\text{CH}^1$, H^{14} , $\text{H}^{14'}$, H^{16} , $\text{H}^{16'}$), 7.29–7.33 m (1H, H^5), 7.34–7.40 m (2H, H^4 , H^6), 7.61 s (1H, H^2). ^{13}C NMR spectrum (30°C), δ , ppm: 68.90 and 69.04 ($\text{C}^{2,12}\text{H}_2\text{O}$, $\text{C}^{2',12'}\text{H}_2\text{O}$), 69.49 and 69.56 ($\text{C}^{3,11}\text{H}_2\text{O}$, $\text{C}^{3',11'}\text{H}_2\text{O}$), 70.33 and 70.36 ($\text{C}^{5,9}\text{H}_2\text{O}$, $\text{C}^{5',9'}\text{H}_2\text{O}$), 70.97 ($\text{C}^{6,8}\text{H}_2\text{O}$, $\text{C}^{6',8'}\text{H}_2\text{O}$), 111.55 (C^{14} , $\text{C}^{14'}$), 113.79 (C^{17} , $\text{C}^{17'}$), 120.47 (C^{16} , $\text{C}^{16'}$), 124.30 (C_{arom}^2), 125.32 (C_{arom}^4 , C_{arom}^6), 126.68 ($2\text{C}^2\text{H}=\text{CH}$), 128.79 (C_{arom}^5), 129.13 ($2\text{CH}=\text{C}^1\text{H}$), 130.85 (C^{15} , $\text{C}^{15'}$), 138.13 (C_{arom}^1 , C_{arom}^3), 149.38 and 149.45 (C^{13a} , $\text{C}^{13a'}$, C^{17a} , $\text{C}^{17a'}$). Mass spectrum, m/z : 662.0 $[M]^+$ (Calculated m/z 662.31 for $[\text{C}_{38}\text{H}_{46}\text{O}_{10}]^+$), 685.0 $[M + \text{Na}]^+$, 701.0 $[M + \text{K}]^+$. Found, %: C 68.70; H 6.69. $\text{C}_{38}\text{H}_{46}\text{O}_{10}$. Calculated, %: C 68.86; H 7.00. M 662.78.

18,18'-{1,3-Phenylenebis[(*E*)-ethene-2,1-diyl]}-bis(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine) or bis(18-crown-6)-1,3-distyrylbenzene (3b). To the reaction mixture 10 mL of water was added, the mixture was extracted with dichloromethane (3×15 mL), the extract was dried with Na_2SO_4 and evaporated in a vacuum. Transparent crystallizing oily substance was washed with 5 mL of pentane, then triturated with 3 mL Et_2O . Yield 53%, fine light-brown crystals, mp 118–119°C. R_f 0.34 (benzene– EtOAc , 1 : 5, with addition of 2–3 drops of pyrrolidine, DC–Alufolien Aluminiumoxid 60 F₂₅₄ neutral, Merck). ^1H NMR spectrum (27°C), δ , ppm: 3.60 s (8H, $2\text{C}^{8,9}\text{H}_2\text{O}$, $2\text{C}^{8',9'}\text{H}_2\text{O}$), 3.64 m (8H, $2\text{C}^{6,11}\text{H}_2\text{O}$, $2\text{C}^{6',11'}\text{H}_2\text{O}$), 3.72 m (8H, $2\text{C}^{5,12}\text{H}_2\text{O}$, $2\text{C}^{5',12'}\text{H}_2\text{O}$), 3.80–3.92 m (8H, $2\text{C}^{3,14}\text{H}_2\text{O}$, $2\text{C}^{3',14'}\text{H}_2\text{O}$), 4.14 m (4H, $\text{C}^2\text{H}_2\text{O}$, $\text{C}^{2'}\text{H}_2\text{O}$), 4.19 m (4H, $\text{C}^{15}\text{H}_2\text{O}$, $\text{C}^{15'}\text{H}_2\text{O}$), 6.85 d (2H, H^{20} , $\text{H}^{20'}$, J 8.1 Hz), 6.99 d (2H, $2\text{C}^2\text{H}=\text{CH}$, J 16.3 Hz), 7.03–7.13 m (6H, $2\text{CH}=\text{CH}^1$, H^{17} , $\text{H}^{17'}$, H^{19} , $\text{H}^{19'}$), 7.29–7.34 m (1H, H^5), 7.34–7.40 m (2H, H^4 , H^6), 7.61 s (1H, H^2). ^{13}C NMR spectrum (30°C), δ , ppm: 68.72 ($\text{C}^{2,15}\text{H}_2\text{O}$, $\text{C}^{2',15'}\text{H}_2\text{O}$), 69.50 and 69.54 ($\text{C}^{3,14}\text{H}_2\text{O}$, $\text{C}^{3',14'}\text{H}_2\text{O}$), 70.47–70.79 ($\text{C}^{5,6,8,9,11,12}\text{H}_2\text{O}$, $\text{C}^{5',6',8',9',11',12'}\text{H}_2\text{O}$), 111.00 (C^{17} , $\text{C}^{17'}$), 113.30 (C^{20} , $\text{C}^{20'}$), 120.29 (C^{19} , $\text{C}^{19'}$), 124.28 (C_{arom}^2), 125.30 (C_{arom}^4 , C_{arom}^6), 126.63 ($2\text{C}^2\text{H}=\text{CH}$), 128.80 ($2\text{CH}=\text{C}^1\text{H}$), 129.12 (C_{arom}^5), 130.68 (C^{18} , $\text{C}^{18'}$), 138.13 (C_{arom}^1 , C_{arom}^3), 149.02 and 149.09 (C^{16a} , $\text{C}^{16a'}$, C^{20a} , $\text{C}^{20a'}$). Mass spectrum, m/z : 789.17 $[M + \text{K}]^+$ 773.17 $[M + \text{Na}]^+$, 750.19 $[M]^+$. Found, %: C 67.37; H 7.15. $\text{C}_{42}\text{H}_{54}\text{O}_{12}$. Calculated, %: C 67.18; H 7.25. M 750.36.

1,1'-{1,3-Phenylenebis[(*E*)-ethene-2,1-diyl]}bis(3,4-dimethoxybenzene) or 3,4,3',4'-tetramethoxy-1,3-distyrylbenzene (6). Into a flask, equipped with a reflux condenser in a flow of argon was added 87 mg (3.6 mmol) of NaH washed from mineral oil and 250 μL of DMF. Then at 0°C a solution of 239 mg (0.63 mmol) of tetraethyl [1,3-phenylenedi(methylene)]bis(phosphonate) **5** in 250 μL of DMF was added dropwise and left for 1.5 h at room temperature. At cooling a solution of 200 mg (1.21 mmol) of veratric aldehyde **7** in 250 μL of DMF was added dropwise. The temperature of reaction mixture was raised to room temperature, the mixture was kept for 2 h, then heated for 1 h at 65°C. To the reaction mixture was added 2.5 mL of water and 1 N HCl till pH 7, the precipitate was filtered off, washed with water, dried in air. Yield 77 mg (32%), light-brown fine crystals, mp 174–175°C (from MeCN) (mp 172–174°C [57]). R_f 0.34 (hexane– EtOAc , 3 : 1 by volume, DC–Alufolien Aluminiumoxid 60 F₂₅₄ neutral, Merck). ^1H NMR spectrum (27°C), δ , ppm: 3.84 s (6H, 4,4'-MeO), 3.89 s (6H, 3,3'-MeO), 6.86 d (2H, H^5 , $\text{H}^{5'}$, J 8.1 Hz), 7.01 d (2H, $2\text{CH}^2=\text{CH}$, J 16.3 Hz), 7.06 d (2H, H^6 , $\text{H}^{6'}$, J 8.1 Hz), 7.10 s (2H, H^2 , $\text{H}^{2'}$), 7.11 d (2H, $2\text{CH}=\text{CH}^1$, J 16.3 Hz), 7.34 m (1H, H^5 , C_6H_4), 7.38 m (2H, H^4 , H^6 , C_6H_4), 7.63 s (1H, H^2 , C_6H_4). ^{13}C NMR spectrum (30°C), δ , ppm: 56.06 (4MeO), 109.25 (C^2 , $\text{C}^{2'}$), 111.76 (C^5 , $\text{C}^{5'}$), 120.20 (C^6 , $\text{C}^{6'}$), 124.37 (C_{arom}^2), 125.42 (C_{arom}^4 , C_{arom}^6), 126.67 ($2\text{C}^2\text{H}=\text{CH}$), 128.94 (C_{arom}^5), 129.26 ($2\text{CH}=\text{C}^1\text{H}$), 130.57 (C^1 , $\text{C}^{1'}$), 138.25 (C_{arom}^1 , C_{arom}^3), 149.59 and 149.68 (C^3 , $\text{C}^{3'}$, C^4 , $\text{C}^{4'}$). Mass spectrum GC/MS (EU), m/z : 402.0 $[M]^+$. $\text{C}_{26}\text{H}_{26}\text{O}_4$. Calculated 402.49.

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