Synthesis and Structure of Bis-crown-Containing Stilbenes

A. I. Vedernikov[1], S. S. Basok[2], S. P. Gromov[1], L. G. Kuz'mina[3], V. G. Avakyan[1], N. A. Lobova[1], E. Yu. Kulygina[2], T. V. Titkov[1], Yu. A. Strelenko[4], E. I. Ivanov[2], J. A. K. Howard[5], and M. V. Alfimov[1]

[1] *Photochemistry Center, Russian Academy of Sciences, ul. Novatorov 7A, Moscow, 119421 Russia*
e-mail: gromov@photonics.ru

[2] *Bogatskii Physicochemical Institute, National Academy of Sciences of Ukraine, Odessa, Ukraine*

[3] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*

[4] *Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia*

[5] *Chemistry Department, Durham University, South Road, Durham DH1 3LE, United Kingdom*

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Abstract—An improved procedure was proposed for the synthesis of stilbenes fused to two crown ether fragments at both benzene rings. The structure of new homologous symmetric bis-crown-containing stilbenes was determined by X-ray analysis. Relations were revealed between the size of the crown ether moiety and stilbene conformation in crystal and the mode of crystal packing. Conformational analysis of the prepared stilbenes in solution and in the solid state was performed by ^{1}H and ^{13}C NMR spectroscopy and by DFT quantum-chemical calculations.

In the recent years, supramolecular chemistry has become one of the most extensively developing fields of organic chemistry [1]. Components of supramolecular systems are often complex and difficultly accessible organic compounds, and their synthesis in many cases constitutes the subject of a separate study. In addition, an important problem in supramolecular chemistry is prediction of properties of compounds in supramolecular systems and development of selective procedures for their self-assembly.

A promising sort of molecules for studying supramolecular organization in solution, monomolecular layers, Langmuir–Blodgett films, and polymeric matrices includes crown ether-fused azobenzenes, azomethines, styryl dyes, and related compounds [2–5] possessing double N=N, C=N, and C=C bonds. Interesting properties of these compounds are the ability to form supramolecules via host–guest-like complex formation with metal and ammonium ions, considerable variations in spectral parameters due to complex formation, and the possibility of varying their structure and properties by irradiation. The most typical photochemical processes occurring in the above self-organized systems and accompanied by considerable variation of their properties are *trans–cis* isomerization of the double bonds, electrocyclic reactions, and

[2+2]-cycloaddition. Crown ether-fused stilbenes were not studied in much detail [6–8], though these compounds might be expected to exhibit equally interesting photochemical behavior and pronounced ability to form complexes.

We recently showed that bis(18-crown-6)–stilbene **Id** and a number of diammonioalkyl derivatives of viologen analogs in dilute solutions give rise to unusual bi- and trimolecular complexes with effective intermolecular charge transfer due to spatial preorganization of the donor and acceptor parts of the initial molecules via hydrogen bonding [9–11]. Such supramolecular systems were found to be very stable; therefore, they can be regarded as convenient models for studying photoinduced intermolecular electron transfer [12] and promising species with versatile electrochemical properties [13]. However, the high potential of bis-crown-containing stilbenes as building blocks for assembly of complex supramolecular systems has not been explored to a sufficient extent. One of the main reasons is relatively difficult preparation of these compounds. Therefore, the goal of the present work was to develop a convenient procedure for the synthesis of symmetric stilbenes containing two 12(15, 18)-crown-4(5, 6) fragments and study their structure.

Scheme 1.
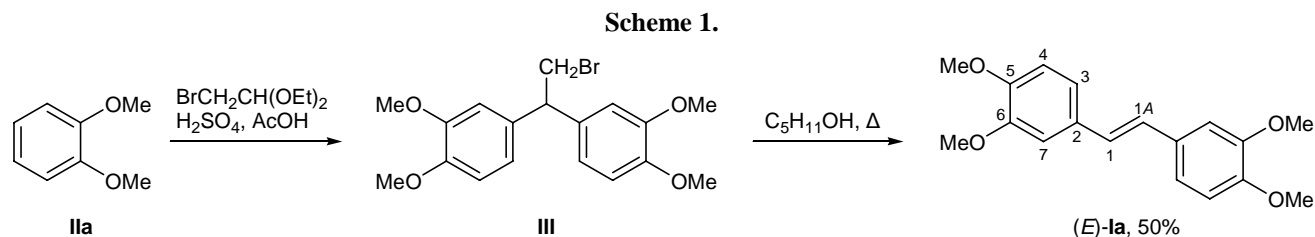
The first representatives of bis-crown-fused stilbenes, bis(15-crown-5)–stilbene **Ic** and bis(18-crown-6)–stilbene **Id** were synthesized by reductive dimerization of the corresponding 4-formylbenzocrown ethers with $TiCl_4$ and zinc in the presence of 1,8-bis-(dimethylamino)naphthalene in anhydrous tetrahydrofuran (yield 26 and 31%, respectively) [7]. A disadvantage of this procedure is the necessity of carrying out the reaction at low temperature (–70°C). We reproduced the synthesis of stilbene **Id** as described in [7] and found that cooling with ice is sufficient to ensure effective reaction. The target product was thus obtained in 40% yield. Other disadvantages of the reported method include the use of aggressive or expensive reagents and thoroughly dehydrated solvent and difficulties in the isolation of products from the reaction mixture. Taking into account the above stated, we analyzed published data [14] with a view to develop a more convenient procedure for the synthesis of bis-crown-containing stilbenes.

One of the most popular methods of synthesis of stilbenes, including crown-fused compounds [8], is based on the Wittig condensation and its modifications.

Table 1. Conditions of rearrangement of 1,1-diaryl-2-bromoethane **IIIc** and yields of bis(15-crown-5)–stilbene **Ic**

Solvent	Temperature, °C	Yield, %
Ethanol	78	29
1-Propanol	98	51
1-Butanol	118	63
1-Pentanol	136–138	73
1-Hexanol	156	70
1-Heptanol	176	69 (62)[a]
1-Octanol	195	65 (60)[a]
Cyclohexanol	161	60
Ethylene glycol	196–198	47[a]
Nitrobenzene	210–211	39[a]
Acetic acid	117–118	17[a]
No solvent (reduced pressure)	135–140	12[a]

[a] After recrystallization from benzene.

However, it implies the use of formyl derivatives of benzocrown ethers and preparation of phosphorylated crown ethers, which make the procedure expensive and laborious. Among simpler procedures for the synthesis of symmetric stilbenes having donor substituents in the aromatic rings, we selected reaction of phenol derivatives with α-haloacetaldehyde diethyl acetal in acid medium, followed by thermal rearrangement of 1,1-diaryl-2-haloethane thus formed into stilbene derivative [15, 16]. We examined the possibility of extending this procedure to the preparation of biscrown-fused stilbenes.

First of all, we studied the synthesis of tetramethoxystilbene **Ia** as model compound in which the four methoxy groups may be regarded as analogs of electron-donor crown-ether moieties. The reaction of 1,2-dimethoxybenzene (**IIa**) with bromoacetaldehyde diethyl acetal in a mixture of acetic and sulfuric acids afforded 1,1-bis(3,4-dimethoxyphenyl)-2-bromoethane (**III**) with a high purity (>90%, according to the ^{1}H NMR data). Compound **III** was converted in a good yield into stilbene (*E*)-**Ia** by heating in 1-pentanol (Scheme 1).

The optimized procedure was then applied to the synthesis of benzocrown ethers **IIb–IId**. The corresponding bromoethanes (analogous to **III**) were obtained as oily substances and were subjected (without identification) to thermal rearrangement to give stilbenes **Ib–Id** (Scheme 2). Thermal rearrangement of 1,1-diaryl-2-haloethanes is usually effected by heating in high-boiling solvents [14]. We examined the effect of the solvent nature and temperature at the rearrangement stage in the synthesis of bis(15-crown-5)–stilbene **Ic** as an example (Table 1). The yield of compound **Ic** was the maximal when the corresponding 1,1-diaryl-2-bromoethane was heated in alcohols. Under these conditions, the released hydrogen bromide is likely to react with the alcohol to give alkyl bromide which is inactive toward crown-fused stilbene. The reaction in acetic acid was accompanied by formation of a considerable amount of tars, and the low yield of stilbene **Ic** can also be explained by sensitivity of the polyether ring to HBr. The rearrangements in high-boiling sol-

Scheme 2.
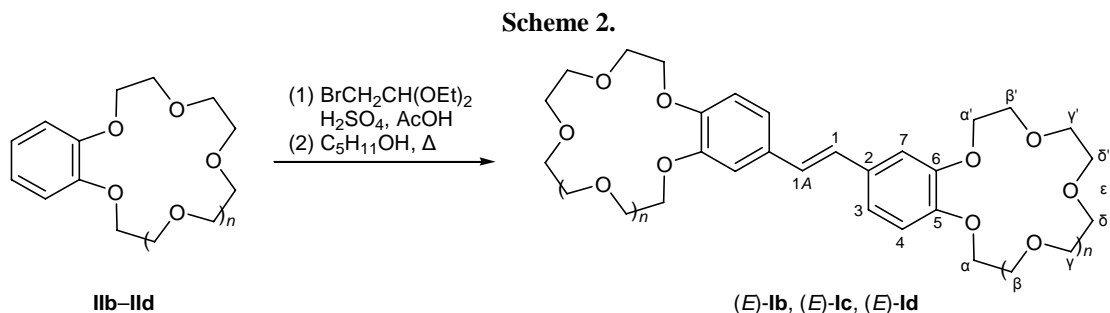
(E)-**Ib**, n = 0, yield 72%; (E)-**Ic**, n = 1, 73%; (E)-**Id**, n = 2, 70%;

vents were also accompanied by partial tarring, and the product yield was lower (for alcohols, starting from 1-heptanol). The optimal temperature for the rearrangement of crown-containing 2-bromoethanes into stilbenes was found to range from 120 to 160°C.

Analysis of the ^{1}H NMR spectra and melting points of the products and comparison with published data showed that stilbenes **Ic** and **Id** are *trans* isomers. The ^{1}H NMR spectrum of newly synthesized bis(12-crown-4)–stilbene **Ib** also contained a single set of signals. The presence of weak signals from protons in the ethylene fragment ($J_{1,1A} = 16.2$ Hz) indicated *E* configuration of compound **Ib**.

Thus the use as starting compounds of accessible benzocrown ethers rather than their formyl derivatives, simple experimental procedure, and high overall yield of the product make the method proposed by us for the synthesis of compounds **Ib**–**Id** more advantageous than that reported previously.
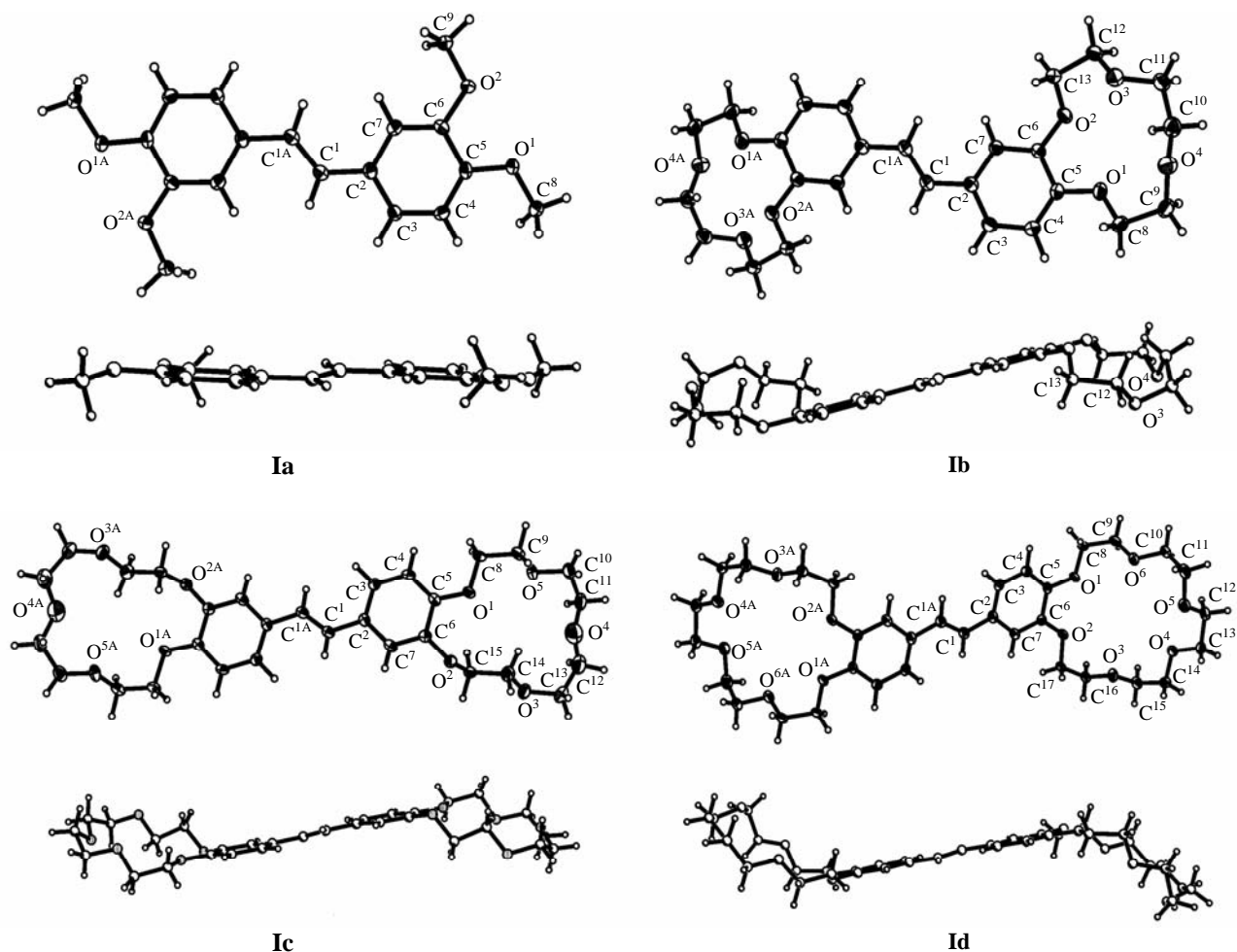
The structures of molecules **Ia**–**Id** (frontal and side views), determined by the X-ray diffraction method, are shown in Fig. 1, and selected bond lengths and bond angles therein are given in Table 2. All molecules occupy a particular position in the crystal symmetry center and are characterized by *trans* configuration of the ethylene fragment and planar structure of the conjugated bond system. On the other hand, molecules **Ia**–**Id** exist in two different conformations, which are retained in going to solution. Molecules **Ia** and **Ib** in crystal adopt a more stable *syn,syn* conformation, while **Ic** and **Id** exist in less favorable *anti,anti* conformation (see below discussion of the NMR data and quantum-chemical calculations).

As seen from Fig. 1 (side views), only molecule **Ia** is planar as a whole; the methoxy groups therein are located almost in the same plane as the benzene rings. The crown ether fragments in molecules **Ib**–**Id** decline to an appreciable extent toward the stilbene plane,

presumably as a result of specific packing of molecules in crystal. The dihedral angle between the mean-square plane passing through the oxygen atoms in the macro-ring and the stilbene system is 46.6° for **Ib**, 24.4° for **Ic**, and 39.7° for **Id**. This specificity gives rise to some new effects which are not typical of benzocrown ethers. In fact, all benzocrown ether systems studied so far, as well as compounds **Ia** and **Id**, are characterized by distortion of the bond angles at the C^5 and C^6 atoms of the benzene ring (i.e., atoms included in the macro-ring; for atom numbering, see Fig. 1). The endocyclic angles $O^1C^5C^6$ and $O^2C^6C^5$ are usually appreciably smaller (~115°) while the exocyclic angles $O^1C^5C^4$ and $O^2C^6C^7$ are greater (~125°) than the corresponding

Table 2. Selected bond lengths d and bond angles ω in molecules **Ia**–**Id**

Bond	d, Å			
	Ia	**Ib**	**Ic**	**Id**
C^1–C^{1A}	1.338(3)	1.341(2)	1.334(8)	1.328(4)
C^1–C^2	1.467(2)	1.464(2)	1.480(5)	1.475(2)
C^2–C^3	1.386(2)	1.396(2)	1.402(6)	1.396(2)
C^3–C^4	1.396(2)	1.393(2)	1.391(6)	1.395(2)
C^4–C^5	1.383(2)	1.387(2)	1.400(6)	1.383(3)
C^5–C^6	1.414(2)	1.407(2)	1.411(5)	1.417(2)
C^6–C^7	1.382(2)	1.381(2)	1.381(6)	1.392(2)
C^7–C^2	1.415(2)	1.411(2)	1.416(6)	1.410(3)
C^5–O^1	1.370(2)	1.369(1)	1.358(5)	1.372(2)
C^6–O^2	1.373(2)	1.373(1)	1.379(5)	1.369(2)
$O^1 \cdots O^2$	2.591	2.606	2.685	2.591
Angle	ω, grad			
$C^{1A}C^1C^2$	127.8(2)	126.2(1)	126.2(5)	127.2(2)
$O^1C^5C^4$	124.9(1)	124.7(1)	125.6(3)	125.2(2)
$O^2C^6C^7$	125.1(1)	123.5(1)	120.0(4)	125.2(2)
$O^1C^5C^6$	115.9(1)	115.7(1)	115.9(3)	115.1(1)
$O^2C^6C^5$	114.9(1)	116.2(1)	119.5(3)	115.6(1)

Fig. 1. Structure of molecules **Ia**–**Id** according to the X-ray diffraction data (frontal and side views).

standard values. These data contradict the concept involving steric repulsion of the O^1 and O^2 atoms: the distance between O^1 and O^2 in molecules **Ia** and **Id** (2.59 Å) is shorter than the sum of their van der Waals radii (~2.8 Å), which is usually interpreted in terms of conjugation between lone electron pairs (LEP) on the O^1 and O^2 atoms (p orbitals) and the benzene ring. The conjugation is favored by the conformation of the $C_{Alk}OC_{Ar}C_{Ar}$ fragment where the corresponding torsion angle approaches either 0 or 180°. In fact, the torsion angles $C_{Alk}OC_{Ar}C_{Ar}$ in molecules **Ia** and **Id** are fairly small: 9.5, –11.7° and 3.5, –15.3°, respectively.

A different pattern is observed for compounds **Ib** and **Ic**. Molecule **Ib** is also characterized by appropriate distortion of the bond angles at C^5 and C^6 (Table 2); however, this distortion is caused by a different factor. The torsion angles $C_{Alk}OC_{Ar}C_{Ar}$ in molecule **Ib** are too large (–33.3 and 46.8°) to ensure effective conjugation between the oxygen LEPs and the benzene ring. There is an empirical rule, according to which the energy of

conjugation is proportional to the squared cosine of the angle between the corresponding p and π orbitals, i.e., of the torsion angles given above. This means that molecule **Ib** retains conjugation by only 70 and 47%, respectively. Undoubtedly, the reason for the observed angular distortion is joint effect of two factors: (1) insufficient flexibility of the relatively small macroring and (2) crystalline field effects leading to declination of the mean-square plane of the macroring from the plane of the stilbene system.

Molecule **Ic** is the first example of structures lacking distortion of bond angles at one benzene carbon atom linked to oxygen atom of the macroring. The bond angles at C^5 are characterized by typical deviations [125.6(3) and 115.9(3)°; Table 2], while the corresponding angles at C^6 are almost similar [120.0(4) and 119.5(3)°]. The torsion angle $C^8O^1C^5C^4$ is 3.3°, which suggests conjugation between O^1 and the benzene ring, whereas the torsion angle $C^{15}O^2C^6C^7$ equal to 110.3° rules out conjugation between O^2 and the

benzene ring. Undoubtedly, this is caused by the crystalline field effect which fixes the molecule in a specific structure lacking for conjugation between the benzene ring and one of the oxygen atoms. No such effect was observed previously for other benzocrown ethers with the same size of the polyether ring.

The presence of a macrocyclic fragment in molecules **Ib–Id** induces considerable changes in bond length distribution in the stilbene conjugation system relative to that found in molecule **Ia**. The latter is characterized by a distinct alternation of bonds in the benzene ring, though this effect is more pronounced in the $C^5C^6C^7C^2$ fragment. Bond alternation in molecules **Ib–Id** is observed only in the $C^5C^6C^7C^2$ fragment where the central C^6–C^7 bond is appreciably shorter than the contiguous bonds. The bonds in the $C^2C^3C^4C^5$ fragment have almost similar lengths. The bridging ethylene double bond in all the examined molecules is essentially localized (Table 2). It should be noted that analogous bond distribution was observed in the benzene rings of molecule **Ic** where conjugation between O^2 and the benzene ring is absent. This means that oxygen atom in the *meta* position with respect to the ethylene bridge only slightly affects conjugation in the stilbene system.

As far as crystal packing was presumed to affect the structure of stilbene molecules **Ia–Id** and electronic effects therein, it is reasonable to consider the modes of crystal packing in more detail. Figure 2 shows two layers of the crystal packing of compound **Ia**. No stacks are formed by molecules in the neighboring layers, and the layers are superimposed in such a way that a stair-like motif is obtained.
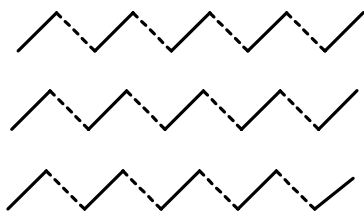
The crystal structure of compound **Ia** is characterized by the existence of hydrophilic domains formed by methoxy groups of the neighboring molecules. Presumably, just the formation of large hydrophilic domains prevents stack-like packing which is more typical of conjugated organic systems than stair motif.

Packing of molecules **Ib** in crystal is shown in Fig. 3. Here, conjugated parts of molecules give rise to a stair–parquet motif. The crown ether moieties in
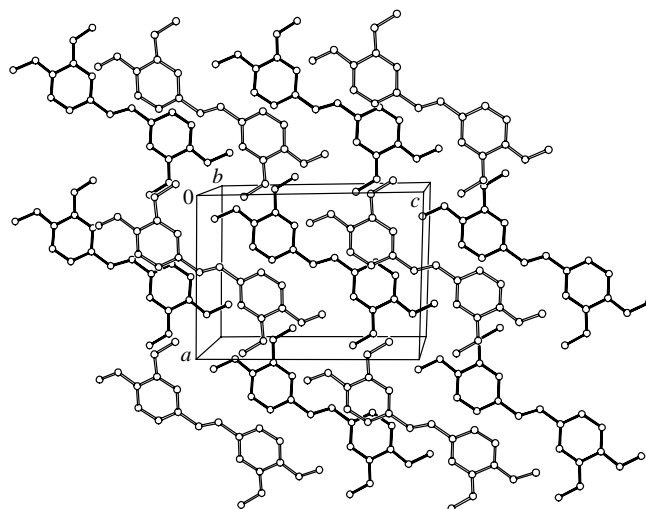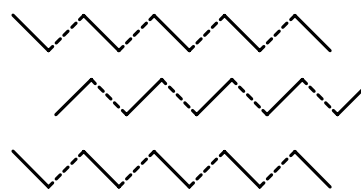
Fig. 2. Two layers of crystal packing of stilbene **Ia**.

the crystal structure of stilbene **Ib** are arranged close to each other, thus forming extended hydrophilic areas.

The tendency to form hydrophilic domains reaches a limit in the crystal structures of stilbenes **Ic** and **Id**, which are characterized by generally similar packing motifs (Figs. 4, 5). It becomes obvious that the principal packing requirement of crown ether fragments is formation of double hydrophilic layers.
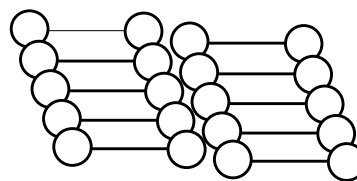
In no case conjugated fragments are packed in stacks, for stack-like motif (a) rules out contact between the stilbene fragments. The only way of ensuring contact between the stilbene fragments is packing according to stair-like motif (b) as shown below:
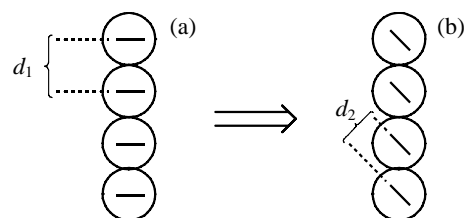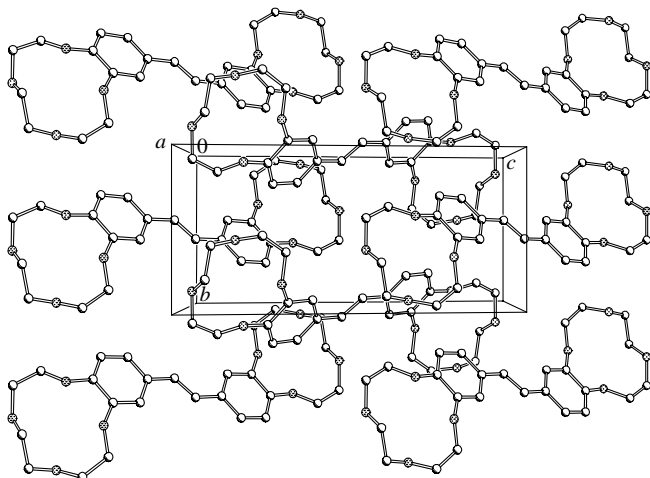
Fig. 3. Crystal packing of stilbene **Ib**.

Here, the dumbbells denoting crown-containing stilbene molecules are shown in a different projection (butt-end view), and the line inside the dumbbell is the projection of the planar stilbene fragment. Obviously, the distance d_2 is shorter than d_1, i.e., only stair-like arrangement of the conjugated fragments ensures formation of tightly packed areas in crystal, taking into account weak contacts between the polyether moieties typical of crown ethers.

Fine structure of organic molecules and their assemblies in solution and in crystal can be established by NMR spectroscopy [17]. Comparison of the NMR data with the structure of a series of homologous compounds, determined by crystallographic analysis, was rarely performed, for it was impossible to obtain suitable crystals for the whole series. As concerns bis-crown-containing stilbenes, study of their conforma-
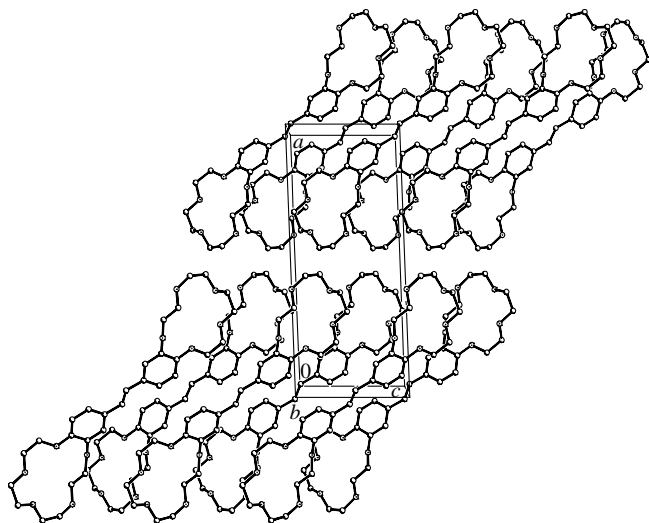

Fig. 4. Crystal packing of stilbene **Ic**.

tional behavior in solution is very important for structure determination of supramolecular systems based thereon [9–13]. Therefore, we examined structural parameters of stilbenes **Ia**–**Id** with the aid of various NMR techniques.

Stilbenes **Ia**–**Id** in crystal exist as symmetric *syn,syn* or *anti,anti* conformers (Fig. 1), presumably due to requirements imposed on their structure to ensure the tightest packing of their molecules. In going to solution, fast equilibrium may establish between the *anti,anti*, intermediate unsymmetrical *syn,anti*, and *syn,syn* conformers (Scheme 3) by analogy with crown-containing styryl and butadienyl dyes studied previously [5, 18]. Unfortunately, the NOESY spectra did not allow us to estimate the fraction of each particular conformer of compounds **I** because of strong interaction between the ethylene protons and both 3-H and 7-H in all conformers (for atom numbering, see Schemes 1 and 2 and Fig. 1). An indirect evidence in favor of *syn,syn* conformers can be derived from the positions of signals of the 3-H and 7-H protons in the benzene ring, which occupy *ortho* positions with respect to the ethylene group. The 7-H proton is also located in the *ortho* position with respect to the strong electron-donor alkoxy group; therefore, its signal should appear in a stronger field relative to the 3-H signal. However, the opposite pattern was observed really; i.e., the 7-H signals in the ^{1}H NMR spectra of stilbenes **Ia**–**Id** were located in a weaker field (by 0.02–0.06 ppm) relative to those belonging to 3-H. This situation is possible when the 7-H proton suffers from deshielding effect by the ethylene fragment, i.e., more compact *syn,syn* conformer of **Ia**–**Id** predominates in the equilibrium mixture. Signals from the CH_2O protons in the crown ether moieties of compounds **Ib**–**Id** are successively displaced upfield as the distance to the benzene ring increases. According to the NOESY spectra, the most downfield CH_2OAr (CH_3OAr) signals are those from the CH_2O^2 (CH_3O^2 in **Ia**) group which (as well as aromatic 7-H proton) fall into the area deshielded by the C=C bond in *syn,syn* conformers.

Compounds **Ia**–**Id** in solution in $CDCl_3$ and in the crystalline state were studied by ^{13}C NMR spectroscopy. Table 3 contains the carbon chemical shifts and the differences $\Delta\delta_C$ in going from crystal to solution.

The positions of signals from analogous ^{13}C nuclei in stilbenes **Ic** and **Id** in solution almost are almost similar, indicating their similar conformational compositions and, probably, the absence of appreciable

Scheme 3.

anti,anti *syn,anti* *syn,syn*
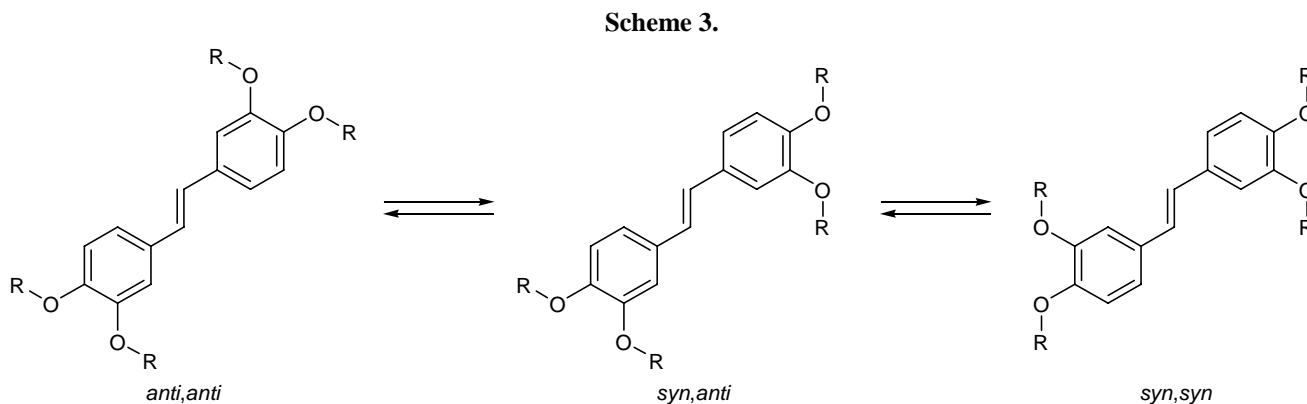
strain in the macrocyclic fragments. In the ^{13}C NMR spectrum of homologous bis(12-crown-4)–stilbene **Ib**, signals from all sp^2-hybridized carbon atoms are displaced downfield relative to the corresponding signals of compounds **Ic** and **Id**, the greatest shifts being observed for C^4 and C^7 (up to 4.0 ppm). Obviously, this pattern results from considerable steric strains in the 12-membered polyether rings of **Ib**, which force LEPs of the O^1 and O^2 atoms out of conjugation with the aromatic system. This is consistent with the X-ray diffraction data (Fig. 1). The positions of most carbon signals in the spectrum of tetramethoxystilbene **Ia** are almost the same as in the spectra of **Ic** and **Id**. Exceptions are the C^4 and C^7 signals which are displaced upfield by 2.7–3.2 ppm. Presumably, methoxy groups are stronger electron donors than alkoxyethoxy, and this effect is reflected in δ_C of the carbon atoms in the *ortho* positions with respect to those groups.

The ^{13}C NMR spectra of all stilbenes **Ia–Id** in the solid state contain a single set of relatively narrow signals (Table 3). Signals from the methylene carbon atoms of crown-containing stilbenes **Ib–Id** give rise to a broad band in the region of δ_C 71 ppm with several poorly resolved maxima. The strongest differences in the solid-state ^{13}C NMR spectra of stilbenes **Ia–Id** are observed in the aromatic region (Fig. 6). As follows from the X-ray diffraction data, the carbon signals belong to *syn,syn* conformers of **Ia** and **Ib** and *anti,anti* conformers of **Ic** and **Id**. Taking into account that rigorous assignment of signals in ^{13}C NMR spectra of solid substances is impossible, approximate assignment was made on the basis of the X-ray diffraction data and comparison with the spectra of their solutions. In going from the solid state to solution, the $|\Delta\delta_C|$ values for most carbon nuclei do not exceed 2.6 ppm. However, the C^3 and C^7 signals are displaced by 6 ppm (except for stilbene **Ic** possessing an unusual conformation of the crown ether fragments in crystal). The

overall variations $|\Delta\delta_C|$ for C^3 and C^7 in **Ia**, **Ib**, and **Id** amount to ~8 ppm, in keeping with the corresponding δ_C values for *anti,anti* and *syn,syn* conformers in crystal. In going from crystal to solution, the C^7 signals of **Ia** and **Ib** shift downfield while the C^3 signals are displaced upfield; the opposite pattern is observed for stilbenes **Ic** and **Id**. The behavior of δ_{C3} and δ_{C7} is consistent with the existence of conformational equilibrium in solution; however, the predominant conformer cannot be determined with certainty on the basis of these data. Presumably, ^{13}C chemical shifts of stilbenes **Ia–Id** strongly depend on the mode of crystal packing whose contribution to $\Delta\delta_C$ is difficult to estimate.

In order to determine the most favorable conformer of the chromophore fragment in (*E*)-stilbenes **Ia–Id** we performed quantum-chemical calculations of the
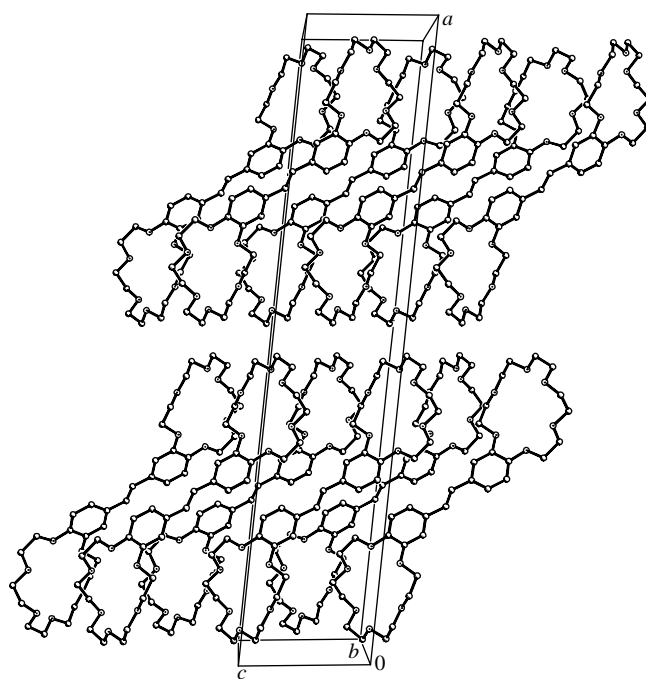
Fig. 5. Crystal packing of stilbene **Id**.

Table 3. ^{13}C NMR spectra of stilbenes **Ia–Id** in solution and in the solid state,[a] δ_C, ppm

Comp. no.	C^7	C^4	C^3	C^2	C^6	C^5	CH=CH	C$^\alpha$ (Me)	C$^{\alpha'}$ (Me)	C$^\beta$, C$^{\beta'}$	C$^\gamma$, C$^\delta$, C$^\varepsilon$
Ia[b]	108.78	111.38	119.56	130.74	149.20	148.77	126.68	55.97	55.88		
Ia[c]	103.9	110.7	123.2	128.1	149.0	149.0	124.7	56.2	53.4		
Ia $(\Delta\delta)$[d]	4.9	0.7	–3.6	2.6	0.2	–0.2	2.0	–0.2	2.4		
Ib[b]	115.81	117.96	121.30	132.43	150.71	150.29	126.99	71.70	71.97	69.94	71.17, 71.27
Ib[c]	113.1	114.4	126.2	132.2	151.5	150.7	126.2	72.2			
Ib $(\Delta\delta)$[d]	2.8	3.6	–4.9	0.2	–0.8	–0.4	0.8	–0.3 to –2.6			
Ic[b]	111.80	114.12	120.10	131.23	149.31	148.91	126.72	69.13	69.24	69.63, 69.67	70.56, 70.59, 71.12
Ic[c]	123.8	114.4	118.5	128.6	151.1	149.9	124.8	71.2			
Ic $(\Delta\delta)$[d]	–12.0	–0.3	1.6	2.6	–1.8	–1.0	1.9	–0.1 to –2.1			
Id[b]	111.96	114.30	120.10	131.25	149.15	148.76	126.70	69.24	69.29	69.69, 69.70	70.78, 70.85
Id[c]	114.1	114.1	114.1	128.7	149.7	147.7	125.3	70.6			
Id $(\Delta\delta)$[d]	–2.1	0.2	6.0	2.6	–0.5	1.1	1.4	–1.4 to 0.3			

[a] Approximate assignment for the solid state.
[b] Solution in CDCl$_3$, c = 0.05 M, 30°C.
[c] Solid state, room temperature.
[d] $\Delta\delta = \delta$(solution) – δ(solid).
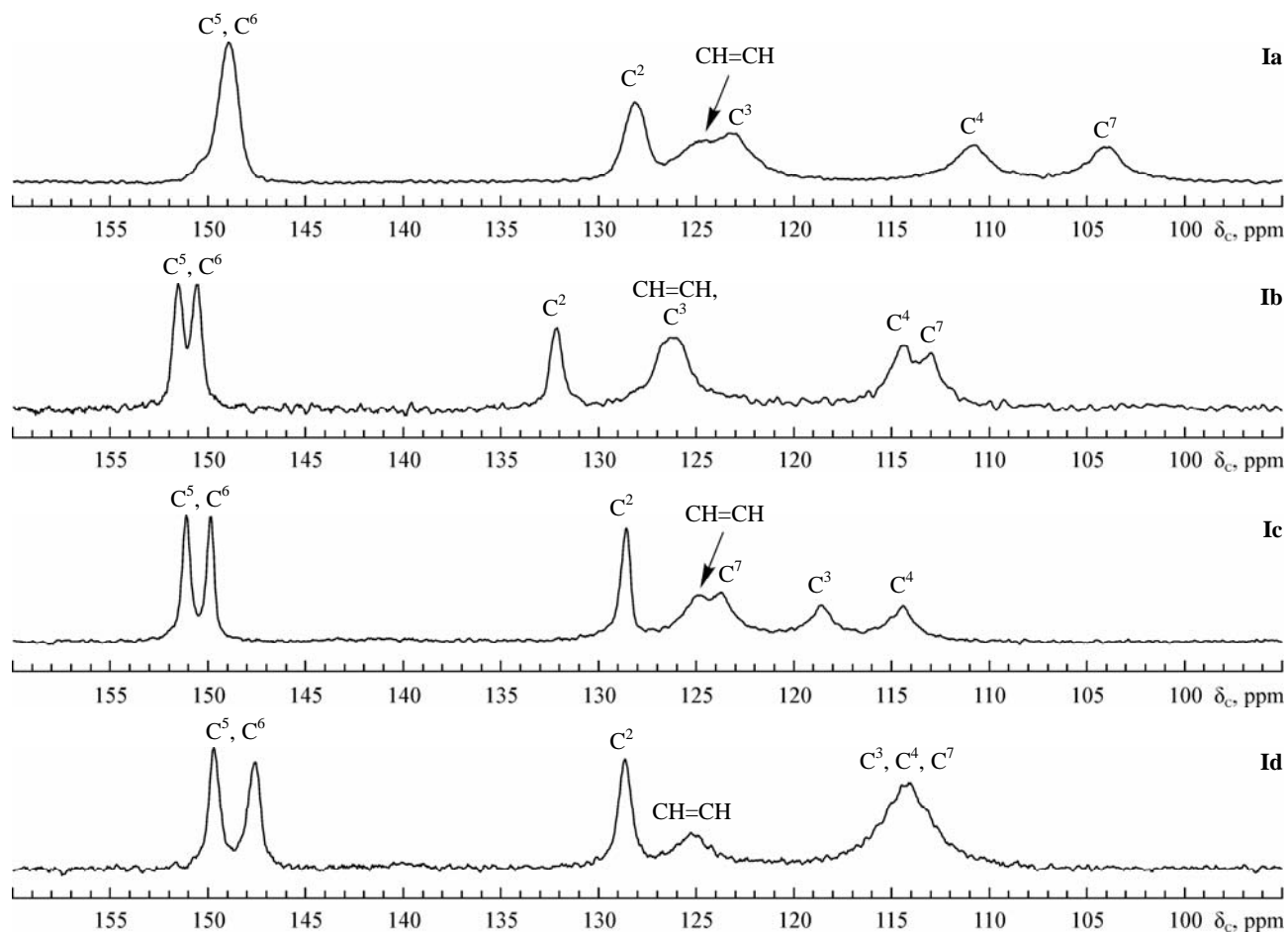
Fig. 6. Solid-state ^{13}C NMR spectra of stilbenes **Ia–Id** in the aromatic region.

Table 4. Parameters of X-ray analysis and crystallographic data for compounds **Ia**–**Id**

Parameter	Ia	Ib	Ic	Id
Molecular formula	$C_{18}H_{20}O_4$	$C_{26}H_{32}O_8$	$C_{30}H_{40}O_{10}$	$C_{34}H_{48}O_{12}$
Molecular weight	300.34	472.53	560.62	648.72
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a, Å	8.9484(5)	10.0733(6)	19.4172(8)	42.778(2)
b, Å	6.7152(3)	7.2364(4)	8.3901(4)	9.0073(3)
c, Å	12.4323(7)	16.1510(8)	8.5481(4)	8.6096(3)
β, deg	92.500(3)	97.464(2)	92.262(2)	95.988(2)
V, Å^3	746.35(7)	1167.34(11)	1391.51(11)	3299.3(2)
Z	2	2	2	4
ρ_{calc}, g/cm^3	1.336	1.344	1.338	1.306
$F(000)$	320	504	600	1392
$\mu(MoK_\alpha)$, mm^{-1}	0.094	0.099	0.100	0.098
Crystal habit, mm	0.36×0.24×0.10	0.36×0.26×0.22	0.38×0.32×0.06	0.56×0.40×0.02
Temperature, K	120.0(2)	120/0(2)	120.0(2)	100.0(2)
Scan range θ, deg	2.28–23.26	2.04–30.00	1.05–27.50	2.31–26.00
Reflection index range	$-8 \le h \le 9$, $-7 \le k \le 7$, $-13 \le l \le 12$	$-8 \le h \le 14$, $-10 \le k \le 10$, $-22 \le l \le 14$	$-25 \le h \le 25$, $-10 \le k \le 8$, $-10 \le l \le 11$	$-43 \le h \le 52$, $-11 \le k \le 11$, $-10 \le l \le 10$
Total number of reflections	2775	8279	8143	9016
Number of independent reflections	1064 ($R_{int} = 0.0278$)	3344 ($R_{int} = 0.0221$)	3172 ($R_{int} = 0.0534$)	3184 ($R_{int} = 0.0679$)
Number of reflections with $I > 2\sigma(I)$	1064	2553	2071	2135
Number of refined parameters	141	218	245	305
Divergence factors R [$I > 2\sigma(I)$]	$R_1 = 0.0339$, $wR_2 = 0.0844$	$R_1 = 0.0425$, $wR_2 = 0.1163$	$R_1 = 0.1025$, $wR_2 = 0.2409$	$R_1 = 0.0435$, $wR_2 = 0.0839$
Divergence factors (all reflections)	$R_1 = 0.0448$, $wR_2 = 0.0892$	$R_1 = 0.0579$, $wR_2 = 0.1287$	$R_1 = 0.1545$, $wR_2 = 0.2637$	$R_1 = 0.0829$, $wR_2 = 0.0949$
Reliability with respect to F^2	1.008	1.029	1.096	1.015
Residual electron density (min/max), e/Å^3	–0.149/0.168	–0.188/0.364	–0.505/1.829	–0.202/0.210

syn,*syn* and *anti*,*anti* conformers of the simplest representative, tetramethoxystilbene **Ia**, in terms of the density functional theory (DFT). Molecule **Ia** contains no flexible macrocyclic fragments which could give rise to numerous local minima on the potential energy surface; calculations of conformations of such structures often give inaccurate results, for these local minima may be close to global. The calculated bond lengths and bond angles in the *syn*,*syn* conformer of **Ia** were in a good agreement with the corresponding parameters determined by X-ray analysis: the maximal

differences between the theoretical and experimental values were 0.013 Å and 0.6°, respectively. A slight difference was observed between the calculated and experimental dihedral angles between the ethylene bond and benzene ring planes (7.8°), as well as for the torsion angles $COC_{Ar}C_{Ar}$ (9.5 and 11.7°). This difference is likely to result from the effect of crystalline field on the structure of stilbene **Ia**. The calculations showed that the *syn*,*syn* conformer of **Ia** is thermodynamically more stable than the *anti*,*anti* conformer by 0.65 kcal/mol. According to the Boltzmann formula,

the ratio of the *syn,syn* and *anti,anti* conformers in equilibrium mixture at room temperature should be 75:25 (with no account taken of solvation effects).

Interconversion of the conformers is controlled by the height of the energy barrier to rotation about the formally single C^1–C^2. The barrier calculated by the DFT method as the energy of transition state for internal rotation was 5.0 kcal/mol in going from the *syn,syn* conformer to *syn,anti* and 5.6 kcal/mol in going from the *anti,anti* conformer to *syn,anti*. These values are approximately twice as high as the barrier to rotation about a single C–C bond in alkanes. The barrier for stilbene **Ia** is higher due to conjugation between the double bond and the benzene ring, which increases π-order of the C^1–C^2 bond. However, this barrier is insufficient to considerably hamper interconversion of the conformers under standard conditions, and both conformers are present in the equilibrium mixture.

Thus we have developed an effective procedure for the synthesis of symmetric bis-crown-fused stilbenes from accessible benzocrown ethers. Conformational analysis of the synthesized stilbenes using the X-ray diffraction data and NMR spectroscopy has revealed specific structural features of crown–stilbenes in the crystalline state and in solution. The results of quantum-chemical calculations have shown that the *syn,syn* conformation of the conjugated fragment in (*E*)-stilbenes possessing four alkoxy substituents is more favorable.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500.13 and 125.76 MHz, respectively, from solutions in CDCl$_3$ and DMSO-d_6 at 30°C; the chemical shifts were measured relative to the corresponding solvent signals (δ 7.27 and 2.50 ppm; δ$_C$ 77.00 ppm); the signals were assigned using homonuclear two-dimensional ^1H–^1H COSY and NOESY spectra and heteronuclear ^1H–^{13}C COSY (HSQC and HMBC) spectra. The chemical shifts were determined with an accuracy of 0.01 ppm, and the coupling constants, with an accuracy of 0.1 Hz. High-resolution solid-state ^{13}C NMR spectra were obtained at room temperature on a Bruker MSL 300 spectrometer (75.47 MHz) with spinning at a magic angle and using the cross-polarization technique (cross-polarization period 1 μs) and powerful decoupling from protons. In all experiments, ZrO$_2$ rotors with a diameter of 7 mm were used; they were rotated at

a rate of 5.2 kHz with a stream of air. The ^{13}C chemical shifts were determined by substitution relative to the high-frequency line of solid glycine (δ$_C$ 176.03 ppm) and were measured with an accuracy of 0.1 ppm. The mass spectra (electron impact, 70 eV) were recorded on a Varian MAT-311A instrument with direct sample admission into the ion source. The elemental compositions were determined at the Microanalysis Laboratory (Nesmeyanov Institute of Organometallic Compounds, Russian Academy of Sciences, Moscow). Benzocrown ethers **IIb**–**IId** were synthesized by the procedure described in [19]. Bromoacetaldehyde diethyl acetal was purchased from Aldrich.

2-Bromo-1,1-bis(3,4-dimethoxyphenyl)ethane (III). Bromoacetaldehyde diethyl acetal, 3.76 ml (0.025 mol), was added to a solution of 6.36 ml (0.05 mol) of 1,2-dimethoxybenzene (**IIa**) in 8 ml of glacial acetic acid. The mixture was cooled to 0°C, and a mixture of 6 ml of glacial acetic acid and 11 ml of concentrated sulfuric acid was added over a period of 30 min at such a rate that the temperature did not exceed 10°C. The mixture was then stirred for 15 min and poured into 100 ml of water. An oily substance separated and was extracted into chloroform (3× 75 ml), and the extract was washed in succession with water, a solution of Na$_2$CO$_3$, and water again, dried over Na$_2$SO$_4$, and evaporated under reduced pressure to isolate 8.62 g of crude bromoethane **III** as a greenish viscous oily substance (purity >90%, according to the NMR data). ^1H NMR spectrum (DMSO-d_6, 30°C), δ, ppm: 3.71 s (6H, MeO), 3.74 s (6H, MeO), 4.11 d (2H, CH$_2$Br, J = 7.9 Hz), 4.25 t (1H, CH, J = 7.9 Hz), 6.86 br.s (4H, 5-H, 6-H), 6.99 br.s (2H, 2-H). Mass spectrum, m/z (I_{rel}, %): 382/380 (15/16) [M]$^+$, 301 (12), 300 (91), 288 (10), 287 (100), 285 (24), 273 (13), 82 (12), 80 (13), 58 (31).

(*E*)-1,2-Bis(3,4-dimethoxyphenyl)ethene (Ia). A solution of 1.35 g of crude bromoethane **III** in 12 ml of 1-pentanol was heated for 6 h under reflux. After cooling, the precipitate was filtered off, washed with 1-pentanol, and dried in air. Yield 0.53 g (50%, calculated on the initial compound **IIa**), slightly yellowish crystals, mp 148–150°C; published data [7]: mp 149–152°C. ^1H NMR spectrum (CDCl$_3$, 30°C, c = 0.05 M), δ, ppm: 3.91 s (6H, 1-OCH$_3$), 3.95 s (6H, 2-OCH$_3$), 6.87 d (2H, 4-H, J = 8.2 Hz), 6.93 s (2H, CH=CH), 7.05 d.d (2H, 3-H, J = 8.2, 1.8 Hz), 7.07 d (2H, 7-H, J = 1.8 Hz).

Stilbenes Ib–Id (*general procedure*)**.** Freshly distilled bromoacetaldehyde diethyl acetal, 3.76 ml

(0.025 mol), was added to a solution of 0.05 mol of benzocrown ether **IIb**–**IId** in 8 ml of glacial acetic acid, the mixture was cooled to 0°C, and a mixture of 6 ml of glacial acetic acid and 11 ml of concentrated sulfuric acid was added over a period of 15 min at such a rate that the temperature did not exceed 10°C. The mixture was stirred for 2 h at 10°C and poured into 100 ml of water. An oily material separated and was extracted with $CHCl_3$ (3×75 ml), and the extract was washed in succession with water, a solution of Na_2CO_3, and water again, dried over $MgSO_4$, and evaporated under reduced pressure to isolate the corresponding 1,1-disubstituted 2-bromoethane as a viscous oily substance. 1-Pentanol, 75 ml, was added to the product, and the mixture was heated for 6 h under reflux. After cooling, the precipitate was filtered off and heated with 100 ml of boiling ethanol. The mixture was cooled, and the precipitate was filtered off and dried in air.

(*E*)-1,2-Bis[3,4-(3,6-dioxaoctamethylenedioxy)-phenyl]ethene (Ib). Yield 9.3 g (72%), mp 183–185°C. ^{1}H NMR spectrum ($CDCl_3$, 30°C, c = 0.05 M), δ, ppm: 3.81 s (8H, γ-CH_2O), 3.88 m (8H, β-CH_2O, β'-CH_2O), 4.20 m (4H, α-CH_2O), 4.23 m (4H, α'-CH_2O), 6.88 s (2H, CH=CH), 6.95 d (2H, 4-H, *J* = 8.2 Hz), 7.08 d.d (2H, 3-H, *J* = 8.2, 1.8 Hz), 7.14 d (2H, 7-H, *J* = 1.8 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 472 (91) [*M*]$^+$, 296 (57), 240 (22), 223 (13), 212 (18), 197 (13), 133 (13), 105 (16), 73 (19), 58 (100). Calculated, %: C 66.09; H 6.83. $C_{26}H_{32}O_8$. Found, %: C 66.01; H 6.89.

(*E*)-1,2-Bis[3,4-(3,6,9-trioxaundecamethylenedioxy)phenyl]ethene (Ic). Yield 10.3 g (73%), mp 190–192°C [7]. ^{1}H NMR spectrum ($CDCl_3$, 30°C, c = 0.05 M), δ, ppm: 3.77 br.s (16H, γ-CH_2O, δ-CH_2O), 3.93 m (8H, β-CH_2O, β'-CH_2O), 4.16 m (4H, α-CH_2O), 4.20 m (4H, α'-CH_2O), 6.85 d (2H, 4-H, *J* = 8.3 Hz), 6.87 s (2H, CH=CH), 7.01 d.d (2H, 3-H, *J* = 8.3, 1.6 Hz), 7.05 d (2H, 7-H, *J* = 1.6 Hz).

(*E*)-1,2-Bis[3,4-(3,6,9,12-tetraoxatetradecamethylenedioxy)phenyl]ethene (Id). Yield 11.3 g (70%), mp 154–156°C [7]. ^{1}H NMR spectrum ($CDCl_3$, 30°C, c = 0.05 M), δ, ppm: 3.69 s (8H, ε-CH_2O), 3.73 m (8H, δ-CH_2O), 3.78 m (8H, γ-CH_2O), 3.93 m (4H, β-CH_2O), 3.95 m (4H, β'-CH_2O), 4.18 m (4H, α-CH_2O), 4.22 m (4H, α'-CH_2O), 6.86 d (2H, 4-H, *J* = 8.3 Hz), 6.87 s (2H, CH=CH), 7.01 d.d (2H, 3-H, *J* = 8.3, 1.7 Hz), 7.06 d (2H, 7-H, *J* = 1.7 Hz).

Study of the solvent and temperature effects on the yield of stilbene (Ic). 2-Bromoethane **IIIc** pre-pared from 64.3 g (0.24 mol) of benzo-15-crown-5 (**IIc**) according to the procedure described above was divided into 12 equal portions. Appropriate solvent, 35 ml, was added to each portion, and the resulting solution was heated for 6 h under reflux or a portion of **IIIc** was heated without a solvent for 6 h at 135–140°C (5 mm). The mixture was cooled, and the precipitate was filtered off (in the reaction with acetic acid, the mixture was poured into 120 ml of water) and heated in 20 ml of boiling ethanol (except for the reaction in ethanol). The mixture was cooled, and the precipitate was filtered off and dried in air. The conditions and yields of compound **Ic** are given in Table 1.

X-Ray analysis. Single crystals of stilbenes **Ia**–**Id** were obtained by slow evaporation of their solutions in a mixture of hexane and methylene chloride. Measurements were performed on a Bruker SMART-6 CCD diffractometer (Mo$K_α$ irradiation, λ = 0.71073 Å). The structures were solved by the direct methods and were refined by the least-squares procedure in full-matrix anisotropic approximation. The crystallographic parameters and parameters of the X-ray diffraction experiments are collected in Table 4. All calculations were performed using SHELXTL-Plus software package [20].

Quantum-chemical calculations of the *syn,syn* and *anti,anti* conformers of stilbene **Ia** with full geometry optimization were performed by the DFT method (B3LYP/6-31G**//B3LYP/6-31G** basis set) using GAUSSIAN 98 software. The barrier to rotation about the C^1–C^2 bond was determined by calculating (with the same basis set) the structure and geometry of the corresponding transition state with account taken of zero-point vibration energy. Calculations of vibrational frequencies for a structure where the torsion angle between the C=C bond and the benzene ring is 89.3° revealed a single negative frequency, which is a necessary and sufficient condition for indicating attainment of a transition state.

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