Stereospecific solid-state [2+2] autophotocycloaddition of a styryl dye containing a 18-crown-6 fragment

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A procedure was developed for the synthesis of a 18-crown-6-containing styryl dye of the pyridine series. Phototransformation products of the dye that formed upon irradiation with visible light in solution, films, and crystals were studied by ^{1}H and ^{13}C NMR spectroscopy and spectrophotometry. Irradiation of solutions of this dye in acetonitrile leads only to reversible *E*—*Z* photoisomerization of the C=C bond. Irradiation of a film of the dye induces stereospecific [2+2] photocycloaddition to form exclusively the *rctt* isomer of tetrasubstituted cyclobutane. The latter was found to undergo base-catalyzed isomerization giving rise to the *rcct* isomer. X-ray diffraction study showed that photocycloaddition occurs in single crystals without their destruction. The structures of the *E* isomer of the dye and the resulting *rctt* isomer of the cyclobutane derivative were established. The characteristic features of the molecular packing of the dye favorable for topochemical photocycloaddition in the crystal and the structural changes that accompany the cyclobutane formation are discussed.

Key words: crown ethers, styryl dyes, structure, photoisomerization, photocycloaddition, topochemical single-crystal-to-single-crystal reaction, cyclobutanes.

Crown-ether-containing styryl and butadienyl dyes have a pronounced ability to undergo light-induced reversible transformations, such as geometric *E*—*Z* isomerization and [2+2] photocycloaddition.[1—5] So far, both photoprocesses have been observed only in solution, the presence of metal cations inducing self-assembly of dye molecules into dimeric complexes being a prerequisite for photocycloaddition of styryl dyes. The transformation giving rise to cyclobutane derivatives is characterized by better color contrast and more stable reaction products compared to *E*—*Z* isomerization. That is why photocycloaddition of styryl dyes holds considerable promise in data recording and storage systems.

Studies of stilbene derivatives and their aza analogues demonstrated that photocycloaddition occurs both in solution and in the solid state.[6—10] In the majority of cases, the compositions of photoproducts have not been thoroughly analyzed and remained uncharacterized because of the formation of stereoisomeric mixtures of cyclobutane derivatives that are difficult to separate. Yet another characteristic feature of photocycloaddition of compounds under consideration is that the reaction is induced by short-wavelength light. This complicates instrumentation for investigations and limits the possibility of using these photosensitive systems. In this connection, it is important to reveal structural requirements for the efficient solid-state stereospecific photocycloaddition of styryl dyes in the absence of metal ions that could allow the use of visible light.

In the present study, we synthesized a new crown-ether-containing styryl dye of the pyridine series **1** and characterized the products formed from compound **1** in solution and in the solid state upon irradiation with visible light.

Synthesis and spectroscopic studies

The synthesis of dye **1** is presented in Scheme 1. Condensation of the formyl derivative of benzo-18-crown-6 ether with 4-methylpyridine was carried out in dry DMF

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1896—1908, August, 2005.

in the presence of potassium *tert*-butoxide as a catalyst[11] to give the previously unknown crown-ether-containing 1-(4-pyridyl)-2-arylethylene **2** in 77% yield. The target dye **1** was synthesized by fusion of compound **2** with ethyl *p*-toluenesulfonate followed by the replacement of the anion by perchlorate upon treatment with perchloric acid (the total yield was 58%). According to the data from of ^{1}H NMR spectroscopy, compounds **1** and **2** were isolated as *E* isomers, as evidenced by the large coupling constants for the olefinic protons ($^3J_{HC=CH}$ = 16.2 and 16.4 Hz, respectively).

Dye *E*-**1** (a solution in acetonitrile) has a characteristic spectrum with a long-wavelength absorption maximum at 399 nm (logε = 4.49) associated with excited-state intramolecular charge transfer from the donor benzocrown fragment to the acceptor pyridinium moiety.[12] Irradiation of a solution of dye *E*-**1** with visible light brings about a rapid decrease in the intensity of the long-wavelength band without changes in the position of its maximum (Fig. 1, curves *1* and *2*). Evidently, visible light induces reversible *E*—*Z* isomerization of the C=C bond of the dye (Scheme 2). This type of photoreaction has been observed for all crown-containing styryl dyes studied earlier.[3]

The formation of the *Z* isomer of dye **1** was proved by studying the ^{1}H NMR spectra of a photostationary mixture. The assignment of the signals is shown in Fig. 2, *b*. The signals for the protons of the ethylene fragment of *Z*-**1** appear as two doublets with the characteristic coupling constants of 12.1 Hz. The *E* : *Z* isomer ratio estimated from the comparison of the integrated intensities of the signals for the aromatic protons is 1.80 : 1 and it remains unchanged upon prolonged storage of the sample in DMSO-d_6 in the dark. This suggests that dark *Z*→*E* isomerization of the *Z* isomer of **1** occurs at a negligibly low rate. A decrease in the intensity of absorption at

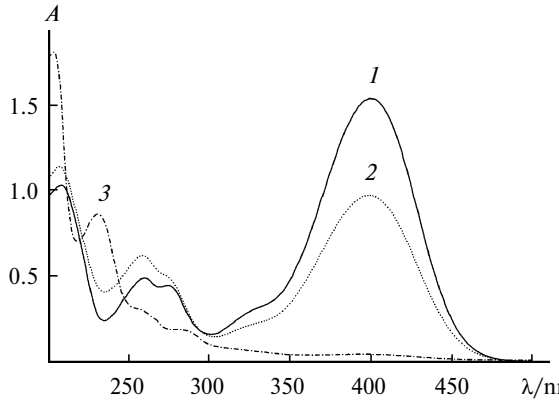
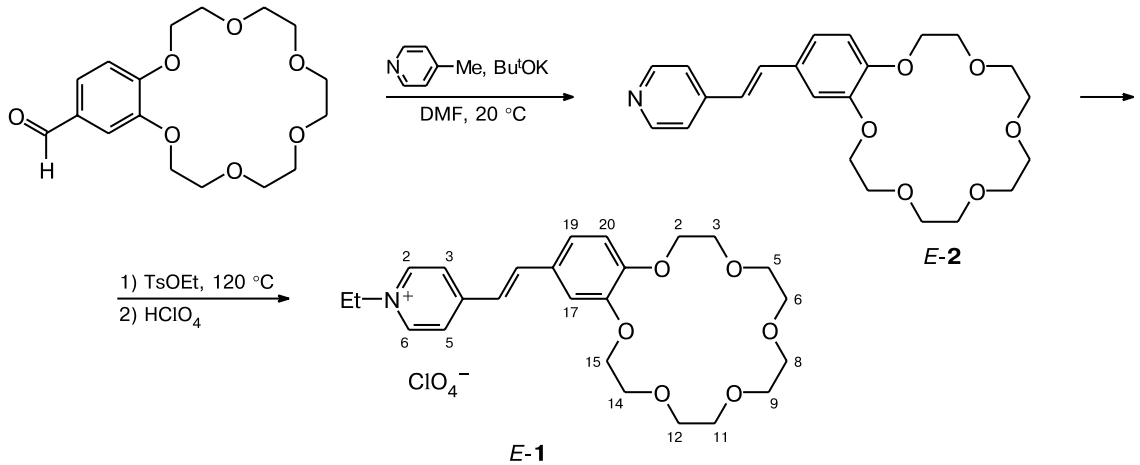


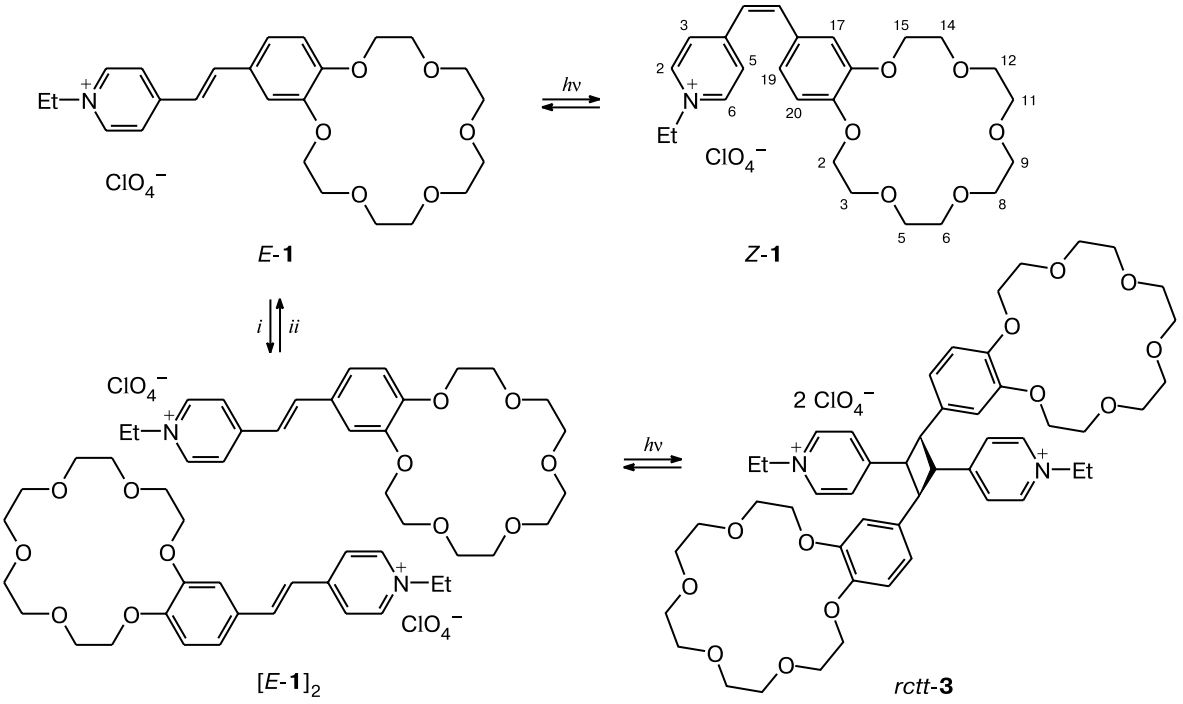
Fig. 1. Electronic absorption spectra of *E*-**1** in acetonitrile (*1*) ($C = 5.0 \cdot 10^{-5}$ mol L^{-1}), a photostationary mixture after irradiation of *E*-**1** with light using an incandescent bulb (60 W) at a distance of 15 cm for 10 min (*2*), and cyclobutane *rctt*-**3**, which was prepared by irradiation of *E*-**1** in a thin film for 40 h (*3*) ($C = 2.5 \cdot 10^{-5}$ mol L^{-1}).

399 nm of the photostationary state to 64% compared to that of pure *E*-**1** (see Fig. 1, curve *2*) corresponds with high accuracy to a decrease in the percentage of the *E* isomer in the reaction mixture (NMR spectroscopic data). Hence, *Z*-**1** shows insignificant absorption, if at all, at 399 nm. This conclusion enabled us to approximately calculate the spectrum of the *Z* isomer, whose long-wavelength absorption maximum is hypsochromically shifted relative to that of *E*-**1** to ~360 nm (logε = 3.4). Thus, a change in the geometry of the *Z* isomer of the dye molecule compared to that of the *E* isomer leads to a substantial decrease in conjugation in the chromophoric fragment and, apparently, to a twist of this fragment due to steric interaction of the bulky aromatic substituents at the ethylene bond. This is reflected in the ^{1}H NMR spectrum as upfield shifts of signals for the majority of the protons,

Scheme 1



Scheme 2



[*E*-**1**]$_2$ is a *syn*-"head-to-tail" dimeric pair

i. In the crystal. *ii*. In solution.

the most substantial shifts being observed for the protons of the unsaturated fragments (up to 1.26 ppm).

It should be noted that no other photoproducts are formed upon prolonged irradiation of a solution of **1** in acetonitrile after establishment of the photostationary state (NMR control).

Irradiation of dye *E*-**1** as a thin film substantially differed from that in solution. In the spectrum of the resulting photoproduct, the long-wavelength absorption band at 400 nm (see Fig. 1, curve *3*) disappeared, which suggests disturbance of the conjugation in styryl chromogen **1**. Studies by ^{1}H and ^{13}C NMR spectroscopy demonstrated that dye **1** almost completely disappeared and one product was present in the reaction mixture. A fragment of the ^{1}H NMR spectrum of this product is shown in Fig. 2, *c*. The signals for the atoms of the ethylene bond are absent in the aromatic region of the spectra. The ^{1}H (Fig. 3, *a*) and ^{13}C NMR spectra each had two new signals at about δ 5 and δ 45, respectively, whose positions are typical of cyclobutane derivatives formed upon photoirradiation of solutions of metal complexes of betaines of styryl dyes studied earlier.[1,4,13] Thus, the solid-state photoreaction of dye *E*-**1** gave a cyclobutane derivative as the only product, the presence of only one set of signals in the ^{1}H and ^{13}C NMR spectra being indicative of the formation of one stereoisomer.

The signals for the protons of the cyclobutane fragment of the resulting photoadduct appear as a symmetric AA´BB´ spin system with the vicinal coupling constants of 9.1 and 7.9 Hz. The formation of five isomers of tetrasubstituted cyclobutane from dye **1** is theoretically possible, and their spectra will be described by the AA´BB´ system. Four isomers can be formed upon photocycloaddition of the *E* or *Z* isomers of the dye closely arranged in *syn*- and *anti*-"head-to-head" dimeric pairs and should be characterized by multiplets for the protons of the cyclobutane ring. The fifth isomer can be formed upon photocycloaddition of *E*-**1** in the *syn*-"head-to-tail" dimeric pair, and the signals for the protons should appear as two doublets of doublets with the coupling constants of 8.97 and 6.78 Hz, which has been predicted by calculations for the analogous isomer of 1,2,3,4-tetraphenylcyclobutane.[13] Hence, the observed shapes of the signals at about δ 5 (see Fig. 3, *a*) and the similarity of the theoretical and experimental coupling constants suggest that the solid-state photocycloaddition afforded the *rctt* isomer of cyclobutane **3** (see Scheme 2). In the preexisted dimeric pair, two molecules of dye *E*-**1** should be arranged in a *syn*-"head-to-tail" fashion (see Scheme 2). This type of molecular packing seems to be most favorable from the point of view of the minimum Coulomb repulsion between two organic cations in the case of the

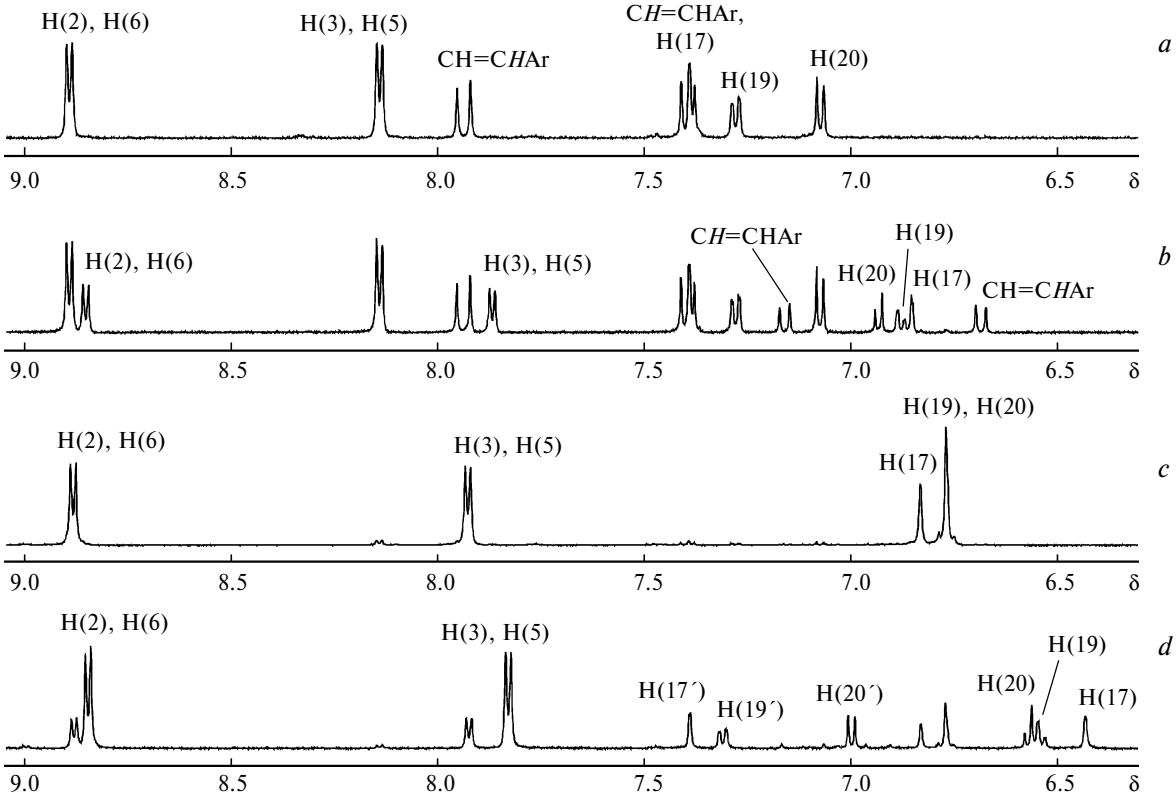


Fig. 2. The ^{1}H NMR spectra (aromatic region, $C \approx 5 \cdot 10^{-3}$ mol L^{-1}) in DMSO-d$_6$ at 30 °C: *a*, dye *E*-**1**; *b*, photoirradiation products of *E*-**1** in acetonitrile for 30 h (a photostationary mixture of the geometric isomers of **1**; the signals of only the *Z* isomer are indicated); *c*, a product obtained upon photoirradiation of *E*-**1** in a thin film for 40 h (*rctt*-**3**); *d*, products prepared by storage of a solution of cyclobutane *rctt*-**3** in commercial-grade acetonitrile for 2 weeks (a mixture of the *rctt* and *rcct* isomers of **3** in a ratio of 1 : 3.69; the signals of only the major *rcct* isomer are indicated).

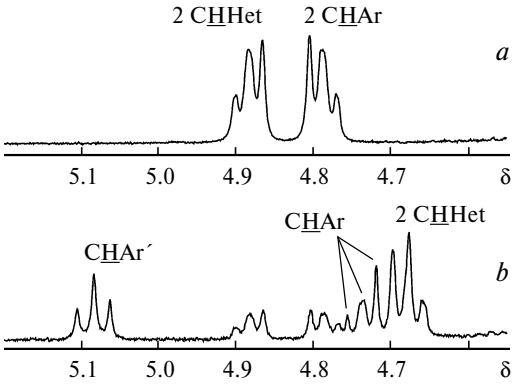


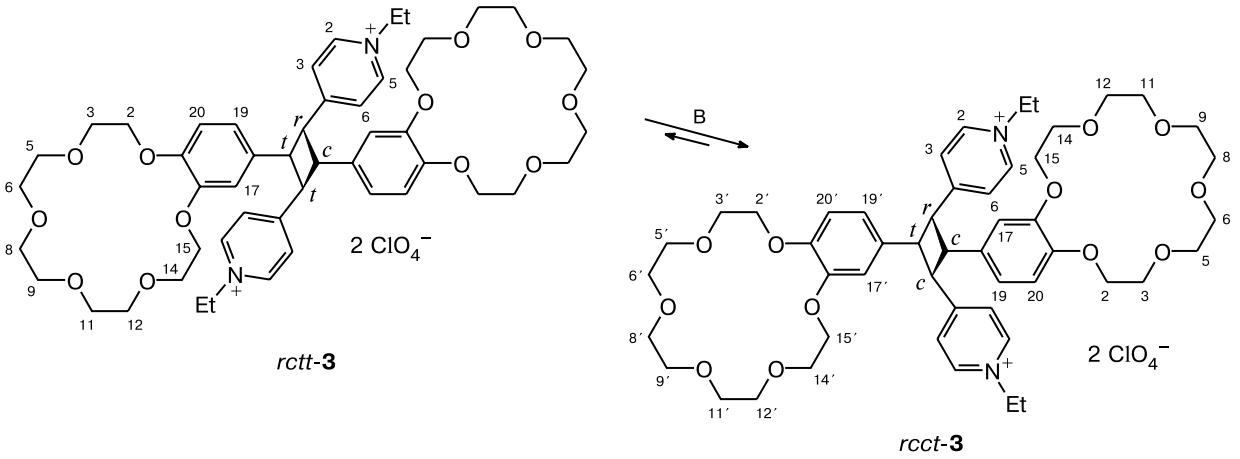
Fig. 3. The ^{1}H NMR spectra (aliphatic region, $C \approx 5 \cdot 10^{-3}$ mol L^{-1}) in DMSO-d$_6$ at 30 °C: *a*, a product of photoirradiation of *E*-**1** in a thin film for 40 h (*rctt*-**3**); *b*, products obtained upon storage of a solution of cyclobutane *rctt*-**3** in industrial acetonitrile for 2 weeks (a mixture of the *rctt* and *rcct* isomers of **3** in a ratio of 1 : 3.69; the signals of only the major *rcct* isomer are indicated).

maximum secondary orbital interaction between the p_z orbitals of their conjugated systems. The results of the spectroscopic study were confirmed by X-ray diffraction analysis.

Cyclobutane derivative *rctt*-**3** is storage-stable in the solid state and in solutions in acetonitrile and DMSO-d$_6$. Irradiation of these solutions with visible light did not lead to any changes in the structure of the photoproduct or the formation of the starting dye **1**. However, the use of the commercial-grade acetonitrile containing nucleophilic impurities as the solvent leads to gradual accumulation of a new product in solution. In the UV spectrum, this is manifested in a slight increase in the intensity with retention of the absorption profile.

An experiment on storage of *rctt*-**3** in pure acetonitrile with an admixture of pyridine confirmed the role of the base in this transformation. The ^{1}H and ^{13}C NMR spectra of the reaction mixture have, in addition to the minor signals of the starting isomer **3**, a new set of signals. Analysis of the COSY and NOESY spectra (Fig. 4) showed that the new signals belong to yet another isomer of cyclobutane **3**. The aromatic region of the ^{1}H (see Fig. 2, *d*) and ^{13}C NMR spectra of the new isomer have signals for two nonequivalent benzocrown fragments and two identical pyridine fragments. This spectral pattern should be

Scheme 3



rctt-**3** *rcct*-**3**

B is a base

observed for a cyclobutane derivative, where the configuration of the carbon atom bound to the pyridine fragment is inverted, *i.e.*, for isomer *rcct*-**3** (Scheme 3). Apparently, the presence of a base leads to deprotonation of the rather acidic protons of cyclobutane at the above-mentioned carbon atoms in **3**, which is responsible for the inversion of the arrangement of the pyridine fragment.

The spectrum of the cyclobutane fragment of the new isomer is described by the ABC_2 spin system (see Fig. 3, *b*) with the vicinal coupling constants of 8.1—10.6 Hz, which corresponds to the structure of *rcct*-**3**. It should be noted that one of the benzocrown fragments in isomer *rcct*-**3** should be fixed between two pyridine rings, which are *cis* with respect to one another, whereas the second benzocrown fragment is rather free. The protons of the *c* fragment are apparently shielded by two pyridine moieties due to which the signals for these protons appear at higher field (Δδ up to 0.40 ppm) compared to those of the starting *rctt*-**3**. To the contrary, the signals for the protons of the *t* fragment in *rcct*-**3** are shifted downfield (Δδ up

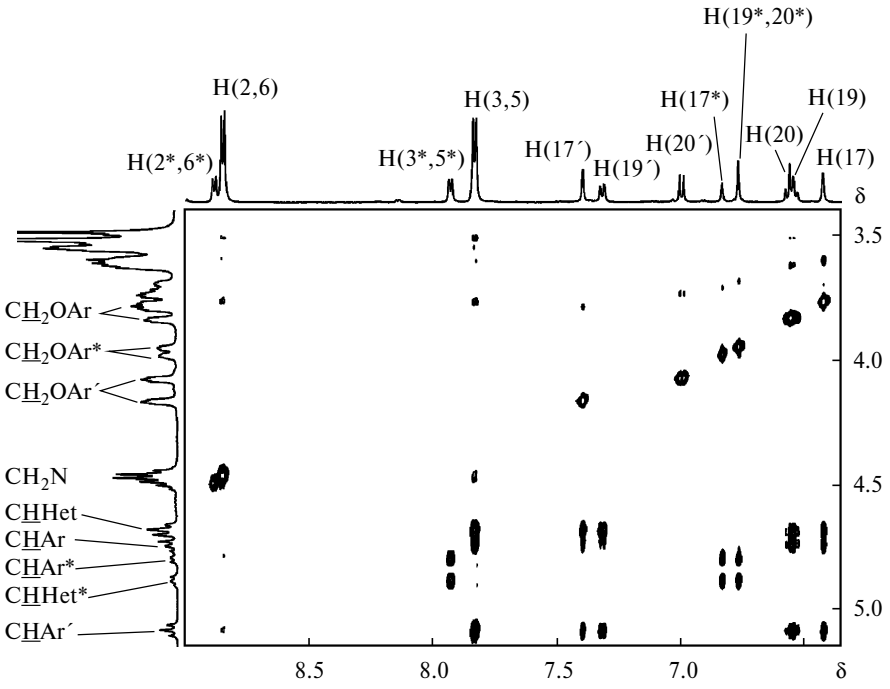


Fig. 4. The NOESY spectrum of a mixture of the *rctt* and *rcct* isomers of cyclobutane **3** in a ratio of 1 : 3.69 (C = 0.023 mol L^{-1}) in DMSO-d_6 at 30 °C; the signals of minor *rctt*-**3** are marked with asterisks.

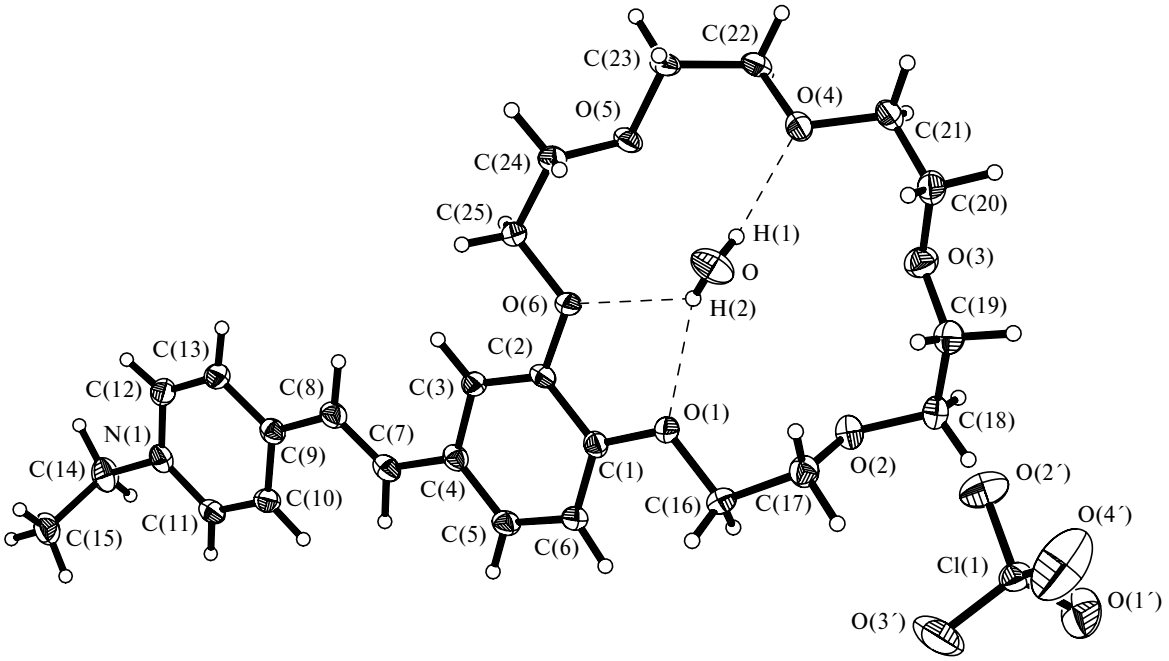


Fig. 5. Components of the asymmetric unit cell of **1** with displacement ellipsoids drawn at the 50% probability level.

to 0.56 ppm) compared to those of *rctt*-**3**, which reflects the absence of groups exhibiting considerable magnetic anisotropy in the vicinity of these protons.

It should be noted that we failed to completely convert the starting isomer of cyclobutane, *i.e.*, the base-catalyzed isomerization of **3** is reversible. In the case of a solution in commercial-grade acetonitrile, the final *rctt* : *rcct* isomer ratio (NMR data) was 1 : 3.69. In pure acetonitrile with an admixture of pyridine, the isomer ratio was 1 : 2.57. This difference may be associated with the specific effect of pyridine on *rctt*-**3**, which is proved by a decrease in the percentage of the *rcct* isomer in the reaction mixture obtained in commercial-grade acetonitrile after its storage in pure acetonitrile with addition of pyridine. The presence of the *rcct* isomer of cyclobutane **3** as the major product is apparently attributed to an optimum ratio between the axial and equatorial substituents in the cyclobutane ring compared to that in the *rctt* isomer.

X-ray diffraction analysis

We succeeded in preparing single crystals of dye **1** and performed X-ray diffraction study of **1**. Independent components of the unit cell are shown in Fig. 5. Selected geometric parameters of the cation of the dye are given in Table 1. The conjugated fragment of the cation is almost planar. The ethyl substituent at the nitrogen atom deviates from the plane of the pyridine ring by 72.8°. The crown-ether fragment includes a solvate water molecule, which forms hydrogen bonds with the O(1), O(6), and O(4) atoms of the crown ether. The corresponding geometric parameters of the hydrogen bonds are as follows: H(1)...O(4), 2.19 Å; O(4)...O, 2.94 Å; O(4)...H(1)—O, 161°; H(2)...O(1), 2.51 Å; H(2)...O(6), 2.59 Å; O(1)...O, 3.20 Å; O(6)...O, 3.14 Å; O—H(2)...O(1), 163°, O—H(2)...O(6), 136°. The H(2) atom of the solvate water molecule is involved in a weak bifurcated hydrogen bond with the O(1) and O(6) atoms.

The crystal packing of dye **1** (Fig. 6) is of particular interest. In the crystal structure, molecules **1** are packed in stacks along the crystallographic *b* axis. The conjugated systems of the cations in different stacks are inclined at different angles with respect to this axis. Any two adjacent molecules in the stack are arranged in a "head-to-tail" fashion and are related by centers of symmetry. The space group of the crystals of this compound ($P2_1/c$) contains two systems of inversion centers, the pairs of cations related by inversion centers of different systems alternating in the stack.

The "head-to-tail" stacking, *i.e.*, the packing in which the adjacent molecules in the stack are related by inversion centers, is one of the most typical packings of crown-containing styryl and butadienyl dyes.[5,14—16] This packing can be schematically represented as follows:

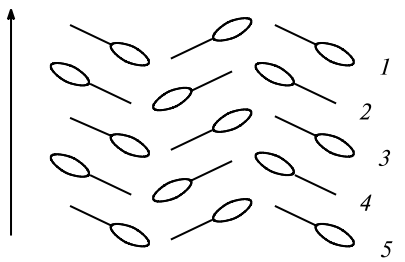


Table 1. Selected bond lengths (*d*), bond angles (ω), and dihedral angles (φ) in compound **1**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Angle	ω/deg
C(1)—C(2)	1.415(3)	O(1)—C(1)—C(2)	115.5(2)
C(2)—C(3)	1.379(3)	O(1)—C(1)—C(6)	125.4(2)
C(3)—C(4)	1.410(3)	O(6)—C(2)—C(1)	115.5(2)
C(4)—C(5)	1.393(3)	O(6)—C(2)—C(3)	124.7(2)
C(4)—C(7)	1.460(3)	C(3)—C(4)—C(5)	118.3(2)
C(5)—C(6)	1.390(3)	C(3)—C(4)—C(7)	122.9(2)
C(6)—C(1)	1.386(1)	C(5)—C(4)—C(7)	118.7(2)
C(7)—C(8)	1.336(3)	C(4)—C(7)—C(8)	127.8(2)
C(8)—C(9)	1.452(3)	C(7)—C(8)—C(9)	123.1(2)
C(9)—C(10)	1.400(3)	C(8)—C(9)—C(10)	122.8(2)
C(10)—C(11)	1.363(3)	C(8)—C(9)—C(13)	120.8(2)
C(11)—N(1)	1.348(3)	C(10)—C(9)—C(13)	116.4(2)
N(1)—C(12)	1.345(3)		
C(12)—C(13)	1.374(3)		
C(13)—C(9)	1.407(3)		

Angle	φ/deg
C(4)—C(7)—C(8)/C(7)—C(8)—C(9)	177.0
C(4)—C(7)—C(8)—C(9)/N(1), C(9)...C(13)	4.6
C(4)—C(7)—C(8)—C(9)/C(1)...C(6)	1.4
N(1),C(9)...C(13)/N(1)—C(14)—C(15)	72.8

Here the lines represent the conjugated moiety of the dyes and the ovals indicate their crown-ether fragments. In this stacking motif, the alternating pairs of the molecules overlap with each other in different fashions, because they are related by different inversion centers. Most often, the stacks are separated in pairs, *i.e.*, there are pairs of molecules characterized by more extensive overlap (stacking pairs, *2* and *3*, *4* and *5*). These pairs can be considerably shifted with respect to each other and their conjugated regions overlap only weakly (*1* and *2*, *3* and *4*).

The same separation of molecules of the stack in pairs is observed in **1**. In the stacking pair, the arrangement of the conjugated fragments of the dye molecules A and B is the closest (see Fig. 6). In the molecules belonging to the adjacent pairs (A and C, B and D), this refers only to the benzene rings. Two projections of the stacking pair are shown in Fig. 7. The distance between the mean planes of the styryl fragments of the molecules A and B is approximately equal to 3.37 Å. The distance between the atoms of the ethylene fragments C(7A)...C(8B) and C(7B)...C(8A) is 3.553 Å. The distance between the ethylene fragments of up to 4.2 Å and the parallel mutual arrangement of these fragments were considered[17,18] as the optimal parameters of the olefin dimer preceding photocyclo-

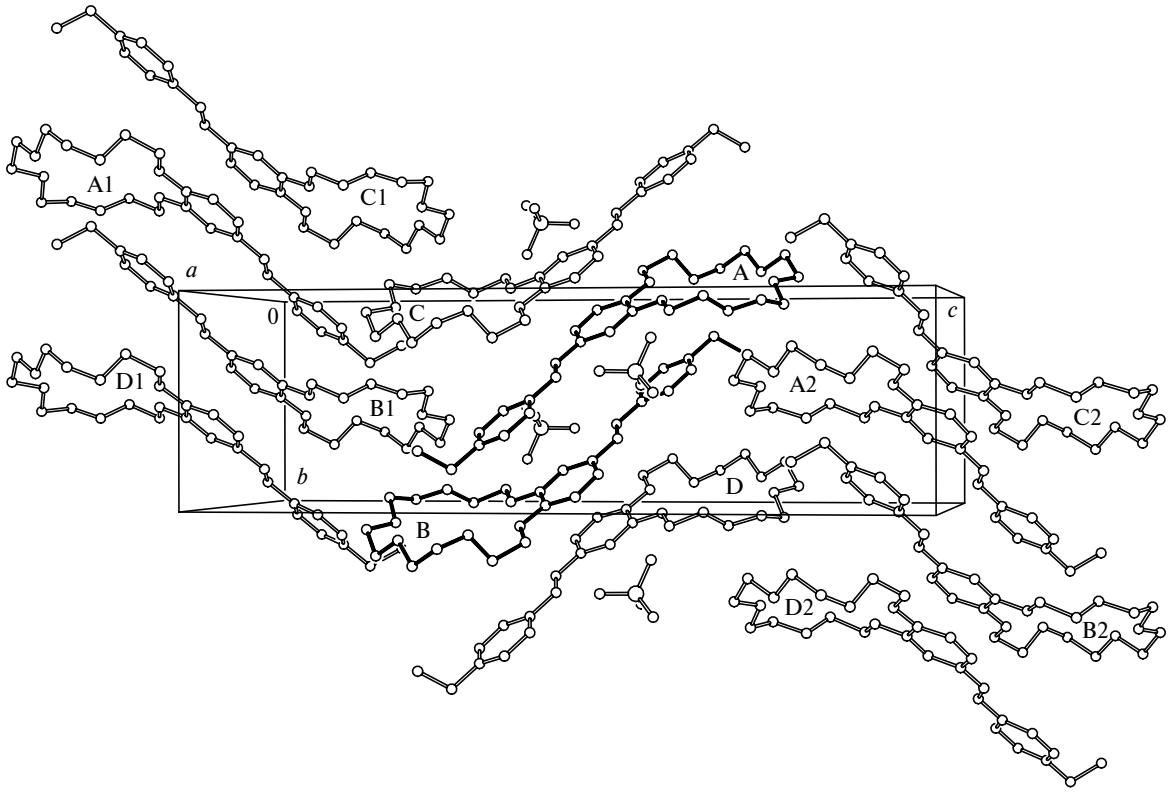


Fig. 6. Fragment of the crystal packing of compound **1**. All hydrogen atoms and the solvate water molecules are omitted. The molecules are indicated by capital letters inside the crown-ether fragment.

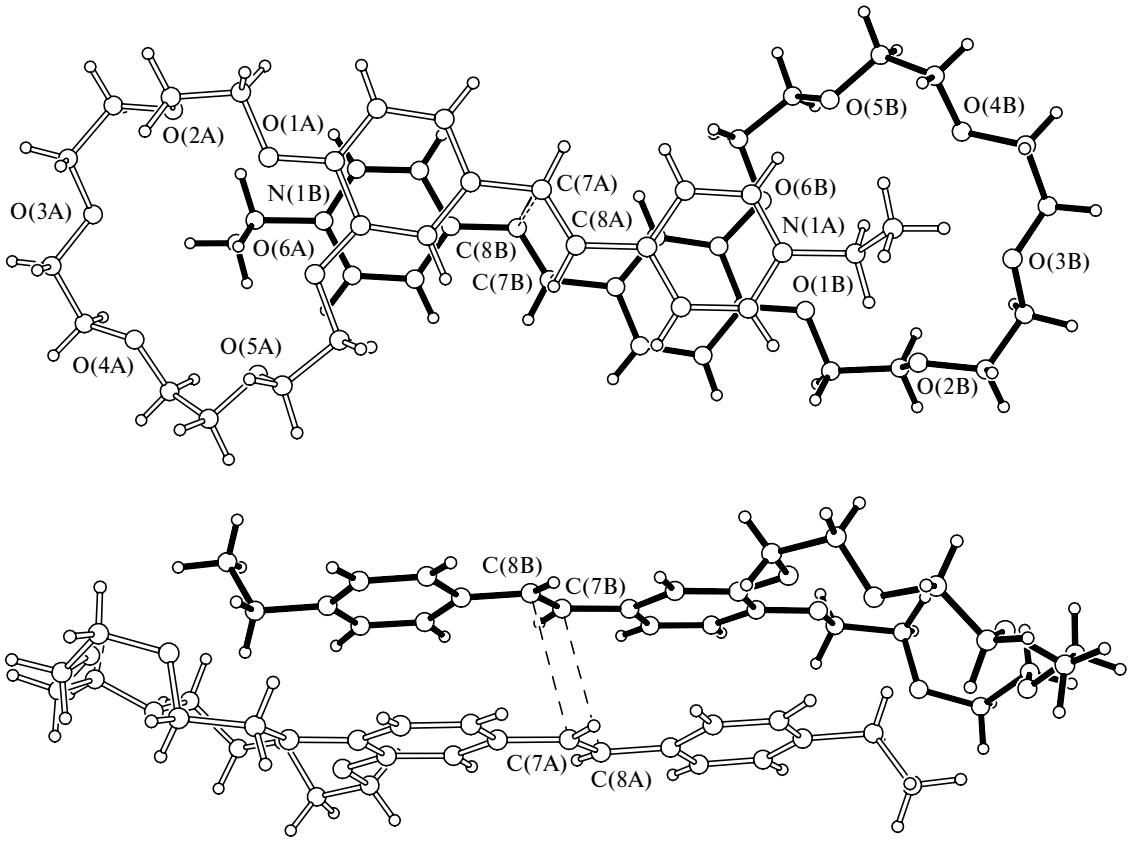


Fig. 7. Frontal and lateral projections of the stacking dimer of **1**.

addition. Consequently, the dimer composed of the molecules A and B is largely preorganized for [2+2] cycloaddition.

According to the results of our earlier crystallographic studies, all crystal packings of crown-ether-containing styryl and butadienyl dyes[5,14–16,19] and derivatives of benzocrown ethers[20–22] are characterized by separation of the regions occupied by conjugated and crown-ether fragments of the molecules. The conjugated fragments form close-packed regions of the crystal, whereas the crown-ether fragments represent loosely packed regions. In the crystal of **1**, each stacking dimer with the closely arranged ethylene fragments is surrounded by loose regions of the crown-ether fragments of the adjacent molecules (Fig. 8). These regions contain the perchlorate anions as well, which are characterized by rotational disorder, *i.e.*, they can rotate about the center of gravity. We hypothesized that this specific "soft" environment of the dimeric pair in the crystal would not hinder substantial atomic displacements of the central fragments of this dimer toward each other if photocycloaddition occurs in the crystal matrix of **1**. At the same time, this environment can level the changes in the exterior shape of the stacking dimer associated with a decrease in its volume in the central region as a result of the transformation into cyclobutane derivative **3**. Hence, topochemical photocycloaddition can presumably occur in a single crystal without its destruction.

With the aim of verifying this assumption, we irradiated the single crystal of dye **1**, which has been studied by X-ray diffraction, with visible light for 20 h. The repeated X-ray analysis of the irradiated single crystal demonstrated that photocycloaddition was brought to completion. The structure of the photocycloaddition product, *viz.*, cyclobutane **3**, is shown in Fig. 9. The cyclobutane dication is located on an inversion center and it is the *rctt* isomer formed under topochemical control of the crystal lattice. Selected geometric parameters of **3** are given in Table 2. Compared to the starting dye, the perchlorate anions of the cycloadduct exhibit considerable rotational disorder, the atoms of the crown-ether fragments are characterized by large atomic displacements, and the H-bonded water molecules are absent in the crown-ether cavities. Thus, photocycloaddition in a single crystal of **1** is accompanied by release of water molecules of crystallization.

It should be noted that the solid-state reaction and release of water molecules of crystallization are accompanied by a decrease in the crystal volume by only ~6%. Figure 10 shows a superposition of the same region of the unit cell of the single crystal before and after irradiation.

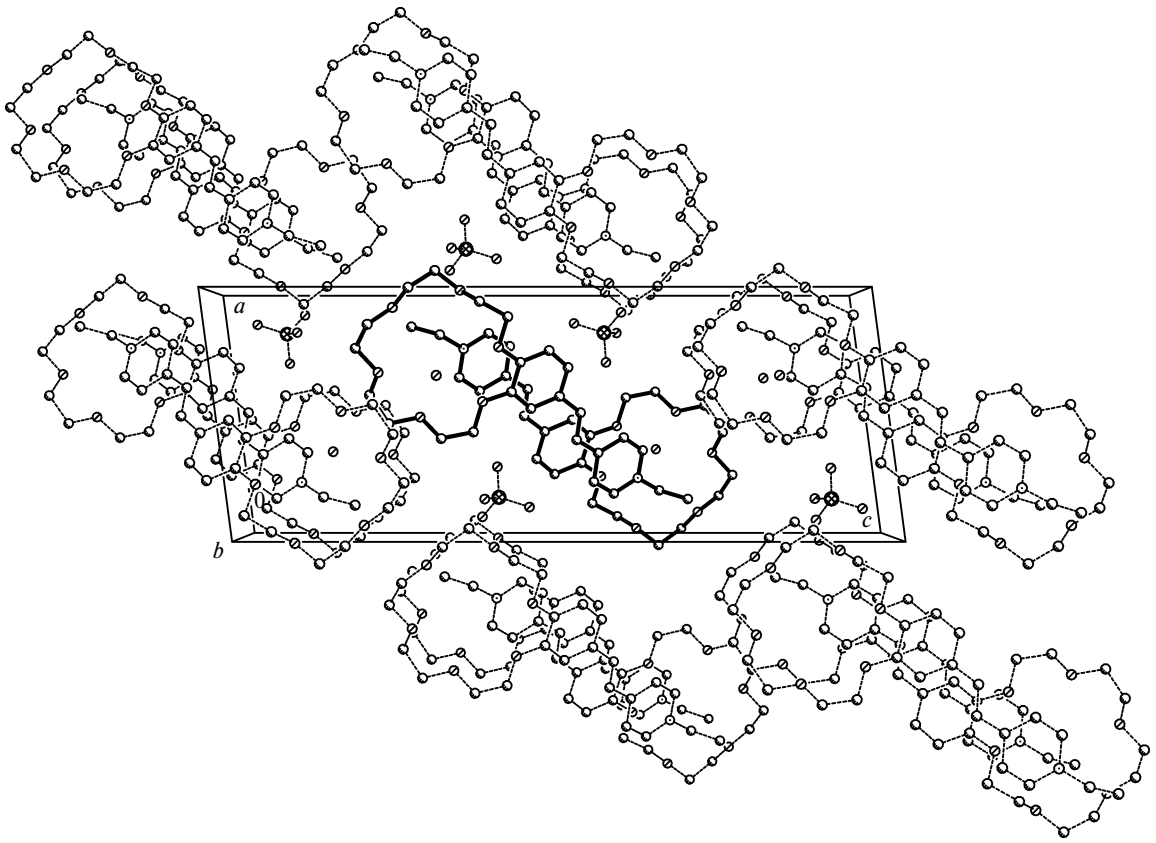


Fig. 8. Crystal environment of the stacking dimer of **1**.

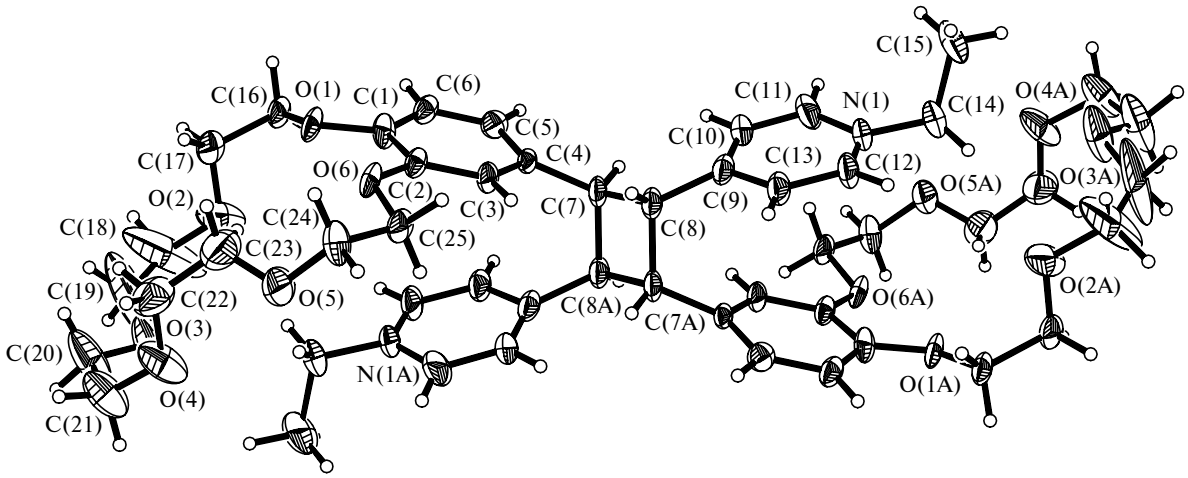


Fig. 9. Structure of the doubly charged cation of cyclobutane *rctt*-**3** with displacement ellipsoids drawn at the 50% probability level.

The reaction is accompanied by substantial atomic displacements not only in the central part of this region but also on the periphery involving the crown-ether fragments and perchlorate anions. This fact confirms our assumption that the "soft" environment of the pre-existing stacking dimer in the crystal can, after small displacements from the starting positions, fit the geometry of photocycloaddition product **3** to the requirements of the starting crystal lattice of **1**. This, in turn, suggests that an analogous reaction can occur without destruction of a single crystal not only for this compound but also for many other crown-ether-containing dyes that can form this most typical packing motif.

It should be noted that, although topochemical photocycloaddition reactions occurring without destruction of single crystals have attracted great attention and have been

Table 2. Selected bond lengths (*d*), bond angles (ω), and dihedral angles (φ) in isomer *rctt*-**3**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Angle	ω/deg
C(1)—C(2)	1.416(9)	O(1)—C(1)—C(2)	115.0(7)
C(2)—C(3)	1.376(9)	O(1)—C(1)—C(6)	125.8(6)
C(3)—C(4)	1.41(1)	O(6)—C(2)—C(1)	116.1(6)
C(4)—C(5)	1.40(1)	O(6)—C(2)—C(3)	125.0(6)
C(5)—C(6)	1.37(1)	C(3)—C(4)—C(5)	117.9(6)
C(6)—C(1)	1.38(1)	C(3)—C(4)—C(7)	122.3(7)
C(4)—C(7)	1.51(1)	C(5)—C(4)—C(7)	119.1(7)
C(7)—C(8)	1.54(1)	C(4)—C(7)—C(8)	120.2(7)
C(8)—C(9)	1.51(1)	C(4)—C(7)—C(8A)	115.8(6)
C(9)—C(10)	1.36(1)	C(8)—C(7)—C(8A)	88.7(6)
C(10)—C(11)	1.38(1)	C(7)—C(8)—C(9)	118.0(7)
C(11)—N(1)	1.39(1)	C(8)—C(9)—C(10)	124.3(7)
N(1)—C(12)	1.34(1)	C(8)—C(9)—C(13)	117.1(8)
C(12)—C(13)	1.39(1)	C(10)—C(9)—C(13)	117.1(7)
C(13)—C(9)	1.43(1)		
C(7)—C(8A)	1.60(1)		

Angle	φ/deg
C(4)—C(7)—C(8)/C(7)—C(8)—C(9)	123.8
C(4)—C(7)—C(8)—C(9)/N(1), C(9)...C(13)	12.1
C(4)—C(7)—C(8)—C(9)/C(1)...C(6)	35.1
N(1),C(9)...C(13)/N(1)—C(14)—C(15)	76.6

extensively investigated,[23—29] such reactions are scarce. In some studies, attempts were made to simulate dimeric structures with the closely arranged parallel ethylene fragments and it was pointed out that for the reaction in a single crystal to proceed without destruction of the latter, the necessary crystal packing should be preformed, which is unpredictable in most cases. Our investigations have shown[5,14—16,19,21] that crown-ether compounds analogous to dye **1** form a very limited set of crystal packings, among which the packing favorable for photocycloaddition without destruction of a single crystal is most typical. Consequently, the targeted design of the structures of crown-ether-containing unsaturated dyes can give rise to new promising data recording and storage systems based on organic single crystals operating with high efficiency in a specified spectral region.

To summarize, we showed that the pathway of the phototransformation of a styryl dye of the pyridine series **1** depends on the aggregate state. Using a crown-ether-containing styryl dye as an example, we demonstrated for the first time that it is possible to perform efficient and stereospecific solid-state photocycloaddition induced by visible light giving rise to a cyclobutane derivative. The reactivity and stereospecificity of photocycloaddition in the crystalline state are determined by the formation of "head-to-tail" stacking dimers of the dye molecules, in which the C=C bonds are closely arranged and are parallel to each other (topochemical control). The photocycloaddition was also possible due to a rather loose environment of the dimeric pairs in the crystal, which does not hinder their considerable structural rearrangement during transformation into a cyclobutane derivative. The characteristic features of the photocycloaddition reaction can be used to construct dye-based data recording systems.

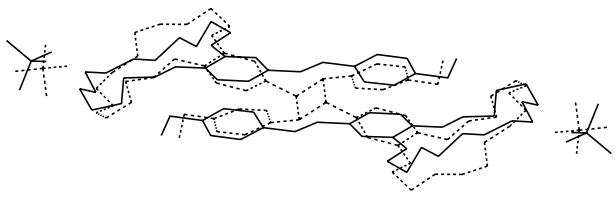


Fig. 10. Superposition of the same region of the unit cell before and after irradiation of a single crystal of dye **1**. The starting compound is shown be solid lines, and photocycloaddition product **3** is represented by dashed lines.

Experimental

The melting points (uncorrected) were measured on a Mel-Temp II instrument. The mass spectrum was obtained on a Finnigan MAT 8430 instrument; the ionization energy was 70 eV; direct inlet of the sample. Elemental analyses were carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). The course of the reactions was monitored by TLC on DC-Alufolien Aluminiumoxide 60 F_{254} neutral (Typ E) plates. Column chromatography was carried out on Al_2O_3 (Aluminiumoxide 90 activ neutral, 0.063—0.200 mm, Merck). The absorption spectra of solutions in acetonitrile were measured on Hitachi 330 and CARY 50 Bio spectrophotometers in 1 cm quartz cells. The ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer (500.13 and 125.76 MHz, respectively) in DMSO-d_6 at 30 °C using the solvent as the internal standard (δ_H 2.50 and δ_C 39.43). The chemical shifts and the coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively. Two-dimensional homonuclear $^1H—^1H$ COSY and NOESY spectra and heteronuclear $^1H—^{13}C$ COSY (HSQC and HMBC) spectra were used to assign the signals for the H and C atoms.

4-Methylpyridine, ethyl *p*-toluenesulfonate, 70% perchloric acid, pyridine (Aldrich), DMF (Fluka), and acetonitrile (Merck) were used without additional purification. 4′-Formylbenzo-18-crown-6 ether was prepared according to a known procedure.[30]

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecen-18-yl)ethen-1-yl]pyridine (*E*-2). A mixture of 4-methylpyridine (2.87 mL, 29.4 mmol) and potassium *tert*-butoxide, which was prepared by dissolution of potassium (0.82 g, 21 mmol) in dry *tert*-butyl alcohol followed by concentration to dryness, in dry DMF (20 mL) was stirred at room temperature for 30 min. Then 4′-formylbenzo-18-crown-6 ether (2.00 g, 5.88 mmol) was added and the reaction mixture was stirred at room temperature for 30 h, after which water (70 mL) was added, the reaction mixture was extracted with $CHCl_3$ (2×70 mL), the organic extracts were concentrated *in vacuo* at 90 °C, and the residue was chromatographed on a column with Al_2O_3 using a gradient of acetonitrile in benzene

(up to 50% of the latter) as the eluent. Compound *E*-**2** was obtained as a white powder in a yield of 1.87 g (77%), m.p. 105—107 °C. Found (%): C, 66.54; H, 7.01; N, 3.37. $C_{23}H_{29}NO_6$. Calculated (%): C, 66.48; H, 7.03; N, 3.37. ^{1}H NMR, δ: 3.54 (s, 4 H, OC(8)H_2, OC(9)H_2); 3.57 (m, 4 H, OC(6)H_2, OC(11)H_2); 3.63 (m, 4 H, OC(5)H_2, OC(12)H_2); 3.77 (m, 2 H, OC(3)H_2); 3.79 (m, 2 H, OC(14)H_2); 4.12 (m, 2 H, OC(2)H_2); 4.17 (m, 2 H, OC(15)H_2); 6.99 (d, 1 H, H(20), J = 8.3 Hz); 7.13 (d, 1 H, C<u>H</u>=CHAr, J = 16.4 Hz); 7.15 (dd, 1 H, H(19), J = 8.3 Hz, J = 1.6 Hz); 7.28 (d, 1 H, H(17), J = 1.6 Hz); 7.45 (d, 1 H, CH=C<u>H</u>Ar, J = 16.4 Hz); 7.50 (d, 2 H, H(3), H(5), J = 6.0 Hz); 8.51 (d, 2 H, H(2), H(6), J = 6.0 Hz). ^{13}C NMR, δ: 68.10, 68.15 (OC(2)H_2, OC(15)H_2); 68.59, 68.64 (OC(3)H_2, OC(14)H_2); 69.71, 69.81 (OC(5)H_2, OC(6)H_2, OC(8)H_2, OC(9)H_2, OC(11)H_2, OC(12)H_2); 110.91 (C(17)); 112.89 (C(20)); 120.44 (C(3), C(5)); 120.97 (C(19)); 123.62 (<u>C</u>H=CHAr); 129.05 (C(18)); 132.89 (CH=<u>C</u>HAr); 144.54 (C(4)); 148.28 (C(16a)); 148.92 (C(20a)); 149.82 (C(2), C(6)). MS, m/z (I_{rel} (%)): 415 $[M]^+$ (100), 240 (55), 239 (89), 226 (17), 224 (23), 213 (47), 184 (13), 182 (13), 167 (13), 154 (21).

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecen-18-yl)ethen-1-yl]-1-ethylpyridinium perchlorate (*E*-1). A mixture of compound *E*-**2** (100 mg, 0.24 mmol) and ethyl *p*-toluenesulfonate (145 mg, 0.72 mmol) was fused at 120 °C for 6 h. The reaction mixture was extracted with a 1 : 1 boiling benzene—light petroleum mixture (3×20 mL). The residue was dissolved with heating in methanol (5 mL). Then 70% perchloric acid (42 μL, 0.48 mmol) was added, the reaction mixture was cooled to −10 °C, and the precipitate was filtered off, washed with cold methanol, and dried. Dye *E*-**1** was obtained as yellow crystals in a yield of 76 mg (58%), m.p. 200—202 °C. Found (%): C, 54.24; H, 6.44; N, 2.35. $C_{25}H_{34}ClNO_{10}\cdot 0.5H_2O$. Calculated (%): C, 54.30; H, 6.38; N, 2.53. ^{1}H NMR, δ: 1.53 (t, 3 H, Me, J = 7.3 Hz); 3.54 (s, 4 H, OC(8)H_2, OC(9)H_2); 3.56 (m, 4 H, OC(6)H_2, OC(11)H_2); 3.62 (m, 4 H, OC(5)H_2, OC(12)H_2); 3.78 (m, 2 H, OC(3)H_2); 3.81 (m, 2 H, OC(14)H_2); 4.16 (m, 2 H, OC(2)H_2); 4.18 (m, 2 H, OC(15)H_2); 4.50 (q, 2 H, CH_2N, J = 7.3 Hz); 7.07 (d, 1 H, H(20), J = 8.4 Hz); 7.28 (dd, 1 H, H(19), J = 8.4 Hz, J = 1.7 Hz); 7.39 (d, 1 H, H(17), J = 1.7 Hz); 7.39 (d, 1 H, C<u>H</u>=CHAr, J = 16.2 Hz); 7.94 (d, 1 H, CH=C<u>H</u>Ar, J = 16.2 Hz); 8.14 (d, 2 H, H(3), H(5), J = 6.9 Hz); 8.90 (d, 2 H, H(2), H(6), J = 6.9 Hz). ^{13}C NMR, δ: 15.95 (Me); 54.98 (CH_2N); 68.13 (OC(2)H_2, OC(15)H_2); 68.45, 68.52 (OC(3)H_2, OC(14)H_2); 69.60, 69.68, 69.79, 69.81 (OC(5)H_2, OC(6)H_2, OC(8)H_2, OC(9)H_2, OC(11)H_2, OC(12)H_2); 111.20 (C(17)); 112.72 (C(20)); 120.72 (<u>C</u>H=CHAr); 123.08 (C(19)); 123.13 (C(3), C(5)); 127.90 (C(18)); 140.98 (CH=<u>C</u>HAr); 143.64 (C(2), C(6)); 148.30 (C(16a)); 150.51 (C(20a)); 153.06 (C(4)).

4-[(*Z*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecen-18-yl)ethen-1-yl]-1-ethylpyridinium perchlorate (*Z*-1). A solution of dye *E*-**1** (12 mg, 0.02 mmol) in dry acetonitrile (15 mL) was irradiated in a thin-walled glass vessel with unfiltered light using a 60 W incandescent bulb at a distance of 15 cm for 30 h. The course of the reaction was monitored spectrophotometrically and by ^{1}H NMR spectroscopy (an aliquot (1 mL) of the reaction mixture was concentrated *in vacuo* and the residue was dissolved in DMSO-d_6). A photostationary mixture of the *E* and *Z* isomers of **1** in a ratio of 1.80 : 1 was obtained (the time of establishment of the photostationary equilibrium was shorter than 1 h). ^{1}H NMR, δ: 1.49 (t, 3 H, Me, J = 7.3 Hz); 3.53 (s, 4 H, OC(8)H_2, OC(9)H_2); 3.55 (m, 4 H, OC(6)H_2, C(11)H_2O); 3.60 (m, 4 H, OC(5)H_2, OC(12)H_2); 3.68 (m, 2 H, OC(14)H_2); 3.75 (m, 2 H, OC(3)H_2); 3.92 (m, 2 H, OC(15)H_2); 4.09 (m, 2 H, OC(2)H_2); 4.50 (q, 2 H, CH_2N, J = 7.3 Hz); 6.68 (d, 1 H, CH=C<u>H</u>Ar, J = 12.1 Hz); 6.85 (d, 1 H, H(17), J = 1.5 Hz); 6.88 (dd, 1 H, H(19), J = 8.4 Hz, J = 1.5 Hz); 6.93 (d, 1 H, H(20), J = 8.4 Hz); 7.16 (d, 1 H, C<u>H</u>=CHAr, J = 12.1 Hz); 7.87 (d, 2 H, H(3), H(5), J = 6.7 Hz); 8.86 (d, 2 H, H(2), H(6), J = 6.7 Hz).

***r*-4-[*c*-2,*t*-4-Bis(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecen-18-yl)-*t*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diperchlorate (*rctt*-3).** The solvent was evaporated from a solution of *E*-**1** (26 mg, 0.05 mmol) in dry acetonitrile (10 mL) in a 7 cm Petri dish to form a thin film of the dye. This was irradiated with unfiltered light using a 60 W incandescent bulb at a distance of 15 cm for 40 h, dissolved in acetonitrile, and concentrated *in vacuo*. A pale-yellow powder was obtained. According to the ^{1}H NMR spectroscopic data, the product contained >96% of *rctt*-**3**, m.p. 88—90 °C. Found (%): C, 55.17; H, 6.30; N, 2.51. $C_{50}H_{68}Cl_2N_2O_{20}$. Calculated (%): C, 55.20; H, 6.30; N, 2.58. ^{1}H NMR, δ: 1.43 (t, 6 H, 2 Me, J = 7.3 Hz); 3.51 (s, 8 H, 2 OC(8)H_2, 2 OC(9)H_2); 3.52—3.61 (m, 16 H, 2 OC(5)H_2, 2 OC(6)H_2, 2 OC(11)H_2, 2 OC(12)H_2); 3.69 (m, 4 H, 2 OC(3)H_2); 3.72 (m, 4 H, 2 OC(14)H_2); 3.95 (m, 4 H, 2 OC(2)H_2); 3.98 (m, 4 H, 2 OC(15)H_2); 4.50 (q, 4 H, 2 CH_2N, J = 7.3 Hz); 4.79 (dd, 2 H, 2 C<u>H</u>Ar, J = 9.1 Hz, J = 7.9 Hz); 4.88 (dd, 2 H, 2 C<u>H</u>Het, J = 9.1 Hz, J = 7.9 Hz); 6.76 (br.d, 2 H, 2 H(19), J = 8.5 Hz); 6.93 (d, 2 H, 2 H(20), J = 8.5 Hz); 6.83 (br.s, 2 H, 2 H(17)); 7.93 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.89 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz). ^{13}C NMR, δ: 16.11 (2 Me); 45.01 (2 <u>C</u>HAr); 45.95 (2 <u>C</u>HHet); 55.47 (2 CH_2N); 67.92, 68.10 (2 OC(2)H_2, 2 OC(15)H_2); 68.58 (2 OC(3)H_2, 2 OC(14)H_2); 69.64, 69.71 (2 OC(5)H_2, 2 OC(6)H_2, 2 OC(8)H_2, 2 OC(9)H_2, 2 OC(11)H_2, 2 OC(12)H_2); 112.62 (2 C(20)); 113.27 (2 C(17)); 120.01 (2 C(19)); 126.96 (2 C(3), 2 C(5)); 130.02 (2 C(18)); 143.24 (2 C(2), 2 C(6)); 147.06 (2 C(20a)); 147.81 (2 C(16a)); 160.02 (2 C(4)).

***r*-4-[*c*-2,*t*-4-Bis(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecen-18-yl)-*c*-3-(1-ethylpyridinium-4-yl)cyclobutyl]-1-ethylpyridinium diperchlorate (*rcct*-3).** A solution of *rctt*-**3** (2 mg) in pure dry acetonitrile (5 mL) with addition of dry pyridine (50 μL) was kept in the dark at room temperature and then concentrated *in vacuo* at 60 °C. According to the ^{1}H NMR spectroscopic data, mixtures of the *rctt* and *rcct* isomers of **3** in a ratio of 3.13 : 1 and 1 : 2.57 were obtained after 30 and 280 h, respectively. ^{1}H NMR, δ: 1.41 (t, 6 H, 2 Me, J = 7.3 Hz); 3.49 (s, 4 H, OC(8)H_2, OC(9)H_2); 3.52—3.64 (m, 20 H, OC(3)H_2, OC(5)H_2, OC(6)H_2, OC(11)H_2, OC(12)H_2, OC(14)H_2, OC(5′)H_2, OC(6′)H_2, OC(11′)H_2, OC(12′)H_2); 3.74 (m, 2 H, OC(3′)H_2); 3.77 (m, 2 H, OC(15)H_2); 3.80 (m, 2 H, OC(14′)H_2); 3.84 (m, 2 H, OC(2)H_2); 4.08 (m, 2 H, OC(2′)H_2); 4.16 (m, 2 H, OC(15′)H_2); 4.47 (q, 4 H, 2 CH_2N, J = 7.3 Hz); 4.68 (m, 2 H, 2 C<u>H</u>Het); 4.74 (dd, 1 H, C<u>H</u>Ar, J = 10.6 Hz, J = 8.1 Hz); 5.08 (t, 1 H, C<u>H</u>Ar′, J = 10.6 Hz); 6.43 (d, 1 H, H(17), J = 1.1 Hz); 6.53 (dd, 1 H, H(19), J = 8.3 Hz, J = 1.1 Hz); 6.57 (d, 1 H, H(20), J = 8.3 Hz); 7.00 (d, 1 H, H(20′), J = 8.3 Hz); 7.31 (dd, 1 H, H(19′), J = 8.3 Hz, J = 1.7 Hz); 7.39 (d, 1 H, H(17′), J = 1.7 Hz); 7.83 (d, 4 H, 2 H(3), 2 H(5), J = 6.7 Hz); 8.85 (d, 4 H, 2 H(2), 2 H(6), J = 6.7 Hz). ^{13}C NMR, δ:

16.00 (2 Me); 43.85 (CHAr′); 47.34 (2 CHHet); 48.75 (CHAr); 55.50 (2 CH_2N); 67.60 ($OC(2)H_2$); 67.94 ($OC(15)H_2$); 68.25 ($OC(2')H_2$); 68.35 ($OC(15')H_2$); 68.45, 68.49 ($OC(3)H_2$, $OC(14)H_2$); 68.66, 68.61 ($OC(3')H_2$, $OC(14')H_2$); 69.59, 69.66, 69.73 ($OC(5)H_2$, $OC(6)H_2$, $OC(8)H_2$, $OC(9)H_2$, $OC(11)H_2$, $OC(12)H_2$, $OC(5')H_2$, $OC(6')H_2$, $OC(8')H_2$, $OC(9')H_2$, $OC(11')H_2$, $OC(12')H_2$); 112.10 (C(20)); 112.64 (C(17′)); 113.54 (C(20′)); 114.70 (C(17)); 119.76 (C(19′)); 122.55 (C(19)); 126.33 (2 C(3), 2 C(5)); 127.55 (C(18)); 133.32 (C(18′)); 143.32 (2 C(2), 2 C(6)); 146.76 (C(20a)); 147.09 (C(16a)); 147.61 (C(20a′)); 148.51 (C(16a′)); 159.79 (2 C(4)).

Table 3. Crystallographic data and characteristics of X-ray diffraction study for compounds **1** and **3**

Parameter	**1**	**3**
Molecular formula	$C_{25}H_{36}ClNO_{11}$	$C_{50}H_{68}Cl_2N_2O_{20}$
Molar weight /g mol^{-1}	562.00	1087.96
Color	Yellow	Pale yellow
Crystal habit	Prism	Prism
Crystal dimensions/mm	0.36×0.22×0.18	0.26×0.22×0.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.0290(6)	10.953(1)
b/Å	8.5403(5)	8.2397(9)
c/Å	28.893(2)	28.705(4)
β/deg	97.570(2)	100.355(6)
V/Å^3	2697.8(3)	2548.5(5)
Z	4	2
ρ/g cm^{-3}	1.219	1.190
μ(Mo-$K\alpha$)/mm^{-1}	0.202	0.203
Temperature/K	123.0(2)	123.0(2)
Radiation	Mo-Kα (λ = 0.71073 Å)	
θ Angle range/deg	1.42—29.00	1.89—28.00
Ranges of indices of measured reflections	$-11 \le h \le 15$ $-11 \le k \le 11$ $-39 \le l \le 33$	$-14 \le h \le 14$ $-10 \le k \le 8$ $-37 \le l \le 37$
Number of measured reflections	16563	20272
Number of independent reflections	7084	6129
R_{int}	0.05353	0.1068
Number of reflections with $I > 2\sigma(I)$	5027	3684
Number of parameters in refinement	487	372
Goodness-of-fit on F^2	1.016	1.235
Final R factors ($I > 2\sigma(I)$)		
R_1	0.0536	0.1822
wR_2	0.1363	0.4238
R factors using all reflections		
R_1	0.0834	0.2393
wR_2	0.1597	0.4471
Residual electron density /e Å^{-3} (min/max)	0.561/−0.336	0.949/−0.493

X-ray diffraction study. Single crystals of dye **1** were grown by slow evaporation of a methanolic solution. A single crystal of **1** that was stored in the dark was mounted on a Bruker SMART-CCD diffractometer under a flow of cooled nitrogen. The X-ray diffraction data were collected using Mo-Kα radiation (graphite monochromator). The structure was solved by the heavy-atom method and refined anisotropically by the full-matrix least-squares method against F^2. A water molecule was found in the cavity of the crown-ether fragment of **1** and all hydrogen atoms, including the hydrogen atoms of the water molecule, were located from difference Fourier syntheses. Then all hydrogen atoms were refined isotropically.

After completion of the first experiment, the crystal was irradiated with visible light using a 60 W incandescent bulb at a distance of ~15 cm for *ca*. 20 h. Then a new X-ray data set was collected from this crystal under a flow of cooled nitrogen. In the course of X-ray data collection, a small fragment of the single crystal was broken off, although the major portion was retained. The visible quality of the crystal was impaired because it was covered with small cracks. A sacrifice in quality of the single crystal was also evidenced by broadening of experimental reflections. It should be noted that the quality of the crystal remained rather high for X-ray diffraction study. A sacrifice in quality of the single crystal is apparently associated with crystal lattice strains due to the appearance of cavities formed as a result of the release of water molecules of solvation.

The structure of cyclobutane *rctt*-**3** was solved by direct methods and refined anisotropically by the full-matrix least-squares method against F^2. The hydrogen atoms were calculated geometrically and refined using a riding model. In this experiment, pronounced anisotropy of atomic vibrations of the crown-ether fragments and considerable rotational disorder of the perchlorate anions were revealed. We failed to take into account all possible models of rotational disorder, which was also evidenced by localization of peaks of residual electron density in the vicinity of the anions.

Characteristics of X-ray diffraction study are given in Table 3. All calculations were carried out using the SHELXTL-Plus program package.[31]

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 03-03-32178 and 03-03-32929), the Council on Grants of the President of the Russian Federation (Program for State Support of Leading Scientific Schools of the Russian Federation, Grant, NSh-2028.2003.3, and the State Program for Support of Young Scientists, Grant MK-3666.2004.3), the Russian Science Support Foundation, the INTAS (Grants 2001-0267 and 03-51-4696), the Russian Academy of Sciences, and the Royal Society of Chemistry (Great Britain, Personal Grants for L. G. Kuz′mina, A. I. Vedernikov, and J. A. K. Howard).

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Received November 19, 2004;
in revised form February 22, 2005