

## Synthesis, complexation, and photochemistry of benzobisthiazole-based bis(crown ether)\*

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Benzobisthiazole-based bis(crown ether) was synthesized and its complexation with alkali and alkaline earth cations was studied. Photochemical transformations of the free ligand and its complexes with alkaline earth cations involve *E,Z*-photoisomerization and [2+2] photocycloaddition.

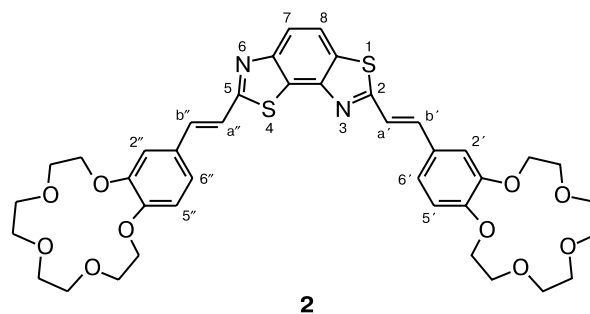
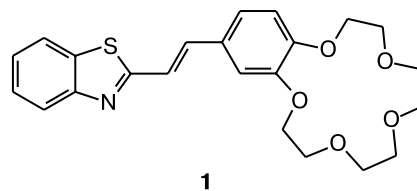
**Key words:** bis(crown ether), benzobisthiazole, 15-crown-5, complexation, photochemistry, *E,Z*-photoisomerization, [2+2] photocycloaddition.

Crown ethers containing photochromic fragments are of obvious interest.<sup>1–4</sup> On the one hand, these compounds proved to be optical molecular sensors for metal cations because they can change the optical characteristics as a result of complexation.<sup>5–7</sup> On the other hand, this process has a substantial effect on the photochemical and photophysical properties of photochromic crown compounds<sup>8,9</sup> due to which this type of compounds holds promise for the design of photochromic materials for different purposes.

Earlier,<sup>10–12</sup> we have synthesized and studied crown-containing 2-styrylbenzothiazole *E*-**1**. This is a ditopic receptor, whose complexation with alkaline earth cations occurs at the crown fragment, whereas the nitrogen atom of the heterocyclic residue is involved in coordination to heavy metal cations and protonation. In the present study, we synthesized and characterized crown-containing benzobis(2-styrylthiazole) **2**. Complexes of bis(crown-ether)s are known<sup>13–16</sup> to be more stable than their monocrown-containing analogs. The complexation involving bis(crown-ether)s is characterized by high selectivity. Bis(crown ether)s have been used also for the synthesis of chiral ligands.<sup>17,18</sup> Although bis(crown-ether)s containing a photochromic group have been docu-

mented,<sup>19–22</sup> the mutual influence of complexation and photochemical transformations in such systems has attracted little attention.<sup>23</sup>

In the present study, we synthesized crown-containing benzobis(2-styrylthiazole) *E,E*-**2**, studied its complexation, and performed detailed analysis of light-induced photochemical transformations occurring in the starting molecule *E,E*-**2** and its complexes with alkaline earth cations.



\* Dedicated to Academician N. S. Zefirov on the occasion of his 70th birthday.

## Experimental

Magnesium, calcium, barium, sodium, potassium, rubidium, and cesium perchlorates were dried *in vacuo* at 230 °C. Spectroscopic-grade acetonitrile containing less than 0.005% water (Aldrich) was used without additional purification.

All experiments, including the preparation of solutions of ligand **2**, were carried out under red light. Potassium *tert*-butoxide was prepared by dissolution of potassium metal in anhydrous Bu<sup>1</sup>OH followed by evaporation of excess Bu<sup>1</sup>OH and drying *in vacuo*. *N*-(3-Acetylaminophenyl)acetamide,<sup>24,25</sup> *N*-(3-thioacetylaminophenyl)thioacetamide,<sup>24,25</sup> and 2,7-dimethylbenzo[1,2-*d*;3,4-*d'*]bisthiazole<sup>24,25</sup> were synthesized according to procedures described earlier.

Elemental analysis was carried out in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (Moscow). The melting points (uncorrected) were measured on an Mel-temp II instrument.

The <sup>1</sup>H NMR spectra were recorded in CD<sub>3</sub>CN at 30 °C on a Bruker DRX-500 spectrometer (500.13 MHz). The chemical shifts and the coupling constants were measured with an accuracy of 0.01 ppm and 0.1 Hz, respectively.

The mass spectra were obtained on a Varian MAT 311A instrument using a direct inlet system; the ionization energy was 70 eV. The electrospray mass spectra (electrospray ionization, ESI method) and high-resolution mass spectra were measured on a JEOL AccuTOF JMS-T100LC mass spectrometer.

The electronic absorption spectra were recorded on a Specord M40 spectrophotometer connected to a computer. The fluorescence spectra were measured on Shimadzu RF-5000 spectrofluorimeter at 20 ± 1 °C. The fluorescence quantum yields of the ligand and its complexes were determined at 20 ± 1 °C for air-saturated acetonitrile solutions with respect to quinine sulfate in 0.5 M H<sub>2</sub>SO<sub>4</sub> as the reference ( $\phi_F = 0.55$ ). The excitation wavelength of 365 nm was used. The quantum yields were calculated using uncorrected fluorescence spectra.

Complexation of *E,E*-**2** with Mg, Ca, Ba, Na, K, and Rb perchlorates was studied by spectrophotometric titration at 20 ± 1 °C by varying the concentration of the corresponding perchlorate at a constant concentration of the ligand. The complexation constants and absorption spectra of the complexes were calculated from the electronic absorption spectra of solutions using the HYPERQUAD program.<sup>26</sup>

Acetonitrile solutions of compound **2** and its complexes were irradiated using a mercury lamp (DRK-120, 120 W). The lines with wavelengths  $\lambda = 313, 365, \text{ and } 405 \text{ nm}$  were separated using UFS-2 + ZHS-3, UFS-6 + BS-7, and PS-13 + ZHS-10 glass light filters, respectively, from a standard kit of optical stained glasses. The light intensity was measured using a ferrioxalate actinometer.

The course of the synthesis was monitored by TLC on DC-Alufolien Kieselgel 60 F<sub>254</sub> and DC-Alufolien Aluminiumoxid 60 F<sub>254</sub> neutral (Type E) plates. Column chromatography was performed on Kieselgel 60 (0.063–0.100 mm) and aluminium oxide 150, basic, Type E (0.063–0.200 mm), and aluminium oxide 90 active, neutral (activity 1) (0.063–0.200 mm) (Merck).

Studies by HPLC were carried out on a Waters instrument (Waters 600 Controller, Waters 600/616S Pump, Waters 486

Tunable Absorbance Detector and Waters 996 Photodiode Array Detector, PDA) using the Millennium 32 software and on a Beckman instrument (System Gold 125 solvent module, System Gold 168 detector, PDA, System Gold 125s solvent module, and System Gold 166 detector) using the Beckman System Gold Chromatography Software 1991 (System Gold Personal Chromatograph). The separation was carried out on reversed-phase columns (Symmetry C<sub>18</sub>, Waters, 3.9 × 150 mm, 5 μm; Beckman Ultrasphere, 4.6 × 250 mm; Beckman Ultrasphere, 2.0 × 250 mm, 5 μm) using a MeCN–H<sub>2</sub>O mixture as the eluent.

**2,5-Dimethylbenzo[1,2-*d*;3,4-*d'*]bisthiazole (4)**. A solution of 1,3-bis(thioacetyl-amido)benzene (3.1 g, 13.8 mmol) and NaOH (9.5 g, 237.5 mmol) in water (150 mL) was mixed with a solution of K<sub>3</sub>[Fe(CN)<sub>6</sub>] (18.7 g, 56.8 mmol) in water (200 mL). The reaction mixture was kept with continuous stirring at ~20 °C for 3 days. The reaction product was isolated by repeated extraction with diethyl ether. The ethereal extract was washed with a large amount of water and concentrated. Compound **4** was obtained in a yield of 0.43 g (8%), m.p. 93 °C (*cf. lit. data*<sup>24,25</sup>: 92–94 °C).

**5-Methyl-2-[2-(*E*)-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecyn-15-yl)ethen-1-yl]benzo[1,2-*d*;3,4-*d'*]bisthiazole (3) and 2,5-bis[2-(*E*)-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecyn-15-yl)ethen-1-yl]benzo[1,2-*d*;3,4-*d'*]bisthiazole (*E,E*-**2**)**. A mixture of bisthiazole **4** (44 mg, 0.2 mmol), 4'-formylbenzo-15-crown-5 ether (130 mg, 0.44 mmol), and Bu<sup>1</sup>OK (49 mg, 0.67 mmol) in anhydrous DMSO (10 mL) was kept at room temperature for 24 h. Then water (20 mL) was added, the products were extracted with chloroform, the solvent was evaporated, and the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> (aluminium oxide 150 basic, type T). After recrystallization from MeCN, compound **3** was obtained in a yield of 5 mg (5%), m.p. 212 °C. Found (%): C, 60.14; H, 5.84; N, 5.31. C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>. Calculated (%): C, 60.22; H, 5.26; N, 5.61. <sup>1</sup>H NMR,  $\delta$ : 3.60 (m, 8 H, 4 OCH<sub>2</sub>); 3.95 and 4.50 (both m, 4 H each, 4 OCH<sub>2</sub>); 7.08 (d, 1 H, H(5'),  $J = 7.5 \text{ Hz}$ ); 7.37 (d, 1 H, H(6'),  $J = 7.6 \text{ Hz}$ ); 7.45 (s, 1 H, H(2'')); 7.60 (d, 1 H, H<sub>a</sub>,  $^3J_{H,H} = 16.1 \text{ Hz}$ ); 7.69 (d, 1 H, H<sub>b</sub>,  $^3J_{H,H} = 16.1 \text{ Hz}$ ); 7.95 (d, 1 H, H(8),  $J = 8.6 \text{ Hz}$ ); 8.19 (d, 1 H, H(7),  $J = 8.6 \text{ Hz}$ ).

The yield of *E,E*-**2** was 28 mg (18%), m.p. 162 °C. Found (%): C, 61.74; H, 5.84; N, 3.71. C<sub>40</sub>H<sub>44</sub>N<sub>2</sub>O<sub>10</sub>S<sub>2</sub>. Calculated (%): C, 61.84; H, 5.71; N, 3.61. <sup>1</sup>H NMR,  $\delta$ : 3.60 (m, 16 H, 8 OCH<sub>2</sub>); 3.95 (m, 8 H, 4 OCH<sub>2</sub>); 4.50 (m, 8 H, 4 OCH<sub>2</sub>); 7.01 (d, 2 H, H(5''), H(5''),  $J = 8.5 \text{ Hz}$ ); 7.31 and 7.33 (both d, 1 H each, H(6'), H(6''),  $J = 8.4 \text{ Hz}, J = 8.4 \text{ Hz}$ ); 7.46 and 7.49 (both s, 1 H each, H(2'), H(2'')); 7.58 and 7.69 (both d, 2 H each, H<sub>a</sub>', H<sub>a</sub>'', H<sub>b</sub>', H<sub>b</sub>'',  $^3J_{H,H} = 16.1 \text{ Hz}, ^3J_{H,H} = 16.1 \text{ Hz}$ ); 7.92 (d, 1 H, H(8),  $J = 8.6$ ); 8.18 (d, 1 H, H(7),  $J = 8.6 \text{ Hz}$ ). MS,  $m/z$ : 776 [M]<sup>+</sup> (100), 500 (87), 224 (13), 184 (14), 144 (24), 125 (21), 114 (20), 77 (15), 58 (45), 51 (27). MS of a solution of ligand *E,E*-**2** in MeCN (ESI, 2 kV, 250 °C, 0.2 mL min<sup>-1</sup>),  $m/z$ : 799.3 [(*E,E*-**2**)·Na]<sup>+</sup>, 1575.6 [2(*E,E*-**2**)·Na]<sup>+</sup>, 1591.6 [2(*E,E*-**2**)·K]<sup>+</sup>.

**Solutions of the complexes of ligand *E,E*-**2** with Mg and Ba perchlorates in MeCN**. A solution of ligand **2** ( $2.4 \cdot 10^{-5} \text{ mol L}^{-1}$ ) in MeCN was prepared by diluting its concentrated solution ( $7.54 \cdot 10^{-5} \text{ mol L}^{-1}$ ). A solution of Mg(ClO<sub>4</sub>)<sub>2</sub> ( $1 \cdot 10^{-2} \text{ mol L}^{-1}$ ) in MeCN (4.8 μL) was added to a solution of **2** ( $C = 2.4 \cdot 10^{-5} \text{ mol L}^{-1}$ ) in MeCN (2 mL) to prepare predominantly the complex of 1 : 1 composition (ligand : cation), or a solution of

Mg(ClO<sub>4</sub>)<sub>2</sub> (1 · 10<sup>-1</sup> mol L<sup>-1</sup>) in MeCN (4.8 μL) was added to prepare predominantly the complex of 1 : 2 composition (ligand : cation). A solution of Ba(ClO<sub>4</sub>)<sub>2</sub> (1 · 10<sup>-2</sup> mol L<sup>-1</sup>) in MeCN (4.8 μL) was added to a solution of *E,E-2* (C = 2.4 · 10<sup>-5</sup> mol L<sup>-1</sup>) in MeCN (2 mL) to prepare predominantly the complex of 2 : 2 composition (ligand : cation), or a solution of Ba(ClO<sub>4</sub>)<sub>2</sub> (1 · 10<sup>-1</sup> mol L<sup>-1</sup>) in MeCN (4.8 μL) was added to prepare predominantly the complex of 1 : 2 composition. A solution of NaClO<sub>4</sub> (5 · 10<sup>-3</sup> mol L<sup>-1</sup>) in MeCN (9.7 μL) was added to a solution of *E,E-2* (C = 2.4 · 10<sup>-5</sup> mol L<sup>-1</sup>) in MeCN (2 mL) to prepare predominantly the complex of 1 : 1 composition (ligand : cation), or a solution of NaClO<sub>4</sub> (5 · 10<sup>-2</sup> mol L<sup>-1</sup>) in MeCN (9.7 μL) was added to prepare predominantly the complex of 1 : 2 composition. The mass spectrum of a solution of ligand *E,E-2* in MeCN in the presence of barium cations (ESI, 2 kV, 250 °C, 0.2 mL min<sup>-1</sup>), *m/z*: 1013.2 [(*E,E-2*)<sub>2</sub>(Ba<sup>2+</sup>)<sub>2</sub>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>], 1054.2 [(*E,E-2*)<sub>2</sub>(Ba<sup>2+</sup>)<sub>2</sub>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>(MeCN)<sub>2</sub>], 457.1 [(*E,E-2*)<sub>2</sub>(Ba<sup>2+</sup>)<sub>2</sub>], 507.2 [(*E,E-2*)(Ba<sup>2+</sup>)<sub>2</sub>(H<sup>+</sup>)(MeCN)<sub>3</sub>(ClO<sub>4</sub><sup>-</sup>)]. The mass spectrum of a solution of ligand *E,E-2* in MeCN in the presence of magnesium cations (ESI, 2 kV, 250 °C, 0.2 mL min<sup>-1</sup>), *m/z*: 899.6 [(*E,E-2*)(Mg<sup>2+</sup>)(ClO<sub>4</sub><sup>-</sup>)], 1023.2 [(*E,E-2*)(Mg<sup>2+</sup>)<sub>2</sub>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>].

The photoprocesses were studied with stirring in a 1-cm quartz cell with a Teflon stopper. The solutions were irradiated with light at a wavelength of 365 nm. The light intensity was *I* = 5.233 · 10<sup>-6</sup> Einstein s<sup>-1</sup> cm<sup>-2</sup>. To calculate the spectrum of the *trans-cis* isomer of compound **2** by the Fisher method, the compound was irradiated with light at 365 and 405 nm.

#### A solution of the cyclodimerization product of ligand **2**.

A solution of ligand **2** (5 · 10<sup>-5</sup> mol L<sup>-1</sup>) and Ba(ClO<sub>4</sub>)<sub>2</sub> (7 · 10<sup>-5</sup> mol L<sup>-1</sup>) in MeCN (2 mL) was irradiated with light at 365 nm with stirring for 12 h until the long-wavelength absorption band at 356 nm disappeared. The products were separated by HPLC. The high-resolution mass spectra:

Product	<i>m</i>		Molecular formula
	Found	Calculated	
1	1598.4706	1598.4670	<sup>12</sup> C <sub>80</sub> <sup>1</sup> H <sub>88</sub> <sup>14</sup> N <sub>4</sub> <sup>23</sup> Na <sub>2</sub> <sup>16</sup> O <sub>20</sub> <sup>32</sup> S <sub>4</sub>
2	1598.4710	1598.4670	<sup>12</sup> C <sub>80</sub> <sup>1</sup> H <sub>88</sub> <sup>14</sup> N <sub>4</sub> <sup>23</sup> Na <sub>2</sub> <sup>16</sup> O <sub>20</sub> <sup>32</sup> S <sub>4</sub>
3	1598.4711	1598.4670	<sup>12</sup> C <sub>80</sub> <sup>1</sup> H <sub>88</sub> <sup>14</sup> N <sub>4</sub> <sup>23</sup> Na <sub>2</sub> <sup>16</sup> O <sub>20</sub> <sup>32</sup> S <sub>4</sub>

<sup>1</sup>H NMR of a mixture of cyclobutane derivatives, δ: 3.80 (m, 16 H, 8 OCH<sub>2</sub>); 3.95 and 4.10 (both m, 8 H each, 8 OCH<sub>2</sub>); 4.90–5.40 (m, 4 H, cyclobutane); 6.72 (m, 2 H, H(5'), H(5'')); 6.86 (m, 2 H, H(6'), H(6'')); 7.00 (m, 2 H, H(2'), H(2'')); 7.35 (d, 1 H, H(8), *J* = 8.1 Hz); 7.60 (d, 1 H, H(7), *J* = 8.0 Hz).

**X-ray diffraction analysis.** Single crystals of **3** suitable for X-ray diffraction analysis were grown by crystallization from a solution in hexane. A single crystal coated with a perfluorinated oil was mounted on a Bruker SMART CCD diffractometer. X-ray diffraction data were collected at low temperature. The crystallographic parameters and characteristics of X-ray diffraction study are given in Table 1. The structure was solved by direct methods and refined by the full-matrix least-squares method against *F*<sup>2</sup> with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were located from difference Fourier maps and refined isotropically. All calculations were carried out using the SHELXS-86<sup>27</sup> and

**Table 1.** Principal crystallographic data and characteristics of X-ray diffraction study for compound **3**

Parameter	Characteristics
Molecular formula	C <sub>25</sub> H <sub>26</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub>
Molar weight/g mol <sup>-1</sup>	498.60
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	21.381(3)
<i>b</i> /Å	7.900(1)
<i>c</i> /Å	14.162(2)
β/deg	95.606(5)
<i>V</i> /Å <sup>3</sup>	2380.5(5)
<i>Z</i>	4
ρ <sub>calc</sub> /g cm <sup>-3</sup>	1.391
<i>F</i> (000)	1048
μ(MoKα)/mm <sup>-1</sup>	0.264
Crystal dimensions/mm	0.22 × 0.14 × 0.02
<i>T</i> /K	120.0(2)
Radiation/Å	Mo-Kα (λ = 0.71073)
Scan mode	ω
θ Scan range/deg	0.96–28.00
Ranges of indices of measured reflections	–27 ≤ <i>h</i> ≤ 28, –10 ≤ <i>k</i> ≤ 9, –18 ≤ <i>l</i> ≤ 13
Number of measured reflections	13776
Number of independent reflections	5721 ( <i>R</i> <sub>int</sub> = 0.1452)
Number of reflections with <i>I</i> > 2σ( <i>I</i> )	2361
Number of parameters in refinement	412
<i>R</i> factor using reflections with <i>I</i> > 2σ( <i>I</i> )	<i>R</i> <sub>1</sub> = 0.0736, <i>wR</i> <sub>2</sub> = 0.1336
<i>R</i> factor using all reflections	<i>R</i> <sub>1</sub> = 0.2095, <i>wR</i> <sub>2</sub> = 0.1756
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.899
Residual electron density/e Å <sup>-3</sup> (min/max)	–0.520/0.535

SHELXL-97<sup>28</sup> program packages. The crystallographic data were deposited with the Cambridge Structural Database.\*

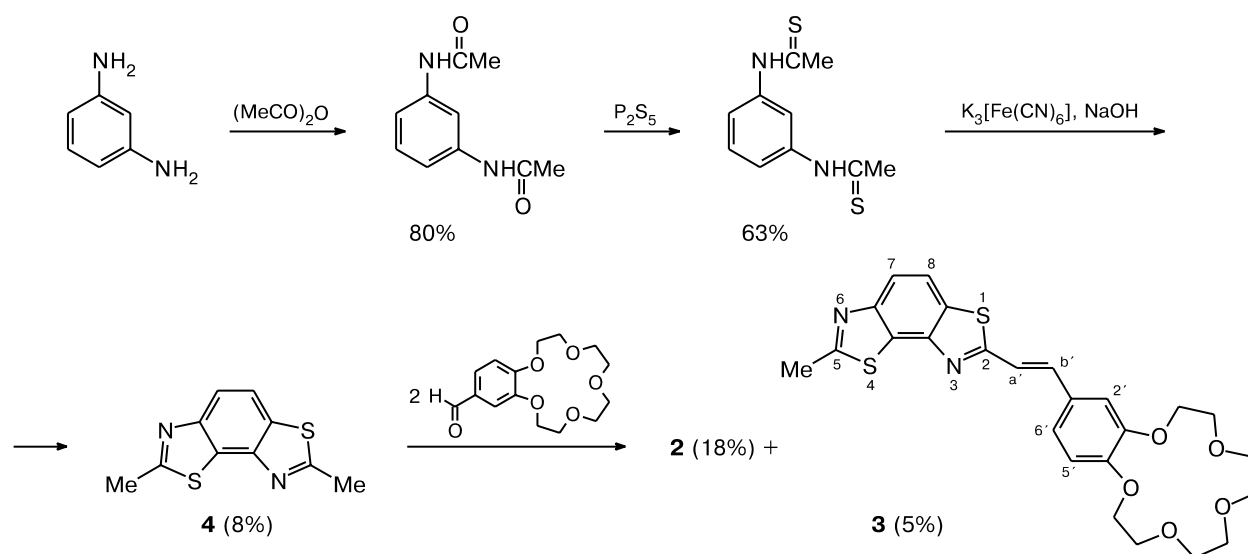
## Results and Discussion

### Synthesis and structure solution

Compound **2** was synthesized by condensation of 2,5-dimethylbenzobisthiazole **4** with the formyl derivative of benzo-15-crown-5 ether in DMSO in the presence of Bu<sup>t</sup>OK at room temperature (Scheme 1). In addition to reaction product **2**, we isolated a small amount of monocondensation product **3**. The starting heterocyclic base **4** was synthesized in three steps according to known procedures.<sup>24,25</sup>

\* These data (refcode 245026) can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

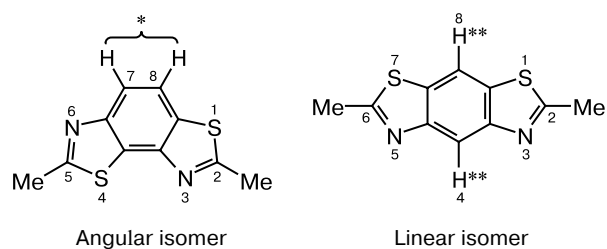
Scheme 1



In the above-mentioned publications, there was no general agreement as to the structure of the resulting heterocyclic base. Hence, we studied the structure of compound **4**.

The cyclization reaction can afford two isomeric benzobisthiazoles with either a linear or angular structure. The  $^1\text{H}$  NMR spectrum of the linear symmetrical isomer should contain two singlets corresponding to the protons H(4) and H(8), whereas the spectrum of the angular isomer should have two doublets corresponding to the protons H(7) and H(8). Analysis of the  $^1\text{H}$  NMR spectra confirmed the formation of angular isomer **4**.

The structure of compound *E,E*-**2** was established by  $^1\text{H}$  NMR spectroscopy. The spin-spin coupling constant for the protons at the C=C bond (16.1 Hz) provides evidence that this compound exists as the *E,E* isomer. The differences in the chemical shifts for the pairs of the protons H(6') and H(6''), H(2') and H(2''),  $\text{H}_{\text{a}'}$  and  $\text{H}_{\text{a}''}$ , and  $\text{H}_{\text{b}'}$  and  $\text{H}_{\text{b}''}$  indicate that molecule *E,E*-**2** is asymmetric. We failed to perform conformational analysis of molecule



\* Two doublets ( $\delta$  7.3 and 7.5). \*\* Both singlets.

*E,E*-**2** based on the  $^1\text{H}$  NMR spectroscopic data. Hence, molecule **2** is presented as an arbitrary chosen conformer in the subsequent schemes of photoprocesses, which show the reactions involving the C=C bonds.

The structure of compound **3** was established by X-ray diffraction analysis. The molecular structure and the atomic numbering scheme are presented in Fig. 1.

Molecule **3** consists of the following three planar fragments: the benzene ring of the benzocrown fragment C(9)...C(14), the C(13)—C(15)=C(16)—C(17) fragment

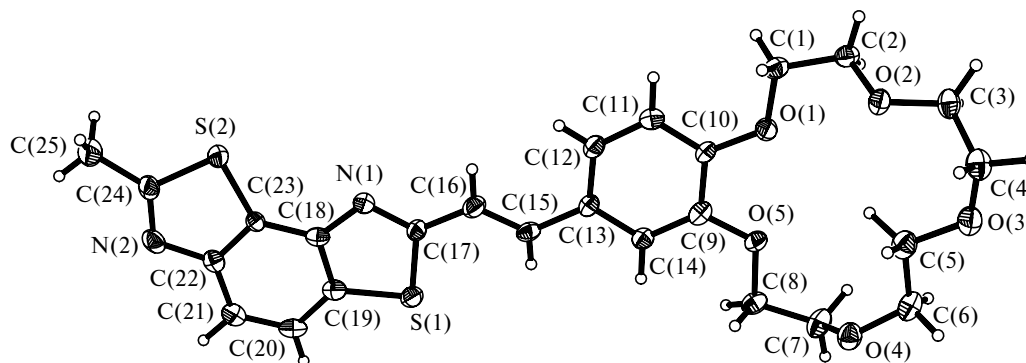


Fig. 1. Molecular structure of benzobisthiazole **3** with displacement ellipsoids drawn at the 50% probability level.

**Table 2.** Selected bond lengths ( $d$ ) and bond angles ( $\omega$ ) in compound **3**

Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$	Angle	$\omega/\text{deg}$
S(1)—C(17)	1.766(5)	C(11)—C(12)	1.387(6)	C(17)—S(1)—C(19)	89.8(2)
S(1)—C(19)	1.742(5)	C(12)—C(13)	1.393(6)	C(23)—S(2)—C(24)	88.9(2)
S(2)—C(23)	1.728(5)	C(13)—C(14)	1.405(6)	C(1)—O(1)—C(10)	117.8(3)
S(2)—C(24)	1.763(2)	C(9)—C(14)	1.386(6)	C(8)—O(5)—C(9)	117.6(3)
N(1)—C(17)	1.318(5)	C(13)—C(15)	1.485(6)	O(5)—C(9)—C(10)	113.9(4)
N(1)—C(18)	1.390(5)	C(15)—C(16)	1.322(6)	O(5)—C(9)—C(14)	125.9(4)
N(2)—C(22)	1.396(6)	C(16)—C(17)	1.438(6)	O(1)—C(10)—C(9)	115.5(4)
N(2)—C(24)	1.308(6)	C(18)—C(19)	1.401(6)	O(1)—C(10)—C(11)	125.3(4)
O(5)—C(9)	1.374(5)	C(19)—C(20)	1.408(7)	C(13)—C(15)—C(16)	126.9(4)
O(1)—C(10)	1.379(5)	C(20)—C(21)	1.367(7)	C(15)—C(16)—C(17)	127.6(4)
C(9)—C(10)	1.422(6)	C(21)—C(22)	1.408(7)		
C(10)—C(11)	1.384(6)	C(22)—C(23)	1.414(7)		

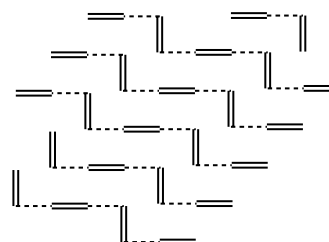
containing the double bond, and the tricyclic heteroaromatic system. The dihedral angles between the first and second planes and between the second and third planes are small ( $4.6^\circ$  and  $3.4^\circ$ , respectively).

Selected bond lengths and bond angles in molecule **3** are given in Table 2.

The ethylenic bond is essentially localized. The bond lengths in the C(13)—C(15)=C(16)—C(17) fragment are 1.485(6), 1.322(6), and 1.438(6) Å, respectively.

The geometry of the benzene ring in the benzocrown moiety is somewhat distorted. The C(9)—C(10) bond shared by two cyclic systems is elongated (1.422(6) Å) compared to two adjacent bonds, C(9)—C(14) and C(10)—C(11) (1.386(6) and 1.384(6) Å, respectively). In addition, the O(1)—C<sub>Ph</sub>—C<sub>Ph</sub> and O(5)—C<sub>Ph</sub>—C<sub>Ph</sub> bond angles at the C(10) and C(9) atoms of the benzene ring have different values. Two angles, which are exocyclic with respect to both cyclic systems, are larger ( $125.3(4)$  and  $125.9(4)^\circ$ ), whereas two other angles are smaller ( $115.5(4)$  and  $113.9(4)^\circ$ ). The character of this distortion is opposite to that, which would be expected based on steric repulsion between the *ortho* substituents, *viz.*, the O(1) and O(5) atoms, because the distance between these atoms (2.572(4) Å) is smaller than twice the van der Waals radius of the oxygen atom ( $\sim 2.8$  Å). At the same time, the C(1)—O(1)—C(10)—C(11) and C(8)—O(5)—C(9)—C(14) torsion angles are small ( $3.9^\circ$  and  $8.6^\circ$ , respectively) and characterize almost planar systems. The bond angles at these oxygen atoms ( $117.8(3)^\circ$  and  $117.6(3)^\circ$ , respectively) correspond to the  $sp^2$ -hybridized state of these atoms. All these geometric features are observed for all benzocrown ethers. Earlier, the same situation has been described<sup>12</sup> for *E-1*. These facts can be explained within the concept of conjugation between the lone pairs of the oxygen atoms occupying the p orbitals and the  $\pi$  system of the benzene ring.

The conjugated moieties of the molecules, which form hydrophobic regions, are arranged in stacking dimers, which, in turn, are packed in a herringbone fashion.<sup>29</sup>



The stacking dimer of compound **3** has a centrosymmetric structure (Fig. 2).

The tricyclic system of one molecule and the benzene ring of another molecule are parallel to each other and are shifted with respect to each other, which is typical of stacking interactions.<sup>30,31</sup> The distances between the N(1A), C(18A), C(19A), C(20A), C(21A), C(22A), and C(23A) atoms and the mean plane of the benzene ring C(9B)...C(14B) are 3.506, 3.405, 3.265, 3.234, 3.324, 3.410, and 3.446 Å, respectively. The dihedral angle between these fragments is small ( $4.9^\circ$ ). The geometric features are typical of systems with stacking interactions.

Two ethylenic bonds are parallel to each other and are located one above another, which is favorable for the photochemical [2+2] cycloaddition reaction giving rise to the centrosymmetric isomer of the cyclobutane derivative. The distances between the C(15A)...C(16B) and C(16A)...C(15B) atoms of the ethylene fragments (3.803 Å) are rather short, which could promote this reaction. However, this reaction is unlikely to occur in this crystal packing because each dimer is surrounded by the adjacent rigid conjugated structural fragments rather than by labile crown-ether chains. Moreover, this rigid structure is stabilized by the cooperative effect of weak intermolecular S...H—C interactions responsible for the formation of infinite chains in the crystal structure.

### Complexation

The electronic absorption spectra of ligand *E,E-2* in MeCN are characterized by an intense long-wavelength

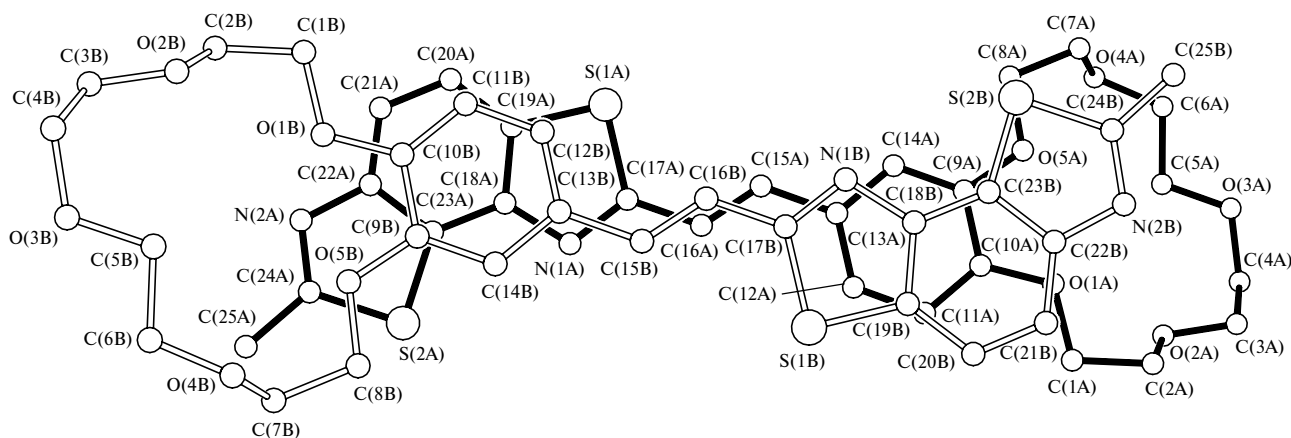


Fig. 2. Structure of the stacking dimer of compound 3 projected along the normal to the mean plane of the molecules.

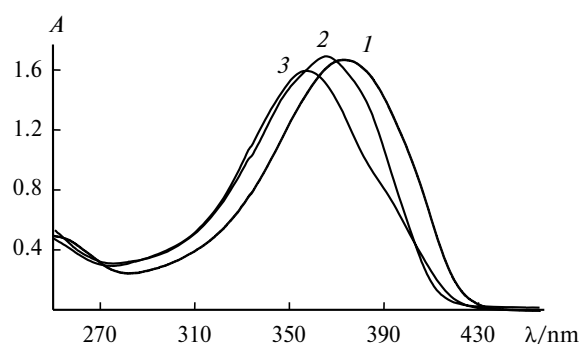


Fig. 3. Absorption spectra (in MeCN) of free ligand *E,E-2* (1) and its complexes (*E,E-2*)·2Ba<sup>2+</sup> ( $C_2 = C_{(E,E-2) \cdot 2Ba^{2+}} = 2.4 \cdot 10^{-5}$  mol L<sup>-1</sup>) (2) and 2(*E,E-2*)·2Ba<sup>2+</sup> ( $C_{2(E,E-2) \cdot 2Ba^{2+}} = 1.2 \cdot 10^{-5}$  mol L<sup>-1</sup>) (3).

Table 3. Spectroscopic characteristics of compounds *E-1* and *E,E-2* and complexes of compound *E,E-2*

Compound	Absorption spectrum		Fluorescence	
	$\lambda_{\max}$ /nm	$\epsilon_{\max} \cdot 10^{-4}$ *	$\lambda_{\max}$ /nm (shift**)	Quantum yield
<i>E-1</i>	359.2	3.36	452	0.0069
<i>E,E-2</i>	374.5	6.26	461	0.011
( <i>E,E-2</i> )·Mg <sup>2+</sup>	365.0	5.92	461 (0)	0.013
( <i>E,E-2</i> )·2Mg <sup>2+</sup>	361.0	6.14	460 (-1)	0.022
2( <i>E,E-2</i> )·2Ba <sup>2+</sup>	356.0	5.73	472 (11)	0.034
( <i>E,E-2</i> )·2Ba <sup>2+</sup>	359.7	5.86	468 (7)	0.025
( <i>E,E-2</i> )·Ca <sup>2+</sup>	363.6	5.86	462 (1)	0.016
( <i>E,E-2</i> )·2Ca <sup>2+</sup>	361.6	6.04	461 (0)	0.022
( <i>E,E-2</i> )·Na <sup>+</sup>	370.0	5.92	461 (0)	0.011
( <i>E,E-2</i> )·2Na <sup>+</sup>	366.3	6.18	452 (-9)	0.014
2( <i>E,E-2</i> )·2K <sup>+</sup>	365.5	5.76	467 (6)	0.033
2( <i>E,E-2</i> )·2Rb <sup>+</sup>	370.4	5.93	467 (6)	0.018
( <i>E,E-2</i> )·2Rb <sup>+</sup>	366.3	6.00	475 (14)	0.030

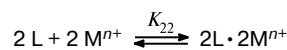
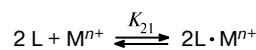
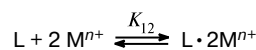
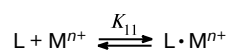
\*  $\epsilon_{\max} \cdot 10^{-4}$  /L mol<sup>-1</sup> cm<sup>-1</sup>.

\*\* The shift relative to the ligand.

absorption band with a maximum at 374 nm ( $\epsilon_{trans} = 6.26 \cdot 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) (Fig. 3, curve 1, Table 3). The long-wavelength absorption band of *E,E-2* is bathochromically shifted relative to that of monocrown-containing analog *E-1*. This shift can, in particular, be attributed to an interaction between two chromophoric systems of molecule *E,E-2*, which has been described earlier.<sup>32</sup>

The addition of metal (Na, K, Rb, Mg, Ca, or Ba) perchlorates to a solution of *E,E-2* ( $2.4 \cdot 10^{-5}$  mol L<sup>-1</sup>) in MeCN leads to a hypsochromic shift of the long-wavelength band in the electronic absorption spectrum, which is indicative of complexation involving the crown fragment (see Table 3).

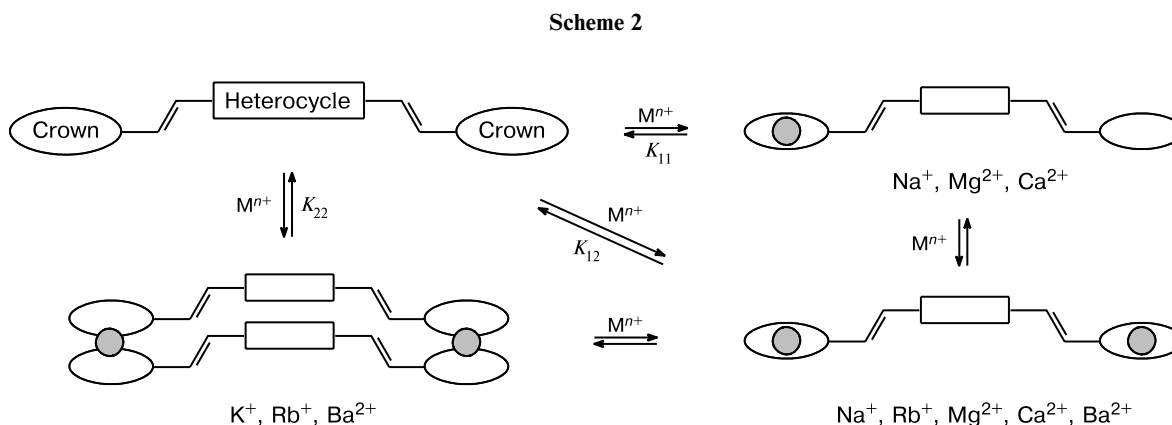
The stability constants of the complexes of *E,E-2* with alkali cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, and Rb<sup>+</sup>) and alkaline earth cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Ba<sup>2+</sup>) were determined by spectrophotometric titration using the HYPERQUAD program.<sup>26</sup> In the calculations, the possibility of complexation according to the following equations was taken into account:



The calculated stability constants are given in Table 4. Ligand *E,E-2* forms two types of complexes with Na<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> cations, viz., (*E,E-2*)·M<sup>n+</sup> and (*E,E-2*)·2M<sup>n+</sup> (see Table 4, Scheme 2). Two types of complexes, (*E,E-2*)·2M<sup>n+</sup> and 2(*E,E-2*)·2M<sup>n+</sup>, were obtained for Rb<sup>+</sup> and Ba<sup>2+</sup> cations. For K<sup>+</sup> cations, only the complex 2(*E,E-2*)·2M<sup>n+</sup> was found. The sandwich complex with Ba<sup>2+</sup> cations is highly stable. The absorption spectra of the (*E,E-2*)·2Ba<sup>2+</sup> and 2(*E,E-2*)·2Ba<sup>2+</sup>

**Table 4.** Stability constants of the complexes of *E-1* and *E,E-2* with Ba<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Rb<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> perchlorates in acetonitrile (293 K) and under conditions of complexation

Complex	$D^*/\text{\AA}$	$\log K_{11}$	$\log K_{12}$	$\log K_{22}$	$\log K_{21}$	Ionic strength/mol L <sup>-1</sup>
( <i>E-1</i> )·Ba <sup>2+</sup>	2.70	4.7±0.1			10.8±0.2	0–0.2
( <i>E,E-2</i> )·Ba <sup>2+</sup>	2.70		7.68±0.065	17.11±0.07		0–1.7·10 <sup>-4</sup> , 1.7·10 <sup>-4</sup> –0.86
( <i>E-1</i> )·Ca <sup>2+</sup>	1.98	5.6±0.1			10.3±0.2	0–2.5·10 <sup>-3</sup>
( <i>E,E-2</i> )·Ca <sup>2+</sup>	1.98	4.66±0.04	8.07±0.11			0–0.155
( <i>E-1</i> )·Mg <sup>2+</sup>	1.30	5.5±0.1				0–2.5·10 <sup>-3</sup>
( <i>E,E-2</i> )·Mg <sup>2+</sup>	1.30	5.64±0.2	10.15±0.2			0–1·10 <sup>-2</sup>
( <i>E,E-2</i> )·Rb <sup>+</sup>	2.96		8.68±0.04	14.08±0.046		0–2.5·10 <sup>-3</sup>
( <i>E,E-2</i> )·K <sup>+</sup>	2.66			15.97±0.084		0–1.67·10 <sup>-4</sup>
( <i>E,E-2</i> )·Na <sup>+</sup>	1.9	4.94±0.097	8.44±0.11			0–3·10 <sup>-3</sup>

\* The diameter of the cation (according to Pauling).<sup>34</sup>

complexes calculated from the results of spectrophotometric titration are presented in Fig. 3 (see curves 2 and 3). The formation of the sandwich complex causes a decrease in the absorption intensity accompanied by a hypsochromic shift of the long-wavelength absorption band. The formation of the (*E,E-2*)·2Ba<sup>2+</sup> complex leads to a slight increase in the absorption intensity.

Table 4 gives the data on complexation of bis(crown ether) *E,E-2* and the results obtained earlier<sup>12</sup> for monocrown-containing analog *E-1*. As can be seen from these data, the corresponding stability constants for compounds *E-1* and *E,E-2* in the case of complexation at one crown fragment have similar values. The involvement of two crown fragments of molecule *E,E-2* in complexation results in the formation of more structurally diverse complexes and stronger binding of metal cations.

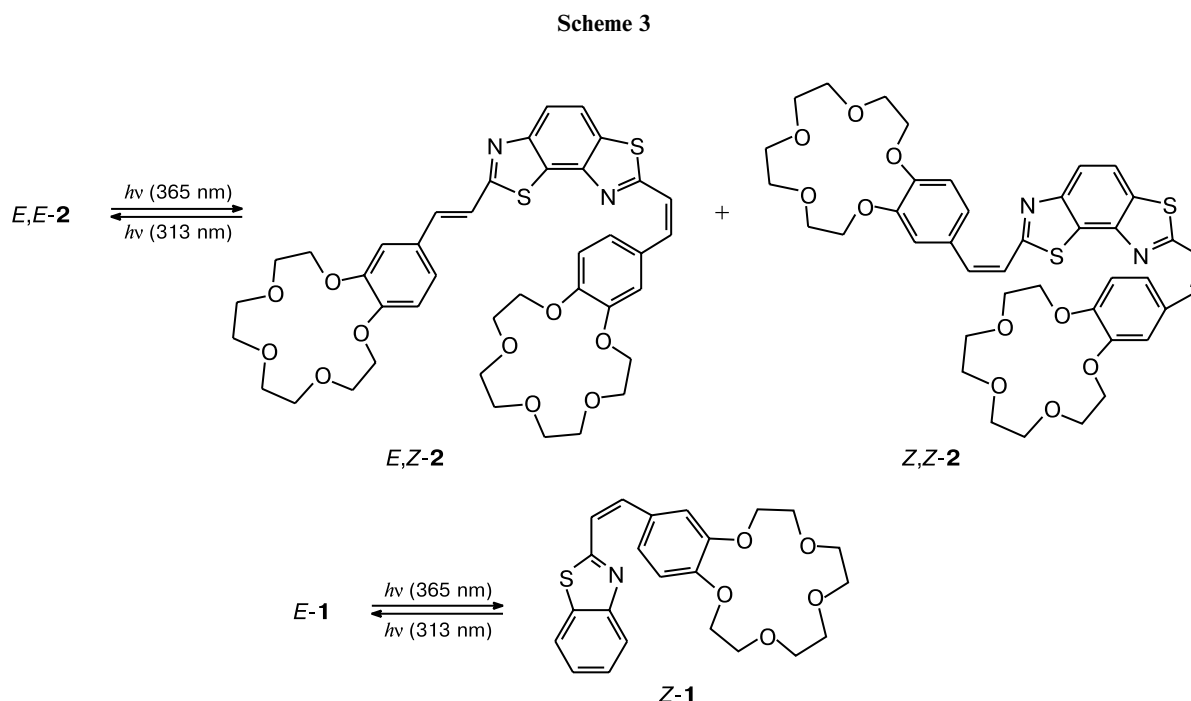
**Fluorescence spectra.** The addition of metal (Na, K, Rb, Mg, Ca, or Ba) perchlorates to a solution of *E,E-2* ( $7.5 \cdot 10^{-6}$  mol L<sup>-1</sup>) in MeCN leads to changes in the stationary fluorescence spectra (see Table 3). Taking into account the calculated stability constants (see Table 4), we prepared solutions of the complexes with the prevailing particular stoichiometry. Interestingly, the

2(*E,E-2*)·2Ba<sup>2+</sup> and 2(*E,E-2*)·2K<sup>+</sup> complexes show a strong fluorescence increase compared to the starting ligand, which can be associated with interactions of the ligands in sandwich complexes. All other complexes under study showed no substantial fluorescence increase.

#### Photochemical transformations

Irradiation of a solution of free ligand *E,E-2* in MeCN at a wavelength of 365 nm leads to a decrease in the absorbance in the region of the long-wavelength absorption band. Analysis of the changes in the electronic absorption spectra upon irradiation led us to conclude that at least two photoprocesses occur.

One process is accompanied by the appearance of an isosbestic point at 320 nm and is characterized by a high quantum yield ( $\phi = 0.48$ ). Another process is accompanied by the appearance of an isosbestic point at 290 nm and is inefficient (the quantum yield is lower than 0.001). Presumably, the former process is *E*→*Z* photoisomerization, which is characteristic of crown-containing 2-styrylbenzothiazoles.<sup>11</sup> Detailed analysis of the *E*→*Z*-photoisomerization products was carried out by HPLC. It was found that two products with retention times of 3 and



3.3 min were formed after irradiation for 4 s. The absorption spectrum of the product with a retention time of 3 min (see Fig. 4, curve 2) coincides with the calculated spectrum of isomer *E,Z-2* (see Fig. 4, curve 3). This isomer is generated by *E*→*Z*-photoisomerization of only one C=C bond of the molecule (Scheme 3).

The spectrum of another photoisomer (see Fig. 4, curve 4) with a retention time of 3.3 min is virtually identical to the spectrum of the *Z* isomer of monocrown ether **1** (see Scheme 3 and Fig. 4, curve 9). This may be evidence

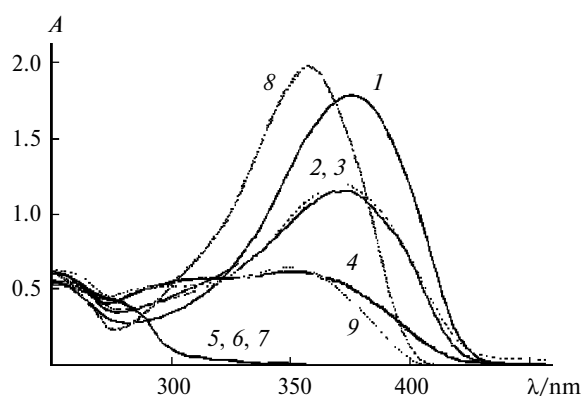
that both C=C bonds in this isomer of compound **2** are in the *Z* position.

Irradiation of bis(crown ether) *E,E-2* in MeCN for 4 h induces a weakly efficient photochemical process giving rise to products with retention times of 15.5 and 17.8 min. The UV spectra of these compounds (see Fig. 4, curves 5–7) are similar to the spectra of cyclobutane derivatives, which have been prepared earlier<sup>32</sup> by photolysis of Ba<sup>2+</sup> complexes with ligand **1**.

The <sup>1</sup>H NMR spectra of products prepared by prolonged photolysis confirmed the formation of isomeric cyclobutanes. In the <sup>1</sup>H NMR spectra of these products, signals for the protons of the double bond are absent, and the spectra show signals at δ 4.90–5.40.

Earlier, we have observed spontaneous dimerization of styryl dyes in the presence of metal cations giving rise to cyclobutanes upon irradiation.<sup>34–36</sup> In the presence of barium cations, compound **1** was demonstrated to form a sandwich complex, in which the molecules are stacked one above another.<sup>32</sup> Photolysis of such complexes affords cyclobutane derivatives. However, in the absence of metal cations, all the above-mentioned compounds are not involved in cycloaddition.

In the case of compound *E,E-2*, the [2+2] photocycloaddition occurs, presumably, in dimers, which are formed in a solution of *E,E-2* as a result of π-stacking interactions between the extended chromophoric systems (Scheme 4). This assumption was additionally confirmed by ESI mass-spectrometric analysis of a solution of ligand *E,E-2*. In addition to the peak of the complexes of the main compound *E,E-2* with Na<sup>+</sup> cations (*m/z* 799.3), the

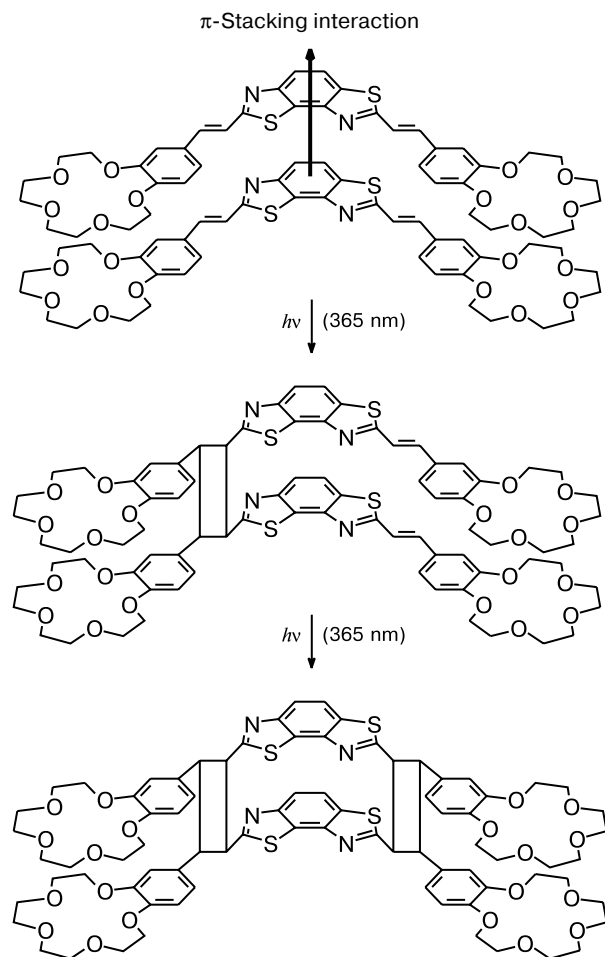


**Fig. 4.** Electronic absorption spectra of isomers *E,E-2* ( $C = 3 \cdot 10^{-5} \text{ mol L}^{-1}$ ) (1), *E,Z-2* (2 and 3; 3, the spectrum of the isomer calculated by the Fisher method), and *Z,Z-2* (4); products of chromatographic separation of a mixture prepared by irradiation of the  $2(E,E-2) \cdot 2\text{Ba}^{2+}$  complex for 8 min ( $C_2 = 2.4 \cdot 10^{-5} \text{ mol L}^{-1}$ ,  $C_{\text{Ba}(\text{ClO}_4)_2} = 1 \cdot 10^{-4} \text{ mol L}^{-1}$ ) (5–7); *E-1* ( $C = 6 \cdot 10^{-5} \text{ mol L}^{-1}$ ) (8); and *Z-1* ( $C = 6 \cdot 10^{-5} \text{ mol L}^{-1}$ ) (9).<sup>11</sup>



spectrum shows peaks of the dimers of  $2(E,E-2) \cdot Na^+$  and  $2(E,E-2) \cdot K^+$  ( $m/z$  1575.6 and  $m/z$  1591.6, respectively).

Scheme 4



The process induced by irradiation of the  $2(E,E-2) \cdot 2Ba^{2+}$  complex with light at 365 nm is [2+2] photocycloaddition, which was confirmed by HPLC, UV spectroscopy, and mass spectrometry. Actually, photolysis afforded products with retention times of 20–24 min. Their absorption spectra (see Fig. 4, curves 5–7) correspond to the spectra of cyclobutane derivatives prepared upon prolonged irradiation of a solution of ligand **2** in the absence of metal cations. Three photolysis products were isolated by HPLC, and their precise weights were determined by ESI mass spectrometry. These results suggest that the photoreaction produced three isomeric cyclobutane derivatives. Unfortunately, the structures of these compounds cannot be studied by NMR spectroscopy because of their low solubilities.

Irradiation of the  $2(E-2) \cdot 2Ba^{2+}$  complex did not give rise to the *Z* isomer. Apparently, the [2+2] photocycloaddition is the major process due to its high effi-

ciency. The measured quantum yield of cyclobutane formation was  $\phi = 0.26$ . Analysis of a solution of the complex by mass spectrometry demonstrated that ligand *E,E-2* is completely dimerized in a solution in the presence of barium cations. In the  $2(E,E-2) \cdot 2Ba^{2+}$  complex, there are  $\pi$ -stacking interactions between the chromophoric groups along with additional binding of the crown fragments of the adjacent molecules giving rise to a sandwich complex. The influence of both factors results in the close arrangement of two molecules **2**, which is favorable for efficient cycloaddition.

The photochemical transformations of the  $(E,E-2) \cdot 2Mg^{2+}$  complex induced by light at 365 nm correspond to photochemical transformations of free ligand **2**. Irradiation of the complex for 4 s gave the  $(Z,Z-2) \cdot 2Mg^{2+}$  complex. More prolonged irradiation for 32 min led to the complete conversion of the complex into cyclobutane derivatives. The data on the compositions of the complexes of **2** with  $Mg^{2+}$  obtained from analysis of the mass spectra suggest that the amount of the dimeric complexes in solution in the presence of  $Mg^{2+}$  ions is smaller than that in the presence of  $Ba^{2+}$  ions, which can explain the low efficiency of cycloaddition in this case.

To summarize, we synthesized new benzobisthiazole-based bis(crown ether). It was found that ligand **2** in acetonitrile forms complexes with alkali and alkaline earth cations, which is accompanied by a hypsochromic shift of the long-wavelength absorption band. Ligand **2** has several binding sites for cations and exhibits different optical properties in complexes with different cations. The optical characteristics of a particular complex depend on the nature of the cation and, correspondingly, on the nature of the group of the ligand coordinated to this cation.

The photochemical transformations of free ligand *E,E-2* and its complexes involve *E,Z*-photoisomerization and [2+2] photocycloaddition. The photoisomerization of the free ligand and its complex with the magnesium cation occurs efficiently. For complexes of ligand *E,E-2* with barium cations, photoisomerization was not observed. The photochemical transformation of this complex efficiently affords [2+2] photocycloaddition products due to preorganization of the ligand molecules in the sandwich-type complex.

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