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# A photochemical electrocyclization of the benzothiazolylphenylethenes involving a C–N bond formation

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**Abstract**

A novel oxidative photodehydrocyclization of benzothiazolylphenylethenes to a polycyclic heteroaromatic cations with good yields was described. Starting from the *trans*-derivative, the phototransformation is a multistep process. It includes two photochemical reactions, a *trans-cis*-isomerization reaction followed by an 1-aza-1,3,5-hexatrienic electrocyclic reaction involving the formation of C–N bond. The cyclized product gives the stable heteroaromatic cations from hydride elimination with oxygen from air.


*Keywords:* Electrocyclic reaction; Photocyclization; 2-Styrylbenzothiazoles; Crown ethers; Benzothiazolo[3,2-*a*]quinolines

## 1. Introduction

Conjugated diarylethylenes, the prototype of which is stilbene, are well known for undergoing a photoreversible cyclization reaction leading to dihydrophenanthrenes [1–5]. When the aryl groups were replaced by furan, thiophen or other heterocyclic rings, which have low aromatic stabilization energies, the closed ring forms were thermally stable and did not return to the open-ring forms in the dark [6–8]. Thermal irreversibility and fatigue resistance of the two photochemical forms are a prerequisite for applications of dihetarylethenes to optoelectronic devices, such as memories and switches [9].

The photochemical behavior of stylbenes in which one phenyl group is substituted by heterocycle reported is not different from the parent carbocyclic compounds: *Z-E*-isomerization [9,10], [2 + 2]-photocyloaddition reaction [11–13] and hexatriene cyclization reaction [14,15] that leads to polycyclic heterocycles after oxidative dehydrogenation. It is remarkable that an N-heteroatom in the *ortho* position of the double bond does not take part in the photocyclization, for example, 2-stilbazole leads to benzo[f]quinoline [16]. Early [17,18] the novel phototransformation of indolinylphenylethenes into the heteroaromatic cations was described. The process includes the electrocyclic reaction through the formation of C–N bond. The found photocyclization has possible preparative value, especially in view of the comparative inaccessibility of heteroaromatic cations by normal chemical synthesis.

In the present work, we studied the photocyclization through the formation of C–N bond for another type of hetarylphenylethene molecule—2-styrylbenzothiazoles (SB) **1**–**8** (Table 1). We evaluate the mechanism of the reaction, to analyze how the electron-donating and electron-withdrawing substituents influence the occurring of the process.

## 2. Experimental

### 2.1. Materials

A synthesis and structures of the SB **1**, **2**, **4**, **5** are described in Ref. [20].

*2-[(E)-2-(2,4-Dimethoxyphenyl)vinyl]-1,3-benzothiazole* (***3***) was synthesized similarly to **1** in 77% yield, m.p. 119–124 °C (from methanol). Anal. calcd. for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.08; N, 4.71; found: C, 68.62; H, 5.09; N, 4.74. $^1$H NMR ($CD_3CN$), $\delta$: 3.87 and 3.90 (2s, 6H, $2OCH_3$); 7.00 (d, 1H, H-6′, $J$ = 8.3 Hz); 7.24 (d, 1H, H-5′, $J$ = 8.3 Hz); 7.32 (s, 1H, H-3′); 7.41 (d, 1H, H-b, $J$ = 16.1 Hz); 7.42 and 7.51 (both m, 2H, H-5, H-6); 7.58 (d, 1H, H-a, $J$ = 16.2 Hz); 7.96 and 7.98 (both d, 2H, H-4, H-7, $J$ = 8.0 Hz, $J$ = 8.1 Hz).

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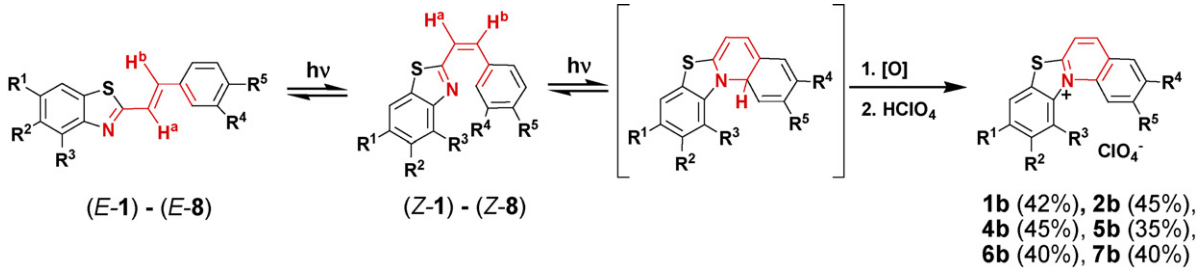



Scheme 1.

*2-[(E)-2-(3,4-Dimethoxyphenyl)vinyl]-1,3-benzothiazole* (***4***) [20]. $^1$H NMR ($CD_3CN$), $\delta$: 3.87 and 3.90 (2s, 6H, $2OCH_3$); 7.00 (d, 1H, H-5′, $J = 8.4$ Hz); 7.14 (d, 1H, H-6′, $J = 8.3$ Hz); 7.32 (s, 1H, H-2′); 7.41 (m, 3H, H-5, H-6, H-b); 7.59 (d, 1H, H-a, $J = 16.1$ Hz); 7.97 and 7.98 (both d, 2H, H-4, H-7, $J = 8.0$ Hz, $J = 8.1$ Hz).

*2-{(E)-2-[3,4-(4,7,10,13-Tetroxacyclooctadec-1,16-ylenedioxy)phenyl]-ethenyl}-1,3-benzothiazole* (***5***) [20]. $^1$H NMR ($CD_3CN$), $\delta$: 3.57 (s, 4H, $2OCH_2$); 3.60 (m, 4H, $2OCH_2$); 3.63 (m, 4H, $2OCH_2$); 3.79 (m, 4H, $2OCH_2$); 4.21 (m, 2H, $ArOCH_2$); 4.25 (m, 2H, $ArOCH_2$); 6.88 (d, 1H, H-5′, $J = 8.2$ Hz); 7.22 (d, 1H, H-6′, $J = 8.3$ Hz); 7.29 (s, 1H, H-2′); 7.42 (d, 1H, H-b, $J = 16.5$ Hz); 7.42 (tr, 1H, H-5, $J = 8.2$ Hz, $J = 7.5$ Hz); 7.51 (tr, 1H, H-6, $J = 8.3$ Hz, $J = 7.5$ Hz); 7.56 (d, 1H, H-a, $J = 16.5$ Hz); 7.47 and 7.63 (both d, 2H, H-4, H-7, $J = 8.2$ Hz, $J = 8.3$ Hz).

*2-{(E)-5,6-Dimethoxy-2-[3,4-(4,7,10,13-Tetroxacyclooctadec-1,16-ylenedioxy)phenyl]-ethenyl}-1,3-benzothiazole* (***6***) was synthesized similarly to **1** in 67% yield, m.p. 129–134 °C (from methanol). Anal. calcd. for $C_{27}H_{33}NO_8S$: C, 61.00; H, 6.26; N, 2.63; found: C, 61.02; H, 6.29; N, 2.71. $^1$H NMR (DMSO), $\delta$: 3.58 (s, 4H, $2OCH_2$); 3.60 (m, 4H, $2OCH_2$); 3.63 (m, 4H, $2OCH_2$); 3.79 (m, 4H, $2OCH_2$); 3.85 and 3.92 (both s, 6H, $2OCH_3$); 4.20 (m, 2H, $ArOCH_2$); 4.24 (m, 2H, $ArOCH_2$); 6.97 (d, 1H, H-5′, $J = 8.3$ Hz); 7.18 (d, 1H, H-6′, $J = 8.3$ Hz); 7.26 (s, 1H, H-2′); 7.34 and 7.48 (both d, 2H, H-a, H-b, $J = 15.8$ Hz, $J = 15.8$ Hz); 7.48 (both s, 2H, H-4, H-7).

*2-{(E)-5-Phenyl-2-[3,4-(4,7,10,13-Tetroxacyclooctadec-1,16-ylenedioxy)phenyl]ethenyl}-1,3-benzothiazole* (***7***) was synthesized similarly to **1** in 27% yield, m.p. 139–143 °C (from methanol). Anal. calcd. for $C_{31}H_{33}NO_6S$: C, 67.99; H, 6.07; N, 2.56; found: C, 67.95; H, 6.09; N, 2.61. $^1$H NMR($CD_3CN$), $\delta$: 3.54 (s, 4H, $2OCH_2$); 3.57 (m, 4H, $2OCH_2$); 3.62 (m, 4H, $2OCH_2$); 3.78 (m, 4H, $2OCH_2$); 4.14 (m, 2H, $ArOCH_2$); 4.21 (m, 2H, $ArOCH_2$); 7.01 (d, 1H, H-5′, $J = 8.7$ Hz); 7.29 (d, 1H, H-6′, $J = 8.7$ Hz); 7.39 (m, 1H, Ph); 7.45 (s, 1H, H-2′); 7.48–7.53 (m, 3H, H-a, Ph); 7.57 (d, 1H, H-b, $J = 16.2$ Hz); 7.73 (m, 2H, Ph); 7.77 (d, 1H, H-6, $J = 7.7$ Hz); 8.14 (d, 1H, H-7, $J = 7.7$ Hz); 8.18 (s, 1H, H-4).

*2-{(E)-2-[3,4-(4,7,10,13-Tetroxacyclooctadec-1,16-ylenedioxy)phenyl]ethenyl}-1,3-naphthothiazole* (***8***) was synthesized similarly to **1** in 22% yield, m.p. 147–149 °C (from methanol). Anal. calcd. for $C_{29}H_{31}NO_6S$: C, 66.77; H, 5.99; N, 2.69; found: C, 66.72; H, 5.96; N, 2.71. $^1$H NMR ($CD_3CN$), $\delta$: 3.72 (s, 4H, $2OCH_2$); 3.74 (m, 4H, $2OCH_2$); 3.81 (m, 4H, $2OCH_2$); 3.98 (m, 4H, $2OCH_2$); 4.22 (m, 2H, $ArOCH_2$); 4.28 (m, 2H, $ArOCH_2$); 6.86 (d, 1H, H-5′, $J = 8.2$ Hz); 7.26 (s, 1H, H-2′); 7.31 (d, 1H, H-6′, $J = 8.1$ Hz); 7.72 (d, 1H, H-b, $J = 15.8$ Hz); 7.73 and 7.90 (both m, 3H, H-5, H-b, H-6); 7.83 and 9.49 (both d, 2H, H-8, H-9, $J = 8.8$ Hz,

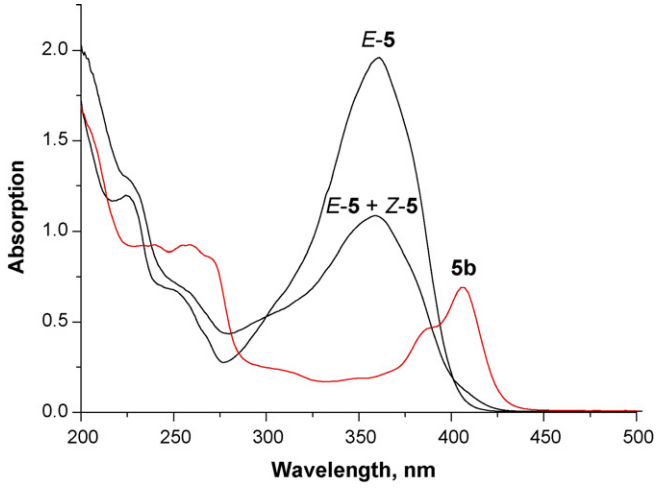
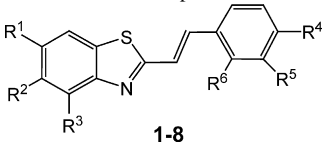



Fig. 1. Electronic absorption spectra of acetonitrile solution of **5**([**5**] = 0.04 mM/L) before (*E*-**5**) and after irradiation with a high pressure Hg-lamp (DRK-120, 120 W), under air: (*E*-**5** + *Z*-**5**), 10 min irradiation at 365 nm; (**5b**), 20 min irradiation at full light.

Table 1
Structure of the compounds SB **1–8**



**1-8**

| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ |
|---|---|---|---|---|---|---|
| **1** | H | H | H | | | H |
| **2** | H | OMe | H | | | H |
| **3** | H | H | H | OMe | H | OMe |
| **4** | H | H | H | OMe | OMe | H |
| **5** | H | H | H | | | H |
| **6** | OMe | OMe | H | | | H |
| **7** | H | Ph | H | | | H |
| **8** | H | | | | | H |

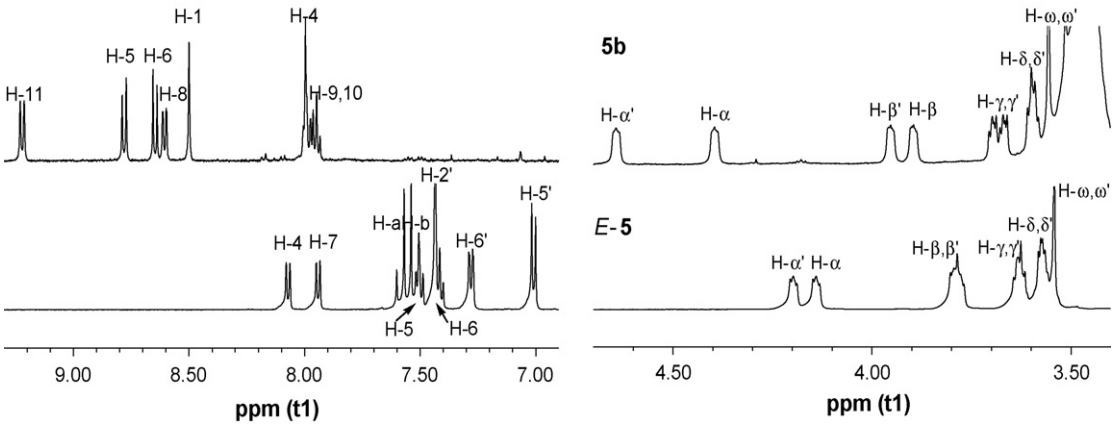



Fig. 2. $^1$H NMR spectra of an acetonitrile solution of *E*-**5** and **5b** (see detailed in Section 2).

$J$ = 8.3 Hz); 8.01 (d, 2H, H-4, H-7, $J$ = 8.5 Hz); 8.41 (d, 1H, H-a, $J$ = 15.8 Hz).

*Analysis of the photostationary mixture of trans and cis-isomers of compounds **3**–**8***. Solution of *trans*-**3**–**8** (0.01 mmol) in 0.6 ml $CD_3CN$ was irradiated with light at 365 nm for 10 min. The obtained spectra correspond to the mixture of *trans* and *cis* isomers of compounds **3**–**8**. So as the $^1$H NMR spectra of *trans*-**3**–**8** were known, the analysis of mixture allows the determination of $^1$H NMR spectra of *cis*-**3**–**8**.

*cis*-***3***. $^1$H ($CD_3CN$), $\delta$: 3.87 and 3.97 (2s, 6H, $2OCH_3$); 6.55 (d, 1H, H-5′, $J$ = 8.6 Hz); 6.56 (s, 1H, H-3′); 7.92 (d, 1H, H-b, $J$ = 13.0 Hz); 7.09 (d, 1H, H-a, $J$ = 13.0 Hz); 7.39 and 7.48 (both tr, 2H, H-5, H-6, $J$ = 8.0 Hz, $J$ = 7.7 Hz); 7.45 (d, 1H, H-6′, $J$ = 8.6 Hz); 7.83 and 7.93 (both d, 2H, H-4, H-7, $J$ = 8.0 Hz).

*cis*-***4***. $^1$H ($CD_3CN$), $\delta$: 3.81 and 3.87 (2s, 6H, $2OCH_3$); 6.82 (d, 1H, H-b, $J$ = 12.3 Hz); 6.98 (d, 1H, H-6′, $J$ = 8.2 Hz); 7.03 (d, 1H, H-a, $J$ = 13.1 Hz); 7.14 (d, 1H, H-5′, $J$ = 8.4 Hz); 7.42 and 7.51 (both m, 2H, H-5, H-6); 7.75 (s, 1H, H-2′); 7.91 and 7.95 (both d, 2H, H-4, H-7, $J$ = 8.1 Hz, $J$ = 8.1 Hz).

*cis*-***5***. $^1$H ($CD_3CN$), $\delta$: 3.57 (s, 4H, $2OCH_2$); 3.60 and 3.63 (both m, 4H, $2OCH_2$); 3.69 and 3.78 (both m, 4H, $2OCH_2$); 4.14 and 4.20 (both m, 4H, $ArO\underline{CH_2}$); 6.83 (d, 1H, H-b, $J$ = 12.2 Hz); 6.97 (d, 1H, H-5′, $J$ = 8.0 Hz); 6.98 (d, 1H, H-a, $J$ = 12.2 Hz); 7.19 (d, 1H, H-6′, $J$ = 8.0 Hz); 7.51 (tr, 2H, H-5, H-6, $J$ = 8.0 Hz, $J$ = 8.0 Hz); 7.67 (s, 1H, H-2′); 7.92 and 7.97 (both d, 2H, H-4, H-7, $J$ = 8.0 Hz).

*cis*-***6***. $^1$H ($CD_3CN$), $\delta$: 3.59 (s, 4H, $2OCH_2$); 3.60 and 3.63 (both m, 4H, $2OCH_2$); 3.71 and 3.79 (both m, 4H, $2OCH_2$); 3.83

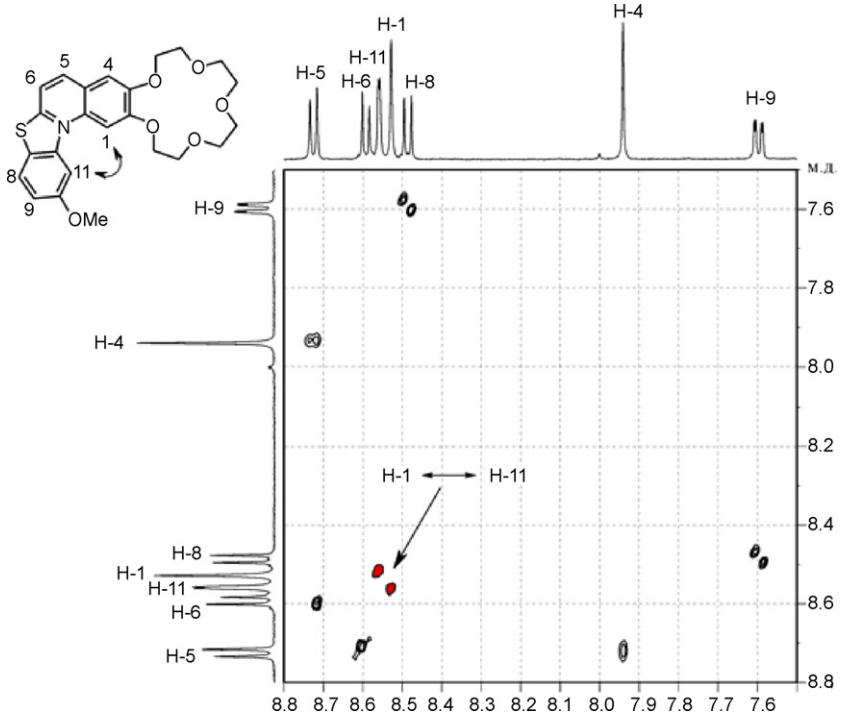
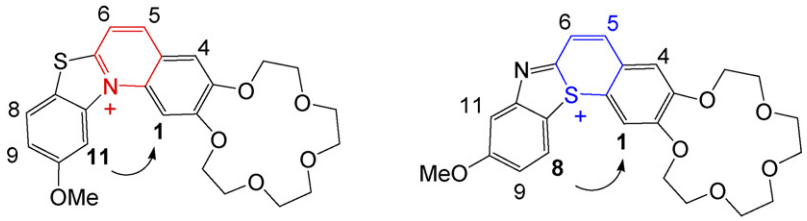



Fig. 3. NOESY spectrum of the product of photochemical cyclization of SB **2**.



Scheme 2.

and 3.91 (2s, 6H, $2OCH_3$); 4.15 and 4.20 (both m, 4H, $ArO\underline{CH_2}$); 6.77 (d, 1H, H-b, $J = 12.6$ Hz); 6.91 (d, 1H, H-a, $J = 12.6$ Hz); 6.96 (d, 1H, H-5′, $J = 8.3$ Hz); 7.08 (d, 1H, H-6′, $J = 8.3$ Hz); 7.41 (s, 1H, H-2′); 7.45 and 7.66 (both s, 2H, H-4, H-7).

*cis*-**7**. $^1$H NMR($CD_3CN$), $\delta$: 3.24 (s, 4H, $2OCH_2$); 3.38 (m, 4H, $2OCH_2$); 3.58 (m, 4H, $2OCH_2$); 3.78 and 3.65 (both m, 4H, $2OCH_2$); 3.85 and 4.04 (both m, 4H, $2ArOCH_2$); 6.78 (d, 1H, H-b, $J = 13.2$ Hz); 6.88 (d, 1H, H-5′, $J = 8.7$ Hz); 6.79 (d, 1H, H-a, $J = 13.2$ Hz); 7.18 (d, 1H, H-6′, $J = 8.7$ Hz); 7.29 (m, 1H, Ph); 7.38–7.43 (m, 2H, Ph); 7.63 (m, 2H, Ph); 7.70 (d, 1H, H-6, $J = 7.7$ Hz); 7.75 (s, 1H, H-2′); 7.84 (d, 1H, H-7, $J = 7.7$ Hz); 8.08 (s, 1H, H-4).

*cis*-***8***. $^1$H NMR ($CD_3CN$), $\delta$: 3.60 (s, 4H, $2OCH_2$); 3.66 (m, 4H, $2OCH_2$); 3.70 (m, 4H, $2OCH_2$); 3.78 and 3.94 (both m, 4H, $2OCH_2$); 4.02 and 4.22 (both m, 4H, $2ArO\underline{CH_2}$); 6.66 (d, 1H, H-b, $J = 12.8$ Hz); 6.68 (d, 1H, H-5′, $J = 8.2$ Hz); 6.69 (d, 1H, H-a, $J = 12.8$ Hz); 7.21 (d, 1H, H-6′, $J = 8.1$ Hz); 7.65 and 7.85 (both m, 3H, H-5, H-6); 7.76 (s, 1H, H-2′); 7.78 and 9.29 (both d, 2H, H-8, H-9, $J = 8.5$ Hz, $J = 8.1$ Hz); 7.95 (d, 2H, H-4, H-7, $J = 8.5$ Hz).

*Synthesis of cyclization products **4b**, **5b**, **7b** (general procedure)*. Solutions of *trans*-**4** (or **5**, **6**, **7**) (0.1 mmol) in MeCN (40 mL) were irradiated with the light of a DRK-120 mercury lamp with simultaneous air oxygen bubbling of for 15–45 min until **4** (or **5**, **6**, **7**) was completely consumed (spectrophotometric monitoring). An inorganic precipitate was filtered off, the filtrate was concentrated *in vacuo*, and the residue was recrystallized from methanol with addition of drop of $HClO_4$.

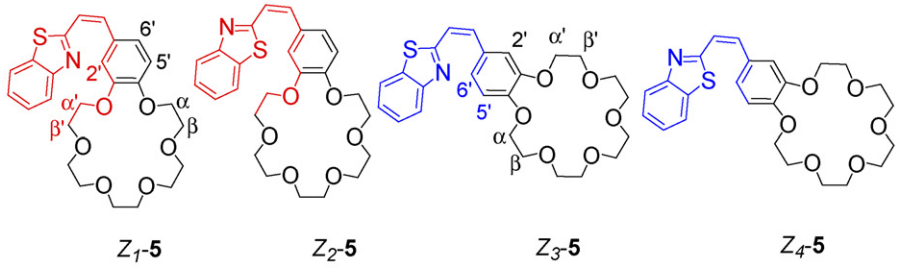
A synthesis and the structures of compounds **1b**, **2b** were described in short communication [21].

*2,3-(Dimethoxy)[1,3]benzothiazolo[3,2-a]quinolin-1a-ium perchlorate (**4b**)*. The yield was 45%, m.p. 224–226 °C. Anal. calcd. for $C_{17}H_{14}ClNO_6S$: C, 51.59; H, 3.57; N, 3.54; found: C, 51.62; H, 3.59; N, 3.51. $^1$H NMR (DMSO), $\delta$: 4.05 (s, 3H, OMe); 4.25 (s, 3H, OMe); 7.95 (tr, 1H, H-9, $J = 8.2$ Hz; $J = 8.8$ Hz); 7.98 (tr, 1H, H-10, $J = 8.2$ Hz; $J = 8.5$ Hz); 7.99 (s, 1H, H-4); 8.50 (s, 1H, H-1); 8.62 (d, 1H, H-8, $J = 8.8$ Hz); 8.67 and 8.83 (both d, 2H, H-5, H-6, $J = 8.3$ Hz, $J = 8.3$ Hz); 9.23 (d, 1H, H-11, $J = 8.5$ Hz).

*2,3-(4,7,10,13-Tetroxacyclooctadec-1,16-ylenedioxy)[1,3]benzothiazolo[3,2-a]quinolin-1a-ium perchlorate (**5b**)*. The yield was 35%, m.p. 245–248 °C. Anal. calcd. for $C_{25}H_{28}ClNO_{10}S$: C, 52.68; H, 4.95; N, 2.46; found: C, 52.62; H, 4.99; N, 2.41. $^1$H NMR (DMSO), $\delta$: 3.56 (m, 4H, $2OCH_2$), 3.60 (m, 2H, $OCH_2$), 3.67 and 3.70 (both m, 4H, $2OCH_2$), 3.89 and 3.95 (both m, 4H, $2OCH_2$), 4.04 and 4.39 (both m, 4H, $2ArOC\underline{H_2}$), 7.95 (tr, 1H, H-9, $J = 7.7$ Hz; $J = 7.3$ Hz); 8.00 (m, 2H, H-5, H-10); 8.50 (s, 1H, H-2); 8.61 (d, 1H, H-8, $J = 8.2$ Hz); 8.62 and 8.78 (both d, 2H, H-6, H-7, $J = 8.6$ Hz, $J = 8.6$ Hz); 9.22 (d, 1H, H-11, $J = 8.2$ Hz).

*9,10-Dimethoxy-2,3-(3,6,9-trioxaundec-1,11-ylenedioxy)[1,3]benzothiazolo[3,2-a]quinolin-1a-ium perchlorate (**6b**)*. The yield was 45%, m.p. 236–238 °C. Anal. calcd. for $C_{27}H_{32}ClNO_{12}S$: C, 51.47; H, 5.12; N, 2.22; found: C, 51.42; H, 5.19; N, 2.21. $^1$H NMR (DMSO), $\delta$: 3.54 (m, 4H, $2OCH_2$); 3.58 (m, 2H, $OCH_2$); 3.64 and 3.66 (both m, 4H, $2OCH_2$); 3.85 and 3.90 (both m, 4H, $2OCH_2$); 3.88 and 3.98 (both s, 6H, $2OCH_3$); 4.00 and 4.38 (both m, 4H, $2ArOC\underline{H_2}$); 8.22 (s, 2H, H-5); 8.58 (s, 1H, H-2); 8.67 (s, 1H, H-8); 8.69 and 8.88 (both d, 2H, H-6, H-7, $J = 8.7$ Hz, $J = 8.7$ Hz); 9.29 (s, 1H, H-11).

*10-Phenyl-2,3-(3,6,9-trioxaundec-1,11-ylenedioxy)[1,3]benzothiazolo[3,2-a]quinolin-1a-ium perchlorate (**7b**)*. The yield was 45%, m.p. 236–238 °C. Anal. calcd. for $C_{31}H_{32}ClNO_{10}S$: C, 57.63; H, 4.99; N, 2.17; found: C, 57.62; H, 4.95; N, 2.21. $^1$H NMR (DMSO), $\delta$: 3.55 (m, 4H, $2OCH_2$), 3.61 (m, 2H, $OCH_2$), 3.64 and 3.70 (both m, 4H, $2OCH_2$), 3.89 and 3.95 (both m, 4H, $2OCH_2$), 4.05 and 4.38 (both m, 4H, $2ArOC\underline{H_2}$), 7.95 (d, 1H, H-9, $J = 7.9$ Hz); 8.00 (s, 1H, H-5); 8.50 (s, 1H, H-2); 8.55 (d, 1H, H-8, $J = 7.9$ Hz); 8.61



Scheme 3.

(m, 5H, Ph); 8.65 and 8.74 (both d, 2H, H-6, H-7, $J = 8.3$ Hz, $J = 8.3$ Hz); 9.28 (s, 1H, H-11).

### 2.2. Methods

Melting points were measured on a Mel-Temp II instrument. $^1$H NMR spectra were recorded on a Bruker DRX-500 spectrometer (working frequency 500.13 MHz) using Me4Si as internal standard. Chemical shifts were measured with an accuracy of 0.01 ppm, and a measurement error of spin–spin coupling constants was 0.1 Hz. Elemental analyses were carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences, Moscow).

The mass spectrum was obtained on a Varian MAT 311A instrument with ionization energy of 70 eV with direct sample injection into the ionization zone.

Electronic absorption spectra were measured on a Specord M_40 spectrophotometer connected to a computer at $20 \pm 1$ °C. Solutions of SB were irradiated with the light of a DRK_120 mercury lamp.

Quantum mechanical calculations were performed by using HyperChem$^{TM}$, Release 6.01 for Windows Molecular Modeling System (Hypercube, Inc., Gainesville, FL). Optimized geometry was calculated by choosing the molecular mechanics MM2 method and the Polak–Ribiere optimization algorithm.

## 3. Results

Compounds **1**–**8** were prepared by condensation of substituted 2-methylbenzothiazole with substituted benzaldehydes in presence of NaOMe in DMSO as has been described early [19]. The thermodynamic *E*-isomers of SB **1**–**8** were obtained as judged by the coupling constants of the olefinic protons (near 16.0 Hz) (See in Experimental part).

Photolysis of these compounds **1**–**8** in acetonitrile in the presence of air oxygen produces new compounds. The structure of products depends on the length of irradiation light. Thus, the photolysis of *E*-SB in MeCN solution at 365 nm results in the formation of *Z*-SB. The quantum yield of the *E*-to-*Z* photoisomerization reaction is equal to 0.5. Our experiments

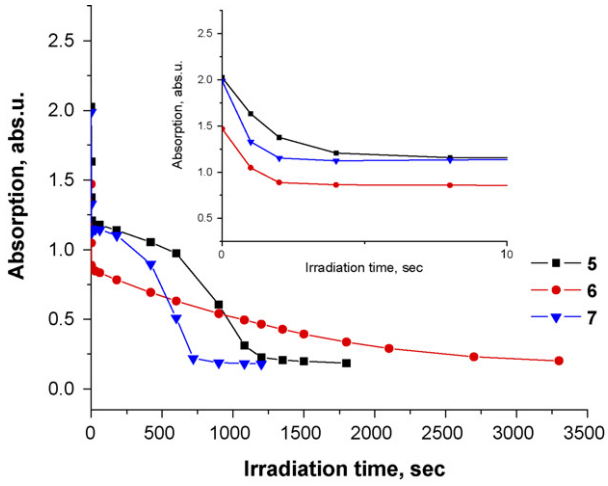



Fig. 4. Dependence of absorption of **3**–**8** (0.04 mM) (at 360 nm) on time of irradiation with a high pressure Hg-lamp, under air.

showed that both *E*-SB and *Z*-SB are stable enough in dark (Scheme 1).

The irradiation of the acetonitrile solution of compounds **1**, **2**, **4**, **5**, **6**, **7** with full high pressure mercury light and simultaneous bubbling of air for 15–45 min results in the appearance of novel photoproducts (Fig. 1; Scheme 1). After the evaporation of acetonitrile the products were isolated by crystallization from MeOH with small addition of $HClO_4$ as the perchlorate. The NMR observation of the reaction mixture showed the disappearance of the olefinic protons (H-a, H-b) and signals of aromatic protons undergo a substantial downfield shift compared to those of the starting SB. The obtained NMR spectra indicated the formation of heteroaromatic cations (Scheme 1; Fig. 2).

Intramolecular cyclization involving both nitrogen and sulfur atoms can be assumed [22,23]. To determine the structure of the product formed, we carried out a detailed analysis of the structure of the heteroaromatic cation formed from SB **2**. As can be seen from the data in Scheme 3, the cyclic products are easily discernible from the NOESY spectra due to the methoxy group. In the case of cyclic product **2b**, whose formation involved the nitrogen atom, the spectrum manifests the interaction of two H-1 and H-11 singlets. A cross peak between the H-1 singlet

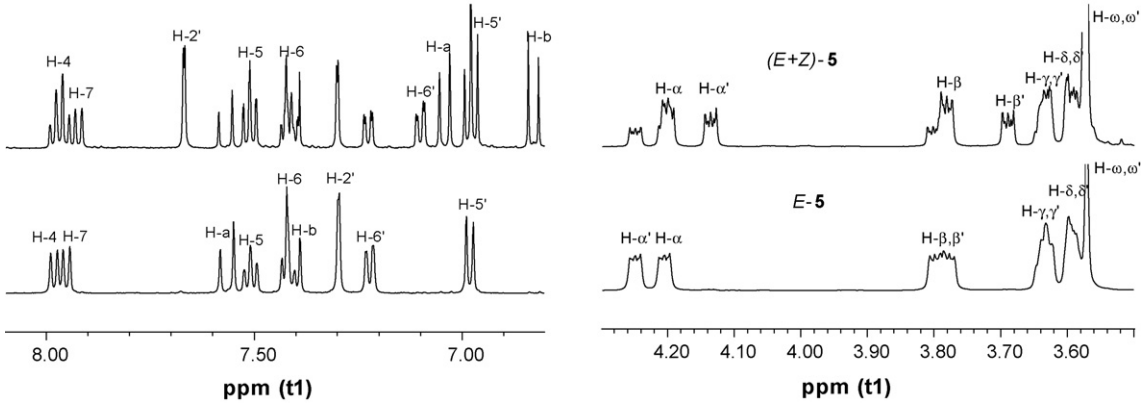



Fig. 5. $^1$H NMR spectra of an acetonitrile solution of *E*-**5** and (*E* + *Z*)-**5** (see detailed in Section 2).

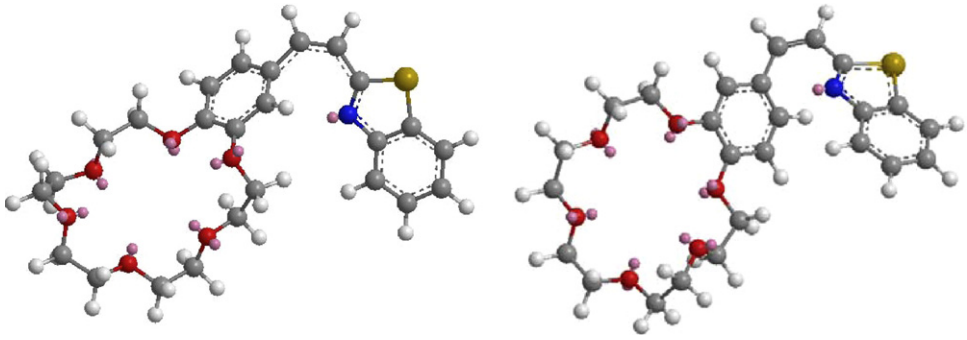


Fig. 6. Calculated structures of $Z_1$-**5** (left) and $Z_3$-**5** (right) (Hyperqaurd, MM2).

and H-11 doublet should be observed for the second theoretically possible product **2b**. As shown in experiment (Fig. 3; Scheme 2), the formation of compound **2b** involves the nitrogen atom.

We propose that the reaction formation of heteroaromatic cations is multistep process. From literature it is known that chromene, spironaphthoxazine derivatives show multistep photochrmism [24–26]. The first step of the photochemical reaction is the formation of *Z*-*E* mixture (Fig. 1). The second step is an intramolecular photocyclization through the formation of C–N bond. The primary product of the photocyclization has not been detected but has been trapped by hydride elimination with oxygen (Fig. 1). Fig. 4 demonstrates the decrease of intensity of the ligands **5**, **6**, **7** absorption long wavelength bands upon the irradiation with full light. The substantial decrease of absorption intensity during the first minute corresponds to the reaction of *E*-*Z*-isomerization which occurs with high quantum yield (near 0.5). More slow changes of absorption intensity were observed during the oxidative photocyclization.

Two factors influence the occurrence of the photocyclization reaction: electronic effect of substituents and space hindrance. Thus, introducing the electron donating substituents OMe group into the benzothiazole residue in SB **6** does the cyclization reaction to be slow, whereas, the presence of acceptor Ph substituent in **7** accelerates the process in comparison with unsbstitutes SB **5** (Fig. 4). In the compound **8** has got large naphthalene residue which is a hindrance in the process formation of cyclic product. The occurrence of electrocyclization with participation of SB **8** has not been observed. The presence of MeO group in benzene ring in *o*-position to the double C=C bond in SB **3** also prevents the photoelectrocyclization reaction.

The formation of photostationary mixture of *E*-*Z*-isomers during the first step of reaction was proved by NMR-spectroscopy. Theoretically it is possible to suggest four conformers of *Z*-isomer presented in Scheme 3. They differ from each other by various orientation of thiozole residue or disposition of benzocrown-ether fragments.

The structure of *Z*-isomer formed after the irradiation of *E*-isomer with light at 365 nm was analyzed by NMR-spectroscopy (see Section 2). The $^1$H NMR spectra of initial *E*-**5** and its photostationary mixture are shown in Fig. 5.

We found the large difference in the position of signals between H-α and H-α′, H-β and H-β′, what is unusual in comparison with *E*-isomer. The position of proton H-2′ are substantially downfield shifted (near 0.4 ppm). The phenomenon was obtained for all studied compounds **1**–**8** (see Section 2). The fact can be explained if the existence of compounds as $Z_1$ or $Z_2$ conformers (Scheme 3) is proposed. In this case the proton H-2′ is located into molecule, its position is closed to *N* ($Z_1$) or *S* ($Z_2$) heteroatoms. Slight interaction (hydrogen bond) between proton H-2′ and heteroatom is probably realized what in NMR spectra causes the substantial downfield change of signal proton H-2′ position.

In the $Z_1$-**5** or $Z_2$-**5** conformers protons H-α′ and H-β′ of crown ether moiety are under the ring-current effect produced by aromatic heterocyclic residue. Anisotropic effect of aromatic system on H-α′ and H-β′ protons results in the shift of its signals in NMR spectrum to downfield region. In the $Z_3$-**5** or $Z_4$-**5** conformers all crown ether protons are located far from the benzothiazole ring. To confirm this suggestion the structures of $Z_1$-**5** and $Z_3$-**5** were calculated with applying of Hyperqard program (version MM2). The calculated structures presented in Fig. 6 clearly show closed position of proton H-2′, H-α′ and H-β′ to benzothiazole residue in $Z_1$-**5** conformer.

It is important to note that the cyclic product observed in electrocyclic reaction forms from the $Z_3$-**5** conformer. Thus, we can propose that the main product of *E*-*Z*-isomerization is $Z_1$-**5** or $Z_2$-**5** conformer which can converts to the $Z_3$-**5** conformer by more prolonged irradiation. In the $Z_3$-**5** conformer disposition of benzene and benzothiazole fragments is favorable for the occurrence of electrocyclic transformation. Perhaps, the first formation of more high stable $Z_1$-**5** or $Z_2$-**5** conformers and that it is required the additional transformation into the $Z_3$-**5** are the reasons of relatively low efficiency of the electrocyclic reaction.

Thus, we described the occurrence of photoinduced oxidative electrocyclic reaction in the series of substituted 2-styrylobenzothiazoles. The reaction involves the formation of C–N bond, the electronic and steric effect of substituents influence the transformation. The mechanism of the reaction includes the consequent formation of the different *Z*-conformers. The reaction is of practical synthetic importance, it opens the photochemical method for obtaining the novel heteroaromatic compounds including crow-containing to be difficulty prepared by the multistep synthetic way.

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