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Photochromic dihetarylethenes

10.* Photochromic 1,2-bis[2-(benzothiazol-2-yl)-3-thienyl]- and 1,2-bis[2-(benzothiazol-2-yl)benzothiophen-3-yl]ethenes

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Dithienylethenes containing the thiophene rings with benzothiazolyl substituents in position 2 were synthesized. 1,2-Bis[2-(benzothiazol-2-yl)benzothiophen-3-yl]hexafluorocyclopentene and 1,2-bis[2,5-di(benzothiazol-2-yl)-3-thienyl]hexafluorocyclopentene possess photochromic properties. The open forms of 1,2-bis(2-benzothiazolylhetaryl)ethenes fluoresce, but introduction of the benzothiazole rings into dihetarylethenes significantly lowers the fatigue resistance of photochromes and favors thermal reversibility.

Key words: 1,2-bis(2-benzothiazolylhetaryl)ethenes, 1,2-dithienylethenes, 1,2-diarylethenes, photochromes, thermal reversibility, fluorescence.

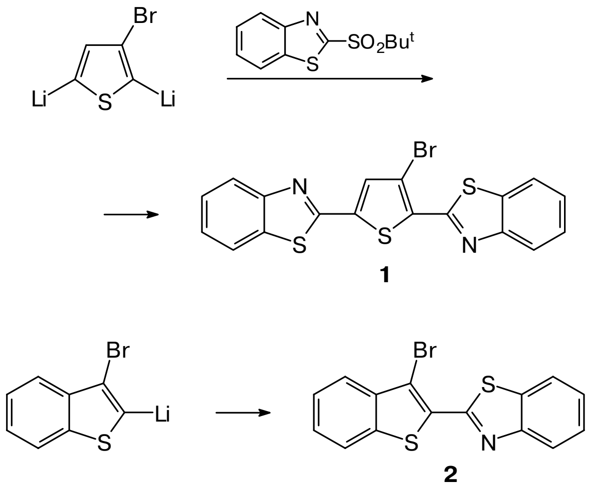
A great variety of thermally irreversible photochromic dihetarylethenes synthesized to date[2,3] mainly differ in heterocyclic systems,[4] in substituents in positions 4 and 5 of the thiophene rings,[5] and in bridges with double bonds between the heterocycles.[6,7] However, the effect of 2-substituents in thiophenes on the photochromic properties has been studied inadequately, though it is rather strong. It was shown[8] that introduction of an RS or RSO_2 group completely deprives dithienylethenes of photochromism. However, the retention of photochromic properties in compounds containing various fragments in the positions mentioned can substantially enlarge the spectra of their physicochemical and optical properties.

The goal of the present work was to synthesize 1,2-bis(benzothiazol-2-ylthienyl)ethenes and compare their photochromic properties with those of their 2-methylthienyl analogs.

Results and Discussion

The starting 2,5-bis(benzothiazol-2-yl)-3-bromothiophene (**1**) was prepared by the reaction of the corresponding dilithiothiophene derivative with 2-*tert*-butylsulfonylbenzothiazole;[9] bromide **2** was synthesized analogously from 3-bromo-2-lithiobenzothiophene (Scheme 1).

Scheme 1



Bromides **2** and **1** react with BuLi and octafluorocyclopentene at −70 °C (Scheme 2) to give compounds **3** and **5** in 49 and 21% yields, respectively. Earlier, their 2-methylthienyl analogs **4** [10] and **6** [11] were obtained.

To study the photochemical properties of compounds **3** and **5**, their solutions in MeCN were irradiated with light with $\lambda = 313$ nm for **3** and $\lambda = 365$ for **5** to induce photocyclization and with $\lambda = 546$ and 578 nm, respectively, for their reverse reactions (Figs. 1, 2). The pronounced photochromism of both products indicates that even such sterically crowded molecules can undergo

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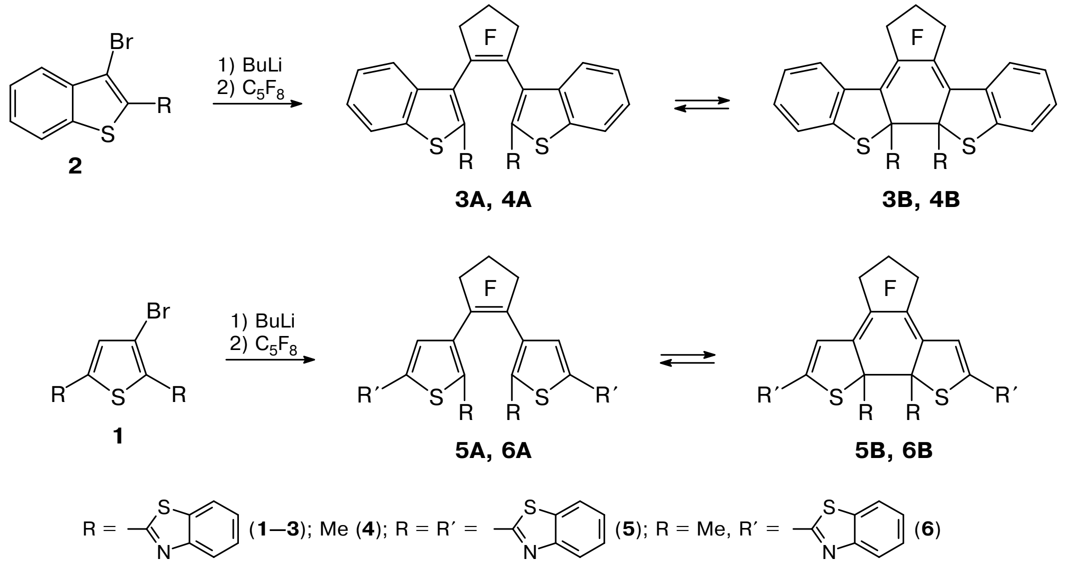
Scheme 2



cyclization, which seemed, quite apparently, to be hardly possible. The absorption spectra recorded for different states of these photochromic systems (*i.e.*, for different ratios between forms **A** and **B**) contain isosbestic points; their positions during the forward and reverse reactions coincide, which suggests completely reversible photocyclization and the absence of side processes. The long-wavelength absorption band of the cyclic form of the (benzothiazolyl)thienyl derivative **5** experiences only a slight hypsochromic shift (4 nm) relative to that of its structural 2-methylthienyl analog **6** (see Ref. 11), the spectral pattern remaining virtually unchanged. For an analogous pair of structures **3B** and **4B**,[10] the hypsochromic shift of the long-wavelength absorption band is somewhat larger (12 nm); this is probably due to substantial distortion of the strained six-membered ring formed upon photocyclization.

In the case of photochrome **3**, dark reactions **A** → **B** and **B** → **A** do not occur, *i.e.*, both its open and cyclic forms are thermally stable.

It should be noted that an increase in the number of electron-withdrawing heterocyclic substituents in the photochrome molecule results in the loss of thermal stability. Thus the cyclic form **B** of product **5** isomerized spontaneously into the open form **A** on storage without irradiation (dark reaction), as evidenced by a decrease in the optical density in the maximum of the long-wave-

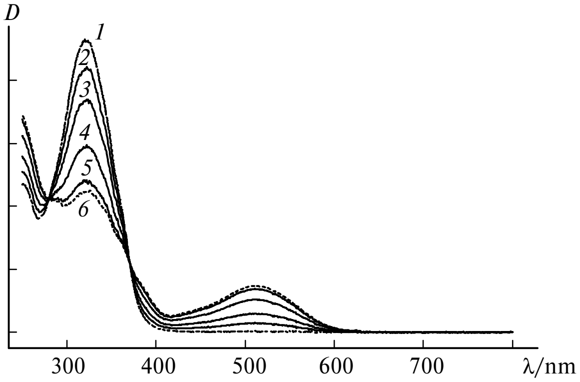


Fig. 1. Electronic absorption spectra of solutions of 1,2-bis[2-(benzothiazol-2-yl)benzothiophen-3-yl]hexafluorocyclopentene (**3**) in acetonitrile upon irradiation at λ = 313 and 546 nm for forward and reverse reactions, respectively: (*1*) the spectrum of the open form, intermediate spectra for exposure times of (*2*) 5, (*3*) 15, (*4*) 40, and (*5*) 90 s, and (*6*) the spectrum in the photosteady state (exposure time 120 s).

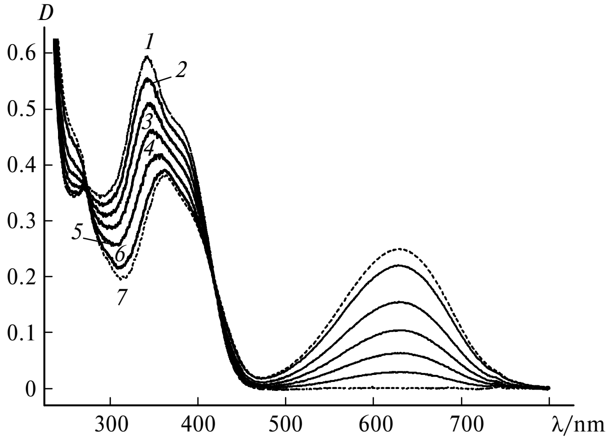


Fig. 2. Electronic absorption spectra of solutions of 1,2-bis[(2,5-dibenzothiazol-2-yl)-thiophen-3-yl]hexafluorocyclopentene (**5**) in acetonitrile upon irradiation at λ = 365 and 578 nm for forward and reverse reactions, respectively: (*1*) the spectrum of the open form, intermediate spectra for exposure times of (*2*) 5, (*3*) 15, (*4*) 35, (*5*) 60, and (*6*) 90 s, and (*7*) the spectrum in the photosteady state (exposure time 120 s).

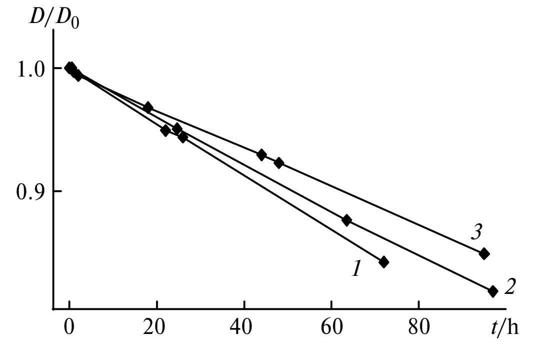


Fig. 3. Changes in the optical density (*D*) in the long-wavelength absorption maximum of cyclic form **5B** upon its dark exposure in (*1*) *n*-hexane, (*2*) ethanol, and (*3*) acetonitrile.

length absorption band of form **B** and a proportional increase in the optical density in the corresponding maximum for form **A**. The presence of the isosbestic point in a series of spectra recorded for different dark exposure times indicates that the thermal ring opening produces no by-products. Note for comparison that 1,2-bis[2-methyl-5-(benzothiazol-2-yl)-3-thienyl]hexafluorocyclopentene (**6**), which is a close analog of compound **5**, is a thermally irreversible photochrome.[11] A study of the dark reaction **5B** → **5A** in different solvents showed that an increase in their polarities inhibits the process, *i.e.*, stabilizes the cyclic form (Fig. 3). This correlates with the results of our quantum-chemical MNDO calculations,[1] which suggest that the cyclization of compound **5** increases 1.4-fold its dipole moment. The quantum yield (for the calculational procedure, see Ref. 12) of the photocyclization **3A** → **3B** was 0.27 and that of the reverse reaction **3B** → **3A** was 0.57.

It is known that photochromes **4** and **6** do not fluoresce.[10,11] When studying the optical properties of their analogs **3** and **5**, we concluded that the introduction of the benzothiazolyl substituents into positions 2 of the thiophene rings results in the appearance of fluorescence of their open forms **3A** and **5A** (Table 1). This is the first example of such a phenomenon. Previously, fluorescence was observed upon introduction of substituents into positions 5 of the thiophene rings.[9,11,13] In some cases, this was due to the structural features of the ethene component[6] of the photochromes. Cyclic forms **B** of both photochromes do not fluoresce.

Table 1. Maxima of the long-wavelength bands (λ_{max}/nm) in the electronic absorption spectra and the maxima in the fluorescence spectrum (λ_{fl}/nm) of the open (**A**) and cyclic (**B**) forms of 1,2-bis(3-thienyl)perfluorocyclopentenes **3** and **5**

Compound	λ_{max}		λ_{fl} (**A**)
	A	**B**	
3	324	502	460
5	342	626	530

1,2-Bis(2-methylbenzothiophen-3-yl)perfluorocyclopentene **4** has a high fatigue resistance ($>1.3 \cdot 10^4$).[14] Replacement of the methyl groups by benzothiazolyl groups decreases it substantially. The fatigue resistance of 1,2-bis[2-(benzothiazol-2-yl)benzothiophen-3-yl)]hexafluorocyclopentene (**3**), determined as described previously,[4] was found to be 150.

Thus, one can state that introduction of benzothiazolyl substituents into positions 2 of the thiophene rings of dithienylethenes results in fluorescence of their open forms and significantly decreases the fatigue resistance of the photochromes. In addition, a dark reaction can occur, *i.e.*, the thermal irreversibility of dithienylethenes is violated.

Experimental

^{1}H NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker SF-300 instruments in $CDCl_3$. Melting points were determined on a Boetius heating stage. Mass spectra were recorded on a Kratos MS-30 instrument (ionizing voltage 70 eV, direct inlet of a substance into the ion source). Thin-layer chromatography was carried out on Silufol UV-254 and Merck 60 F_{254} plates; column chromatography was performed on Merck 60 silica gel. All reactions involving organolithium compounds were carried out in highly purified, moisture- and oxygen-free argon under elevated pressure. Reagents and solvents were dried by standard methods. Reagents were introduced into preliminarily dried reaction vessels through rubber septa using disposable syringes.

Samples were irradiated with a DRSh-500 mercury lamp through light filters to isolate mercury spectral lines with λ = 313, 365, 546, and 578 nm. The radiation intensity of the mercury lamp was measured with an F-4 photocell calibrated with a ferrioxalate actinometer[15] for λ = 313 and 365 nm and a Reinecke salt actinometer[16] for λ = 546 and 578 nm. Electronic absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer, and fluorescence spectra were recorded on an Elumin-2M spectrofluorimeter. The quantum yields of photochromic transformations were determined by irradiating ethanolic solutions of compounds with light with the corresponding wavelengths. The irradiation time was increased stepwise from 5 s to 1—2 min (in total, seven to ten experimental points). After each exposure, an absorption spectrum of the irradiated solution was recorded.

2-(3-Bromobenzothiophen-2-yl)benzothiazole (2). A 1.45 *M* solution of BuLi in hexane (14.5 mmol, 10 mL) was added to a stirred solution of 2,3-dibromobenzothiophene (3.8 g, 13 mmol) in 60 mL of anhydrous ether in an atmosphere of Ar at −5 °C, and stirring was continued at this temperature for 30 min. The reaction mixture was cooled to −70 °C, a solution of (benzothiazol-2-yl) *tert*-butyl sulfone[9] (3.5 g, 13.8 mmol) in anhydrous toluene (35 mL) was added, and stirring was continued for 40 min. The resulting solution was warmed to ~20 °C, kept under Ar for 16 h, and cooled to −5 °C. Then MeOH (20 mL) was added, and the reaction mixture was stirred at ~20 °C for 20 min. The solvents were removed, and the residue was washed with water and MeOH and dried. The yield of compound **2** was 2.78 g (61%), m.p. 214—215 °C (from ethanol—benzene). Found (%): C, 52.30; H, 2.40. $C_{15}H_8BrNS_2$. Calculated (%): C, 52.03; H, 2.33. ^{1}H NMR, δ: 6.09 (t, 1 H, H(5′), *J* = 7.5 Hz); 6.95 (t, 1 H, H(6′), *J* = 7.5 Hz); 6.70 (d, 1 H, H(7′), *J* = 7.5 Hz); 7.39—7.56 (m, 3 H, H(4′), H(5), H(6)); 7.75 (d, 1 H, H(7), J = 8.0 Hz); 7.97 (d, 1 H, H(4), J = 8.0 Hz). MS, m/z (I_{rel} (%)): 345, 347 $[M]^+$ (100).

1,2-Bis[2-(benzothiazol-2-yl)benzothiophen-3-yl]hexafluorocyclopentene (3). A 1.45 M solution of BuLi in hexane (1.45 mmol, 1.0 mL) was added with stirring in an atmosphere of Ar at −70 °C to a solution of compound **2** (0.46 g, 1.33 mmol) in 50 mL of anhydrous THF. The reaction mixture was stirred at this temperature for 15 min. Then C_5F_8 (0.145 g, 0.68 mmol) in 1 mL of anhydrous THF was added at −70 °C, and stirring was continued for 2 h. The reaction mixture was warmed to ~20 °C, left under Ar for ~14 h, and then cooled to −5 °C. After addition of 5 mL of EtOH, the resulting solution was stirred at 20 °C for 40 min. The solvents were removed, and the residue was washed with water and dried. The product was isolated by chromatography on silica gel in benzene. The yield of compound **3** was 0.23 g (49%), m.p. 272—273 °C. Found (%): C, 59.57; H, 2.54. $C_{35}H_{16}F_6N_2S_4$. Calculated (%): C, 59.48; H, 2.28. ^{1}H NMR, δ: 6.18 (t, 1 H); 6.98 (t, 1 H, H(5), H(6), J = 7.5 Hz); 7.10 (d, 1 H, H(7′), J = 7.5 Hz); 7.45 (t, 1 H, H(5′), J = 8.0 Hz); 7.79 (d, 1 H, H(7′), J = 8.0 Hz); 8.01 (d, 1 H, H(4′), J = 8.0 Hz). MS, m/z (I_{rel} (%)): 706 $[M]^+$ (100).

1,2-Bis[(2,5-dibenzothiazol-2-yl)-thiophen-3-yl]hexafluorocyclopentene (5) was obtained analogously from bromide **1** in a mixture of anhydrous THF and anhydrous toluene. The product was isolated by chromatography in benzene. The yield of compound **5** was 21%, m.p. 294—297 °C. Found (%): C, 56.76; H, 1.85. $C_{41}H_{18}F_6N_4S_6$. Calculated (%): C, 56.41; H, 2.08. ^{1}H NMR, δ: 6.80 (s, 1 H, H(4), thiophene ring); 7.10, 7.19, 7.42 (all t, 1 H each); 7.51 (t, 1 H, H(5), H(6), J = 8.0 Hz); 7.60, 7.81, 7.90 (all d, 1 H each); 8.10 (d, 1 H, H(4), H(7), J = 8.0 Hz). MS, m/z (I_{rel} (%)): 872 $[M]^+$ (3).

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