Photochromic dihetarylethenes

2.* Synthesis and photochromic properties of 5,5′-alkylthio(alkylsulfonyl)-substituted 1,2-bis(2-alkylthien-3-yl)perfluorocyclopentenes

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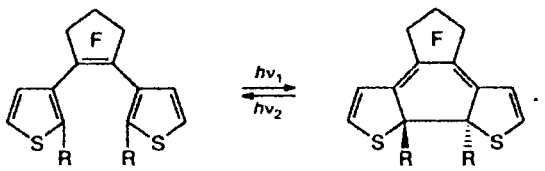
Novel 1,2-bis(2-alkylthien-3-yl)hexafluorocyclopentenes containing the alkylthio or alkylsulfonyl groups in positions 5 and 5′ of the thiophene rings were synthesized. These compounds are photochromes; their photochromic properties were studied.

Key words: 1,2-(dithienyl)perfluorocyclopentenes, photostationary state, reversible photocyclization, photochromes.

Dithienylperfluorocyclopentenes (**1**) containing alkyl substituents in positions 2 and 2′ are used as basic compounds for the creation of various photochromic systems.[2–4] Photochromism of dithienylperfluorocyclopentenes is based on reversible photocyclization:



1A **1B**

We have shown[1] that when the alkyl group in position 2 is replaced by the alkylthio or alkylsulfonyl group, compounds **1** exist in the open form **A** only and are not cyclized in the **B** form under UV irradiation. It was of interest to reveal the influence of the alkylthio and alkylsulfonyl substituents in other positions of the thiophene ring on the ability of compounds **1** for photocyclization.

In this work, the synthesis of isomeric structures containing the alkylthio and alkylsulfonyl groups in positions 5 and 5′ of the thiophene rings (Scheme 1) from 2-ethyl-5-(ethylthio)thiophene (**2**) is described, and their photochromic properties have been studied.

The bromination of sulfide **2** with two equivalents of Br_2 in glacial AcOH or $CHCl_3$ resulted in the formation of dibromide **3** in a high yield. Treating **3** with one equivalent of Bu^nLi in Et_2O led to a mixture of isomeric monobromides **4** and **5** in a ratio of ~1 : 4 (according to the ^1H NMR spectra). This mixture gave (after column chromatography) pure 3-bromo-2-ethyl-5-(ethylthio)thiophene (**5**), which was used for the subsequent synthesis. Its isomer, 4-bromo-2-ethyl-5-(ethylthio)thiophene (**4**), was described previously.[5]

The successive action of Bu^nLi and octafluorocyclopentene on monobromides **5** and **4** at −70 °C resulted in the corresponding isomeric 1,2-bis[2-ethyl-5-(ethylthio)thien-3-yl]perfluorocyclopentene (**6**) and 1,2-bis[5-ethyl-2-(ethylthio)thien-3-yl]perfluorocyclopentene (**7**), which were oxidized by 30% H_2O_2 to bissulfones **8** and **9**, respectively (see Scheme 1).

1,2-Bis[5-ethyl-2-ethylthio(ethylsulfonyl)thien-3-yl]perfluorocyclopentenes **7** and **9** obtained are not photochromes. By contrast, their isomers **6** and **8** exhibit pronounced photochromic properties.

UV irradiation (λ = 313 nm) of an ethanolic solution of the colorless open form **6A** results in its transformation to the colored cyclic form **6B**. The electronic spectrum exhibits a decrease in the optical density at the absorption maximum of form **6A** (λ_{max} = 243 nm, ε_{243} = $2.45 \cdot 10^4$ L mol^{-1} cm^{-1}) and an increase in the optical density at the absorption maximum of form **6B** (λ_{max} = 563.5 nm, $\varepsilon_{563.5}$ = $1.68 \cdot 10^4$ L mol^{-1} cm^{-1}). When an ethanolic solution containing form **6B** is irradiated with light with λ = 546 nm, the optical density at the absorption maximum of form **6B** decreases, and that of form **6A** increases (Fig. 1). The **6A** → **6B** transformation does not completely occur because of overlapping

* For Part 1, see Ref. 1.

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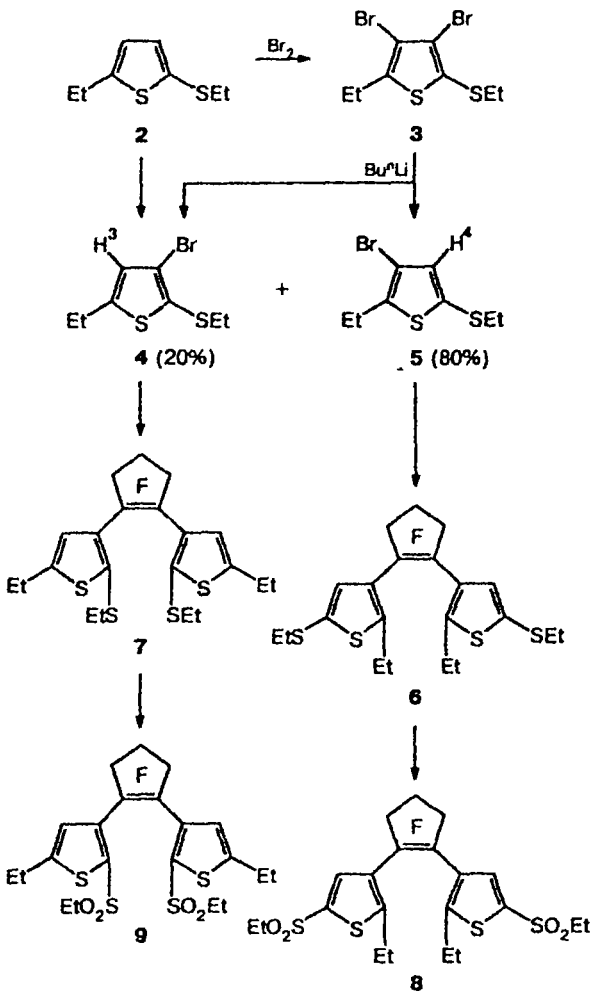
Scheme 1



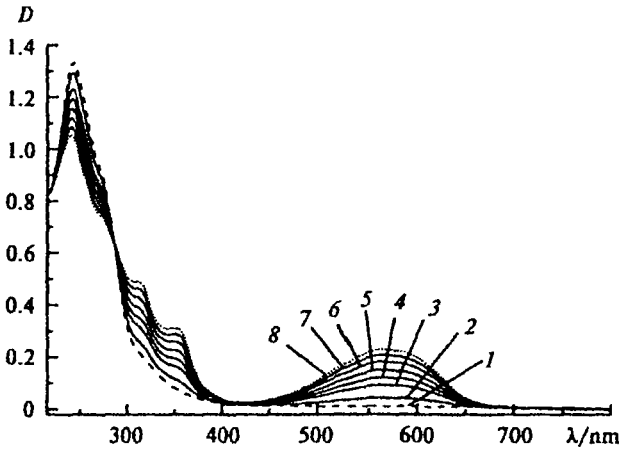


Fig. 1. Change in the absorption spectrum of an ethanolic solution of 1,2-bis[2-ethyl-5-(ethylthio)thien-3-yl]perfluorocyclopentene (**6**) during irradiation with light with λ = 313 nm. Spectra: *1*, initial solutions; *2*, after 5-s irradiation; *3*, after 13 s; *4*, after 18 s; *5*, after 27 s; *6*, after 37 s; *7*, after 48 s; and *8*, after 60 s.

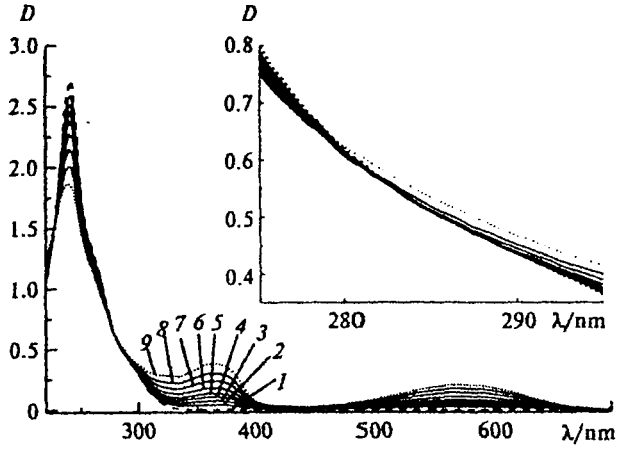


Fig. 2. Change in the absorption spectrum of an ethanolic solution of 1,2-bis[2-ethyl-5-(ethylsulfonyl)thien-3-yl]perfluorocyclopentene (**8**) during irradiation with light with λ = 313 nm. Spectra: *1*, initial solution; *2*, after 11-s irradiation; *3*, after 21 s; *4*, after 33 s; *5*, after 45 s; *6*, after 65 s; *7*, after 101 s; *8*, after 160 s; and *9*, after 280 s.

of the electronic absorption spectra of forms **6A** and **6B** at λ = 313 nm, and at some irradiation dose, a photostationary state is established for which the rates of the direct and reverse photoreactions are equal, and the concentrations of both forms of the photochromic compound remain unchanged during further irradiation. The ratio of the concentrations of forms **A** and **B** in the photostationary state depends on the irradiation wavelength and is reversely proportional to the ratio of extinction coefficients of these forms at the given wavelength. For λ = 313 nm, the concentrations of forms **6A** and **6B** in the photostationary states are 71 and 29 mol.%, respectively. Isosbestic points are observed in the absorption spectra of the solution. Their positions for the direct and reverse reactions coincide, which indicates complete photoreversibility of the photocyclization of compound **6** and the absence of side processes. The quantum yield of the **6A** → **6B** phototransformation is equal to 0.14; that of the **6B** → **6A** phototransformation amounts to 0.01. The dark reaction **6A** → **6B** is absent, and the dark reaction **6B** → **6A** is almost absent as well: the optical density of an ethanolic solution of **6B** remains unchanged after 500-h storage in darkness.

When an ethanolic solution of **8A** is irradiated with light with λ = 313 nm, the colored form **8B** appears accompanied by the redistribution of the optical density; however, isosbestic points in the absorption spectra are absent (Fig. 2) when this ethanolic solution is further irradiated with light with λ = 546 nm. This indicates that, along with the photochromic process, compound **8** undergoes transformations that differ from photocyclization.

Experimental

NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz) in $CDCl_3$. Mass spectra were recorded on a Kratos MS-30 mass spectrometer at an ionizing voltage of 70 eV with the direct introduction of the substance into an ion source. Column chromatography was carried out on silica gel L (100—160 mesh), and Silufol UV-254 plates (heptane as the eluent) were used for thin layer chromatography.

Samples were irradiated with a resonance mercury lamp (λ = 254 nm) and a DRSh-500 mercury lamp using light filters to separate the lines in the mercury spectrum (313 and 546 nm). The intensity of the mercury lamp radiation was determined by actinometry. Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer.

To determine quantum yields (Φ) of the direct and reverse reactions, an ethanolic solution of a substance was irradiated with light with λ = 313 nm for the direct reaction or λ = 546 nm for the reverse reaction, increasing gradually the irradiation duration from 5 s to 1—2 min (7—10 experimental points). The absorption spectrum of the irradiated solution was recorded after each exposure.

The quantum yield (Φ) was calculated by the formula

$$\Phi = V\Delta D^{B}(t)/[\varepsilon^{B} l J_{abs}(t)],$$

where V is the volume of the solution under irradiation, $\Delta D^{B}(t)$ is the change in the optical density of the solution at the absorption maximum of form **B** over time t, ε^{B} is the extinction coefficient of form **B**, l is the optical path length, and $J_{abs}(t)$ is the flux absorbed by the solution over time t. For the reverse reaction, the dependence of $\Delta D^{B}(t)$ on $J_{abs}(t)$ is linear; hence, $\Delta D^{B}(t)/J_{abs}(t)$ = const and Φ is independent of t. For the direct reaction, $\Delta D^{B}(t)/J_{abs}(t)$ was determined as the tangent slope at the origin of coordinates of the plot of $\Delta D^{B}(t)$ *vs.* $J_{abs}(t)$.

The extinction coefficient of form B (ε^{B}) was calculated from the assumption that at short times of irradiation (a low conversion), the contribution of the absorption of form **B** to the absorption maximum of form **A** is negligible. Then

$$C^{B}(t) = C^{A}(t_0) - C^{A}(t) = \frac{D^{A}(t_0) - D^{A}(t)}{\varepsilon^{A} l} = \frac{\Delta D^{A}(t)}{\varepsilon^{A} l},$$

where $C^{A}(t)$ ($C^{B}(t)$) is the molar concentration of form **A** (**B**) after irradiation over time t, $C^{A}(t_0)$ is the molar concentration of form **A** in the nonirradiated solution, $D^{A}(t)$ is the optical density of the solution at the absorption maximum of form **A** after irradiation over time t, and $D^{A}(t_0)$ is the optical density of the nonirradiated solution at the absorption maximum of form **A**. Inserting the expression obtained for $C^{B}(t)$ into the formula $\varepsilon^{B} = D^{B}/(C^{B} l)$, one can obtain $\varepsilon^{B} = \varepsilon^{A} D^{B}(t)/\Delta D^{A}(t)$.

The absorbed flux (J_{abs}) was determined from the formula

$$J_{abs} = J_0 \int_0^t (1 - 10^{-D_\lambda}) dt = J_0 \sum_{\Delta t} (1 - 10^{-\overline{D_\lambda(\Delta t)}}) \Delta t,$$

where J_0 is the light intensity at the irradiation wavelength, and D_λ is the optical density of the solution at the irradiation wavelength.

3,4-Dibromo-2-ethyl-5-(ethylthio)thiophene (3). Bromine (21.1 g) in $CHCl_3$ (50 mL) was added during 30 min to a solution of sulfide **2** (10.84 g, 62.9 mmol) in $CHCl_3$ (25 mL) at 45 °C. The reaction mixture was stirred for 2 h at the same temperature, washed with a 8% solution of NaOH (2×30 mL) and water, and dried with $CaCl_2$. $CHCl_3$ was distilled off, and the residue was distilled *in vacuo*. The yield of compound **3** was 14.4 g (70%), b.p. 161—162 °C (8 Torr), n_D^{20} 1.6182. Found (%): C, 29.49; H, 3.29; Br, 48.26; S, 19.36. $C_8H_{10}Br_2S_2$. Calculated (%): C, 29.11; H, 3.06; Br, 48.41; S, 19.43. ^{1}H NMR, δ: 1.25 (t, 6 H, CH_3CH_2, CH_3CH_2S); 2.7 (m, 4 H, CH_2S, CH_2CH_3).

Reaction of 1 equiv. Bu^{n}Li with dibromide 3. An ethereal solution of Bu^{n}Li (2.5 g, 39 mmol) cooled to −70 °C was added during 10 min to compound **3** (11.3 g, 34.6 mmol) in anhydrous Et_2O (50 mL) in an argon flow. The reaction mixture was stirred for 10 min at the same temperature, cooling was removed, and EtOH (2 mL) and then water (20 mL) were added. The ethereal layer was separated, washed with dilute HCl (1 : 10) and water, and dried with $CaCl_2$. The ether was distilled off, and the residue (8.96 g of light-yellow oil) was distilled *in vacuo* to obtain a fraction (5.31 g, 63%) with b.p. 127—130 °C (8 Torr), n_D^{20} 1.5870. ^{1}H NMR, δ: 1.27 (t, 6 H, 2 CH_3); 2.8 (m, 4 H, 2 CH_2); 6.72, 6.92 (both s, 0.2 H and 0.8 H, H(3), H(4)). A mixture of compounds **4** and **5** (1.5 g) as well as pure bromide **5** (1.55 g, n_D^{20} 1.5792) were isolated from the fraction (3.1 g) by column chromatography.

3-Bromo-2-ethyl-5-(ethylthio)thiophene (5). Found (%): C, 38.15; H, 4.37; Br, 30.65; S, 24.59. $C_8H_{11}BrS_2$. Calculated (%): C, 38.25; H, 4.41; Br, 31.60; S, 25.52. ^{1}H NMR, δ: 1.30 (t, 6 H, 2 CH_3); 2.80 (q, 4 H, 2 CH_2); 6.92 (s, 1 H, H(4)). TLC data: R_f 0.46.

4-Bromo-2-ethyl-5-(ethylthio)thiophene (4).[5] ^{1}H NMR, δ: 1.30 (t, 6 H, 2 CH_3); 2.80 (q, 4 H, 2 CH_2); 6.72 (s, 1 H, H(3)). TLC data: R_f 0.34.

1,2-Bis[2-ethyl-5-(ethylthio)thien-3-yl]perfluorocyclopentene (6). A solution of Bu^{n}Li (4.0 g, 6.3 mmol) in Et_2O cooled to −70 °C was added in an Ar flow to bromide **5** (1.43 g, 5.69 mmol) in anhydrous Et_2O (7 mL). The reaction mixture was stirred for 1 h at the same temperature, and octafluorocyclopentene (0.42 mL, 0.67 g, 3.15 mmol) was introduced in two portions. The reddish-brown solution was stored at −70 °C for 2 h and left to stand for 12 h at 20 °C. The mixture was hydrolyzed under cooling with 8% HCl (5 mL) and H_2O (10 mL). The organic layer was separated, washed with water to the neutral reaction, and dried with $CaCl_2$. Then Et_2O was removed, and a dark-red oil (1.57 g) was obtained, from which highly volatile components with b.p. below 160 °C were distilled off (8 Torr). The residue (0.79 g) was chromatographed on a column to obtain fluoride **6A** (0.44 g, 25%) in the form of a dense light heptane-containing oil. Found (%): C, 55.21; H, 6.13. $C_{21}H_{22}F_6S_4 \cdot C_7H_{16}$. Calculated (%): C, 54.51; H, 6.21. ^{1}H NMR, δ: 0.97 (t, 3 H, CH_3CH_2); 1.25 (t, 3 H, CH_3CH_2S); 2.25 (q, 2 H, CH_2CH_3); 2.80 (q, 2 H, CH_2S); 7.02 (s, 1 H, H(4)). MS, m/z (I_{rel} (%)): 516 $[M]^+$ (100), 459 (50), 427 (57). After UV irradiation (λ = 254 nm) of form **6A** without a solvent for 3 h, the ^{1}H NMR spectrum contains, along with signals of **6A**, signals from protons of **6B**, δ: 1.10 (t, 3 H, CH_3CH_2); 1.35 (t, 3 H, CH_3CH_2S); 2.38 (q, 2 H, CH_2CH_3); 2.95 (q, 2 H, CH_2S); 6.03 (s, 1 H, H(4)). The ratio of the intensities of signals of the corresponding protons **6B** : **6A** ≈ 2 : 1.

1,2-Bis[5-ethyl-2-(ethylthio)thien-3-yl]perfluorocyclopentene (7) was obtained similarly to isomer **6** from bromide **4** (1.4 g, 5.6 mmol) in 24% yield, m.p. 68—69 °C (from heptane, at −50 °C). Found (%): C, 48.68; H, 4.37. $C_{21}H_{22}F_6S_4$. Calculated (%): C, 48.62; H, 4.29. ^{1}H NMR, δ: 1.10 (t, 3 H, CH_3CH_2); 1.30 (t, 3 H, CH_3CH_2S); 2.50 (q, 2 H, CH_2CH_3); 2.82 (q, 2 H, CH_2S); 6.88 (s, 1 H, H(4)).

1,2-Bis[2-ethyl-5-(ethylsulfonyl)thien-3-yl]perfluorocyclopentene (8). 30% H_2O_2 (0.2 mL, 1.35 mmol) was added to a solution of perfluorocyclopentene **6** (70 mg, 0.135 mmol) in

glacial AcOH (5 mL). The mixture was heated on a boiling water bath (95 °C) for 1.5 h and left to stand at 20 °C for 12 h. The mixture was poured in water and extracted with AcOEt. The extract was washed with H_2O, Na_2CO_3, and H_2O and dried with $MgSO_4$, and the solvent was distilled off. Bis-sulfone **8** (50 mg, 78%) with m.p. 168—170 °C (from EtOH) was obtained. Found (%): C, 43.36; H, 3.87. $C_{21}H_{22}F_6O_4S_4$. Calculated (%): C, 43.44; H, 3.82. ^{1}H NMR, δ: 1.10 (t, 3 H, CH_3CH_2); 1.36 (t, 3 H, CH_3CH_2S); 2.38 (q, 2 H, CH_2CH_3); 3.25 (q, 2 H, CH_2SO_2); 7.58 (s, 1 H, H(4)). MS, m/z (I_{rel} (%)): 580 $[M]^+$ (27), 487 $[M - SO_2C_2H_5]^+$ (70), 394 $[M - 2SO_2C_2H_5]^+$ (70), 379 (100).

1,2-Bis[5-ethyl-2-(ethylsulfonyl)thien-3-yl]perfluorocyclopentene (9) was synthesized by the procedure described for bis-sulfone **8** from compound **7** (210 mg, 0.406 mmol) in 68% yield (m.p. 98—99 °C from heptane). Found (%): C, 43.41; H, 3.99. $C_{21}H_{22}F_6O_4S_4$. Calculated (%): C, 43.44; H, 3.82. ^{1}H NMR, δ: 1.32 (m, 6 H, CH_3CH_2S, CH_3CH_2); 2.85 (q, 2 H, CH_2CH_3); 3.12 (q, 2 H, CH_2SO_2); 7.8 (s, 1 H, H(4)).

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