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Photochromic dihetarylethenes
18.* New approach to the synthesis of dithienothiophene and preparation of its photochromic derivative

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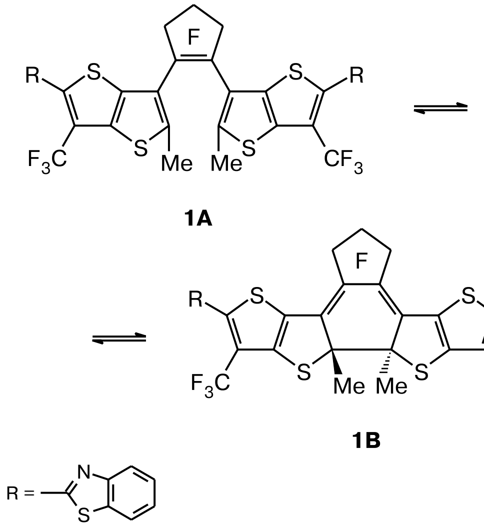
A new approach to the synthesis of dithienothiophene was developed, and 1,2-bis(2,6-dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophen-3-yl)hexafluorocyclopent-1-ene was prepared. The latter compound is the first representative of photochromic dihetarylethenes with the fused tricyclic fragments linked through the perfluorocyclene bridge.

Key words: 1,2-bis(2,6-dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophen-3-yl)hexafluorocyclopent-1-ene, 1,2-dihetarylethenes, hexafluorocyclopentene derivatives, photochromes.

Previously,[2] we have reported that hexafluorocyclopentene derivatives of thieno[3,2-*b*]thiophene (**1**) exhibit photochromic properties. Their open (colorless, **1A**) and cyclic (colored, **1B**) forms possess high thermal stability due to which the direct and reverse photoinduced transformations **1A** $\rightleftharpoons$ **1B** with retention of the structure can be repeatedly performed (Scheme 1).

Scheme 1



It was demonstrated that the maximum of the long-wavelength absorption band for the cyclic form of photochrome **1B** is located in the region of 622 nm. It seemed reasonable to synthesize derivatives of the closest analog of thienothiophene structure **1**, *viz*., dithieno[3,2-*b*;2´,3´-*d*]thiophene, with the aim of elucidating the influence of the length of conjugation on the properties of photochromes.

In the present study, we developed a new procedure for the preparation of the dithieno[3,2-*b*;2´,3´-*d*]thiophene structure and synthesized 1,2-bis(2,6-dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophen-3-yl)hexafluorocyclopent-1-ene (**2**). The latter compound is the first representative of photochromic systems in which the perfluorocyclopentene bridge is directly bound to the tricyclic fragments (Scheme 2).

The key intermediate **7** was synthesized with the use of a new approach to the construction of the dithieno[3,2-*b*;2´,3´-*d*]thiophene system. Our method differs from those described previously[3,4] and is based on selective bromination of 5,5´-dimethyl-2,2´-bithiophene (**3**) at positions 3 and 3´ under the action of NBS in a 1 : 1 AcOH—$CHCl_3$ mixture. 3,3´-Dibromo-5,5´-dimethyl-2,2´-bithiophene (**4**) thus prepared was transformed under the successive action of 1 equiv. of Bu^nLi and 1 equiv. of elemental sulfur to form 3´-bromo-3-thio derivative **5** in 67% yield. Bromide **5** underwent cyclization in the presence of Cu_2O in DMF to give 2,6-dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophene (**6**). The latter was brominated by NBS to yield bromo derivative **7** (see Scheme 2). The reaction proceeded nonregioselectively and compound **7** was isolated from the mixture of bromination products by column chromatography in 10.4% yield. The further synthesis of model compound **2** was carried out according to a procedure described previously.[2]

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* For Part 17, see Ref. 1.

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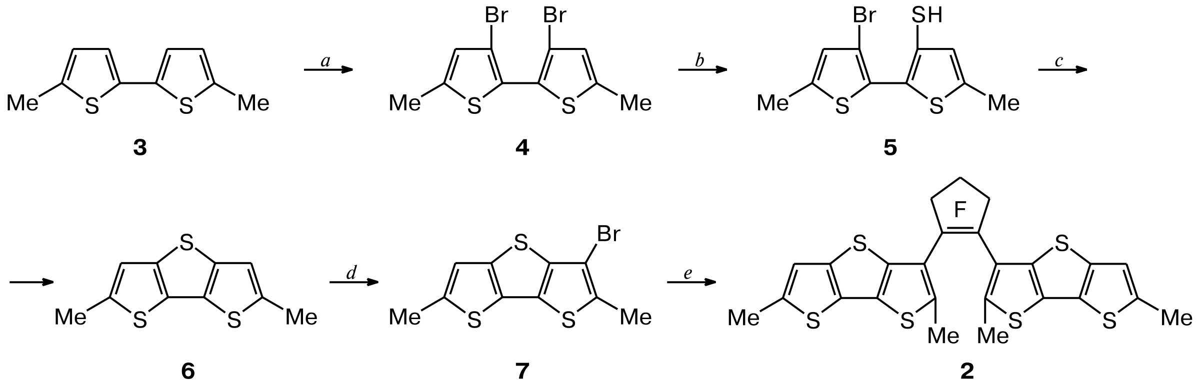
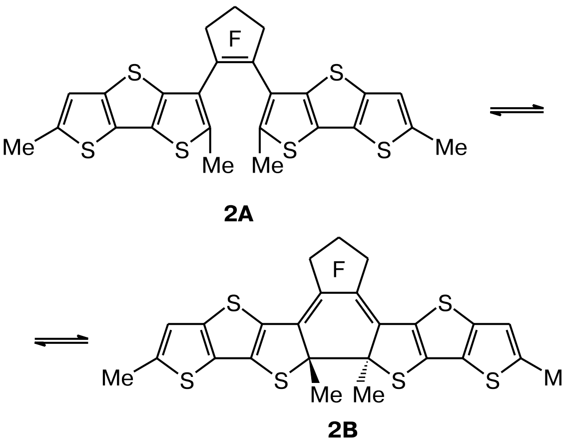
Scheme 2



Reagents and conditions: *a*. NBS, AcOH—$CHCl_3$, 10 °C. *b*. 1) Bu^{n}Li, –70 °C; 2) S_8, –35 °C. *c*. Cu_2O, KOH, DMF. *d*. NBS, AcOH—$CHCl_3$, 5 °C. *e*. 1) Bu^{n}Li, –78 °C, hexane—THF; 2) octafluorocyclopentene.

The photochromic characteristics of compound **2** were studied in a solution in MeCN. Photocyclization **2A** $\longrightarrow$ **2B** was performed under irradiation with light with λ = 313 nm and the reverse reaction was carried out under irradiation with light with λ = 578 nm (Scheme 3). Compound **2** was demonstrated to exhibit the photochromic properties. The maxima of the long-wavelength absorption bands for the open (**2A**) and cyclic (**2B**) forms are observed at 290 and 612 nm, respectively, which are comparable with the corresponding characteristics of benzothiazole derivatives **1**.

Scheme 3



The available data are insufficient for the detailed estimation of the spectroscopic characteristics of model compound **2**. However, it is quite probable that the introduction of the benzothiazole groups at positions 2 and 6 of the dithienothiophene ring can lead to a substantial bathochromic shift of the long-wavelength absorption band of the cyclic form of the photochrome.

Experimental

The ^{1}H NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and SF-300 instruments in $CDCl_3$ and DMSO-d_6. The melting points were determined on a Boetius stage and were not corrected. The mass spectra were measured on a Kratos MS-300 instrument with direct inlet of the sample into the ion source; the energy of ionizing electrons was 70 eV. The high-resolution mass spectrum was obtained on a Finnigan MAT instrument. Thin-layer chromatography was carried out on Silufol UV-254 and Merck-60 plates. Column chromatography was performed on silica gel Merck-60. All reactions with organolithium compounds were carried out under a low pressure of highly pure moisture- and oxygen-free argon. The reagents and solvents were prepared according to standard procedures. The reagents were introduced into a pre-dried apparatus with the use of rubber stoppers and disposable syringes.

The photochromic characteristics of compound **2** were studied in a solution in MeCN. The samples were irradiated with a DRSh-500 mercury lamp using light filters to separate lines of the mercury spectrum (λ = 313 and 578 nm). The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer.

3,3´-Dibromo-5,5´-dimethyl-2,2´-bithiophene (4). *N*-Bromosuccinimide (3.20 g, 0.018 mol) was added to a suspension of 5,5´-dimethyl-2,2´-bithiophene (**3**)^5 (8.70 g, 0.045 mol) and hydroquinone (6.87 g, 0.062 mol) in a 1 : 1 AcOH—$CHCl_3$ mixture (276 mL) at 6—10 °C during 10 min and the reaction mixture was stirred at this temperature for 20 min. Then water (113 mL) was added. The aqueous layer was separated and extracted with $CHCl_3$ (2×20 mL). The extract was combined with the organic layer, washed with water (2×20 mL) and solutions of Na_2CO_3 (2×20 mL) and NaCl (2×20 mL), and dried over $CaCl_2$. The solvent was evaporated. Column chromatography (hexane as the eluent) afforded compound **4** in a yield of 10.60 g (67%), m.p. 80.0—82.5 °C (from hexane). Found (%): C, 34.22; H, 2.31; Br, 45.25; S, 18.17. $C_{10}H_8Br_2S_2$. Calculated (%): C, 34.11; H, 2.29; Br, 45.39; S, 18.21. MS, *m/z*: 350, 352, 354 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 2.50 (s, 6 H, 2 Me); 6.75 (s, 2 H, H of thiophene).

3-Bromo-3´-mercapto-5,5´-dimethyl-2,2´-bithiophene (5). A 1.75 *N* Bu^nLi solution (0.016 mol) in hexane (9.25 mL) was added to a solution of compound **4** (5.70 g, 0.016 mol) in anhydrous ether (20 mL) under argon at −70 °C during 7 min and the reaction mixture was stirred at −70 °C for 30 min. Then elemental sulfur (0.56 g) was added during 7 min, the reaction mixture was stirred at a temperature from −26 to −35 °C for 2 h, water (102 mL) was added during 10 min, and the mixture was stirred for 15 min. The aqueous layer was separated, extracted with ether (5×15 mL), and combined with the organic layer. The combined extracts were washed with water, a 8% NaOH solution, and again with water. All washing liquors and the aqueous layer were combined and cooled to 5 °C. Then ether was added. The mixture was acidified with concentrated HCl (Congo dye) and extracted with ether. The extract was washed with water and dried over $MgSO_4$. The ether was evaporated to obtain compound **5** in a yield of 2.27 g (46%). This compound was used in the subsequent step without additional purification. MS, *m/z*: 304, 306 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 2.45 and 2.52 (both s, 3 H each, 2 Me); 6.65 and 6.75 (both s, 1 H each, 2 H of thiophene).

2,6-Dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophene (6). A suspension of KOH (4.93 g) and Cu_2O (1.14 g) in DMF (149 mL) was added to a solution of compound **5** (2.27 g, 7.4 mmol) in DMF (42 mL). The reaction mixture was stirred at 20 °C for 1.5 h and then refluxed for 40 h. The dimethylformamide was distilled off and benzene (100 mL) was added to the residue. The reaction mixture was refluxed for 20 min and the benzene solution was decanted from the precipitate. The precipitate was washed several times with dilute HCl (1 : 1). Then the precipitate was washed with water and an NaCl solution and dried over $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a column with SiO_2 (hexane as the eluent). Compound **6** was obtained in a yield of 1.32 g (78.6%), m.p. 76—78 °C (from hexane). Found (%): C, 53.62; H, 3.47; S, 42.78. $C_{10}H_8S_3$. Calculated (%): C, 53.54; H, 3.59; S, 42.87. MS, *m/z*: 224 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 2.50 (s, 6 H, 2 Me); 6.75 (s, 2 H, H of thiophene).

3-Bromo-2,6-dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophene (7). *N*-Bromosuccinimide (4.20 g, 23.59 mmol) was added to a suspension of compound **6** (1.32 g, 5.89 mmol) and hydroquinone (0.91 g, 8.27 mmol) in a 1 : 1 AcOH—$CHCl_3$ mixture (35 mL) at 3—5 °C during 10 min and the reaction mixture was stirred at this temperature for 20 min. Then cold water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$ (2×15 mL) and combined with the organic layer. The combined layers were washed with a solution of NaCl and Na_2CO_3 (2×10 mL) and then with water (2×10 mL) and dried over $MgSO_4$. The solvent was evaporated and the residue was twice chromatographed on a column with SiO_2 (hexane as the eluent). Compound **7** was obtained in a yield of 0.185 g (10.4%), m.p. 76—77 °C (from hexane). Found (%): C, 39.72; H, 2.26; Br, 26.54; S, 31.60. $C_{10}H_7BrS_3$. Calculated (%): C, 39.75; H, 2.33; Br, 26.14; S, 31.77. MS, *m/z*: 302, 304 $[M]^+$. ^1H NMR ($CDCl_3$), δ: 2.50 and 2.62 (both s, 3 H each, 2 Me); 6.95 (s, 1 H, H of thiophene).

1,2-Bis(2,6-dimethyldithieno[3,2-*b*;2´,3´-*d*]thiophene-3-yl)hexafluorocyclopent-1-ene (2). A solution of Bu^nLi in hexane (0.46 mL; the concentration was 0.09 g mL^{-1}, 0.65 mmol) was gradually added to a solution of compound **7** (0.18 g, 0.59 mmol) in anhydrous THF (20 mL) under argon at −78 °C. After 15 min, a solution of octafluorocyclopentene (0.04 mL, 0.30 mmol) in anhydrous THF (0.26 mL) was added. The reaction mixture was stirred at −78 °C for 2 h and then the temperature was raised to 20 °C. The reaction mixture was kept for 12 h and then cooled to −15 °C. Then MeOH (5 mL) was added and the mixture was stirred for 2 h. The solvent was evaporated and water was added to the residue. The mixture was extracted with CH_2Cl_2 and the extract was washed with water and dried over $CaCl_2$. The solvent was evaporated and the residue was chromatographed on a column with SiO_2 (light petroleum as the eluent). Compound **6** was obtained in a yield of 0.085 g (64%). Compound **2** was obtained in a yield of 0.01 g (5.4%) as a viscous oil. MS, Found: *m/z* 620.7336 $[M]^+$. $C_{25}H_{14}F_6S_6$. Calculated: M = 620.7360. ^1H NMR ($CDCl_3$), δ: 2.50 (s, 6 H, 2 Me); 6.93 (s, 2 H, H of thiophene).

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