Photochromic dihetarylethenes
3.* Synthesis and photochromic properties of 1,2-bis[2-methyl-5-(benzoxazol-2-yl)thien-3-yl]hexafluorocyclopentene

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1,2-Bis[2-methyl-5-(benzoxazol-2-yl)thien-3-yl]hexafluorocyclopentene was synthesized, and its photochromic properties were studied.

Key words: dithienylperfluorocyclopentenes, photochromes, photostationary state, reversible photocyclization.

Among organic photochromic substances appropriate for recording and prolonged storage of information, derivatives of 1,2-bis(thien-3-yl)perfluorocyclopentene are of great interest, because they possess a high thermal stability of the open and cyclic forms and allow one to choose an appropriate change in color during irradiation due to a change in the structure.[2] It is significant for the use of similar photochromic compounds to read out information without a substantial influence on mutual transitions of the cyclic and open forms. As shown previously,[3] this possibility can be achieved due to fluorescence excited in the region that does not result in the mutual transformation of these forms.

For the purpose of the preparation of substances with similar properties, but simpler in structure and more accessible from the synthetic viewpoint, we decided to introduce into the molecule "fluorophoric" fragments that provide fluorescence of the compound. The benzoxazole cycle was chosen as such a fragment. 2,5-Bis(benzoxazol-2-yl)thiophene, for example, has been used as a fluorophore.[4]

We synthesized 1,2-bis[2-methyl-5-(benzoxazol-2-yl)thien-3-yl]perfluorocyclopentene (**1**) according to Scheme 1. 2-(4-Bromo-5-methylthien-2-yl)benzoxazole (**2**) was obtained by the condensation of 4-bromo-5-methylthiophene-2-carboxylic acid (**3**) with *ortho*-aminophenol in xylene in the presence of H_3BO_3 in a 45% yield. The replacement of bromine by lithium in bromide **2** under the action of Bu^nLi at −70 °C gave Li derivative **4**, whose reaction with octafluorocyclopentene resulted in the formation of adduct **5** (49% yield). The reaction of the latter with the Li derivative **4** gave the target product **1A** in a 31% yield. It is noteworthy that the formation of monoadduct **5** demonstrates the possibility of the synthesis of nonsymmetrical derivatives of octafluorocyclopentene by this method.

The photochemical parameters of compound **1** were studied in an ethanolic solution. The absorption maximum of form **1A** was observed at λ = 324 nm, and that of form **1B** lies at λ = 620 nm. The **1A** → **1B** photocyclization was performed under irradiation with light with λ = 313 nm, and light with λ = 578 nm was used for the reverse reaction. The absorption spectra exhibit isosbestic points, and the coincidence of their positions for the direct and reverse reactions indicates the complete photoreversibility of photocyclization of compound **1** and the absence of side processes (Fig. 1).

The quantum yield was calculated by the procedure described previously.[1] The quantum yield of the **1A** → **1B** phototransformation is equal to 1±0.1, and that of the **1B** → **1A** phototransformation is equal to 0.01±0.001. The dark reaction **1A** → **1B** is absent, and the dark reaction **1B** → **1A** is virtually absent as well: the optical density of an ethanolic solution of **1B** remained almost unchanged during its 500-h keeping in darkness. The extinction coefficient of form **1A** was determined by us as $4.6 \cdot 10^4$ L mol^{-1} cm^{-1} at λ = 324 nm. Since the quantum yields of the direct and reverse reactions differ by two orders of magnitude, the absorption spectrum observed during prolonged irradiation of form **1A** with the light with λ = 313 nm can be assigned to form **1B**, and then the extinction coefficient of conformer **1B** at λ = 620 nm is equal to $1.6 \cdot 10^4$ L mol^{-1} cm^{-1}. Com-

* For Part 2, see Ref. 1.

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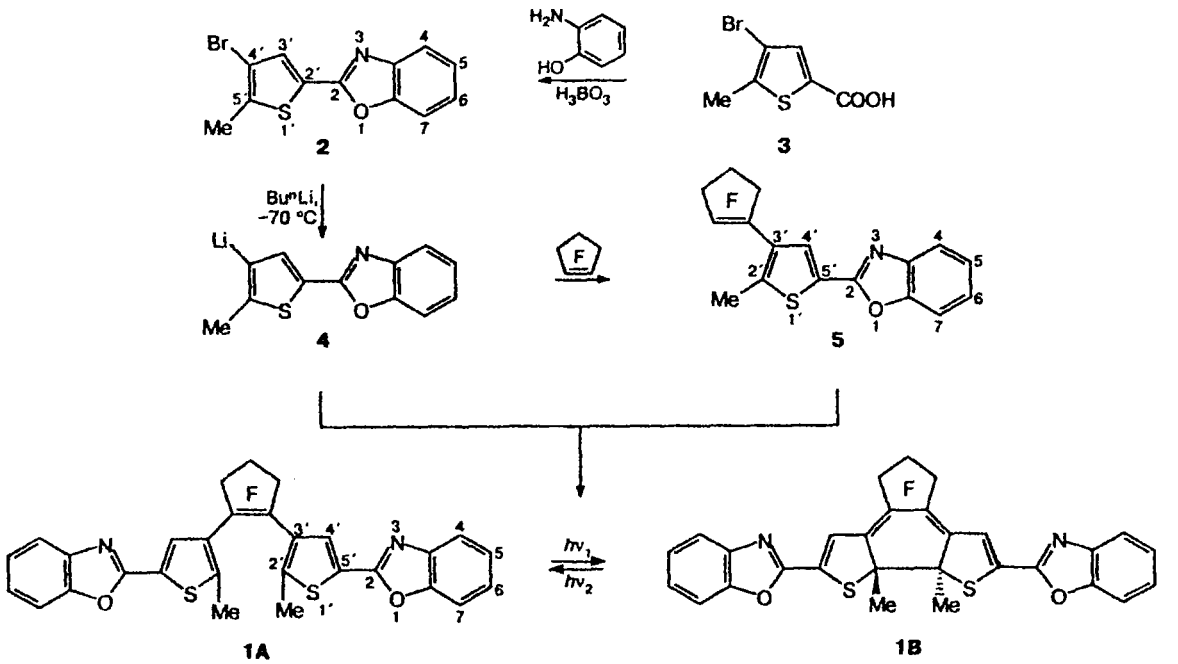
Scheme 1



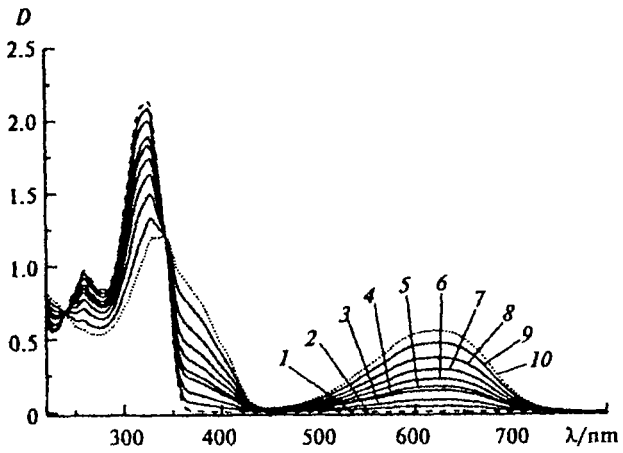


Fig. 1. Change in the absorption spectrum of an ethanolic solution of 1,2-bis[2-methyl-5-(benzoxazol-2-yl)thien-3-yl]hexafluorocyclopentene **1** during irradiation with light with λ = 313 nm. Spectra: *1*, initial solution; *2*, 5 s after the beginning of irradiation; *3*, 10 s after; *4*, 16 s after; *5*, 20 s after; *6*, 28 s after; *7*, 37 s after; *8*, 50 s after; *9*, 70 s after; and *10*, 90 s after.

pound **1** does not exhibit fluorescent properties in either open or cyclic form.

Experimental

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

Samples were irradiated by a DRSh-500 mercury lamp using light filters to separate the lines in the mercury spectrum (313 and 578 nm). The intensity of the mercury lamp radiation was determined by an F4 photocell calibrated by a ferrioxalate actinometer[5] for λ = 313 nm and by an actinometer based on Reinecke salt[6] for λ = 578 nm. Absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. Fluorescence was studied on a Perkin—Elmer LS-50 spectrofluorimeter.

To determine the quantum yield, a solution of a substance in ethanol was irradiated with light with λ = 313 nm to perform the direct reaction (578 nm for the reverse reaction), increasing gradually the irradiation duration from 5 s to 1—2 min (7—10 experimental points) and recording the absorption spectrum of the irradiated solution for each exposure.

2-(4-Bromo-5-methylthien-2-yl)benzoxazole (2). A mixture of *ortho*-aminophenol (330 mg, 3 mmol), 4-bromo-5-methylthiophene-2-carboxylic acid **3** (660 mg, 3 mmol), and H_3BO_3 (186 mg, 3 mmol) in xylene (30 mL) was refluxed for 31 h with a Dean—Stark trap. Xylene was removed *in vacuo*. The product was isolated by preparative TLC using benzene as the eluent. Compound **2** (400 mg, 45%) with m.p. 143—144 °C was obtained. Found (%): C, 49.17; H, 3.01; Br, 26.72; S, 10.73. $C_{12}H_8BrNOS$. Calculated (%): C, 48.99; H, 2.74; Br, 27.16; S, 10.90. ^{1}H NMR (DMSO-d_6), δ: 2.51 (s, 3 H, CH_3); 7.39—7.45 (m, 2 H, H(5), H(6)); 7.71—7.77 (m, 2 H, H(4), H(7)); 7.83 (s, 1 H, H(3')). MS, m/z (I_{rel} (%)): 294 $[M]^+$ (100%).

1-[2-Methyl-5-(benzoxazol-2-yl)thien-3-yl]heptafluorocyclopentene (5). A 1.25 *N* solution (0.9 mL) of Bu^nLi (1.1 mmol) in hexane was added to a solution of compound **2** (300 mg, 1 mmol) in THF (4 mL) with stirring at −70 °C, and the mixture was kept for 15 min. Then octafluorocyclo-

pentene (320 mg, 1.5 mmol) was added at −70 °C, and the mixture was stored for 2 h. The temperature of the reaction mixture was brought to room temperature, 2 mL of water and a solution of 0.1 mL of concentrated HCl in 1 mL of water were added. The solvents were removed *in vacuo*, and the residue was dissolved in $CHCl_3$, washed with water, and dried with $CaCl_2$. $CHCl_3$ was removed, and the product was isolated by preparative TLC using $CHCl_3$ as the eluent. Compound **5** (200 mg, 49%) with m.p. 122—124 °C was obtained. ^{1}H NMR ($DMSO$-d_6), δ: 2.59 (s, 3 H, CH_3); 7.39—7.48 (m, 2 H, H(5), H(6)); 7.73—7.81 (m, 2 H, H(4), H(7)); 7.91 (s, 1 H, H(4′)). ^{19}F NMR ($CDCl_3$), δ: −128.1 (s, 2 F, CF_2); −124.5 (s, F, CF); −116.2 (s, 2 F, CF_2); −106.7 (s, 2 F, CF_2). MS, *m/z* (I_{rel} (%)): 407 $[M]^+$ (100%).

1,2-Bis[2-methyl-5-(benzoxazol-2-yl)thien-3-yl]hexafluorocyclopentene (1). A 1.75 *N* solution (0.32 mL) of Bu^nLi (0.56 mmol) in ether was added to a solution of compound **2** (150 mg, 0.51 mmol) in THF (4 mL) with stirring at −70 °C (Ar), and the mixture was kept for 10 min. Then a solution of compound **5** (200 mg, 0.49 mmol) in THF (2 mL) was added at −70 °C, and the mixture was stored for 2 h. The temperature of the reaction mixture was brought to room temperature, and the solution was left to stand for ~12 h. Water (5 mL) and concentrated HCl (0.1 mL) were added. The solvents were removed *in vacuo*, and the residue was dissolved in $CHCl_3$, washed with water, a 5% solution of Na_2CO_3, and again with water, and dried above $CaCl_2$. $CHCl_3$ was removed. The product was isolated on a chromatographic column (Silpearl, benzene as the eluent). Compound **1** (92 mg, 31%), with m.p. 194—195 °C was obtained. Found (%): C, 57.26; H, 2.95. $C_{29}H_{16}F_6N_2O_2S_2$. Calculated (%): C, 57.80; H, 2.67. ^{1}H NMR ($CDCl_3$), δ, 1A (open form): 2.06 (s, 3 H, CH_3); 7.30—7.42 (m, 2 H, H(5), H(6)); 7.5—7.6 (m, 1 H, H(4)); 7.7—7.8 (m, 1 H, H(7)); 7.92 (s, 1 H, H(4′)); 1B (cyclic form): 2.32 (s, 3 H, CH_3); 5.30 (s, 1 H, H(4′)). ^{19}F NMR ($CDCl_3$), δ: −131.5 (s, 2 F, CF_2); −110 (s, 4 F, $(CF_2)_2$). MS, *m/z* (I_{rel} (%)): 602 $[M]^+$ (60%).

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High-pressure alkylation of azomethines
1. Synthesis of *N*-monoalkylanilines

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Reaction of anils with alkyl halides under high pressure (10 kbar) was studied. Alkylation in polar media (dioxane or acetonitrile) followed by hydrolysis yields pure *N*-monoalkylanilines in high yields. Optimum conditions for high-pressure alkylation were found.

Key words: azomethines, alkylation, immonium salts, *N*-monoalkylanilines, high pressure.

It is well known that direct alkylation of primary amines yields mixtures of products that are difficult to separate, pure dialkylamines being especially hard to isolate. Pure *N*-monoalkylanilines can be obtained in various ways,[1] including alkylation of easily available azomethines followed by hydrolysis of the resulting quaternary immonium salts.[2]

This method is quite promising, but it works well only with active alkylating agents, probably, because of the low nucleophilicity of azomethines. Even when highly

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