Photochromic dihetarylethenes
6.* Photochromic derivatives of thieno[3,2-*b*]thiophene**

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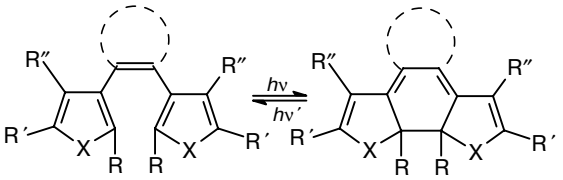
1,2-Bis{5-(2-benzothiazolyl)-2-methyl-6-trifluoromethylthieno[3,2-*b*]thiophen-3-yl}hexafluorocyclopentene possessing high fatigue resistance was synthesized for the first time. Its photochromic and fluorescence properties were studied. The structure of its cyclic form was established by X-ray diffraction analysis.

Key words: 1,2-bis{5-(2-benzothiazolyl)-2-methyl-6-trifluoromethylthieno[3,2-*b*]thiophen-3-yl}hexafluorocyclopentene, 1,2-dithienylethenes, hexafluorocyclopentene derivatives; photochromes, X-ray diffraction analysis, fluorescence.

Among photochromic compounds, 1,2-dihetarylethenes have attracted considerable recent attention due to the high thermal stability of the open (colorless, **A**) and cyclic (colored, **B**) forms and the possibility to repeatedly perform direct and reverse photoinduced processes with retention of the structure (high fatigue resistance).[2]

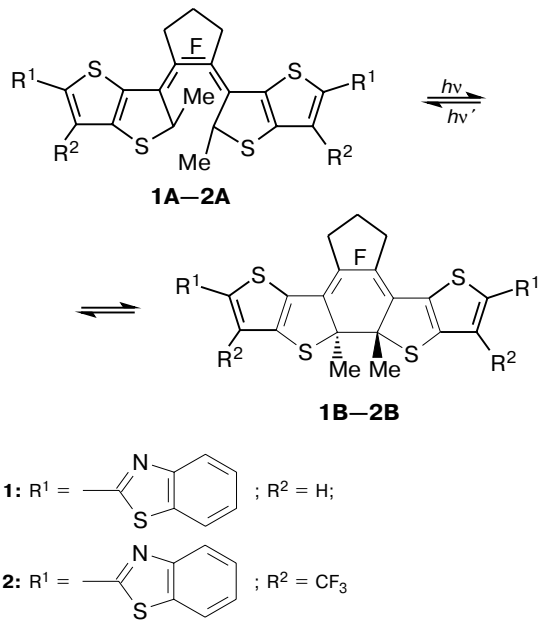


A **B**

Benzo[*b*]thiophene derivatives whose fatigue resistance in the absence of atmospheric oxygen reaches 10^4 cycles are of particular interest.[3] In this connection, it was of interest to study the photochromic properties of thieno[3,2-*b*]thiophene derivatives of types **1**—**2** (Scheme 1) as the closest heterocyclic analogs of benzo[*b*]thiophene.

When using such photochromes, the possibility to read out information without a significant effect on interconversions of the cyclic and open forms is of great importance. Previously, it has been demonstrated[4] that this possibility can be realized due to fluorescence excited with light with the wavelength λ such that it does not induce interconversions of two forms. However, fluorescent 1,2-dihetarylethenes are few in number.[5—7]

Scheme 1



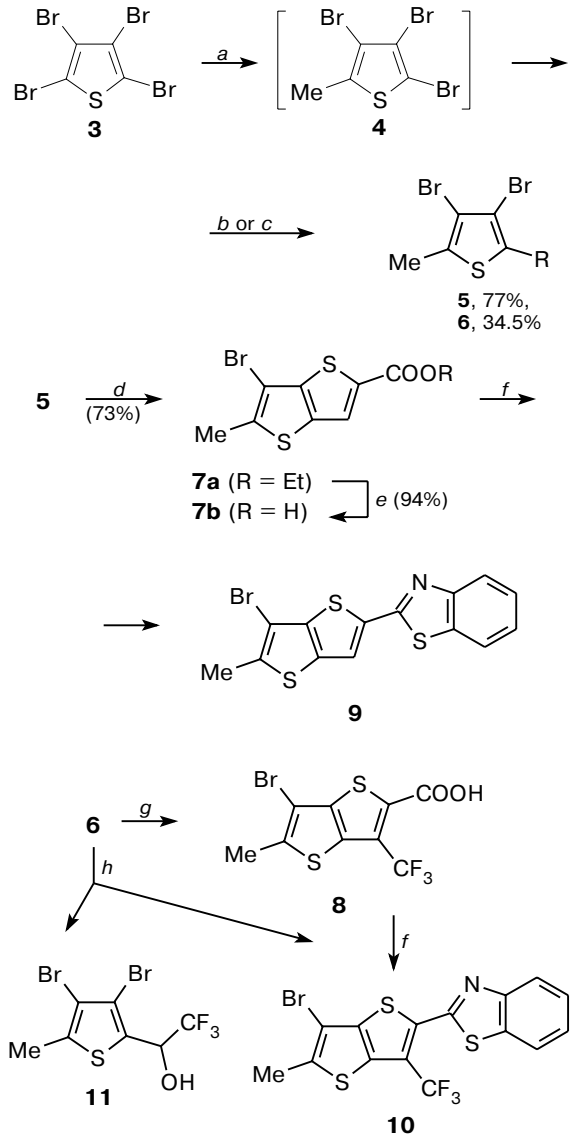
* For Part 5, see Ref. 1.
** Dedicated to the memory of Professor Ya. L. Gol'dfarb on the occassion of his 100th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 107—112, January, 2001.
1066-5285/00/5001-0110 $25.00

We believed that the introduction of the benzothiazole fragments into molecules of thienothiophene photochromes can lead to the appearance of fluorescence properties.

We used tetrabromothiophene (**3**) as the starting compound for preparing compounds **1** and **2**. The reaction of compound **3** with BuLi and methyl benzenesulfonate at 0 °C[8] afforded 3,4,5-tribromo-2-methylthiophene (**4**). Treatment of the latter with BuLi and DMF gave rise to 3,4-dibromo-5-methyl-2-thiophene aldehyde (**5**), whereas the reaction of **4** with ethyl trifluoroacetate yielded trifluoromethyl ketone **6** (Scheme 2). Both stages can be performed as a one-pot procedure without isolation of bromide **4**. Cyclization of compounds **5** and **6** with ethyl thioglycolate afforded acids **7** and **8**, respectively, of which only compound **7** underwent condensation with *ortho*-aminophenol to form thieno[3,2-*b*]thiophene derivative (**9**). Thienothiophene **10** was synthesized by the reaction of ketone **6** with 2-mercaptomethylbenzothiazole. This approach can be extended to other aryl-substituted derivatives of thienothiophene. However, it should be remembered that this reaction is accompanied by side reduction of ketone **6** with 2-mercaptomethylbenzothiazole to form carbinol **11**.

Scheme 2

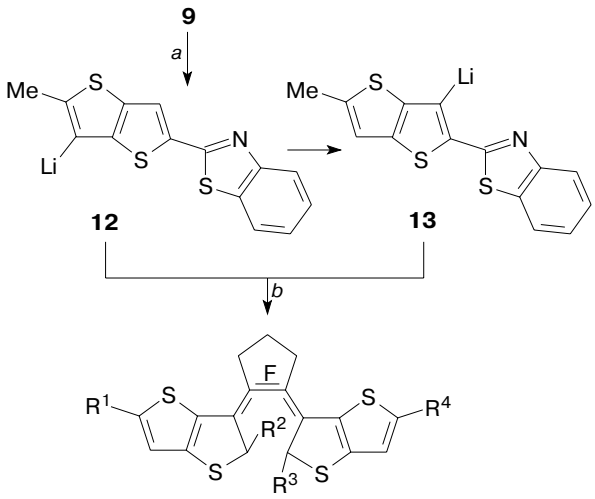


5: R = CHO; **6:** R = $COCF_3$; **7a:** R = Et; **7b:** R = H

Reagents and conditions: *a*) 1) Bu^nLi, 0 °C, 2) $PhSO_3Me$; *b*) 1) Bu^nLi, 0 °C, 2) DMF, −65 °C; *c*) 1) Bu^nLi, 0 °C, 2) CF_3CO_2Et, −70 °C; *d*) $HSCH_2CO_2Et$—K_2CO_3/DMF; *e*) LiOH/THF—H_2O, 65 °C; *f*) 2-aminothiophenol/*N*-MP; *g*) $HSCH_2CO_2Et$—NaOEt/EtOH; *h*) 2-mercaptomethylbenzothiazole—NaOEt/EtOH.

The reaction of compound **9** with BuLi at −70 °C followed by the coupling with octafluorocyclopentene (C_5F_8) gave rise to a mixture that could not be separated and that contained not only the desired dihetarylethene **1** but also other compounds possessing very similar photochromic properties. The formation of this mixture gave grounds to suggest that the lithium atom in intermediate hetaryllithium **12** can partially migrate from position 6 to position 3 followed by the reaction of the resulting Li-containing derivatives **12** and **13** with C_5F_8 (Scheme 3).

Scheme 3

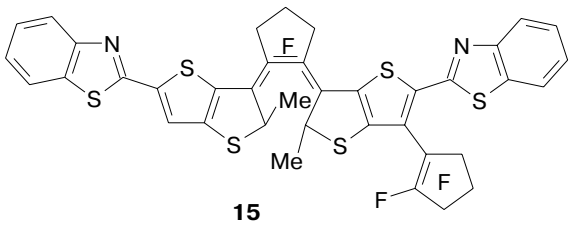


$R^1 = R^4 = Z$; $R^2 = R^3 = Me$; $R^1 = R^3 = Z$; $R^2 = R^4 = Me$; $R^2 = R^3 = Z$; $R^1 = R^4 = Me$; Z = 2-benzothiazolyl

Reagents and conditions: *a*) Bu^nLi, −70 °C; *b*) C_5F_8.

To confirm this suggestion, Li derivative **12**, which was prepared from bromide **9**, was introduced into the reaction with bromine. Based on the ^1H NMR spectral data of the product isolated, it was established that it contained the 3-bromine-substituted analog (4%), bromine-free 2-(2-benzothiazolyl)-5-methylthieno[3,2-*b*]thiophene (**14**) (11%), and the initial bro-

mide **9** (85%). Apparently, the migration of the lithium atom is caused by the high acidity of the proton at position 3 due to the activating effect of the benzothiazole substituent. Based on the fact that the lithium atom in compound **12** readily migrates, it can also be assumed that direct metallation of bromide **9** (see Scheme 2) or the resulting photochrome **1** (see Scheme 1) under the action of butyllithium can occur at position 3 followed by the reaction of this lithium-containing derivative with C_5F_8. This is also supported by the fact that the mass spectrum of the mixture has a peak at $m/z = 939$, which corresponds to structure **15**.



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The reaction of BuLi and C_5F_8 with hetarene **10** in which the hydrogen atom at position 3 is replaced by the trifluoromethyl group gave rise to photochromic compound **2** as the single product. Its structure was established by spectral methods. The formation of cyclic form **2B** was confirmed by X-ray diffraction study.

The structure of molecule **2B** is shown in Fig. 1. The perfluorocyclopentene fragment (*F*) adopts an envelope conformation. The C(9) flap of the envelope deviates from the mean plane through the remaining four atoms by −0.380 Å. The thiophene rings in the thieno[3,2-*b*]thiophene fragments (*T* and *T′*) also adopt an envelope conformation. The C(1) and C(1′) flaps of the envelopes deviate in opposite directions from the corresponding planes of the remaining seven atoms by −0.331 and 0.313 Å, respectively. Therefore, molecule **2B** contains a six-membered ring (*C*) adopting the "twisted sofa" conformation with the *trans*-oriented methyl substituents at the C(1) and C(1′) atoms. The remaining portion of the molecule (except for the fluorine atoms) is virtually planar as evidenced by the dihedral angles between the fragments. Thus the angle of rotation of the benzothiazole fragment (*B*) with respect to the *T* fragment is 1.39°. The angle of rotation of the *B′* fragment with respect to the *T′* fragment is somewhat larger (13.42°), which, apparently, results from the molecular packing in the crystal. The *F*/*T*, *F*/*T′*, and *T*/*T′* dihedral angles are 1.15°, 2.44°, and 3.40°, respectively.

Analysis of the geometric parameters of molecule **2B** revealed the following facts. First, the thienyl fragments lose their aromaticity, and the alternation of the bond lengths in the chain —C(3)—C(2)—C(7)—C(11)—C(2′)—C(3′)— is indicative of the formation of a new planar conjugated system. Second, the exocyclic bond angles at the C(2) (133.9°) and C(2′) atoms (134.4°) in the cyclic form of the molecule are substantially larger (by 7—12°) than the analogous angles in the structures of the open forms of dithienylperfluorocyclopentenes,[9] which results in additional steric hindrance in the fused *T*(*T′*) and *C* rings and, apparently, favors the conversion of the molecule from form **B** to **A**. The remaining bond lengths and bond angles in the structure of **2B** have standard values. No shortened intermolecular contacts were found.

The photochemical characteristics of compound **2** were studied in an *n*-hexane solution. Photocyclization **A**→**B** was carried out upon irradiation with λ = 313 nm. The reverse reaction was performed upon irradiation with λ = 578 nm. The absorption spectra have isobestic points. Their positions for the direct and reverse reactions coincide, which is indicative of the complete reversibility of photocyclization and the absence of side processes (Fig. 2). The dark reactions **A**→**B** and **B**→**A** are absent. The quantum yields of photocyclization (the calculation procedure has been reported previously[13]) and of the reverse reaction were 0.9 and 0.006, respectively. Open form **2A** exhibits fluorescence in an ethanolic solution (Fig. 3). The intensity of fluorescence decreases sharply after cyclization under the action of UV light

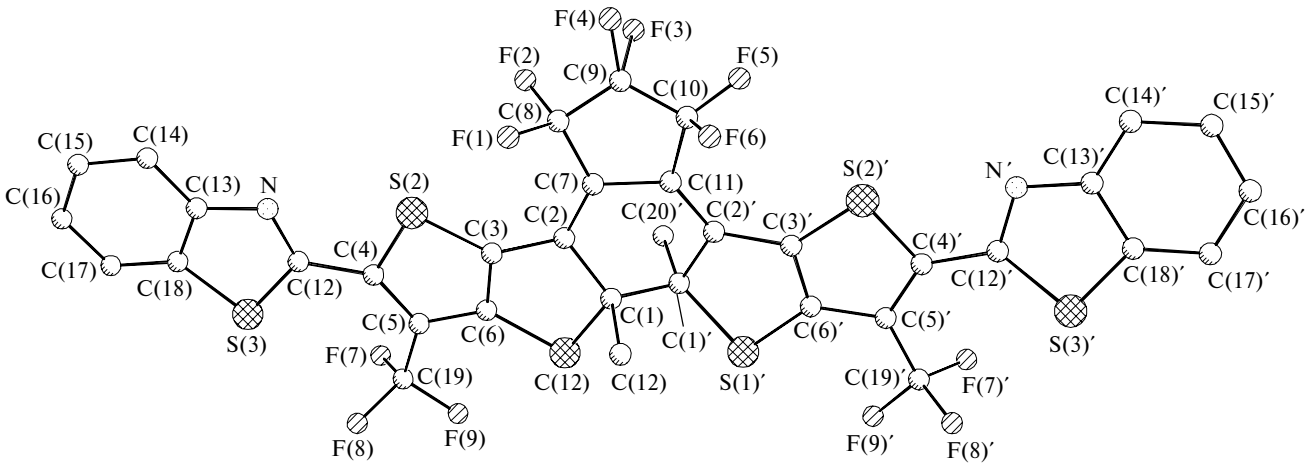

Fig. 1. Structure of molecule **2B**.

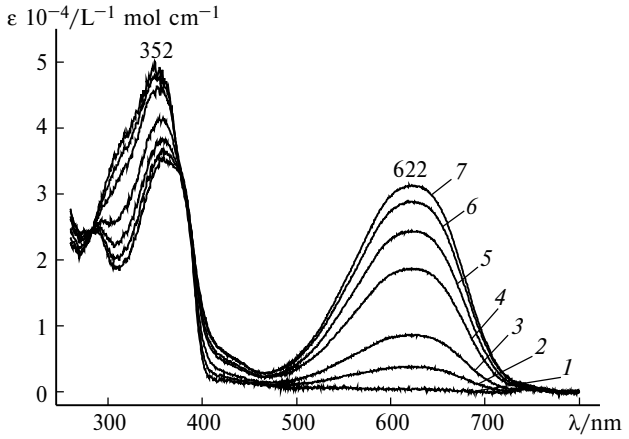

Fig. 2. Changes in the absorption spectrum of an *n*-hexane solution of 1,2-bis{5-(2-benzothiazolyl)-2-methyl-6-trifluoromethylthieno[3,2-*b*]thiophen-2-yl}hexafluorocyclopentene **3** before irradiation (open form) (*1*) and after irradiation with light at λ = 313 nm and at λ = 578 nm; the time of exposure: 5 s (*2*), 15 s (*3*), 1 min (*4*), 2 min (*5*), 3 min (*6*), and 4 min (*7*, the photostationary state (the maximum content of the cyclic form)).

with λ = 365 nm (*i.e.*, after the establishment of the photostationary state in which this compound exists predominantly in nonfluorescent cyclic form **2B**). The maximum of fluorescence emission of **2A** is observed at λ = 427 nm. The fluorescence excitation spectrum coincides with the long-wavelength absorption band of form **2A** (λ = 352 nm). This indicates that it is form **2A** which is fluorescent. Interestingly, 1,2-bis[5-(benzothiazol-2-yl)-2-methylthien-3-yl]perfluoropentene, which we have synthesized previously[11] and which is the closest structural analog of compound **2**, is not fluorescent.

We measured the fatigue resistance of compound **2**, which was determined as the number of photocycles N_c (*i.e.*, conversions from the open form to the cyclic form and back with respect to the complete photoconversion) which the substance can undergo until its amount decreases to 80% of the initial value. The N_c value in an *n*-hexane solution was $5 \cdot 10^3$.

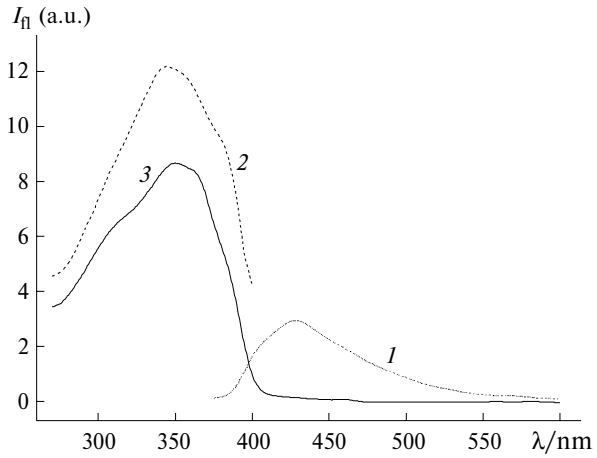

Fig. 3. Fluorescence spectra (*1* and *2*) and the absorption spectrum (*3*) of an ethanolic solution of 1,2-bis{5-(2-benzothiazolyl)-2-methyl-6-trifluoromethylthieno[3,2-*b*]thiophen-2-yl}hexafluorocyclopentene **2A**; excitation at λ = 350 (*1*) and 425 nm (*2*).

To summarize, photochromic compound **2** prepared based on thieno[3,2-*b*]thiophene possesses high fatigue resistance and its open form is fluorescent due to which **2** can be considered as a promising compound of practical significance for recording and storage of information.

Experimental

The ^{1}H NMR spectra were recorded on Bruker AC-200, WM-250, and SF-300 instruments in $CDCl_3$ and $(CD_3)_2SO$. The melting points were measured on a Boetius heating stage. The mass spectra were obtained on a Kratos MS-30 instrument with direct introduction of the sample into the ion source; the energy of ionizing electrons was 70 eV. Thin-layer chromatography was carried out on Silufol UV-254 and Merck 60 F_{254} plates. Column chromatography was performed on silica gel Merck 60. All reactions with organolithium compounds were carried out in highly purified moisture- and oxygen-free argon under moderate pressure. The reagents and solvents were dried according to standard procedures. The reagents were introduced into a predried apparatus using rubber stoppers and single-use syringes.

In photochemical studies, the samples were irradiated with the use of a DRSh-500 high-pressure mercury lamp. The intensity of irradiation of the mercury lamp was determined using an F4 photodetector calibrated against a ferrioxalate actinometer[10] for λ = 313, 365, 405, and 436 nm and against an actinometer based on Reinecke salt[12] for λ = 546 and 578 nm. The absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. Fluorescence was studied on a Perkin—Elmer LS-50 spectrofluorometer. To determine the quantum yield, a solution of the compound in ethanol was irradiated with light at λ = 313 and 578 nm in the case of photocyclization and the reverse reaction, respectively, using light filters for separation of the mercury-spectrum lines. The duration of irradiation was gradually increased from 5 s to 1—2 min (a total of 7—10 experimental points). For each exposure, the absorption spectrum of the irradiated solution was recorded.

To determine the fatigue resistance, a solution of compound **2**, which was not purified from gases, was subjected to irradiation in a wide range of wavelengths including the mercury-spectrum lines of 313, 365, 405, 436, 546, and 578 nm. The intensity ratio of the mercury-spectrum lines in the UV and visible regions was varied using broad-band light filters. In the case of photochrome **2**, this ratio was chosen in such a way that the photostationary state was substantially shifted to the cyclic form. This was associated with the fact that photodecyclization is the governing stage of the photoreversible process because its quantum yield for this compound is two orders of magnitude smaller than that of photocyclization. The time of irradiation during which one photocycle occurred was determined by the formula

$$\tau = C_0 \Phi_{\mathbf{B}\rightarrow\mathbf{A}} / J_a^{\mathbf{B}},$$

where C_0 is the initial concentration of the compound, $\Phi_{\mathbf{B}\rightarrow\mathbf{A}}$ is the quantum yield of the conversion of **B** into **A**, and $J_a^{\mathbf{B}}$ is the intensity of light absorbed by form **B** in the photostationary state. Other methods for the determination of the fatigue resistance have been reported previously.[12,13]

X-ray diffraction study of compound 2B. Bright-red pyramidal single crystals of compound **2B** were grown from a solution in $CHCl_3$ and had the composition of the solvate $C_{35}H_{14}F_{12}N_2S_6 \cdot 0.5CHCl_3$. The crystals are monoclinic, a = 21.320(8) Å, b = 20.659(7) Å, c = 19.638(7) Å, β = 104.08(3)°, V = 8389.93 Å^3, d_{calc} = 1.566 g cm^{-3}, the space group $C2/c$, Z = 8. The intensities of 5053 independent reflections were measured on an automated four-circle Syntex $P2_1$ diffractometer (graphite monochromator, Mo-Kα radiation, θ/2θ scanning technique). The structure was solved by the direct method. The positions of the hydrogen atoms were revealed from difference electron density syntheses. The structure was refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms (with isotropic thermal parameters for H atoms) using 4386 reflections with $I > 3\sigma(I)$ to the reliability factor R_1 = 0.081. The refinement based on all reflections converged to wR = 0.107. Further improvement of the reliability factor was hindered by partial disorder of the Cl atoms in the chloroform molecule of solvation and disorder of the F(3)—F(6) atoms. Calculations were carried out with the use of the SHELXTL PLUS (Version 5.03+) and AREN-90 program packages. The atomic coordinates, thermal parameters, and geometric parameters of molecule **2B** were deposited with the Cambridge Structural Database.

3,4-Dibromo-5-methyl-2-thiophene aldehyde (5). A 1.79 *N* solution of BuLi (46 mL, 82 mmol) in ether was added with stirring and cooling to a suspension of tetrabromothiophene **3** (32 g, 80 mmol; Aldrich) in anhydrous ether (160 mL) at −5 °C. The reaction mixture was stirred at 0 °C for 15 min and cooled to −65 °C. Then $PhSO_3Me$ (13.76 g, 80 mmol) was added and the mixture was heated to ~20 °C and stirred for 1 h. Then a 1.79 *N* solution of BuLi (46 mL, 82 mmol) was added at −2—0 °C. The mixture was stirred at this temperature for 15 min and cooled to −70 °C. Then DMF (12 g, 164 mmol) was rapidly added and the reaction mixture was stirred with a gradual increase in the temperature to ~20 °C after which it was kept under a pressure of Ar for ~12 h. A 10% HCl solution (170 mL) was added with cooling. The mixture was stirred at 20 °C for 2 h and then extracted with ether. The ethereal layer was washed with water, dried with $MgSO_4$, and concentrated. Aldehyde **5** was obtained in a yield of 17.9 g (77%), m.p. 89.5—90 °C (from hexane). Found (%): C, 25.51; H, 1.86. $C_6H_4Br_2OS$. Calculated (%): C, 25.37; H, 1.42. ^{1}H NMR ($CDCl_3$), δ: 2.56 (s, 3 H, CH_3); 9.90 (s, 1 H, CHO).

3,4-Dibromo-5-methyl-2-trifluoroacetylthiophene (6). A 1.32 *N* BuLi solution (30 mL, 40 mmol) in ether was added to a suspension of bromide **3** (16 g, 40 mmol) in ether (60 mL) at 0 °C for 10 min. The mixture was stirred at this temperature for 15 min and then $PhSO_3Me$ (6.9 g, 40 mmol) was added at −65 °C. The temperature was increased to ~20 °C and the mixture was stirred for 30 min and cooled to 0 °C. Then a 1.32 *N* BuLi solution (34 mL) was added, the mixture was stirred for 15 min, and CF_3COOEt (5.7 g, 40 mmol) was rapidly added at −65 °C (the mixture warmed up to −30 °C). Then the mixture was cooled to −65 °C, stirred at this temperature for 2 h, and kept at 20 °C for ~12 h. A 10% HCl solution (100 mL) was added and the aqueous layer was extracted with ether. The ethereal extract was washed successively with a solution of $NaHCO_3$ and water and dried with $MgSO_4$. After removal of the solvent, the residue was distilled. Compound **6** was isolated in a yield of 6.10 g (34.5%), b.p. 109—115 °C (2.5 Torr). The reaction with tribromide **4**, which has been preliminarily isolated, afforded compound **6** in 44% yield. Found (%): C, 24.40*; H, 0.95. $C_7H_3Br_2F_3OS$. Calculated (%): C, 23.89; H, 0.86. ^{1}H NMR ($CDCl_3$), δ: 2.61 (s, 3 H, CH_3).

6-Bromo-5-methylthieno[3,2-*b*]thiophene-2-carboxylic acid (7). Aldehyde **5** (5 g, 17.6 mmol) was added to a mixture of potassium carbonate (3.28 g, 23.7 mmol) and ethyl thioglycolate (2.13 g, 17.7 mmol) in DMF (60 mL) and the reaction mixture was stirred under an Ar atmosphere for 77 h. Then the mixture was poured into water (200 mL) and extracted with CH_2Cl_2. The organic layer was washed with water and dried with $CaCl_2$. The solvent was removed *in vacuo*. Ethyl ester of acid **7** (**7a**) was obtained in a yield of 3.9 g (73%), m.p. 82—83 °C (from heptane). ^{1}H NMR ($CDCl_3$), δ: 1.40 (t, 3 H, CH_3); 2.53 (s, 3 H, CH_3); 4.39 (q, 2 H, CH_2); 7.93 (s, 1 H, H(4)).

A solution of the ester (3 g, 9.8 mmol) in THF (20 mL) was mixed with a 1 *N* aqueous solution of LiOH (20 mL) and refluxed for 3 h. Then THF was removed *in vacuo* and the aqueous solution was acidified with dilute HCl. The precipitate that formed was filtered off and washed with water. Acid **7** was obtained in a yield of 2.7 g (94%), m.p. >280 °C (decomp.) (from EtOAc). Found (%): C, 34.69; H, 2.05. $C_8H_5BrO_2S_2$. Calculated (%): C, 34.67; H, 1.82. ^{1}H NMR (acetone-d_6), δ: 2.59 (s, 3 H, CH_3); 8.12 (s, 1 H, H(3)).

6-Bromo-5-methyl-3-trifluoromethylthieno[3,2-*b*]thiophene-2-carboxylic acid (8). Ethyl thioglycolate (1.72 g, 14.3 mmol) was added with stirring under an Ar atmosphere to an ethanolic solution of sodium ethoxide, which was prepared from Na (0.3 g) and anhydrous ethanol (15 mL). After 20 min, compound **6** (4.58 g, 13 mmol) was added. The mixture was heated with boiling for 3 h. Then a solution of sodium ethoxide, which was prepared from Na (0.74 g) and anhydrous ethanol (67 mL), was added, and the mixture was refluxed for 10 h. The ethanol was removed *in vacuo*, the residue was dissolved in water, and the aqueous solution was washed with ether and acidified. The product was filtered off and washed with water. Acid **8** was obtained in a yield of 2.5 g (56%), m.p. 255—256 °C (from $CHCl_3$). Found (%): C, 32.37; H, 1.31. $C_9H_4BrF_3O_2S_2$. Calculated (%): C, 31.32; H, 1.17.

^{13}C NMR (DMSO-d_6), δ: 15.5 (3 C, CH_3); 101.4 (3 C, CF_3); 118.4, 123.8, 124.9, 132.6, 141.7, and 142.7 (6 C, the thienothiophene ring); 160.6 (C, CO_2H). MS (EI), m/z (I_{rel} (%)): 346 [M$^+$] (100).

2-(2-Benzothiazolyl)-6-bromo-5-methylthieno[3,2-*b*]thiophene (9). Thionyl chloride (0.15 mL, 2.16 mmol) was added to a solution of acid **7** (0.5 g, 1.8 mmol) in *N*-methylpyrrolidone (9 mL) under an Ar atmosphere at 5 °C and the mixture was stirred at 20 °C for 20 min. Then *o*-aminothiophenol (0.24 g, 1.9 mmol) was added and the mixture was heated at 137—140 °C for 4.5 h. A 1 *N* solution of NaOH (20 mL) was added to the reaction mixture at 5 °C and the mixture was stirred at 20 °C for 0.5 h. The precipitate that formed was filtered off and washed successively with a 2% solution of NaOH and water. The product was purified by chromatography (benzene as the eluent). Compound **9** was obtained in a yield of 0.48 g (72%), m.p. 184—185 °C (hexane). Found (%): C, 46.12; H, 2.57. $C_{14}H_8BrNS_3$. Calculated (%): C, 45.90; H, 2.20. ^{1}H NMR ($CDCl_3$), δ: 2.55 (s, 3 H, CH_3); 7.38 and 7.50 (both t, 1 H each, H(5) and H(6) of the benzothiazole ring); 7.78 (s, 1 H, H(3)); 7.87 and 8.05 (both d, 1 H each, H(4) and H(7) of the benzothiazole ring).

2-(2-Benzothiazolyl)-6-bromo-5-methyl-3-trifluoromethylthieno[3,2-*b*]thiophene (10). 2-Mercaptomethylbenzothiazole

* For the fluorine- and bromine-containing compounds, analysis for the carbon content generally gives inadequate results.

(1.6 g, 8.8 mmol) was prepared from the corresponding isothiuronium chloride (2.5 g, 9.6 mmol) upon treatment with a 2 *N* Na_2CO_3 solution (20 mL) and MeOH (10 mL) in an ultrasonic bath under an Ar atmosphere for 4 h followed by acidification with CH_3COOH and extraction with ether. A solution of this compound in anhydrous ethanol (20 mL) was added to a solution of sodium ethoxide (Na (0.184 g) in anhydrous ethanol (10 mL)) at 10 °C. The reaction mixture was stirred for 20 min and then ketone **6** (2.83 g, 8.0 mmol) was added. The mixture was refluxed for 4 h. Then a solution of sodium ethoxide (Na (0.45 g) in anhydrous ethanol (25 mL)) was added and the mixture was refluxed for 19 h. The solvent was distilled off, water was added to the residue, and the resinous product that precipitated was dissolved in $CHCl_3$ and dried with $CaCl_2$. Product **10** was isolated by chromatography (hexane as the eluent) in a yield of 0.5 g (15%), m.p. 173—174 °C (from heptane). Found (%): C, 42.48; H, 1.64. $C_{15}H_7BrF_3N_3S_3$. Calculated (%): C, 41.48; H, 1.62. ^{1}H NMR ($CDCl_3$), δ: 2.56 (s, 3 H, CH_3); 7.45 and 7.55 (both t, 1 H each, H(5) and H(6) of the benzothiazole ring); 7.92 and 8.12 (both d, 1 H each, H(4) and H (7) of the benzothiazole ring). MS (EI), *m/z* (I_{rel} (%)): 433 [M^+] (100).

The aqueous solution was extracted with CH_2Cl_2. (3,4-Dibromo-5-methyl-2-thienyl)trifluoromethylcarbinol **11** was isolated from the extract by chromatography (a 5 : 1 hexane—ethyl acetate mixture as the eluent) in a yield of 0.56 g (20%) (from heptane), m.p. 55—56.5 °C. Found (%): C, 23.91; H, 1.48. $C_7H_5Br_2F_3OS_3$. Calculated (%): C, 23.75; H, 1.42. ^{1}H NMR ($CDCl_3$), δ: 2.50 (s, 3 H, CH_3); 2.95 (d, 1 H, OH); 5.44—5.57 (m, 1 H, CH). MS (EI), *m/z* (I_{rel} (%)): 354 [M^+] (10).

Attempt to synthesize 1,2-bis{5-(2-benzothiazolyl)-2-methylthieno[3,2-*b*]thiophen-3-yl}hexafluorocyclopentene (1A). A 1.88 *N* BuLi solution (0.48 mL, 0.9 mmol) in ether was added to a solution of hetarene **9** (300 mg, 0.82 mmol) in THF (5 mL) at −70 °C, the mixture was stirred for 15 min, and a solution of C_5F_8 (0.06 mL, 0.45 mmol) in THF (1 mL) was added. The mixture was stirred at this temperature for 2 h and kept at 20 °C under Ar for ~12 h. Then 5% HCl (2 mL) was added to the mixture with cooling, the solvents were removed *in vacuo*, and the residue was dissolved in CH_2Cl_2, washed with water, dried with $CaCl_2$, and concentrated. Column chromatography (a 7 : 1 hexane—$CHCl_3$ mixture as the eluent) afforded the initial compound **9**, debromination product **14**, and a mixture of photochromic products in yields of 90 mg (30%), 60 mg (26%), and 30 mg, respectively. Attempts to separate the mixture failed (MS (EI), *m/z*: 939 [M^+] for compound **5** and 746 [M^+] for compound **1** or the mixture of isomers). Compound **14**: m.p. 176—178 °C. Found (%): C, 58.56; H, 3.29. $C_{14}H_9NS_3$. Calculated (%): C, 58.50; H, 3.16. ^{1}H NMR ($CDCl_3$), δ: 2.61 (s, 3 H, CH_3); 6.98 (s, 1 H, H (6)); 7.35 and 7.48 (both t, 1 H each, H(5) and H(6) of the benzothiazole ring); 7.75 (s, 1 H, H (3)); 7.85 and 8.02 (both d, 1 H each, H(4) and H(7) of the benzothiazole ring).

1,2-Bis{5-(2-benzothiazolyl)-2-methyl-6-trifluoromethylthieno[3,2-*b*]thiophen-3-yl}hexafluorocyclopentene (2). A mixture was prepared from dihetarene **10** (252 mg, 0.58 mmol), a 1.48 *N* BuLi solution (0.64 mmol) in hexane, and a solution of C_5F_8 (62 mg, 0.29 mmol) in THF (1 mL) analogously to compound **1**. Chromatography (a hexane—$CHCl_3$ mixture (from 100 : 4 to 5 : 3) as the eluent) of the mixture afforded the initial bromide **10**, 2-(2-benzothiazolyl)-5-methyl-3-trifluoromethylthieno[3,2-*b*]thiophene (**16**), and photochrome **2A** in yields of 40 mg (16%), 60 mg (20%), and 50 mg (20%), respectively. Compound **16**: m.p. 147.5—148 °C (from heptane). Found (%): C, 50.99; H, 2.06. $C_{15}H_8F_3NS_3$. Calculated (%): C, 50.69; H, 2.27. ^{1}H NMR ($CDCl_3$), δ: 2.62 (s, 3 H, CH_3); 6.99 (s, 1 H, H (3)); 7.43 and 7.54 (both t, 1 H each, H(5) and H(6) of the benzothiazole ring); 7.91 and 8.11 (both d, 1 H each, H(4) and H(7) of the benzothiazole ring). Compound **2A**: m.p. 288—289 °C. ^{1}H NMR ($CDCl_3$), δ: 2.19 and 2.33 (both s, 3 H each, CH_3, parallel and antiparallel open forms (2 : 1)); 7.46 and 7.54 (both t, 1 H each, H(5) and H(6) of the benzothiazole ring); 7.93 and 8.12 (both d, 1 H each, H(4) and H(7) of the benzothiazole ring).

2-(2-Benzothiazolyl)-6-bromo-5-methylthieno[3,2-*b*]thiophene from bromide **9**. A 1.45 *N* BuLi solution (0.9 mmol) in ether was added to a solution of compound **9** (300 mg, 0.82 mmol) in THF (7 mL) at −70 °C. The mixture was stirred at this temperature for 10 min and a solution of Br_2 (140 mg, 0.9 mmol) in ether (1 mL) was added. The mixture was stirred at this temperature for 1 h and then at 20 °C for 40 min. Then 5% HCl (5 mL) was added with cooling. After removal of the solvents *in vacuo*, the residue was extracted with $CHCl_3$, the organic layer was washed successively with water and a 5% $NaHCO_3$ solution and dried, and the solvent was removed *in vacuo*. According to the ^{1}H NMR spectral data, the residue (297 mg) contained the initial compound **9** (85%), 2-(2-benzothioazolyl)-5-methylthieno[3,2-*b*]thiophene **14** (11%; 6.98 s, 1 H, H(6); 7.73 s, 1 H, H(3)), and 2-(2-benzothiazolyl)-3-bromo-5-methylthieno[3,2-*b*]thiophene (4 %; 7.03 s, 1 H, H(6)). The compounds were identified based on the signals for the thienothiophene protons.

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Received July 24, 2000;
in revised form September 12, 2000