## Photochromic dihetarylethenes 5.\* Synthesis, structure, and photochromic properties of 4,4'-disubstituted 1,2-bis{2-ethyl-5-ethylthio(ethylsulfonyl)-3-thienyl]perfluorocyclopentenes

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A series of new photochromic compounds were obtained for the first time from 1,2-bis(2ethylthio-3-thienyl)perfluorocyclopentene by substituting bromine atoms or carboxy, alkoxycarbonyl, and carbamoyl groups for hydrogen atoms in positions 4 and 4'. Introduction of these substituents causes a slight bathochromic shift (by 20-30 nm) of a long-wavelength absorption band for the cyclic form and significantly increases the quantum yields of photocyclization  $\Phi_{A\to B}$  and ring opening  $\Phi_{B\to A}$ . Depending on the nature of a substituent,  $\Phi_{A\to B}$  decreases in the order COOH > COOMe > CONHAr. The quantum yields are markedly reduced when the ethylthio groups in positions 5 and 5' are replaced by ethylsulfonyl groups (a tenfold reduction in  $\Phi_{A\to B}$  and a four- to fivefold reduction in  $\Phi_{B\to A}$ ). The most considerable bathochromic shift of a long-wavelength band and the highest quantum yields of forward and reverse photoreactions were observed for 1,2-bis(4-bromo-2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentene. 1,2-Bis(2-ethyl-5-ethylthio-4-methoxycarbonyl-3-thienyl)perfluorocyclopentene was structurally characterized by X-ray diffraction analysis.

Key words: bisthienylperfluorocyclopentenes, molecular structure, photochromic compounds, reversible photocyclization, quantum yield.

Previously, we described the synthesis of 1,2-bisthienylperfluorocyclopentenes containing alkylthio- or alkylsulfonyl groups in the positions 2.2° and 5,5° of the thiophene rings, 1-3 reported the relevant crystallographic data, and studied the possibility of their reversible photocyclization **A**  $\longrightarrow$  **B**.

It was shown that bisthienylperfluorocyclopentenes with sulfur-containing groups in positions 2 and 2' are not photochromes, whereas 2,2'-dialkyl derivatives exhibit such properties. Introduction of an ethylthio or ethylsulfonyl group into positions 5 and 5' significantly shifts the long-wavelength band maximum of the cyclic photochromes ( $\lambda_{max}^{B}$ ). Thus for 1.2-bis(2-methyl-3thienyl)perfluorocyclopentene,  $\lambda_{max}^{B}$  is 505 nm,<sup>4</sup> while for 1.2-bis(2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentene 1 and 1.2-bis(2-ethyl-5-ethylsulfonyl-3thienyl)perfluorocyclopentene 2, these values are 564 and 572 nm, respectively.<sup>3</sup>

In the present work, the synthesis and photochromic properties of 4,4'-disubstituted bis(2-ethyl-5-ethylthioand 2-ethyl-5-ethylsulfonylthienyl)perfluorocyclopen-

\* For part 4, see Ref. 1.

tenes are described. The literature data on the effect of functional groups in these positions on the photochromicity are lacking. In addition, such derivatives are convenient starting reagents for the synthesis of other promising photochromic products. Of particular importance is the relationship between the type of substituents and the position of the long-wavelength absorption band of form **B**, because the photochromes with such a band lying above 780 nm can be irradiated with standard semiconducting lasers.<sup>5,6</sup>

## **Results and Discussion**

Compounds 4-8 were synthesized according to Scheme 2. The key intermediate was the known 1,2-bis(2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentene 1, <sup>3</sup> in which the thiophene ring is substantially activated by the alkylthio group as regards electrophilic substitution, thus facilitating its subsequent functionalization.

In the present work, a method for the synthesis of 3-bromo-2-ethyl-5-ethylthiothiophene (3), a precursor for compound 1, from 2-ethylthiophene was proposed.

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 $\label{eq:rescaled} \begin{array}{cccc} R^1 = \text{SEt, } \text{SO}_2\text{Et, } R^2 = \text{H}, \text{ Et, CHO, COOH, } R^3 = \text{H} \\ & & & \\ R^1 & R^2 & R^3 \\ \textbf{1} & & \\ \text{Et} & & & \\ \textbf{2} & & \\ \text{Et} & & & \\ \text{SO}_2\text{Et} & \text{H} \end{array}$ 

Unlike the previous method,<sup>3</sup> bromide 3 free from an impurity of isomeric 4-bromo-2-ethyl-5-ethylthio-

thiophene is formed in good yield (-75%) from 3,5-dibromo-2-ethylthiophene. Starting from compound **1**, we synthesized 4,4'-dibromo- and -dicarboxy derivatives, which were used in subsequent transformations.

Bromination of bissulfide 1 afforded dibromide 4 in quantitative yield. The latter was oxidized with  $H_2O_2$  to give the corresponding sulfone 5. Treatment of dibromide 4 with BuLi in ether followed by carbonization results in dicarboxylic acid 6 in 60–70% yield. Then, diester 7 and some arylamides **8a**–d were obtained from acid 6 according to the known methods.

Attempts to formylate compound 1 in positions 4 and 4' using the Vilsmeier or Rieche reactions<sup>7</sup> employed in the synthesis of sterically hindered aromatic aldehydes and by the reaction of dibromide 4 with BuLi and HCONMe<sub>2</sub> or HCOOEt failed. In all cases, the starting compounds were recovered, with traces of the reaction products. Such a result is probably due to steric hindrances which prevent the reactions of bulky intermediates with 1,2-dithienylperfluorocyclopentene 1.

Compounds 4-8 were characterized by data from NMR spectroscopy and mass spectrometry; the structures of amides 8 were additionally confirmed by IR spectra. It is of note that the <sup>1</sup>H NMR spectra of





Fig. 1. Molecular structure of ester 7.

arylamides 8b-d show doubled signals for the amide protons and for an aromatic proton (in the case of amide 8b, the signals for the methylene protons of the OCH<sub>2</sub>CF<sub>3</sub> group are also doubled). Apparently, this indicates the presence of two conformers in solution.

The molecular structure of ester 7 was determined using X-ray diffraction analysis (Fig. 1). The perfluorocyclopentene fragment (F) exists in the flattened envelope conformation with the C(5) atom deviating from the plane of the other four ring atoms by 0.12 Å. The greatest torsion angle is C(4)-C(5)-C(1)-C(2) $(10.06^{\circ})$ . Orientation of the substituents with reference to the thiophene rings ( $T^{I}$  and  $T^{2}$ ) is determined by dihedral and torsion angles (Table 1).

Note that small dihedral angles between the substituents and the thiophene rings allow the substituted thiophene fragments to be regarded as nearly planar. The C(17) and C(25) atoms of the ethylthio groups and the C(21) atom of the ethyl group deviate from the least-squares planes calculated for these fragments by -1.474, 1.182, and -1.204 Å, respectively.

The main parameters of molecular geometry are presented in Tables 2 and 3. The bond lengths and angles are standard within the experimental error, except for the unusually short C(16)--C(17), C(24)--C(25), and C(18)--C(19) bonds. This is explained by the fact that the C(17), C(19), and C(25) atoms cannot be located precisely because of considerable thermal vibrations of the terminal methyl groups, their equivalent thermal factors ( $U_{equiv}$ ) being three to four times higher than those for the other atoms.

The thiophene rings  $(T^{I}, T^{2})$  are planar with an accuracy of 0.01 Å. The dihedral angles  $F/T^{I}$  and  $F/T^{2}$  are 84.7(0.4)° and 86.7(0.4)°, respectively; these values are much larger than the corresponding angles (~55°) in the previously studied analogs containing 2,2'- and 5,5'-disubstituted thienyl rings.<sup>1,2</sup>

The dihedral angle between the *T* rings is equal to 79.0(0.2)°, which also exceeds the average value of the analogous angle in the aforesaid photochromes (56.0°). The alkoxycarbonyl and ethyl groups of both thiophene rings are in unusual *anti*-configuration to each other; as a result, the distance between the potential reaction centers, C(6)...C(10) (4.45 Å), becomes significantly longer than the van der Waals C...C contact (3.42 Å). This altogether suggests that the molecular conformation of 7 in the crystalline state is unfavorable for the open form **A** to undergo cyclization into form **B**. Indeed, no coloration was observed upon irradiation of a colorless crystal of ester 7 with UV light ( $\lambda = 313$  nm), *i.e.*, cyclization did not occur.

Nevertheless, when a solution of compound 7 (form A) in ethanol is irradiated with the same light ( $\lambda = 313$  nm), cyclization does take place to give form B.

The photochemical parameters of compounds 1 and 2 (see Ref. 3) and new derivatives 4--8 (Table 4) were studied in an ethanolic solution in the range 220-800 nm; all of them are photochromes. A typical

Table 1. Conformational parameters ( $\varphi$ ) in molecule 7

Angle	φ/deg
$T^{1}/C(8)-O(1)-C(14)-O(2)$	10.2
$T^{\prime}/C(9)-S(2)-C(16)$	14.9
$T^{i}/C(6) - C(18) - C(19)$	22.7
$T^{I}/C(14) = O(2) = C(15)$	13.5
C(8) - C(14) - O(2) - C(15)	3.5
C(1) - S(2) - C(16) - C(17)	82.4
$T^{2}/C(12) - C(22) - O(3) - O(4)$	5.1
$T^2/C(13) - S(4) - C(24)$	6.1
$T^2/C(10) - C(20) - C(21)$	60.6
$T^{2}/C(22) - O(4) - C(23)$	7.5
C(12) - C(22) - O(4) - C(23)	3.2
C(13) - S(4) - C(24) - C(25)	73.8

Bond	$d/\lambda$	Bond	d/Å
S(1)C(6)	1.708(8)	C(2) - C(3)	1.40(2)
S(1) - C(9)	1.718(9)	C(3) - C(4)	1.53(2)
S(2)C(9)	1.725(10)	C(4) - C(5)	1.476(12)
S(2)-C(16)	1.75(2)	C(5) - C(11)	1.506(12)
S(3)-C(13)	1.677(11)	C(6) - C(7)	1.375(10)
S(3)C(10)	1.731(10)	C(6) - C(18)	1.491(13)
S(4)-C(13)	1.766(11)	C(7) - C(8)	1.432(H)
S(4)C(24)	1.77(2)	C(8) - C(9)	1.419(11)
O(1)C(14)	1.170(11)	C(8) - C(14)	1.495(12)
O(2) - C(14)	1.313(12)	C(10)~C(11)	1.346(12)
O(2) - C(15)	1.475(14)	C(10)C(20)	1.47(2)
O(3)-C(22)	1.163(11)	C(11) - C(12)	1.411(10)
O(4)+C(22)	1.319(12)	C(12) - C(13)	1.382(13)
O(4)C(23)	1.438(12)	C(12) - C(22)	1.485(13)
C(1) - C(5)	1.322(10)	C(16) - C(17)	1.31(3)
C(J) = C(7)	1.491(11)	C(18) - C(19)	1.13(3)
C(1) = C(2)	1.500(13)	C(20) - C(21)	1.47(2)
C(24)C(25)	1.26(3)		

Table 2. Bond lengths (d) in compound 7

absorption spectrum (namely, that of ester 7) is shown in Fig. 2. The observed long-wavelength bands are associated with  $\pi,\pi^*$ -transitions, because they experience a bathochromic shift when a nonpolar solvent (*n*-hexane) is replaced by a polar one (ethanol).

For all compounds, there are isosbestic points which coincide for the forward  $(A \rightarrow B)$  and reverse reactions  $(B \rightarrow A)$ . The long-wavelength absorption bands of open forms  $(\lambda_{max}^{A})$  appear at 245–308 nm, while those of cyclic forms  $(\lambda_{max}^{B})$ , at 562–610 nm. Extinction coefficients of forms A and B,  $\lambda_{max}^{A}$  and  $\lambda_{max}^{B}$ , and the quantum yields (the calculational procedure was described earlier<sup>3</sup>) of photocyclization and ring-opening are given in Table 4.

While analyzing the effect of substituents in positions 4 and 4' on the absorption spectra of forms **B**, it should be noted that a long-wavelength band in the spectrum of compounds 4, 6, and 8a-d is slightly bathochromically

Table 3. Main bond angles  $(\omega)$  in compound 7

shifted (568-578 nm) as compared to the 4.4 '-unsubstituted analog 1 ( $\lambda_{max}^{B} = 564$  nm). One can see that  $\lambda_{max}^{B}$  lies within a narrow range, which becomes even narrower for arylamides 8a-d (571-578 nm). The bathochromic shift of the long-wavelength band of form B is considerable only for bromides 4 and 5 ( $\lambda_{max}^{B} = 592$  and 610 nm, respectively). When the ethylthic groups in positions 5 and 5' are replaced by ethylsulfonyl groups, the long-wavelength band of form B is also shifted bathochromically (cf., compounds 1 and 2 or 4 and 5).

1,2-Bis(2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentenes 1, 4, and 6--8 are characterized by very different quantum yields of photocyclization,  $\Phi_{A\rightarrow B}$ . The highest  $\Phi_{A \rightarrow B}$  value is observed for 4.4 -dibromosulfide 4 (1.0):  $\Phi_{A\to R}$  of the other sulfides decreases in the order carboxylic acid > ester > arvlamide, which corresponds to a decrease in the electron-donating properties of the substituents in positions 4 and 4'. Almost all 1,2-bis(2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentenes are superior to 4,4'-unsubstituted analog I in  $\Phi_{A \rightarrow B}$ . Note that the passage from sulfide 4 to sulfone 5 reduces  $\Phi_{A \rightarrow B}$  by a factor of 10 (!) and causes the aforesaid bathochromic shift of the long-wavelength band of form B. The quantum yields of the reverse photoreaction,  $\Phi_{B\to A}$ , for compounds 4-8 are one order of magnitude lower than the corresponding  $\Phi_{A \rightarrow B}$  values.

Thus, while comparing the photochromic properties of compounds 4 and 6--8 with those of 4,4'-unsubstituted analog 1, one can note that substitution of bromine atoms possessing +M and -I effects in positions 4 and 4' sharply increases the quantum yields of photocyclization ( $\Phi_{A\rightarrow B}$ ) and the reverse reaction ( $\Phi_{B\rightarrow A}$ ) and results in the most considerable bathochromic shift of  $\lambda_{max}^{\ B}$  among all the compounds under discussion.

## Experimental

NMR spectra were recorded on a Bruker WM-250 instrument. Mass spectra were recorded on a Kratos MS-30 instrument (ionizing voltage 70 eV, direct inlet of the substance into the ion

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Angle	∞/deg	Angle	ംഗ/deg	Angle	₀/deg
C(6) - S(1) - C(9)	93.9(4)	C(7) - C(6) - S(1)	111.5(6)	C(13)-C(12)-C(22)	118.6(8)
C(9) - S(2) - C(16)	103.9(7)	C(18) - C(6) - S(1)	120.3(6)	C(11) - C(12) - C(22)	128.6(8)
C(13) - S(3) - C(10)	92.4(5)	C(6) - C(7) - C(8)	112.7(7)	C(12) - C(13) - S(3)	111.4(7)
C(13)-S(4)C(24)	102.3(9)	C(6) - C(7) - C(1)	123.4(7)	C(12) - C(13) - S(4)	126.4(7)
C(14) - O(2) - C(15)	113.8(9)	C(8) - C(7) - C(1)	123.8(6)	S(3) - C(13) - S(4)	122.3(6)
C(22)-O(4)-C(23)	117.0(8)	C(9) - C(8) - C(7)	112.3(7)	O(1) - C(14) - O(2)	124.8(9)
C(5) - C(1) - C(7)	128.7(7)	C(9) - C(8) - C(14)	124.5(7)	O(1) - C(14) - C(8)	123.0(9)
C(5) - C(1) - C(2)	110.6(7)	C(7) - C(8) - C(14)	123.2(7)	O(2) - C(14) - C(8)	112.0(9)
C(7) - C(1) - C(2)	120.5(7)	C(8) - C(9) - S(1)	109.5(6)	C(17) - C(16) - S(2)	115.0(2)
C(3) - C(2) - C(1)	104.5(9)	C(8) - C(9) - S(2)	128.1(6)	C(19) - C(18) - C(6)	131.0(2)
C(2) - C(3) - C(4)	110.8(8)	S(1) = C(9) = S(2)	122.1(5)	$C(2) \rightarrow C(20) \rightarrow C(10)$	113.2(10)
C(5) - C(4) - C(3)	101.2(7)	C(11)-C(10)-C(20)	130.6(9)	O(3)-C(22)-O(4)	123.9(10)
C(1) - C(5) - C(4)	112.0(7)	C(11) - C(10) - S(3)	111.0(7)	O(3) - C(22) - C(12)	124.3(10)
C(1) - C(5) - C(11)	128.1(7)	C(20) - C(10) - S(3)	118.2(8)	O(4) - C(22) - C(12)	111.7(8)
C(4) - C(5) - C(11)	119.6(7)	C(10) - C(11) - C(12)	112.8(8)	C(25) - C(24) - S(4)	109.0(2)
C(7) - C(6) - C(18)	127.9(8)	C(13) - C(12) - C(11)	112.5(7)		

Com-	λ <sub>max</sub> /nm (ε/	$(M^{-1} \text{ cm}^{-1})$	Φ	
pound	A	B	A-→B	B-→A
1	243 (24500)	564 (16800)	0.14	0.01
2	242 (20100)	572 (1520)		
4	206 (33100)	592 (5350)	1.0	0.04
5	250 (25100)	610 (1000)	0.1	0.009
6	307 (14500)	568 (7930)	0.80	0.02
7	308 (33200)	562 (21900)	0.35	0.012
8a	295 (15000)	578 (7940)	0.26	0.03
8b	249 (60600)	571 (10400)	0.12	0.019
8c	245 (68500)	573 (9050)	0.21	0.013
8d	290 (31000)	578 (9700)	0.22	0.02

 
 Table 4. Photochemical parameters of 1,2-bis(3-thienyl)perfluorocyclopentenes

source). Column chromatography was carried out on silica gel L (100--160 mesh). TLC was performed on Silufol UV-254 plates.

Compounds were irradiated with a DRSh-500 mercury lamp through light filters of 313 and 578 nm. The radiation intensity of the mercury lamp was measured with an F4 photocell calibrated with a ferrioxalate actinometer<sup>8</sup> for  $\lambda = 313$  nm and a Reinecke salt actinometer<sup>9</sup> for  $\lambda = 578$  nm. Absorption spectra were recorded on a Shimadzu UV-2101PC spectrophotometer. The quantum yield was determined by irradiating an ethanolic solution of a compound with light with  $\lambda = 313$  and 578 nm for the forward and reverse reactions, respectively. The exposure time was extended stepwise from 5 s to 1-2 min (in total, seven to ten experimental points), with recording of absorption spectra of the irradiated solution for each exposure time.

**3.5-Dibromo-2-ethylthiophene.** A solution of Br<sub>2</sub> (111.3 g, 0.697 mol) in 90 mL of glacial AcOH was added at 2-4 °C



Fig. 2. Spectra of an ethanolic solution of 1,2-bis(2-ethyl-5ethylthio-4-methoxycarbonyl-3-thienyl)perfluorocyclopentene 7 irradiated with light with  $\lambda = 313$  nm (forward reaction) and 578 nm (reverse reaction): 1, absorption spectrum of form A; 2, absorption spectrum in the photosteady state (irradiation time 350 s). Intermediate spectra were recorded for an exposure time of 5, 15, 40, 100, and 225 s.

over 4 h to a solution of 2-ethylthiophene (37.21 g, 0.332 mol) in 170 mL of glacial AcOH. The reaction mixture was kept at 20 °C for 1 h and poured into 800 mL of cold water. The product was extracted with Et<sub>2</sub>O, and the extract was washed successively with water, a solution of Na<sub>2</sub>CO<sub>3</sub>, and water (to neutral reaction) and dried with CaCl<sub>2</sub>. The solvent was removed, and the residue was twice distilled *in vacuo* to give the title dibromide (35 g, 40%), b.p. 109–-112 °C (13 Torr),  $n_D^{20}$  1.6026. <sup>1</sup>H NMR,  $\delta$ : 1.27 (t, 3 H, Me, hereinafter J = -7 Hz); 2.75 (q, 2 H, CH<sub>2</sub>); 6.86 (s, 1 H, H(4)) (cf. Ref. 10: <sup>1</sup>H NMR,  $\delta$ : 6.80 (s, 1 H, H(4)), b.p. 90–95 °C (3 Torr)).

**3-Bromo-Z-ethyl-5-ethylthiothiophene (3).** A solution of Bu<sup>o</sup>Li (9.95 g, 0.155 mol) in 100 mL of Et<sub>2</sub>O was cooled to -70 °C and added in an atmosphere of Ar at the same temperature over 10 min to a solution of 3,5-dibromo-2-ethylthiophene (38.1 g, 0.141 mol) in 100 mL of dry Et<sub>2</sub>O. Then, a cold (-70 °C) solution of diethyl disulfide (Et<sub>2</sub>S<sub>2</sub>) (21.6 g, 0.176 mol) in 60 mL of Et<sub>2</sub>O was added in two steps, and the reaction mixture was kept at -70 °C for 2 h and left at 20 °C for 12 h. After hydrolysis with 5% NaOH, the organic layer was separated, washed with water, and dried with CaCl<sub>2</sub>. The solvent was removed, and the residue was distilled in *vacuo* to give bromide 3 (26.6 g, 75%), b.p. 114–116 °C (5 Torr),  $n_D^{20}$  LSS52. The product is identical with the known compound<sup>3</sup> (TLC and <sup>1</sup>H NMR,  $\delta$ : 6.92 (s, 1 H, H(4), characteristic signal)).

1.2-Bis(4-bromo-2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentene (4). A solution of Br<sub>2</sub> (0.495 g, 0.158 mL, 3.1 mmol) in 5 mL of CHCl<sub>3</sub> was gradually added at 20 °C over 1 h to a solution of compound  $1^{3}$  (0.8 g, 1.548 mmol) in 12 mL of dry CHCl<sub>3</sub>. The reaction mixture was heated at 50-60 °C for 1 h. cooled, washed successively with H2O, 5% NaOH, and H2O, and dried with CaCl<sub>b</sub>. Removal of the solvent gave dibromide 4 in quantitative yield (1.02 g) as a heavy, light green oil, which was purified by column chromatography in benzene. Found (%): C, 37.62; H, 2.83,  $C_{21}H_{20}Br_2F_6S_4$ . Calculated (%); C, 37.40; H, 2.98. <sup>1</sup>H NMR, δ: 1.20 (m, Me); 2.83 (m, CH<sub>2</sub>) (signal intensity ratio 3 : 2), MS, m/z (Iret (%)): 676/674/672 [M]\* (7.5).  $595/594 [M - Br]^+ (17.7), 514 [M - 2Br]^+ (91).$  The <sup>1</sup>H NMR spectrum of the oil irradiated with UV light ( $\lambda = 254$  nm) shows not only the signals corresponding to the open form but also those from the ring protons (8: 1.10 (t, 3 H, CH<sub>3</sub>CH<sub>2</sub>C); 1.41 (t, 3 H. CH<sub>3</sub>CH<sub>2</sub>S); 2.40 (q, 2 H, CCH<sub>2</sub>CH<sub>3</sub>); 3.02 (q, 2 H, CH<sub>2</sub>S)).

**1.2-Bis(4-bromo-2-ethyl-5-ethylsulfonyl-3-thienyl)perfluorocyclopentene (5).** A solution of dibromide **4** (80 mg, 0.118 mmol) in 3 mL of glacial AcOH and 40%  $H_2O_2$  (0.2 mL, 1.80 mmol) was heated at 95 °C for 2 h and left at 20 °C for 12 h. AcOH was removed *in vacuo*, and the residue was dried *in vacuo* to give bissulfone **5** (80 mg, 95%). m.p. 65 °C (from aqueous EtOH). Found (%): C, 34.65; H, 2.85. C<sub>21</sub>H<sub>20</sub>Br<sub>2</sub>F<sub>6</sub>O<sub>4</sub>S<sub>4</sub>. Calculated (%): C, 34.1; H, 2.71. <sup>1</sup>H NMR, δ: 1.30 (t. CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>S); 2.95 (q. CH<sub>2</sub>SO<sub>2</sub>) (signal intensity ratio 3 : 1 : 1). MS, *m/z* ( $I_{rel}$  (%)): 647/645/643 [M - SO<sub>2</sub>Et]<sup>+</sup> (100), 553/551/549 [M - 2SO<sub>2</sub>Et - H]<sup>+</sup> (90), 474/472 (30), 392 (17).

**1,2-Bis(4-carboxy-2-ethyl-5-ethylthio-3-thienyl)perfluorocyclopentene (6).** A solution of Bu<sup>n</sup>Li (0.313 g, 4.89 mmol) in 3.29 mL of *n*-hexane was gradually added at -5 to -10 °C to a solution of dibromide 4 (1.5 g, 2.22 mmol) in 15 mL of dry Et<sub>2</sub>O. The reaction mixture was kept at 0 °C for 30 min, poured into solid CO<sub>2</sub> in ether, and left at 20 °C for 12 h. Water was added to the resulting dark solution, the organic layer was separated, and the aqueous layer was washed with Et<sub>2</sub>O and acidified with dilute HCl (1 : 1). The precipitate that formed was filtered off, washed with water, and dried in a desiccator over CaCl<sub>3</sub> to give dicarboxylic acid 6 (0.91 g, 68%), m.p. 255-257 °C (from 70% EtOH). Found (%): C, 45.95; H, 3.87.

Com- pound	M.p./°C (solvent)	<u>Found</u> Calcul	ated (%)	Molecular formula	Yield (%)	IR, v/cm <sup>-1</sup> (CHCl <sub>3</sub> )	<sup>1</sup> Η NMR, δ
		С	н				
8a	232–235 (EtOH, CHCl <sub>3</sub> )	<u>53.48</u> 53.42	<u>4.03</u> 4.10	C <sub>35</sub> H <sub>32</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S <sub>4</sub>	* 45	1640 (CO), 3280(NH)	1.30 (m, 6 H, C $\underline{H}_3$ CH <sub>2</sub> , C $\underline{H}_3$ CH <sub>2</sub> S); 2.75, 2.90 (2 q, 4 H, C $\underline{H}_2$ Me, SC $\underline{H}_2$ Me); 6.85–7.20 (m, 4 H, Ph); 8.3 (s, 1 H, OH); 9.20 (s, 1 H, NH)
8b	178–180 (CHCl <sub>3</sub> )	<u>45.22</u> 45.00	<u>3.32</u> 3.10	$C_{39}H_{32}F_{12}N_4O_8S_6$	, 60	1660, 1670, 3345(NH)**	1.26 (m, 6 H, $CH_3CH_5$ , $CH_3CH_5S$ ); 2.55–2.90 (m, 4 H, $CH_5Me$ , $SCH_2Me$ ); 4.25, 4.28 (2 q, 2 H, $OCH_2CF_3$ ); 7.35, 7.45, 7.55, 7.85, 7.90 (all s, 3 H, Pb); 8.80, 8.90 (2 s, 1 H, NH)
8c	203 - 205 (C <sub>6</sub> H <sub>6</sub> - hexane)	<u>53.20</u> 53.19	<u>3.55</u> 3.62	C <sub>47</sub> H <sub>38</sub> F <sub>6</sub> N <sub>4</sub> O <sub>6</sub> S <sub>5</sub>	40	1680 (CO), 3280 (NH)	1.25 (m, 6 H, $CH_3CH_2$ , $CH_3CH_2S$ ); 2.70, 2.90 (2 q, 4 H, $CH_2Me$ , $SCH_2Me$ ); 7.55–7.60 (m, 5 H, Ph); 7.75–7.80 (2 s, 1 H, Ph); 8.15 (br.s, 1 H, Ph); 8.82, 8.92 (2 s, 1 H, NH)
8d	149–151 (EtOH)	<u>60.51</u> 60.40	<u>4.26</u> 4.25	$C_{43}H_{36}F_{6}N_{2}O_{2}S_{4}$	50	1680 (CO), 3345(NH)**	1.22 (m, 6 H, C $\underline{H}_3$ CH $_2$ S, C $\underline{H}_3$ CH $_2$ ); 2.55–2.90 (m, 4 H, C $\underline{H}_2$ Me, SC $\underline{H}_2$ Me); 7.38–7.90 (m, 5 H, β-C $_{10}$ H $_7$ ); 8.15, 8.70 (2 s, 2 H, β-C $_{10}$ H $_7$ ); 8.28, 9.12 (2 s, 1 H, NH)

Table 5. Physicochemical characteristics of amides 8a-d

\* MS,  $m/z (I_{ret} (\%))$ ; 787 [M]<sup>+</sup> (<5), 569 [M - 2NH(OH)C<sub>6</sub>H<sub>4</sub>]<sup>+</sup> (8), 513 (10).

\*\* Pellets with KBr.

 $\begin{array}{l} C_{23}H_{22}F_6O_4S_4, \mbox{ Calculated (\%): } C, 45.69; \mbox{ H}, 3.67, {}^{1}\mbox{ H} \mbox{ NMR, } \delta; \\ 1.25 \ (t, \ 3 \ H, \ C\underline{H}_3CH_2); \ 1.38 \ (t, \ 3 \ H, \ C\underline{H}_3CH_2S); \ 2.65 \ (m, \ 2 \ H, \\ C\underline{H}_2CH_3); \ 2.98 \ (m, \ 2 \ H, \ C\underline{H}_3C\underline{H}_2S), \ MS, \ m/z \ (I_{rel} \ (\%)); \\ 604 \ \{M\}^{+} \ (70), \ 564 \ (85), \ 530 \ (50). \end{array}$ 

The other was removed from the organic layer to give an oil (0.38 g) containing bissulfide 1 as a major component (TLC).

1,2-Bis(2-ethyl-5-ethylthio-4-methoxycarbonyl-3-thienyl)perfluorocyclopentene (7). An excess of an ethereal solution of diazomethane was added to a suspension of dicarboxylic acid 6 (60 mg, 0.1 mmol) in 2 mL of ether. The reaction mixture was left at 20 °C for 12 h. The solvent was removed, and ester 7 (55 mg, 90%) was obtained as heavy green oil, which crystallized with time, M.p. 108–110 °C (from *n*-hexane). Found (%): C, 47.69; H, 4.32,  $C_{25}H_{26}F_6O_4S_4$ , Calculated (%): C, 47.45; H, 4.14, <sup>1</sup>H NMR, &: 1.10 (t, 3 H, CH<sub>3</sub>CH<sub>2</sub>); 1.38 (t, 3 H, CH<sub>3</sub>CH<sub>2</sub>S); 2.60 (m, 2 H, CH<sub>2</sub>Me); 2.98 (m, 2 H, CH<sub>3</sub>CH<sub>2</sub>S).

Synthesis of N,N'-bisaryl-1,2-bis(2-ethyl-5-ethylthio-3thienyl)perfluorocyclopentene-4,4'-dicarboxamides (8a-d). A suspension of dicarboxylic acid 6 (0.1 g, 0.166 mmol) in 2 mL of dry benzene was refluxed with an excess of SOCl<sub>2</sub> (1 mL) for 1 h. The resulting brown solution was concentrated *in vacuo*, and the residue was dissolved in benzene. The corresponding arylamine (0.408 mmol) was added, and the reaction mixture was refluxed for 1 h, left at 20 °C for 12 h, and then filtered. The filtrate was washed with water and dried with MgSO<sub>4</sub>. The solvent was removed, and the residue was recrystallized from appropriate solvents (Table 5).

X-ray diffraction analysis of 1,2-bis(2-ethyl-5-ethylthio-4methoxycarbonyl-3-thienyl)perfluorocyclopentene (7). The transparent colorless crystals ( $C_{25}H_{26}S_4O_4F_6$ ) grown from a solution in heptane are monoclinic. The unit cell parameters are a = 12.405(6) Å, b = 24.45(2) Å, c = 9.876(4) Å,  $\beta = 103.51(4)^\circ$ , V = 2912(3) Å<sup>3</sup>,  $d_{calc} = 1.443$  g cm<sup>-3</sup>, space group *Cc*, Z = 4. Intensity data were collected at 20 °C on a Syntex *P2*<sub>1</sub> automated four-circle diffractometer (graphite monochromator, MoK $\alpha$  radiation,  $\theta/2\theta$  scan mode). The number of independent reflections is 3975. The structure was solved by the direct method and refined on *F*<sup>2</sup> for all independent reflections by full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were located from an electron-density difference map and refined isotropically by the least-squares method. The discrepancy factor  $R_1 = 0.065$  (from 1374 reflections with  $F^2 > 2\sigma$  ( $F^2$ )). For all observed reflections,  $wR_2 = 0.153$ . All calculations were performed with SHELXTL PLUS 5 and AREN-90 program packages. Atomic coordinates, thermal factors, and geometric parameters of molecule 7 have been deposited with the Cambridge Structural Database.

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## References

- L. G. Vorontsova, M. M. Krayushkin, Z. A. Starikova, M. A. Kalik, F. M. Stoyanovich, O. Yu. Zolotarskaya, and D. L. Dzhavadov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 74 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 77 (Engl. Transl.)].
- M. M. Krayushkin, M. A. Kalik, D. L. Dzhavadov, and L. G. Vorontsova, *Khim. Geterotsikl. Soedin.*, 1998, 927 [*Chem. Heterocycl. Compd.*, 1998 (Engl. Transl.)].
- M. M. Krayushkin, M. A. Kalik, D. L. Dzhavadov, A. Yu. Martynkin, A. V. Firsov, and B. M. Uzhinov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 979 [*Russ. Chem. Bull.*, 1999, 48, 971 (Engl. Transl.)].
- T. Saika, M. Irie, and T. Shimidzu, J. Chem. Soc., Chem. Commun., 1994, 2123.
- 5. M. Irie and K. Uchida, Bull. Chem. Soc. Jpn., 1998, 71, 985.
- 6. S. L. Gilat, S. H. Kawai, and J.-M. Lehn, Chem. Eur. J., 1995, 1, 275.
- M. Emmelis, G. Pawłowski, and H. W. Vollmann, *Angew. Chem.*, 1989, 28, 1445.
- B. Hatchard and C. A. Parker, Proc. R. Soc., 1956, A235, 518.
- E. W. Wagner and A. W. Adamson, J. Am. Chem. Soc., 1966, 88, 394.
- S. Kano, J. Yuasa, and T. Yokomatsu, *Heterocycles*, 1983.
   20, 2035.

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