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SYNTHESIS, STRUCTURE, AND SOME REACTIONS OF 1,2-BIS(2-ALKYLTHIO-3-THIENYL)PERFLUOROCYCLOPENTENE

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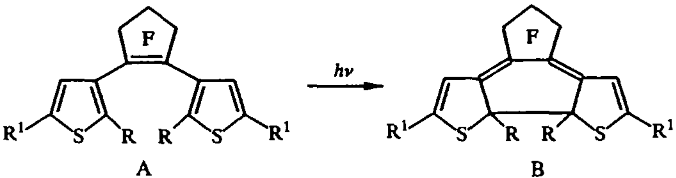
The synthesis of 1,2-bis(2-ethylthio-3-thienyl)perfluorocyclopentene is described. Metallation with n-BuLi and subsequent treatment with DMF or CO_2 gave the corresponding 5,5'-diformyl and dicarboxy derivatives. The structure of 1,2-bis(2-ethylthio-3-thienyl)perfluorocyclopentene was studied by x-ray structural analysis. It was established that the unit cell contains two crystallographically independent molecules with geometrical and conformational parameters close to one another. The thiophene rings were inclined at an angle of 60° to the plane of the perfluorocyclopentene fragment, the thioalkyl groups were disposed antiparallel to it.

Compounds containing diaryl- or diheteryl(dithienyl)alkene fragments, potentially capable of valence tautomerism, are widely used to obtain organic materials applicable in information technics and optoelectronics [1]. A characteristic of such materials is the possibility of a wide variation in physicochemical and photochromic properties with even small changes in molecular structure. For example, replacement of methyl groups by n-hexyl in positions 2 of the thiophene rings in compounds of type A not only increases the solubility in certain organic solvents 30 fold but also shifts the absorption maximum in the electronic spectrum by 20-30 nm [2]. A change in the nature of the substituent at position 5 of the thiophene ring proved to have a significant effect on the photochromic properties and thermal stability of one of the tautomeric forms [3, 4]. The effect of the nature of the substituent at positions 2 of the thiophene rings in similar systems has not been studied.



R = Me, R¹ = CHO, Ar, Het

In the present work derivatives have been obtained for the first time of 1,2-bis(thienyl)perfluorocyclopentene (I) containing an alkylthio group in position 2 of the thiophene ring. This activates the thiophene ring in electrophilic substitution and metallation reactions, facilitating the subsequent introduction of various functional substituents into the free positions of the heterocycle.

Compound (I) was synthesized from 2-ethylthiophene according to the scheme shown below. Bromination of the latter and subsequent debromination of the obtained dibromosulfide (II) with n-BuLi at −70°C leads to 3-bromo-2-ethylthiothiophene (III) in good yield. The bisulfide (I) was synthesized in 60% yield by the successive action on bromide (III) of BuLi in ether and then octafluorocyclopentene. Compound (I) was converted practically quantitatively by an excess of 30% H_2O_2 into the bisulfone (IV). The bisulfide (I) is metallated in both of the thiophene rings in a few minutes with BuLi in ether and after treatment with DMF or CO_2 is converted in good yield into the dialdehyde (V) or the dicarboxylic acid (VI) respectively. Metallation of the alkyl analog 1,2-bis(2-hexyl-3-thienyl)perfluorocyclopentene proceeds with significantly more difficulty and requires the use of TMEDA [2].

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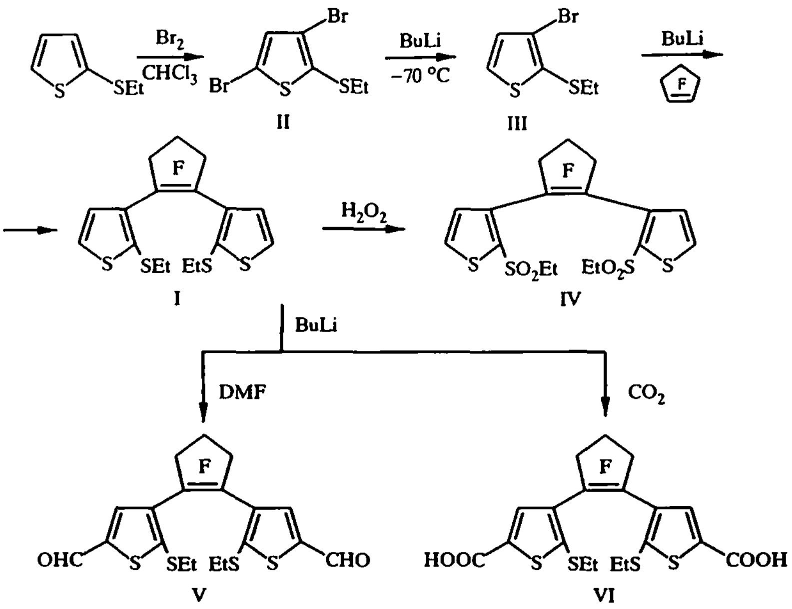

The structure of the obtained alkylthiothienylperfluorocyclopentene was confirmed by data of elemental analysis, PMR and mass spectra. Fluoride (I) was also investigated by x-ray structural analysis.

The unit cell of crystals of compound (I) contain two crystallographically independent molecules (Ia, b), the geometrical parameters of which differed by no more than ±0.1 Å and ±1.5°. All the bond lengths and valence angles were within the limits of the standard statistical mean values [5]. The structure of molecule (Ia) is shown in Fig. 1. The values of the geometrical parameters averaged for the two molecules are given in Tables 1 and 2. It is evident from Table 3 that the conformation of molecules (Ia, b) are also the same except for the different angle of the thioalkyl groups relative to the thiophene rings (T^1 and T^2), viz. 113.67 and 68.98° respectively. The perfluorocyclopentene fragment (F) is planar. The angles between T^1 or T^2 and F are close to 60°, the angle between rings T^1 and T^2 is 75.7° (Ia) and 73.20° (Ib). The thioalkyl groups have an antiparallel orientation relative to ring F. In the structure of 1,2-bis(5-formyl-2-methyl-3-thienyl)perfluorocyclopentene, as mentioned [4], the methyl substituents are also oriented antiparallel, and the thiophene rings are turned relative to the perfluorocyclopentene fragment by an angle of 45°.

The obtained 2-ethylthio-substituted perfluorocyclopentene possesses a high solubility in the usual organic solvents (it is frozen out from heptane at −50°C). On UV irradiation it, its 5-formyl and 5-carboxy derivatives (V) and (VI), and also the bisulfone (IV) display no photochromic properties, which indicates the exceptional stability of the open (aromatic) form A of this set of compounds.

EXPERIMENTAL

The PMR spectra were taken in $CDCl_3$ on a Bruker WM 250 (250 MHz) instrument. Mass spectra were obtained with a Kratos MS 30 instrument with an ionizing voltage of 70 eV with direct insertion of the substance into the ion source.

2,4-Dibromo-5-ethylthiophene (II). Bromine (23.66 g, 148 mmole) in $CHCl_3$ (100 ml) was added with vigorous stirring at 0-5°C during 30 min to a solution of 2-ethylthiothiophene (10.65 g, 74 mmole) in $CHCl_3$ (50 ml) and the mixture was kept at 20°C for 4 h. The reaction mixture was poured onto ice, the organic layer was separated, washed with water, with 3% NaOH, with 5% $Na_2S_2O_3$, with water, dried over $CaCl_2$, and the solvent evaporated. Dibromide (II) (15.9 g, 71.2%) was isolated from the residue (16.2 g green oil) by distillation in vacuum, bp 138-139°C (10.6 GPa), n_D^{20} 1.6409. PMR spectrum: 6.99 (1H, s, 3-H); 2.84 (2H, q, CH_2); 1.29 (3H, t, CH_3); $J_{CH2,CH3}$ = 7.42 Hz. Found, %: C 24.21; H 2.09; Br 52.49; S 21.06. $C_6H_6Br_2S_2$. Calculated, %: C 23.83; H 2.00; Br 52.83; S 21.20.

3-Bromo-2-ethylthiothiophene (III). A solution of BuLi (2.3 g, 36 mmoles) in dry ether (19.8 ml) was added to a solution of dibromide (II) (10 g, 33 mmole) in dry ether (100 ml) at −75°C during 40 min in a stream of argon. The reaction mixture was kept for 1 h at −70°C, then MeOH (1.5 ml) and water (30 ml) were added sequentially. The organic layer was separated, washed with water to neutral reaction, dried over $CaCl_2$, and the ether distilled off. Monobromide (III) (5.56 g,

TABLE 1. Bond Lengths in Structure (I) Averaged for the Two Crystallographically Independent Molecules (Ia, b)

Bond	d, Å	Bond	d, Å
$S_{(1)}-C_{(7)}$	1,735	$C_{(14)}-C_{(15)}$	1,435
$S_{(1)}-C_{(8)}$	1,724	$S_{(4)}-C_{(15)}$	1,722
$S_{(2)}-C_{(7)}$	1,701	$S_{(4)}-C_{(16)}$	1,686
$S_{(2)}-C_{(6)}$	1,834	$C_{(13)}-C_{(16)}$	1,440
$C_{(5)}-C_{(6)}$	1,545	$S_{(3)}-C_{(16)}$	1,783
$C_{(8)}-C_{(9)}$	1,377	$S_{(3)}-C_{(17)}$	1,810
$C_{(9)}-C_{(10)}$	1,480	$C_{(17)}-C_{(18)}$	1,480
$C_{(7)}-C_{(10)}$	1,480	$C_{(12)}-C_{(19)}$	1,506
$C_{(10)}-C_{(11)}$	1,430	$C_{(19)}-C_{(22)}$	1,510
$C_{(11)}-C_{(12)}$	1,277	$C_{(20)}-C_{(21)}$	1,521
$C_{(12)}-C_{(13)}$	1,445	$C_{(11)}-C_{(21)}$	1,480
$C_{(13)}-C_{(14)}$	1,420	$(C-F)_{mean}$	1,321

TABLE 2. Valence Angles in Structure (I) Averaged for the Two Crystallographically Independent Molecules (Ia, b)

Angle	ω, (deg)	Angle	ω, (deg)
$C_{(7)}-S_{(1)}-C_{(8)}$	95,1	$C_{(22)}-C_{(25)}-C_{(11)}$	102,1
$S_{(1)}-C_{(8)}-C_{(9)}$	111,3	$C_{(12)}-C_{(13)}-C_{(14)}$	124,8
$C_{(8)}-C_{(9)}-C_{(10)}$	114,0	$C_{(12)}-C_{(13)}-C_{(16)}$	120,9
$C_{(9)}-C_{(10)}-C_{(7)}$	110,1	$C_{(14)}-C_{(13)}-C_{(16)}$	113,5
$C_{(9)}-C_{(10)}-C_{(11)}$	127,5	$C_{(13)}-C_{(14)}-C_{(15)}$	109,1
$C_{(7)}-C_{(10)}-C_{(11)}$	121,9	$C_{(14)}-C_{(15)}-S_{(4)}$	112,6
$C_{(10)}-C_{(7)}-S_{(2)}$	127,0	$C_{(15)}-S_{(4)}-C_{(16)}$	92,4
$S_{(1)}-C_{(7)}-C_{(10)}$	109,0	$S_{(4)}-C_{(16)}-C_{(13)}$	111,6
$S_{(1)}-C_{(7)}-S_{(2)}$	123,6	$C_{(13)}-C_{(16)}-S_{(3)}$	126,6
$C_{(7)}-S_{(2)}-C_{(6)}$	98,2	$S_{(3)}-C_{(16)}-S_{(4)}$	121,6
$S_{(2)}-C_{(6)}-C_{(5)}$	114,1	$C_{(16)}-S_{(3)}-C_{(17)}$	102,9
$C_{(10)}-C_{(11)}-C_{(12)}$	128,2	$S_{(3)}-C_{(17)}-C_{(18)}$	115,3
$C_{(10)}-C_{(11)}-C_{(25)}$	116,3	$F_{(23)}-C_{(19)}-F_{(22)}$	105,6
$C_{(11)}-C_{(12)}-C_{(13)}$	131,0	$F_{(24)}-C_{(20)}-F_{(25)}$	104,4
$C_{(19)}-C_{(12)}-C_{(13)}$	117,9	$F_{(26)}-C_{(21)}-F_{(27)}$	103,2
$C_{(11)}-C_{(12)}-C_{(19)}$	111,9		
$C_{(12)}-C_{(19)}-C_{(20)}$	105,9		
$C_{(19)}-C_{(20)}-C_{(21)}$	108,2		

TABLE 3. Conformational Angles (φ, deg) in Molecules (Ia) and (Ib)

Fragment	(Ia)	(Ib)
$C_{(5)}-C_{(6)}-S_{(2)}-C_{(7)}$	121,52	116,72
$C_{(6)}-S_{(2)}-C_{(7)}/T^1$	113,67	68,98
T^1/F	57,80	53,98
T^2/F	59,80	59,39
$C_{(16)}-S_{(3)}-C_{(17)}/T^2$	118,98	114,15
$C_{(18)}-C_{(17)}-S_{(3)}-C_{(16)}$	116,87	54,59
T^1/T^2	75,73	73,20

75.5%) was isolated from the residue (7.12 g dark oil) by distillation in vacuum, bp 106-107°C (10.6 GPa); n_D^{20} 1.6085. PMR spectrum: 7.32 (1H, d, 5-H); 7.02 (1H, d, 4-H); $J_{H4,H5} = 5.47$ Hz; 2.87 (2H, q, CH_2); 1.29 (3H, t, CH_3); $J_{CH2,CH3} = 7.46$ Hz. Found, %: C 32.86; H 3.18; Br 35.52; S 28.50. $C_6H_7BrS_2$. Calculated, %: C 32.29; H 3.16; Br 35.52; S 28.74.

1,2-Bis(2-ethylthio-3-thienyl)perfluorocyclopentene (I). A solution of BuLi (0.68 g, 10.65 mmole) in dry ether (6 ml) was added during 5 min to a solution of bromide (III) (2.15 g, 9.68 mmole) in dry ether (30 ml) at −70°C in a stream

TABLE 4. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) in the (Ia, b) Molecules

Atom	x	y	z
1	2	3	4
	(Ia)		
$S_{(1)}$	4802(3)	8800(4)	8206(3)
$S_{(2)}$	4541(3)	6713(3)	8867(3)
$S_{(3)}$	5809(3)	9113(3)	12936(3)
$S_{(4)}$	4252(3)	7692(2)	13930(3)
$C_{(5)}$	5569(8)	6224(8)	6191(10)
$C_{(6)}$	4607(8)	6267(6)	6937(9)
$C_{(7)}$	5173(5)	7853(7)	8809(9)
$C_{(8)}$	5726(6)	9611(7)	8551(9)
$C_{(9)}$	6307(5)	9238(7)	9201(11)
$C_{(10)}$	5993(5)	8189(6)	9436(8)
$C_{(11)}$	6436(5)	7542(6)	9945(8)
$C_{(12)}$	6164(5)	7046(5)	10997(8)
$C_{(13)}$	5358(4)	7049(7)	11910(9)
$C_{(14)}$	4763(6)	6177(7)	12113(9)
$C_{(15)}$	4142(6)	6461(7)	13292(9)
$C_{(16)}$	5215(5)	7892(7)	12885(8)
$C_{(17)}$	6147(6)	9362(7)	14701(11)
$C_{(18)}$	6769(6)	8658(8)	14908(11)
$C_{(19)}$	6821(6)	6389(9)	11108(12)
$C_{(20)}$	7617(11)	6716(9)	10134(10)
$C_{(21)}$	7353(6)	7403(6)	9268(13)
$F_{(22)}$	7141(4)	6460(5)	12299(8)
$F_{(23)}$	6573(4)	5452(5)	10787(8)
$F_{(24)}$	7946(10)	5979(8)	9270(12)
$F_{(25)}$	8294(6)	7179(11)	10820(12)
$F_{(26)}$	7953(3)	8201(4)	9426(7)
$F_{(27)}$	7419(4)	7085(8)	7893(8)
$H_{(55,C5)}$	560(5)	598(5)	516(6)
$H_{(56,C5)}$	585(7)	577(5)	663(5)
$H_{(57,C5)}$	590(5)	690(5)	634(5)
$H_{(58,C18)}$	695(6)	879(6)	1588(6)
$H_{(59,C18)}$	731(6)	873(5)	1421(5)
$H_{(60,C18)}$	646(5)	797(6)	1474(6)
$H_{(67,C6)}$	432(6)	672(5)	649(7)
$H_{(68,C6)}$	427(6)	559(6)	678(5)
	(Ib)		
$S_{(28)}$	8477(3)	10756(4)	7079(4)
$S_{(29)}$	7345(3)	12236(4)	8737(3)
$S_{(30)}$	7896(3)	13208(5)	4001(5)
$S_{(31)}$	7557(4)	11106(3)	2505(7)
$C_{(32)}$	9673(6)	11293(8)	9112(12)
$C_{(33)}$	8847(7)	10599(9)	8699(12)
$C_{(34)}$	8238(5)	11905(7)	7552(10)
$C_{(35)}$	7567(6)	13500(8)	8677(11)
$C_{(36)}$	8292(6)	13687(7)	7707(10)
$C_{(37)}$	8683(6)	12830(7)	6996(7)
$C_{(38)}$	9455(5)	12831(5)	5940(9)
$C_{(39)}$	9544(5)	12287(5)	4799(9)
$C_{(40)}$	8915(5)	11646(7)	3923(8)
$C_{(41)}$	8945(5)	10644(6)	3375(10)
$C_{(42)}$	8260(8)	10243(8)	2487(10)
$C_{(43)}$	8163(6)	11992(8)	3507(8)
$C_{(44)}$	8054(8)	13694(10)	2372(10)
$C_{(45)}$	8889(10)	13666(10)	1532(9)
$C_{(46)}$	10482(6)	12393(7)	4060(11)
$C_{(47)}$	10923(5)	13206(12)	5051(14)
$C_{(48)}$	10269(7)	13417(7)	6361(12)

TABLE 4 (continued)

1	2	3	4
F(49)	10881(4)	11603(5)	3837(9)
F(50)	10607(4)	12771(7)	2912(8)
F(51)	11590(6)	12952(11)	5493(12)
F(52)	11399(8)	13879(9)	4599(12)
F(53)	10499(8)	13460(6)	7552(8)
F(54)	10214(4)	14386(5)	6328(9)
H(61,C32)	988(6)	1121(6)	1001(6)
H(62,C32)	1016(5)	1118(6)	834(6)
H(63,C32)	954(7)	1198(5)	921(5)
H(64,C45)	898(6)	1394(6)	063(6)
H(65,C45)	935(6)	1404(6)	212(5)
H(66,C45)	899(5)	1296(6)	130(5)
H(71,C33)	835(6)	1071(5)	946(6)
H(72,C33)	898(6)	991(5)	860(6)
H(73,C44)	759(6)	1331(6)	178(5)
H(74,C44)	795(6)	1440(5)	260(5)

of argon. The mixture obtained was stirred at the same temperature for 1 h, then octafluorocyclopentene (0.98 g, 4.84 mmole) was added to it in two portions of 0.49 g (0.31 ml). The cooling was removed after 2 h at −70°C and the reaction mixture hydrolyzed at 0°C with a mixture of 10% HCl (5 ml) and water (10 ml). The organic layer was separated, washed with water until neutral reaction, and dried over $CaCl_2$. After removing the ether a cinnamon oil (2.14 g) was obtained, from which the volatile components (0.26 g) with bp < 160°C (10.6 Pa) were distilled in vacuum. This fraction contained mainly the initial bromide (III) (0.18 g). Fluoride (I) (1.32 g, 62%) was isolated from the residue by column chromatography on silica gel (L 100-160 μ, eluent heptane) as a thick oil which crystallized, and was readily soluble in organic solvents. After recrystallization from heptane (−50°C) mp 47.5-48.5°C. PMR spectrum: 7.4 (1H, d, 5-H); 7.23 (1H, d, 4-H); $J_{H4,H5}$ = 5.79 Hz; 2.57 (2H, q, CH_2); 1.12 (3H, t, CH_3); $J_{CH2,CH3}$ = 7.47 Hz. Mass spectrum: 460 (80) $[M]^+$; 399 (98) $[M-SC_2H_5]^+$; 370 (65), 338 (100) $[M-2SC_2H_5]^+$. Found, %: C 44.68; H 3.11. $C_{17}H_{14}F_6S_5$. Calculated, %: C 44.34; H 3.06. M 460.54.

1,2-Bis(2-ethylsulfonyl-3-thienyl)perfluorocyclopentene (IV). Hydrogen peroxide (30%, 0.16 ml; 1.57 mmole) was added to a solution of fluoride (I) (60 mg, 0.13 mmole) in glacial acetic acid (2 ml). The mixture was heated on a boiling water bath for 2 h, cooled, and poured onto ice. The precipitated solid was filtered off, washed with water, dried, and bisulfone (IV) (62 mg, 90.6%) obtained having mp 184-185°C (from EtOH). PMR spectrum: 7.71 (1H, d, 5-H); 7.42 (1H, d, 4-H); $J_{H4,H5}$ = 5.14 Hz; 3.17 (2H, q, CH_2); 1.38 (3H, t, CH_3); $J_{CH2,CH3}$ = 7.57 Hz. Found, %: C 38.34; H 2.60. $C_{17}H_{14}F_6S_4O_4$. Calculated, %: C 38.93; H 2.69.

1,2-Bis(2-ethylthio-5-formyl-3-thienyl)perfluorocyclopentene (V). An ether solution (0.5 ml) of BuLi (47 mg, 0.75 mmole) was added in a stream of argon to a solution of fluoride (I) (140 mg, 0.3 mmole) in dry ether (7 ml) at 0°C. The mixture was stirred for 30 min at 20°C, cooled to −40°C, and dry DMF (0.22 g, 3 mmole) added. The suspension was stirred for 20 min at −40°C, and 1.5 h without cooling, and then hydrolyzed with 5% HCl. The aqueous layer was separated, extracted with ether, the extract was combined with the organic layer, washed with water, dried over $MgSO_4$, and the ether evaporated. The yellow oil crystallized on standing and according to PMR data was a 85:15 mixture of compounds (V) and (I). The mixture was chromatographed on a column of silica gel (L 100-160 μ, eluent benzene), and the bisaldehyde (V) (100 mg, 65%) was isolated, mp 88-89°C (from heptane). PMR spectrum: 9.82 (1H, s, CHO); 7.87 (1H, s, 4-H); 2.89 (2H, q, CH_2); 1.22 (3H, t, CH_3); J_{CH2CH3} = 7.69 Hz. Mass spectrum: 516 (100) $[M]^+$, 456 (90), 398 (33), 338 (28). Found, %: C 44.52; H 2.97. $C_{19}H_{14}F_6O_2S_4$. Calculated, %: C 44.19; H 2.73. M 516.6.

1,2-Bis(2-ethylthio-5-carboxy-3-thienyl)perfluorocyclopentene (VI). An ether solution of BuLi (143 mg, 2.2 mmole) was added to a solution of fluoride (I) (410 mg, 0.89 mmole) in dry ether as described for aldehyde (V). The suspension obtained was kept for 30 min at 20°C, poured onto dry ice in ether, and kept for 12 h at 20°C. Water was added to the reaction mixture, the aqueous layer was separated, extracted with ether, and acidified under cooling with 5% HCl. The acid which precipitated was extracted with ether, the extract washed with water, and dried over $MgSO_4$. The ether was distilled off, and crude acid (290 mg) obtained, which was washed with heptane, and reprecipitated from AcOH with water. Pure acid (V) (160 mg) was obtained, mp 202-203°C (with decomposition). PMR spectrum: 7.98 (1H, s, 4-H); 2.83 (2H, q, CH_2); 1.22 (3H, t, CH_3); J_{CH2CH3} = 7.66 Hz. Mass spectrum: 548 (60) $[M]^+$, 504 (60), 443 (50), 414 (70), 382 (78), 338 (60), 208 (100). Found, %: C 41.86; H 3.03. $C_{19}H_{14}F_6O_4S_4$. Calculated, %: C 41.60; H 2.57. M 548.56.

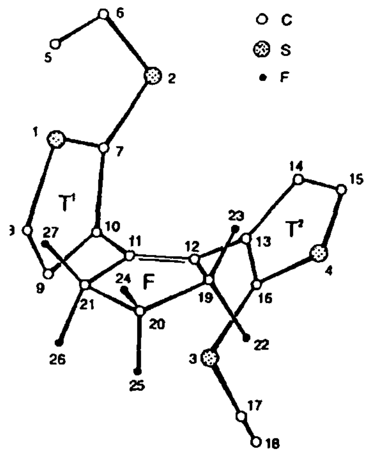

Fig. 1. Structure and conformation of the (Ia) molecule (without allowing for hydrogen atoms). The numbering of the atoms is given in the machine code.

X-Ray Structural Investigation of 1,2-Bis(2-alkylthio-3-thienyl)perfluorocyclopentene (I). Colorless transparent monocrystals of compound (I) of composition $C_{17}H_{14}F_6S_4$, grown in methanol, belong to the triclinic crystal system. Unit cell parameters: $a = 15.392(2)$, $b = 13.922(2)$, $c = 9.724(2)$ Å, $\alpha = 99.89(1)°$, $\beta = 82.38(1)°$, $\psi\gamma = 98.96(1)°$, $V = 2015.68$ Å^3, space group P1, Z = 4. The intensities of 1862 reflections with $I > 2\sigma(I)$ were measured on an automatic four-circle RED-4 diffractometer (λCuKα, graphite monochromator, $\theta/2\theta$ scanning). The structure was solved by the direct method, the coordinates of the nonhydrogen atoms were refined by the least squares method in an anisotropic approach, and the hydrogen atoms an isotropic. The final value of the divergence factor was 0.08. Calculations were carried out with the AREN 90 program [6]. The atomic coordinates and the equivalent isotropic temperature parameters for the two crystallographically independent molecules (Ia, b) are given in Table 4.

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