Crystal structure of 1,2-bis(2-methyl-5-formyl-thien-3-yl)perfluorocyclopentene, $C_5F_6(C_4HSCH_3)_2(CHO)_2$, *a photochromic diarylethene*

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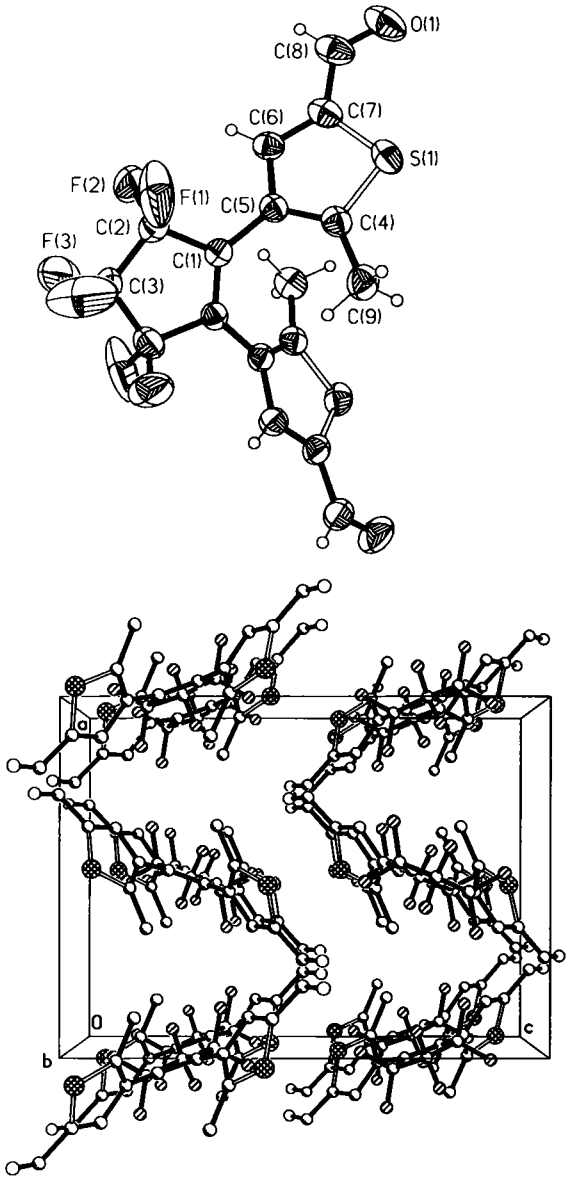

Abstract

$C_{17}H_{10}F_6O_2S_2$, orthorhombic, *Pbcn* (No. 60), $a = 12.182(2)$ Å, $b = 8.706(1)$ Å, $c = 16.622(3)$ Å, $V = 1762.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.068$, $wR_{ref}(F^2) = 0.131$, $T = 293$ K.

Source of material

Bromination of 5-methythiophene-2-carbaldehyde in acetic acid afforded 3-bromo-5-methylthiophene-2-carbaldehyde as a regioisomer (mp 332 K; 95%) [1]. The carbonyl group was protected as the dioxolane acetal (oil; 93%) prior to coupling with the fluorinated ring to give 1,2-bis[2-methyl-5-(2-(1,3-dioxolane))-thien-3-yl]perfluorocyclopentene (syrup; 35%). Then, the goal compound was gained by hydrolyzing the above compound (solid; 95%). Finally, suitable colorless crystals were obtained by slow vapour diffusion of chloroform and hexane (mp 456 K). ^{1}H NMR results are included in the deposited CIF-file.

Discussion

Photochromic diarylethene derivatives have received much attention as potential materials for high density optical storage and other optoelectronic devices [1-4]. Although the compound has been reported before [1,5], we synthesised it by a new method and gained the crystalline material. In general, diarylethenes have parallel and antiparallel forms in solution, and they are interconverting. However, in the crystals, there is no exchange between the two formers, and the dithienylethenes are fixed in a reactive antiparallel conformation and undergo effective photocyclization reactions by a conrotatory mode [6].

The molecular structure is shown in the upper figure (35% probabilty ellipsoids) and its packing diagram is shown in the lower figure (along the *b* direction) which indicates that the compound is packed in an antiparallel conformation in the crystal. The dihedral angles between the cyclopentene ring and the two thiophene rings are both 46.1°. The distance between C4 and C4^i (*i*: 1–*x*, *y*, 0.5–*z*), which are reactive carbon atoms, was estimated to be 3.60 Å, that is short enough for the reaction to take place in the crystalline phase [7].

Table 1. Data collection and handling.

Crystal:	colorless, prism, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.72 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	49.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2087, 1558
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1118
$N(param)_{refined}$:	124
Programs:	SHELXTL [8], DIFABS [9]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(6A)	8*d*	0.3077	–0.1368	0.3903	0.068
H(8A)	8*d*	0.2173	0.039	0.5014	0.094
H(9A)	8*d*	0.6582	–0.0052	0.283	0.105
H(9B)	8*d*	0.6951	0.0756	0.3628	0.105
H(9C)	8*d*	0.6415	0.1722	0.2935	0.105

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	8*d*	0.4780(1)	0.1725(1)	0.42525(7)	0.093(1)	0.0578(7)	0.0545(7)	0.0102(7)	–0.0107(6)	–0.0088(5)
F(1)	8*d*	0.5110(5)	–0.3945(4)	0.3848(2)	0.372(8)	0.063(2)	0.100(3)	–0.025(3)	–0.101(4)	0.024(2)
F(2)	8*d*	0.3550(3)	–0.3915(4)	0.3302(3)	0.134(3)	0.082(2)	0.196(4)	–0.042(2)	0.104(3)	–0.036(3)
F(3)	8*d*	0.4225(4)	–0.5584(6)	0.2267(3)	0.239(5)	0.200(5)	0.205(5)	–0.156(4)	0.127(5)	–0.134(4)
O(1)	8*d*	0.2762(4)	0.2224(5)	0.5344(2)	0.133(4)	0.098(3)	0.082(3)	0.039(3)	0.015(3)	–0.024(2)
C(1)	8*d*	0.4811(3)	–0.2034(4)	0.2881(2)	0.045(2)	0.049(2)	0.052(2)	0.001(2)	–0.001(2)	0.003(2)
C(2)	8*d*	0.4614(4)	–0.3646(5)	0.3172(3)	0.081(3)	0.057(3)	0.063(3)	–0.010(3)	0.003(3)	0.009(2)
C(3)	4*c*	1/2	–0.4678(7)	1/4	0.077(5)	0.042(4)	0.103(6)	0	0.016(4)	0
C(4)	8*d*	0.5304(4)	0.0468(5)	0.3560(2)	0.069(3)	0.057(3)	0.044(2)	0.003(2)	–0.008(2)	0.001(2)
C(5)	8*d*	0.4593(3)	–0.0743(5)	0.3428(2)	0.058(2)	0.049(2)	0.044(2)	0.005(2)	–0.003(2)	0.001(2)
C(6)	8*d*	0.3635(4)	–0.0639(5)	0.3909(2)	0.060(3)	0.061(3)	0.049(2)	0.008(2)	0.001(2)	0.004(2)
C(7)	8*d*	0.3614(4)	0.0644(5)	0.4382(3)	0.075(3)	0.066(3)	0.047(2)	0.022(3)	–0.001(2)	0.003(2)
C(8)	8*d*	0.2760(5)	0.1063(6)	0.4950(3)	0.097(4)	0.084(4)	0.053(3)	0.034(3)	0.005(3)	0.005(3)
C(9)	8*d*	0.6412(4)	0.0748(6)	0.3207(3)	0.073(3)	0.072(3)	0.065(3)	–0.014(3)	–0.009(2)	–0.004(3)

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