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3,3,4,4,5,5-Hexafluoro-1,2-bis{3-methyl-5-[3-(trifluoromethyl)phenyl]-2-thienyl}cyclopent-1-ene

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Key indicators

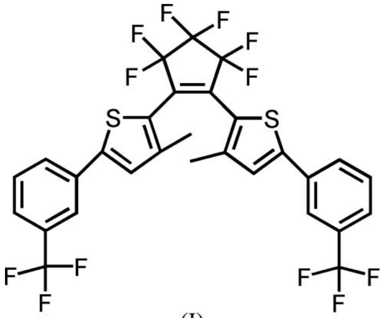
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
R factor = 0.075
wR factor = 0.145
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{29}H_{16}F_{12}S_2$, a photochromic dithienylethene, is a potential material for optical storage. It adopts a photo-active antiparallel conformation in the single crystalline phase. The distance between the two reactive C atoms is 3.624 (8) Å. The molecule has crystallographic twofold rotation symmetry. The dihedral angles between the cyclopentene ring and the attached thiophene and benzene rings are 47.2 (2) and 17.9 (2)°, respectively.

Comment

Owing to their highly efficient photo-isomerization reactions, good thermal stability of both isomers and excellent fatigue resistance, photochromic diarylethene dervatives are the most promising candidates for optical memory devices and photo switches (Irie, 2000; Tian & Yang, 2004).



(I)

In particular, perfluorocyclopentene derivatives can be recycled 10 000 times with no chemical change (Gilat *et al.*, 1995; Matsuda & Irie, 2004). In general, diarylethenes have two interconverting conformations, *viz*. the parallel conformer and antiparallel conformer, and photocyclization reaction proceeds in a conrotatory fashion only from the anti-parallel conformer according to the Woodward–Hoffmann rule (Pu *et al.*, 2003; Kobatake & Irie, 1999). Both in solution and in the crystal, diarylethenes undergo a photochromic-type reaction between 1,3,5-hexatriene and cyclohexadiene by alternate irradiation with UV and visible light. In order to improve the optical storage density, it was necessary to develop diarylethenes which absorb at a short wavelength. Although many photochromic diarylethene crystals have been reported so far (Kobatake & Irie, 2004; Pu *et al.*, 2004, 2005; Sun *et al.*, 2003), crystals which absorb at a short wavelength are quite rare. In this paper, a new photochromic diarylethene, (I), which has a relatively shorter wavelength absorption spectrum was synthesized, and its structure is presented here.

Figs. 1 and 2 show the molecular structure of (I) and its packing diagram, respectively. Compound (I) is a bis(2-

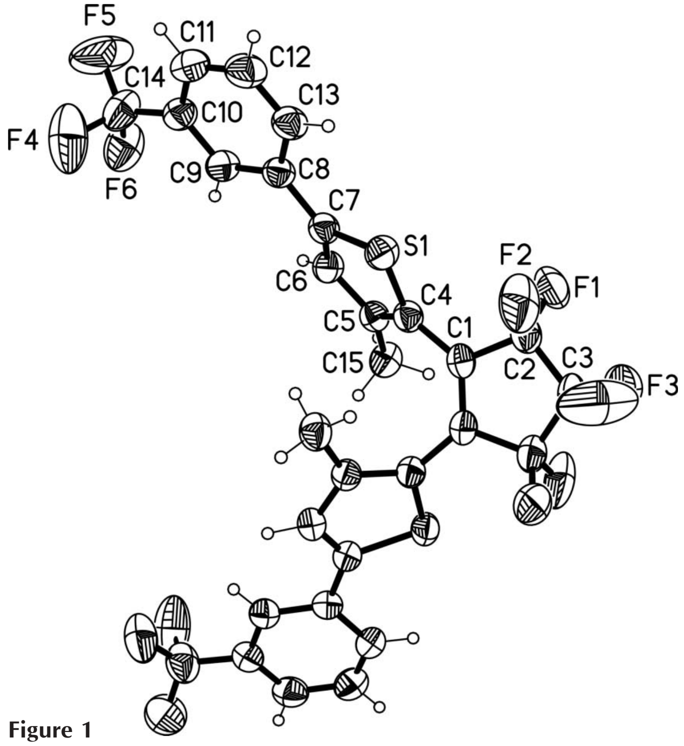


Figure 1
View of the structure of (I), showing the atomic numbering scheme and 35% probability ellipsoids for the non-H atoms. Unlabeled atoms are related to labeled atoms by the symmetry code $(-x, y, \frac{1}{2} - z)$.

thienyl)perfuorocyclopentene derivative. The molecules pack in an anti-parallel conformation, with the two thiophene rings related to each other by C_2 symmetry. In the perfluorocyclopentene ring, the C1—C1^{i} bond is a double bond and is significantly shorter than the C1—C2 and C1^{i}—C2^{i} single bonds [symmetry code: (i) $-x$, y, $-z + \frac{1}{2}$]. The distance between the reactive C atoms (C5 and C5^{i}) is 3.624 (8) Å, which is short enough theoretically for a photocyclization reaction to take place in the crystalline phase (Ramamurthy & Venkatesan, 1987). The molecule has crystallographic twofold rotation symmetry, the axis passing through F3, C3 and the mid-point of the C1—C1^{i} bond. In addition, the dihedral angle between the hexafluorocyclopentene ring and the attached thiophene ring is 47.2 (2)°, and that between the thiophene ring and the adjacent benzene ring is 17.9 (2)°.

Experimental

The title compound was derived originally from 3-methylthiophene. First, n-butyl lithium hexane solution (8.2 ml of 2.5 mol l^{-1}) was gradually added at 273 K to a diethyl ether solution (40 ml) containing 2 g 3-methylthiophene. The solution was heated for 1 h under reflux. After cooling the solution to 273 K, 8.2 ml trimethyl borate was added. The solution was then stirred for 1 h at room temperature, 20% (w/w) Na_2CO_3 aqueous solution (25 ml), 3-trifluorobenzene (4.6 g), tetrahydrofuran (40 ml), and tetrakis(triphenylphosphine)palladium(0) (0.29 g) were added and heated for 6 h under reflux with vigorous stirring to give 3.2 g 4-methyl-2-[3-(trifluoromethyl)phenyl]thiophene in 65% yield. This compound was dissolved in diethyl ether (40 ml) and n-butyl lithium hexane solution (5.2 ml 2.5 mol l$^{-1)}$ was added at 273 K under an argon gas atmosphere. After the mixture was heated under reflux for 1 h, the reaction mixture was cooled to 273 K. Octafluorocyclopentene (0.89 ml) was added and stirred for 2 h at this temperature. After extracting with diethyl ether and evaporation *in vacuo*, the residue was purified by comlumn chromatography on silica gel (hexane) to give 3.7 g of the title compound in 43% yield. Finally, colorless crystals of the title compound suitable for X-ray analysis were obtained by recrystallization from chloroform. Its structure was confirmed by the melting point, NMR and high resolution mass spectrometry (m.p. 407–408 K). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (s, 6H), 7.18 (s, 2H), 7.53–7.57 (t, 2H), 7.60–7.62 (d, 2H), 7.76–7.76 (d, 2H), 7.84 (s, 2H); HRMS (ESI): $M + H^+$, found 657.0575, $C_{29}H_{16}F_{12}S_2$ requires 657.0571.

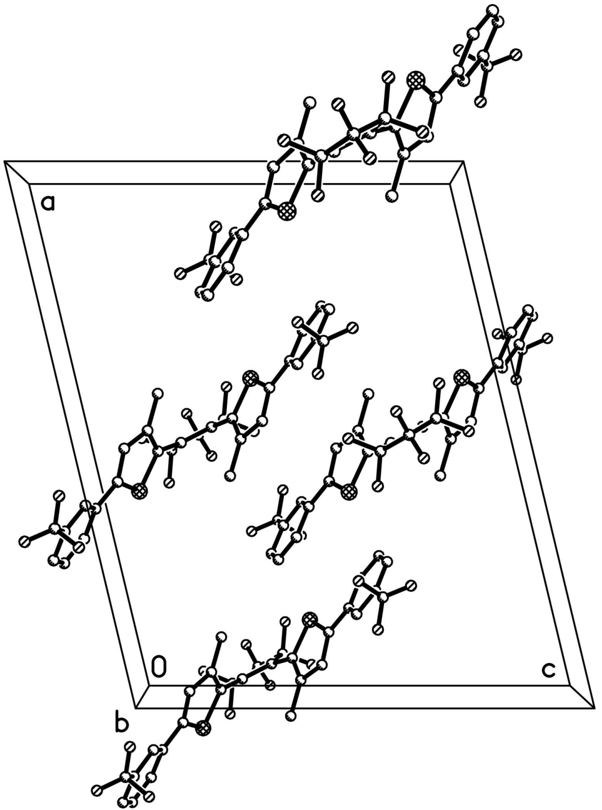


Figure 2
The packing of (I), viewed along the b axis.

Crystal data

$C_{29}H_{16}F_{12}S_2$
$M_r = 656.54$
Monoclinic, $C2/c$
$a = 20.011$ (2) Å
$b = 8.6936$ (8) Å
$c = 16.3481$ (16) Å
$\beta = 103.498$ (8)°
$V = 2765.5$ (5) Å^3
$Z = 4$
$D_x = 1.577$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 4.8$–12.5°
$\mu = 0.29$ mm^{-1}
$T = 295$ (2) K
Prism, yellow
0.5 × 0.4 × 0.4 mm

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: empirical (using intensity measurements) (North *et al.*, 1968)
$T_{\min} = 0.843$, $T_{\max} = 0.889$
2996 measured reflections
2422 independent reflections
1876 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 23$
$k = -10 \rightarrow 1$
$l = -19 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: none

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.075$
$wR(F^2) = 0.145$
$S = 1.01$
2422 reflections
196 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 13P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C7	1.721 (4)	C2—C3	1.502 (6)
C1—C1^i	1.354 (8)	C8—C9	1.390 (6)
C1—C2	1.502 (6)	C8—C13	1.420 (6)
C7—S1—C4	92.2 (2)	C4—C5—C6	111.0 (4)
C1^i—C1—C2	110.8 (2)	C6—C7—C8	129.3 (4)
F2—C2—F1	104.0 (4)	C6—C7—S1	110.4 (3)
F2—C2—C3	111.1 (4)	C8—C7—S1	120.3 (3)
C3—C2—C1	105.2 (4)	C11—C10—C14	119.6 (5)
F3—C3—F3^i	103.6 (9)	C12—C13—C8	120.9 (5)
C2—C3—C2^i	107.7 (6)	F5—C14—F6	110.4 (6)
C5—C4—S1	111.6 (3)	F5—C14—F4	103.1 (6)
C1—C4—S1	120.4 (3)	F6—C14—F4	98.2 (5)

Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.

The H atoms were positioned theoretically and allowed to ride on their parent atoms in the final refinement [C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C)]. The methyl groups were treated as rigid groups and allowed to rotate about the C—C bond.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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