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1-(2,5-Dimethyl-3-thienyl)-2-[5-(1,3-dithiolan-2-yl)-2-methyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene: a new photochromic diarylethene compound

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The title compound, $C_{19}H_{16}F_6S_4$, is a new asymmetric photochromic diarylethene which contains 3-thienyl substituents. The distance between the two reactive C atoms in the molecule is 3.548 (3) Å. The dihedral angles between the central cyclopentene ring and two thiophene rings are 45.7 (1) and 44.5 (1)°.

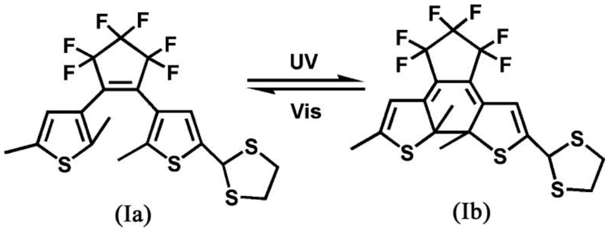
Key indicators

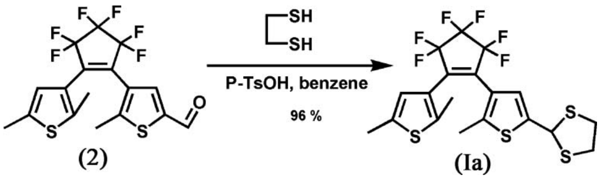
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.111
Data-to-parameter ratio = 13.5

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

Comment

Photochromic diarylethene derivatives have attracted much attention in the field of optical memory and photoswitches because of their excellent thermal stability, fatigue resistance, rapid response and high reactivity in the solid state (Irie, 2000; Tanifuji *et al.*, 2005; Tian & Yang, 2004). For further background information, see Pu, Liu *et al.* (2005) and Pu, Yang *et al.* (2005). Although many diarylethene compounds have been reported to date, they are mainly limited to symmetrical and amorphous diarylethenes (Irie, 2000; Kobatake & Irie, 2004; Morimoto & Irie, 2005). Asymmetric crystalline diarylethenes are very rare (Pu, Xiao *et al.*, 2005). We have synthesized a new asymmetric photochromic diarylethene compound, (I*a*), and its structure is presented here.





The molecular structure of (I*a*) and its packing diagram are shown in Figs. 1 and 2, respectively. Selected geometric parameters are given in Table 1. Compound (I*a*) is an asymmetric bis(3-thienyl)perfluorocyclopentene derivative.

The two thiophene ring systems have essentially identical geometries and the dihedral angles between the plane of the central cyclopent-1-ene ring and those of the adjacent thiophene rings (S1/C6–C9 and S4/C14–C17) are 45.7 (1) and 44.5 (1)°, respectively. The intramolecular distance between the two reactive C atoms (C6···C14) is 3.548 (3) Å. This

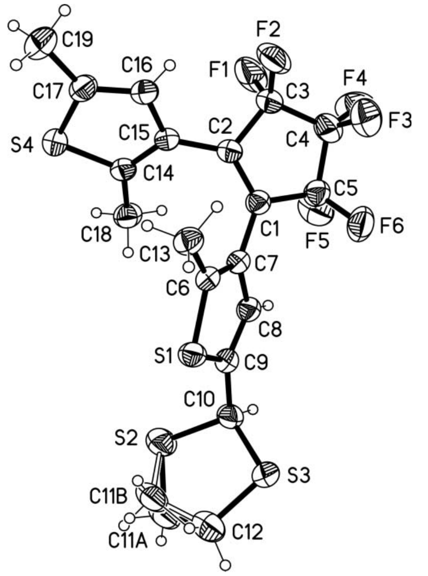


Figure 1
The structure of (I*a*), showing 35% probability ellipsoids and the atom-numbering scheme. One of the two disordered C atom components is shown with full bonds and the other with open bonds.

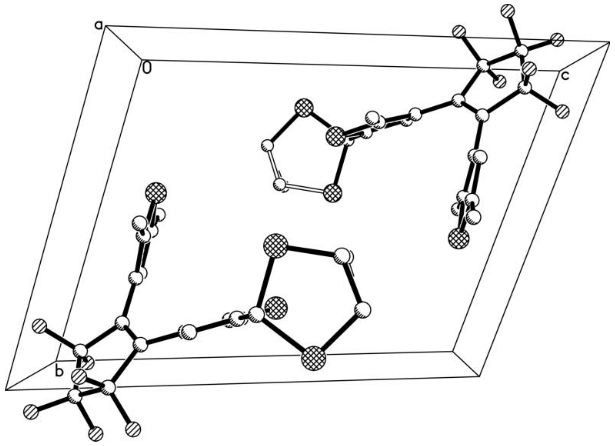


Figure 2
A packing diagram for (I*a*), viewed down the *a* axis. H atoms have been omitted for clarity. One of the two disordered C atom components is shown with full bonds and the other with open bonds.

distance indicates that the crystal can be expected to undergo photochromism to generate compound (I*b*) (see scheme), because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 Å (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).

In fact, crystals of (I*a*) showed photochromism to form (I*b*) in accordance with the expected ring closure. Upon irradiation with 254 nm light, the colourless crystals rapidly turned red, and the colour remained stable in the dark. When the red crystals were dissolved in dichloromethane, the resulting solution also showed a red colour with an absorption maximum at 526 nm, consistent with the presence of the closed-ring isomer, (I*b*). Upon irradiation with visible light of a wavelength greater than 450 nm, the red crystals returned to the initial colourless crystals, and the absorption spectrum of a dichloromethane solution containing the colourless material was the same as that of solutions of the open-ring form, (I*a*), with an absorption maximum at 243 nm.

Experimental

Compound (I*a*) was synthesized by the condensation reaction (Pu, Xu *et al.*, 2005) of 1-(2,5-dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-2-(5-formyl-2-methyl-3-thienyl)cyclopent-1-ene [compound (2); Pu, Luo *et al.*, 2006] with 1,2-ethanedithiol. A solution of compound (2) (0.41 g, 1.0 mmol), 1,2-ethanedithiol (0.184 g, 2.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.2 g) in benzene (150 ml) was refluxed for 17 h with a Dean–Stark condenser. After cooling the reaction mixture to room temperature, the solvent was removed under vacuum. Column chromatography (silica gel, ethyl acetate–petroleum ether 1:5) afforded the title compound (0.47 g, 96%). The compound was recrystallized from chloroform at room temperature and yielded crystals suitable for X-ray analysis. The structure of (I*a*) was confirmed by melting point, elemental analysis and NMR spectroscopy (see CIF for details);m.p. 387.7 K. Analysis, calculated for $C_{19}H_{16}F_6S_4$: C 46.90, H 3.31%; found: C 46.99, H 3.42%.

Crystal data

$C_{19}H_{16}F_6S_4$
$M_r = 486.56$
Triclinic, $P\overline{1}$
$a = 8.954$ (3) Å
$b = 10.305$ (3) Å
$c = 13.329$ (3) Å
$\alpha = 100.471$ (14)°
$\beta = 106.617$ (16)°
$\gamma = 111.010$ (17)°
$V = 1043.1$ (6) Å^3
$Z = 2$
$D_x = 1.549$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.51$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.5 × 0.4 × 0.3 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: none
4403 measured reflections
3638 independent reflections
3109 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\rm max} = 25.0°$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.111$
$S = 1.02$
3638 reflections
269 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 2P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.006$
$\Delta\rho_{\rm max} = 1.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.46$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.719 (2)	C1—C5	1.498 (3)
S1—C9	1.723 (3)	C2—C15	1.471 (3)
S4—C17	1.720 (3)	C2—C3	1.504 (4)
S4—C14	1.722 (2)	C3—C4	1.509 (4)
C1—C2	1.343 (3)	C4—C5	1.526 (4)
C1—C7	1.467 (3)		
C7—C1—C2—C15	−10.1 (5)	C2—C3—C4—C5	11.6 (3)
C1—C2—C3—C4	−3.1 (3)	C2—C1—C5—C4	14.4 (3)
C15—C2—C3—C4	−179.6 (2)		

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Atom C11 is disordered over two sites, with site-occupancy factors of 0.423 (6) and 0.577 (6). H atoms were positioned geometrically, with C–H = 0.93 and 0.96 Å, for aromatic and methyl C atoms, respectively, and were constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), or 1.5$U_{\rm eq}$(C) for methyl H. The highest peak is located 1.42 Å from atom F4.

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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