

## 2-[4-[2-(2,5-Dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl]-5-methyl-2-thienylmethyl-ene]propanedinitrile: a new photochromic diarylethene compound

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## Key indicators

Single-crystal X-ray study  
T = 295 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$   
R factor = 0.079  
wR factor = 0.155  
Data-to-parameter ratio = 14.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

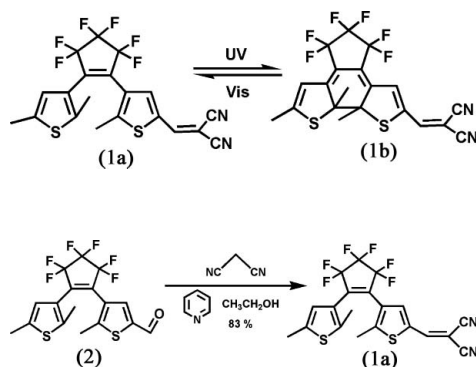
The title compound,  $\text{C}_{20}\text{H}_{12}\text{F}_6\text{N}_2\text{S}_2$ , is a new asymmetric photochromic diarylethene which contains 3-thienyl substituents. The distance between the two reactive C atoms in the molecule is 3.677 (8) Å. The dihedral angles between the central cyclopentene ring and the two thiophene rings are 47.6 (2) and 49.2 (2)°.

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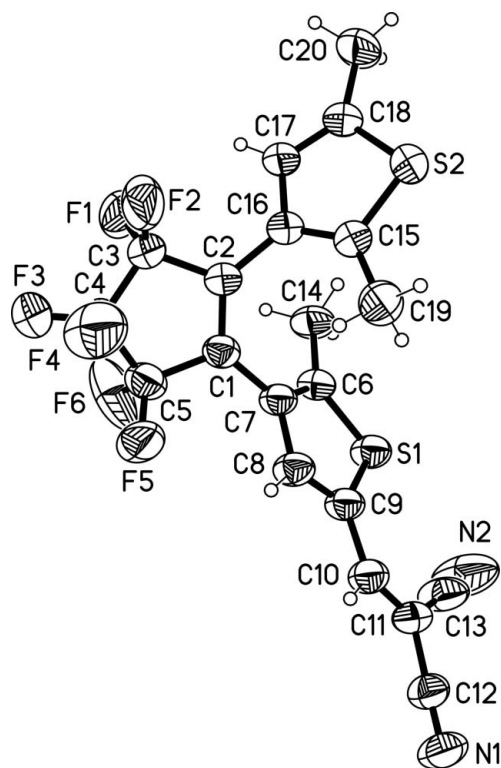
## Comment

Photochromic compounds have been extensively investigated for their optoelectronic properties, for example as materials for optical recording, full-colour displays, photoswitches *etc.* (Irie, 2000; Higashiguchi *et al.*, 2005; Tian & Yang, 2004). Among the various types of photochromic compounds, diarylethenes are regarded as the most promising candidates for these applications because of their excellent thermal stability, fatigue-resistant character, rapid response and high reactivity in the solid state (Tanifuji *et al.*, 2005). For further background information, see Pu, Liu *et al.* (2005) and Pu, Yang *et al.* (2005).

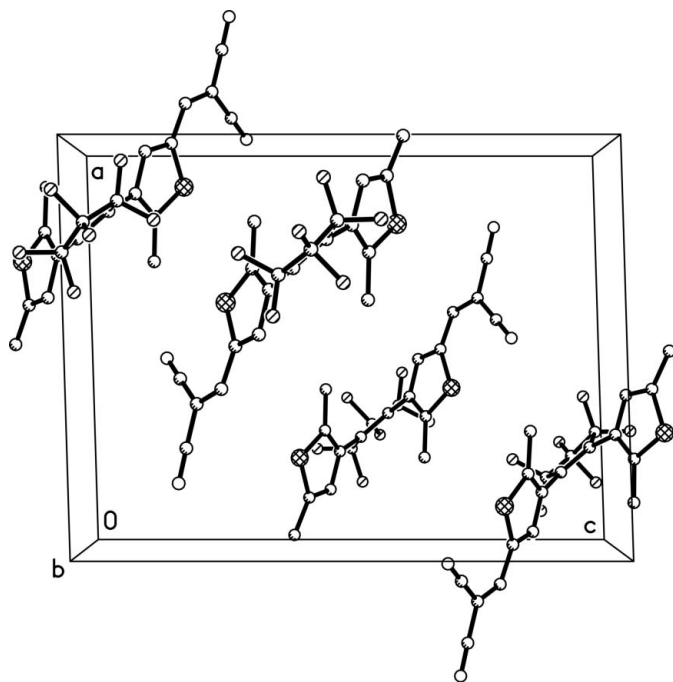


Crystals of diarylethenes attract much attention from both fundamental and practical points of view because they have some characteristic properties, such as dichroism under polarized light, thermal stability and fatigue-resistant photochromic performance (Morimoto *et al.*, 2004; Pu, Li *et al.*, 2005). To date, many crystal structures of diarylethene derivatives and their properties have been reported (Morimoto & Irie, 2005; Kobatake & Irie, 2004), including some structures determined by our group (Pu *et al.*, 2003, 2004; Pu, Li *et al.*, 2006; Pu, Xu *et al.*, 2005; Yang *et al.*, 2006). The synthesis and structure of the title photochromic diarylethene compound, (1a), are reported here.

The molecular structure of (1a) and a packing diagram are shown in Figs. 1 and 2, respectively. Selected geometric parameters are given in Table 1. Compound (1a) is an asym-



**Figure 1**  
The molecular structure of (1a), showing 35% probability ellipsoids and the atom-numbering scheme.



**Figure 2**  
A packing diagram for (1a), viewed down the *b* axis. H atoms have been omitted for clarity.

metric bis(3-thienyl)perfluorocyclopentene derivative. In the hexafluorocyclopentene ring, the C1–C2 bond is clearly a double bond, being significantly shorter than the other single bonds from atoms C1 and C2 (Table 1). The two methyl

groups attached to atoms C6 and C15 are located on different sides of the C1=C2 double bond, as reflected in the torsion angles C1–C2–C16–C15 [−47.4 (8)°] and C2–C1–C7–C6 [−49.6 (8)°] (Fig. 1). Such a conformation is crucial for the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970).

The two independent planar 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 S2/C15–C18) are 47.6 (2) and 49.2 (2)°, respectively.

The intramolecular distance between the two reactive C atoms (C6···C15) is 3.677 (8) Å. This indicates that the crystal can be expected to undergo photochromism to generate compound (1b) (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 (1a) showed photochromism to yield (1b) in accordance with the expected ring closure. Upon irradiation with 365 nm light, the yellowish single crystals turned rapidly to green, and the colour remained stable in the dark. When the green crystals were dissolved in dichloromethane, the resulting solution also showed a green colour, with a maximum absorption at 669 nm, consistent with the presence of the closed-ring isomer, (1b). We have not, so far, been able to determine the crystal structure of (1b) because of the limitation of experimental conditions. The structure of the closed-ring isomer should be determined below 213 K (Yamaguchi & Irie, 2005). Upon irradiation with visible light of wavelength longer than 550 nm, the green-coloured crystals reverted to the initial yellowish crystals; the absorption spectrum of a dichloromethane solution of the yellowish crystal showed a maximum absorption at 366 nm, *i.e.* it is a solution of the open-ring form, (1a).

## Experimental

Compound (1a) was synthesized by the Knoevenagel condensation reaction (Pu *et al.*, 2003) 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 malonodinitrile. A very small quantity of piperidine was added dropwise at room temperature to a stirred solution of compound (2) (0.410 g, 1.0 mmol) and malonodinitrile (0.079 g, 1.2 mmol) in anhydrous ethanol (20 ml), and the mixture was refluxed for 27 h at 351 K. The reaction mixture was then dried over anhydrous MgSO<sub>4</sub>, the solvent was removed, and column chromatography (silica gel, chloroform) gave the title compound, (1a) (0.380 g, 0.83 mmol), in 83% yield. The compound was recrystallized from chloroform at room temperature and yielded crystals suitable for X-ray analysis. Compound (1a) was further characterized by its melting point (m.p. 402.5 K) and by elemental analysis and NMR measurements. Analysis calculated for C<sub>20</sub>H<sub>12</sub>F<sub>6</sub>N<sub>2</sub>S<sub>2</sub>: C 52.40, H 2.64%; found: C 52.43, H 2.71%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, p.p.m.): 1.830 (s, 3H, –CH<sub>3</sub>), 2.061 (s, 3H, –CH<sub>3</sub>), 2.426 (s, 3H, –CH<sub>3</sub>), 6.682 (s, 1H, thiophene-H), 7.651 (s, 1H, thiophene-H), 7.789 (s, 1H, –CH=); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, δ, p.p.m.): 109.72 (2F), 110.53 (2F), 131.78 (2F).

## Crystal data

$C_{20}H_{12}F_6N_2S_2$   
 $M_r = 458.44$   
 Monoclinic,  $P2_1/n$   
 $a = 13.6074$  (15) Å  
 $b = 8.4990$  (11) Å  
 $c = 17.9494$  (19) Å  
 $\beta = 91.745$  (9)°  
 $V = 2074.9$  (4) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.468$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.32$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Prism, yellow  
 $0.4 \times 0.3 \times 0.3$  mm

## Data collection

Bruker  $P4$  diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 5015 measured reflections  
 3873 independent reflections  
 2280 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.017$   
 $\theta_{max} = 25.5^\circ$   
 3 standard reflections  
 every 97 reflections  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.079$   
 $wR(F^2) = 0.155$   
 $S = 1.00$   
 3873 reflections  
 274 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 5P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 1.10$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.44$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

S1—C6	1.711 (5)	C1—C7	1.474 (6)
S1—C9	1.725 (5)	C1—C5	1.495 (7)
S2—C18	1.705 (5)	C2—C16	1.471 (6)
S2—C15	1.713 (5)	C2—C3	1.505 (7)
N1—C12	1.139 (6)	C3—C4	1.498 (7)
N2—C13	1.127 (8)	C4—C5	1.476 (8)
C1—C2	1.341 (6)	C10—C11	1.339 (7)
C7—C1—C2—C16	−8.4 (9)	C1—C2—C16—C17	136.4 (6)
C2—C1—C7—C8	135.2 (6)		

The highest peak in the final difference Fourier map is located 1.519 Å from F3. All H atoms were positioned geometrically and refined using a riding model, fixing the aromatic and olefinic C—H distances at 0.93 Å and methyl C—H distances at 0.96 Å, and with  $U_{iso}(H) = 1.2U_{eq}(\text{aromatic and olefinic C})$  or  $1.5U_{eq}(\text{methyl C})$ .

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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