

3,3,4,4,5,5-Hexafluoro-1,2-bis(3-methyl-5-phenyl-2-thienyl)cyclopent-1-ene, a new photochromic diarylethene compound

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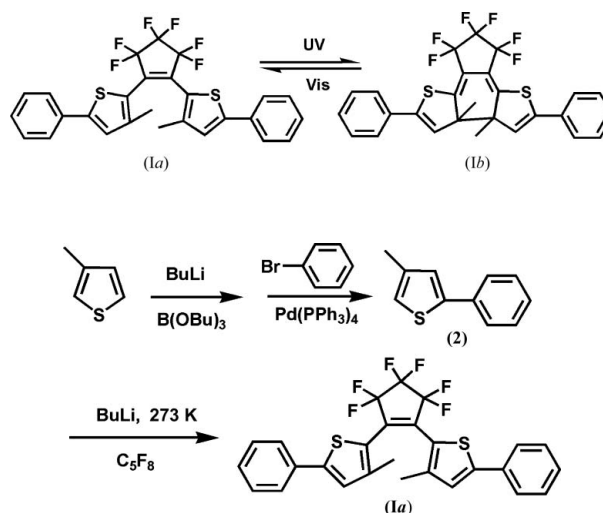
Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
Disorder in main residue
 R factor = 0.052
 wR factor = 0.153
Data-to-parameter ratio = 11.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_{27}\text{H}_{18}\text{F}_6\text{S}_2$, there are two independent molecules in the asymmetric unit. In the two molecules, the distances between the two reactive C atoms, *i.e.* the ring C atoms to which the methyl groups are attached, are 3.500 (6) and 3.562 (5) Å. The dihedral angles between the thiophene ring and the adjacent benzene rings are 7.7 (5) and 8.8 (6)° in one molecule, and 6.8 (5) and 44.0 (7)° in the other.

Comment

Of all the photochromic compounds, diarylethene derivatives are the most promising candidates because of their good thermal stability, high sensitivity, fast response and high fatigue resistance (Irie, 2000; Tian & Yang, 2004). For application in full-colour displays and for increasing the density of optical recording media, it is desirable to develop diarylethene compounds whose ring-closure isomers show yellow or red colours (Takami & Irie, 2004). In order to achieve this goal, it is effective to attach 2-thienyl rings to the ethene unit of diarylethenes (Pu, Liu & Yan, 2005; Uchida *et al.*, 1998). To date, many diarylethene derivatives and their properties have been reported (Irie, 2000; Matsuda & Irie, 2004; Tian & Yang, 2004), and we have also reported some perfluorocyclopentene derivatives that undergo single-crystalline photochromism (Pu *et al.*, 2004; Pu, Liu, Chen *et al.*, 2005; Pu, Liu & Yan, 2005; Pu, Xiao *et al.*, 2005; Pu, Xu *et al.*, 2005; Pu, Yang *et al.*, 2005a,b; Pu, Yang & Yan, 2005). For further background information see Pu, Liu & Chen *et al.* (2005). In the present work, a new photochromic diarylethene, (Ia), was synthesized, and its crystal structure is presented here.



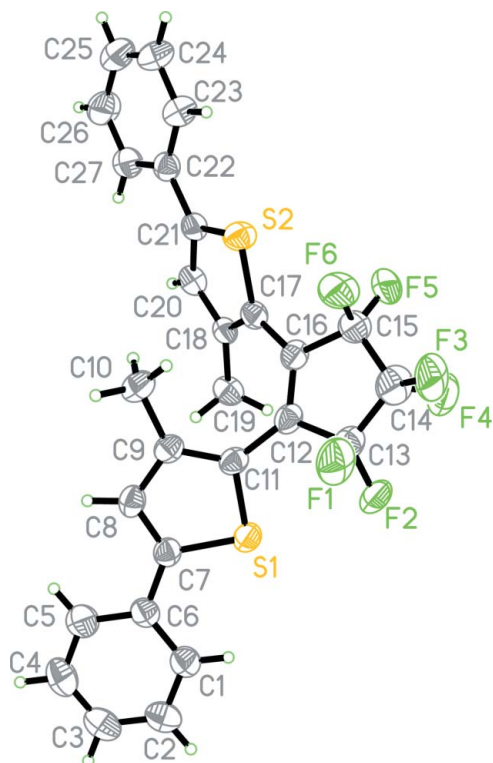


Figure 1

A view of one independent molecule of the title compound, shown with 35% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii. The minor components of disorder for the F atoms are not shown.

The two independent molecules of (*Ia*) are shown in Figs. 1 and 2, and selected geometric parameters are given in Table 1. Both molecules show a photoactive anti-parallel conformation, *i.e.* the molecules have molecular C_2 symmetry (Higashiguchi *et al.*, 2003; Matsuda & Irie, 2000; Pu *et al.*, 2003). In the hexafluorocyclopentene rings of the two molecules, the C12–C16 [1.360 (5) Å] and C39–C43 [1.355 (5) Å] bonds are clearly double bonds, while the other bonds in the ring are single. The thiophene rings are linked by the C12=C16 and C39=C43 double bonds; the methyl groups are located on different sides of the double bond and thus are *trans* with respect to the double bond. Such a conformation is crucial for the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970).

In one independent molecule of (*Ia*), the dihedral angles between the least-squares plane of the atoms of the central cyclopent-1-ene ring and those of the thiophene rings are 139.9 (9)° for S1/C7–C9/C11 and 138.2 (7)° for S2/C17–C18/C20/C21, and those between the thiophene rings and the adjacent benzene rings are 7.7 (5)° for C1–C6 and 8.8 (6)° for C22–C27. The orientations of the methyl groups at C9 and C18 are defined by the torsion angles C10–C9–C11–C12 [–2.7 (7)°] and C16–C17–C18–C19 [–1.8 (7)°]. The distance between the two reactive C atoms (C9···C18) is 3.500 (6) Å and this distance indicates that the compound can undergo photochromism in the crystalline phase (Ramarurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).

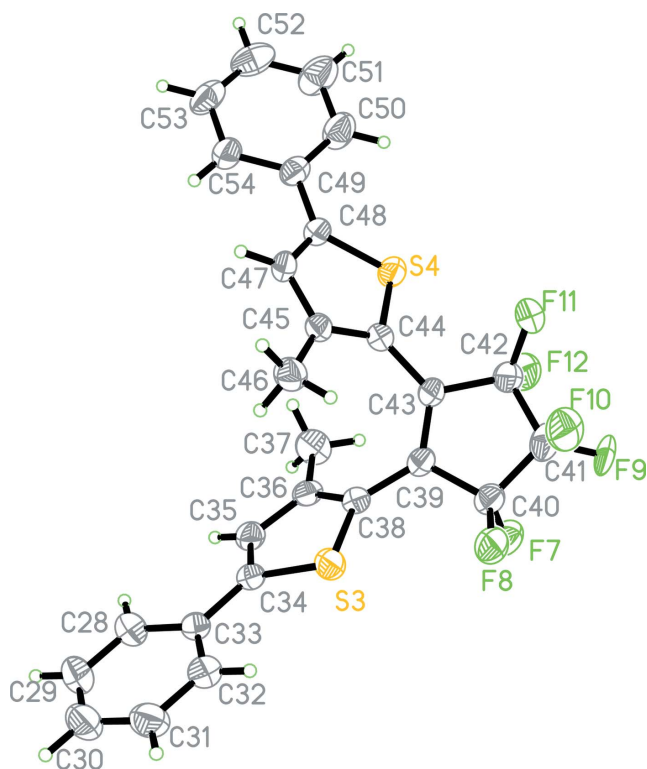


Figure 2

A view of the second molecule of the title compound, shown with 35% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii. The minor components of disorder for the F atoms are not shown.

Similarly, for the other independent molecule, the dihedral angles between the central cyclopent-1-ene ring and the thiophene rings are 134.3 (7)° for S3/C34–C36/C38 and 58.5 (8)° for S4/C44–C45/C47/C48, and those between the thiophene rings and the adjacent benzene rings are 6.8 (5)° for C28–C33 and 44.0 (7)° for C49–C54. The distance between the two reactive C atoms (C36···C45) is 3.562 (5) Å, which again is less than the value of 4.2 Å, allowing photochromism. The orientations of the methyl groups at C36 and C45 are defined by the torsion angles C37–C36–C38–C39 [3.1 (7)°] and C43–C44–C45–C46 [0.6 (7)°].

In the structure of the related isomer (Pu, Liu & Chen *et al.*, 2005), the corresponding values for the dihedral angles between the central cyclopentene ring and the thiophene rings are 44.9 (1) and 38.8 (1)°, resulting in a reactive C-atom separation of 3.430 (4) Å.

Experimental

The title compound, (*Ia*), was derived originally from 3-methylthiophene, (1). First, *n*-butyllithium in a hexane solution (12.2 ml, 2.5 M) was gradually added at 273 K to a diethyl ether solution (40 ml) containing 3-methylthiophene (3.0 g). The solution was heated for 1 h under reflux. After cooling the solution to 273 K, trimethyl borate (12.3 ml) was added. The solution was then stirred for 1 h at room temperature, and then aqueous Na₂CO₃ (20% w/w, 32 ml), 1-bromobenzene (4.4 g), tetrahydrofuran (30 ml) and tetrakis(triphenylphosphine)palladium(0) (0.45 g) were added. The mixture was heated for 15 h under reflux with vigorous stirring to give

4-methyl-2-phenylthiophene, (2), in 55% yield (2.9 g). Under an argon gas atmosphere, compound (2) was dissolved in diethyl ether (40 ml) and *n*-butyllithium in a hexane solution (6.8 ml, 2.5 M) was added at 273 K. After heating under reflux for 1 h, the reaction mixture was cooled to 273 K. Octafluorocyclopentene (1.2 ml) was added and the mixture was stirred for 1 h at this temperature. After extraction with diethyl ether and evaporation *in vacuo*, the residue was purified by column chromatography on silica gel (hexane) to give the title compound in 65% yield (2.9 g). The compound was recrystallized from hexane at room temperature to produce crystals suitable for X-ray analysis (m.p. 369–370 K). Analysis calculated for C₂₇H₁₈F₆S₂: C 62.30, H 3.49%, found: C 62.37, H 3.51%. Spectroscopic analysis: ¹H NMR (400 MHz, CDCl₃, δ, p.p.m.): 1.854 (*s*, 6H, –CH₃), 7.083 (*s*, 6H, thiophene-H), 7.322–7.340 (*d*, 2H, *J* = 7.2 Hz, benzene-H), 7.389–7.407 (*t*, 4H, *J* = 7.2 Hz, benzene-H), 7.567–7.594 (*d*, 4H, *J* = 7.2 Hz, benzene-H); ¹⁹F NMR (400 MHz, CDCl₃, δ, p.p.m.): 108.91 (4 F), 131.10 (2 F); ¹³C NMR (400 MHz, CDCl₃, δ, p.p.m.): 15.019, 125.338, 126.068, 127.973, 128.525, 132.668, 141.763, 147.463; IR (KBr, ν, cm⁻¹): 1592, 1462, 1439, 1384, 1337, 1270, 1191, 1119, 1065, 986, 845, 808, 756, 686.

Crystal data

C ₂₇ H ₁₈ F ₆ S ₂	<i>D</i> _x = 1.426 Mg m ⁻³
<i>M</i> _r = 520.53	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 3885 reflections
<i>a</i> = 18.252 (2) Å	<i>θ</i> = 2.3–21.9°
<i>b</i> = 17.012 (2) Å	<i>μ</i> = 0.28 mm ⁻¹
<i>c</i> = 16.073 (2) Å	<i>T</i> = 294 (2) K
<i>β</i> = 103.686 (3)°	Rod, yellow
<i>V</i> = 4849.0 (11) Å ³	0.24 × 0.12 × 0.10 mm
<i>Z</i> = 8	

Data collection

Bruker SMART CCD area-detector diffractometer	8541 independent reflections
<i>φ</i> and <i>ω</i> scans	4154 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.060
<i>T</i> _{min} = 0.833, <i>T</i> _{max} = 0.970	<i>θ</i> _{max} = 25.0°
24412 measured reflections	<i>h</i> = –21 → 20
	<i>k</i> = –20 → 19
	<i>l</i> = –12 → 19

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.7856P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	(Δ/σ) _{max} = 0.003
<i>S</i> = 0.99	$\Delta\rho_{max} = 0.66 \text{ e } \text{Å}^{-3}$
8541 reflections	$\Delta\rho_{min} = -0.35 \text{ e } \text{Å}^{-3}$
745 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

S1–C7	1.717 (4)	C12–C16	1.360 (5)
S1–C11	1.734 (4)	C12–C13	1.495 (6)
S2–C21	1.719 (4)	C15–C16	1.491 (6)
S2–C17	1.728 (4)	C16–C17	1.459 (5)
S3–C34	1.722 (4)	C38–C39	1.453 (5)
S3–C38	1.731 (4)	C39–C43	1.355 (5)
S4–C48	1.718 (4)	C39–C40	1.494 (5)
S4–C44	1.736 (4)	C42–C43	1.496 (5)
C11–C12	1.458 (5)	C43–C44	1.451 (5)
C10–C9–C11–C12	–2.7 (7)	C37–C36–C38–C39	3.1 (7)
C11–C12–C16–C17	–10.0 (7)	C38–C39–C43–C44	11.5 (7)
C16–C17–C18–C19	–1.8 (7)	C43–C44–C45–C46	0.6 (7)

The F atoms of the CF₂ groups are disordered and two distinct conformations were modelled. The site occupancies are 0.723 (9):0.277 (9) for the F atoms attached to C13 to C15, and 0.715 (7):0.285 (7) for the F atoms attached to C40 to C42. All H atoms were placed in calculated positions, with C–H distances of 0.93 (aromatic) and 0.96 Å (CH₃). They were included in the refinement in the riding-model approximation with *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms, and 1.5*U*_{eq}(C) for CH₃.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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