

3,3,4,4,5,5-Hexafluoro-1,2-bis[2-methyl-5-(3-methylphenyl)-3-thienyl]cyclopent-1-ene, a new photochromic diarylethene compound**Shou-Zhi Pu,* Tian-She Yang,
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Republic of ChinaCorrespondence e-mail:
pushouzhi@tsinghua.org.cn**Key indicators**Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
Disorder in main residue
 R factor = 0.041
 wR factor = 0.112
Data-to-parameter ratio = 12.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The new title symmetric photochromic diarylethene compound, $\text{C}_{29}\text{H}_{22}\text{F}_6\text{S}_2$, which contains a 3-methylphenyl substituent, adopts an antiparallel conformation in the crystal structure. The distance between the two reactive C atoms, *i.e.* the ring C atoms to which the methyl groups are attached, is 3.559 (8) Å. The dihedral angles between the central cyclopentene ring and the adjacent thiophene rings are 40.8 (7) and 45.1 (5)°, and those between the thiophene rings and the adjacent benzene rings are 3.3 (6) and 25.7 (9)°.

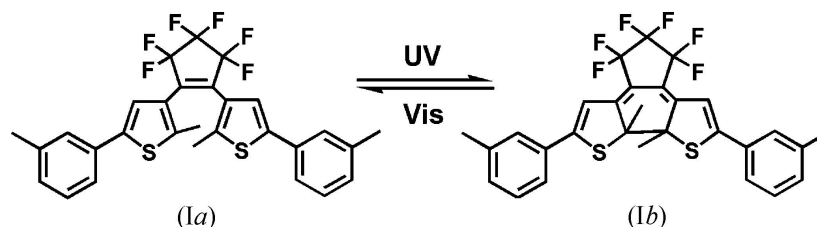
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Comment

A photochromic compound is defined as one that can be transformed reversibly between two isomers having different absorption spectra (Brown, 1971; Dürr & Bouas-Laurent, 1990). Although various types of photochromic compounds have been reported, compounds that undergo thermally stable photochromic reactions are limited to diarylethenes, fulgides and phenoxynaphthacenequinones (Kobatake & Irie, 2003). Of all the photochromic compounds, diarylethenes are the most promising candidates because of their good thermal stability, high sensitivity, fast response and high fatigue resistance (Irie, 2000; Tian & Yang, 2004). A large number of diarylethene crystal structures and their properties have already been reported (Matsuda & Irie, 2004; Morimoto *et al.*, 2004; Morimoto & Irie, 2005; Kobatake & Irie, 2004), including some structures we have determined (Pu *et al.*, 2003, 2004; Pu, Fan *et al.*, 2005; Pu, Li *et al.*, 2005; Pu, Liu *et al.*, 2005; Pu, Xu *et al.*, 2005; Pu, Xiao *et al.*, 2005; Pu, Yang, Wang *et al.*, 2005; Pu, Yang, Yan *et al.*, 2005). For further background information see Pu, Liu *et al.* (2005). A new diarylethene compound, (*Ia*), with methyl groups at the *meta*-positions of both terminal phenyl groups was synthesized, and its crystal structure is reported here.



The molecular structure of (*Ia*) is shown in Fig. 1 and selected geometric parameters are given in Table 1. The molecule contains two thiophene rings substituted by two *meta*-methylbenzene rings in a photoactive antiparallel conformation, *i.e.* the molecule has molecular C_2 symmetry. The central hexafluorocyclopentene ring is disordered over

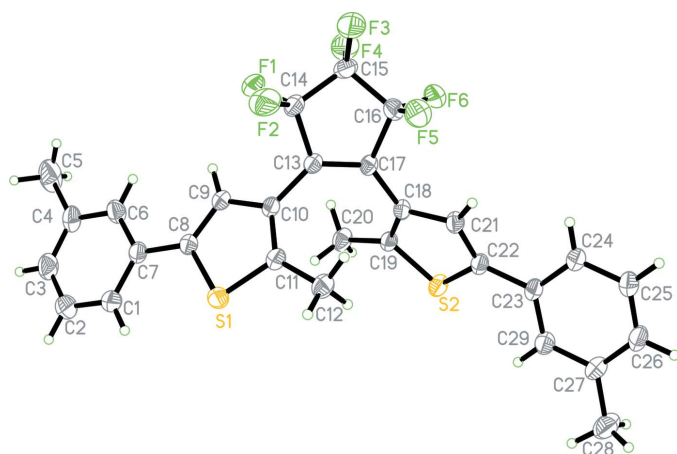


Figure 1
The molecular structure of the title compound, showing 30% probability displacement ellipsoids. Only one disorder component is shown.

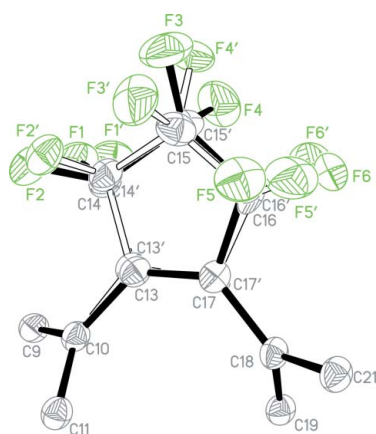


Figure 2
A view of a portion of (Ia), showing the disorder. Displacement ellipsoids are drawn at the 30% probability level, and primed (') atom labels and open bonds indicate the minor component of disorder.

two sites (see Fig. 2 and *Experimental* section). In the cyclopent-1-ene ring, the C13=C17 bond is clearly a double bond, and the other bonds in the ring are clearly single bonds (see Table 1).

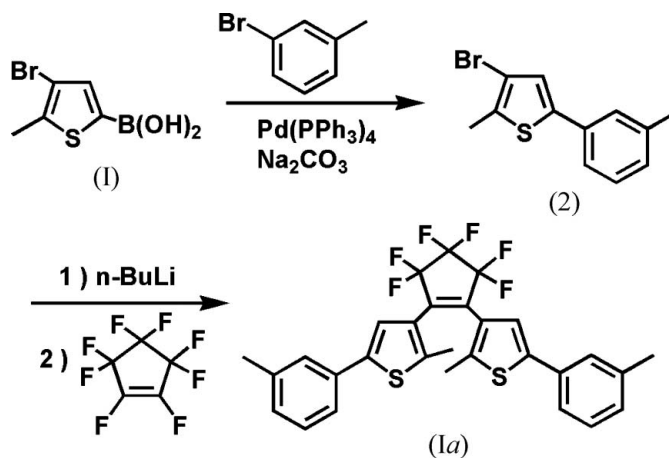
The two thiophene rings are linked by the C13=C17 double bond. The two methyl groups are located on different sides of the double bond and are thus *trans* with respect to the double bond. Such a configuration is crucial for the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970). The dihedral angles between the least-squares plane of the atoms of the central cyclopent-1-ene ring and the adjacent thiophene rings are 40.8 (7)° for S1/C8–C11 and 45.1 (5)° for S2/C18–C22, and those between thiophene rings and the adjacent benzene rings are 3.3 (6)° for C1–C4/C6/C7 and 25.7 (9)° for C23–C27/C29, respectively. The distance between the two reactive C atoms (C13...C17) is 3.559 (8) Å. This distance indicates that the crystal can undergo photochromism in the crystalline phase because the photochromic reactivity of crystals depends on the distance between the reactive C atoms being less than 4.2 Å (Rama-

murthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).

Upon irradiation with 313 nm light, colorless single crystals of (Ia) turned to blue rapidly, and the blue color remained stable in the dark. When the blue crystals were dissolved in hexane, the solution also remained blue. The absorption maximum of this solution was observed at a wavelength of 580 nm, consistent with the presence of the closed-ring isomer, (Ib). This result suggests that the title compound undergoes a photochromic reaction to produce the closed-ring molecule of (Ib) in the single-crystal phase. We have not, so far, been able to determine the crystal structure of (Ib). Furthermore, upon irradiation with wavelengths longer than 450 nm, the blue crystal changes back to colorless, and the absorption spectrum of a hexane solution of the colorless crystals was the same as that of a solution of the open-ring form, (Ia), with the absorption maximum at 279 nm.

Experimental

The title compound was originally derived from 2-methylthiophene (I). 3-Bromo-2-methyl-5-(3-methylphenyl)thiophene, (2) (3.57 g, 13.4 mmol), in 83.7% yield was synthesized by reacting (I) (3.53 g, 16.0 mmol) (Pu, Liu *et al.*, 2005) with 3-bromo-1-methylbenzene (2.74 g, 16.0 mmol) in the presence of Pd(PPh₃)₄ (0.5 g) and Na₂CO₃ (2 mol l⁻¹, 30 mmol) in tetrahydrofuran (THF, 80 ml) for 16 h at 343 K. To a stirred THF solution (60 ml) of (2) (3.57 g, 13.4 mmol) 5.4 ml of *n*-BuLi/hexane solution (2.5 mol l⁻¹, 13.5 mmol) was slowly added at 195 K under a nitrogen atmosphere. 30 min later, octafluorocyclopentene (0.91 ml, 6.7 mmol) was added and the mixture was stirred for 2 h. The reaction mixture was extracted with diethyl ether and evaporated *in vacuo*, then purified by column chromatography (petroleum ether) to give the title compound (1.25 g, 2.3 mmol) in 34.3% yield. The compound crystallized from hexane at room temperature and produced single crystals suitable for X-ray analysis. The structure of (Ia) was confirmed by melting point, element analysis and NMR (m.p. 417 K). Analysis calculated for C₂₉H₂₂F₆S₂: C 63.49, H 4.04%; found: C 63.53, H 4.09%; ¹H NMR (400 MHz, CDCl₃): δ 1.948 (*s*, 6H, –CH₃), 2.373 (*s*, 6H, –CH₃), 6.720 (*s*, 2H, thiophene-H), 7.049–7.127 (*m*, 4H, ben-H), 7.288 (*s*, 2H, ben-H), 7.338–7.380 (*t*, 2H, *J* = 8.4 Hz, ben-H); ¹⁹F NMR (400 MHz, CDCl₃): δ 109.96 (4F), 131.79 (2F).



Crystal data

C₂₉H₂₂F₆S₂
M_r = 548.59
 Monoclinic, *P*₂₁/*n*
a = 11.9825 (16) Å
b = 9.2708 (12) Å
c = 22.935 (3) Å
 β = 92.934 (2)°
V = 2544.4 (6) Å³
Z = 4

D_x = 1.432 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3825 reflections
 θ = 2.4–25.3°
 μ = 0.27 mm⁻¹
T = 294 (2) K
 Prism, colorless
 0.24 × 0.22 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.728, *T*_{max} = 0.970
 13927 measured reflections

5176 independent reflections
 3308 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.033
 θ_{max} = 26.4°
h = -14 → 14
k = -11 → 11
l = -13 → 28

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.041
wR (*F*²) = 0.112
S = 1.02
 5176 reflections
 426 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.4455P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1–C11	1.720 (2)	C16–C17	1.500 (6)
S1–C8	1.729 (2)	C13'–C17'	1.34 (2)
S2–C19	1.724 (2)	C13'–C14'	1.514 (10)
S2–C22	1.727 (2)	C14'–C15'	1.522 (10)
C13–C17	1.354 (11)	C15'–C16'	1.525 (10)
C13–C14	1.504 (5)	C16'–C17'	1.511 (10)
C14–C15	1.526 (6)	C17'–C18	1.476 (10)
C15–C16	1.518 (6)		
C6–C7–C8–S1	179.81 (19)	C10–C13'–C17'–C18	-20 (18)
C11–C10–C13–C17	40 (5)	C13'–C17'–C18–C19	66 (9)
C10–C13–C17–C18	18 (6)	C13–C17–C18–C19	35 (3)
C11–C10–C13'–C17'	59 (14)	S2–C22–C23–C24	156.91 (19)

An intermediate stage in the refinement, it was obvious from electron-density maps that the hexafluorocyclopentene ring atoms, and hence the F atom substituents, were disordered over two sites. The site occupancies refined to 0.758 (5):0.242 (5). All H atoms were placed in calculated positions, with C–H distances of 0.93 Å (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) or 1.5*U*_{eq}(C) for methyl C atoms.

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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