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## Key indicators

Single-crystal X-ray study  
 $T = 294\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.046  
 $wR$  factor = 0.147  
Data-to-parameter ratio = 13.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

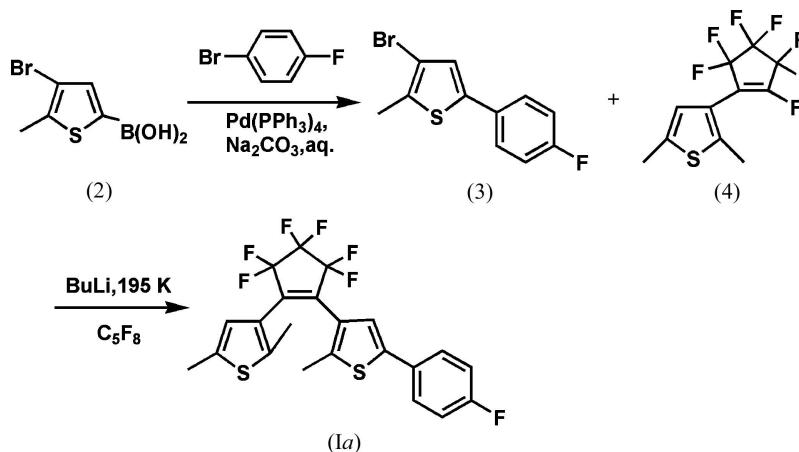
## 1-(2,5-Dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-2-[5-(4-fluorophenyl)-2-methyl-3-thienyl]cyclopent-1-ene: a new photochromic diarylethene compound

The title compound,  $\text{C}_{22}\text{H}_{15}\text{F}_7\text{S}_2$ , is a new unsymmetrical photochromic diarylethene derivative which can potentially be used for photoelectronic applications such as high-density optical recording and photoswitches. The distance between the two reactive C atoms is 3.572 (5) Å; the dihedral angles between the central cyclopentene ring and the thiophene rings are 44.7 (7) and 46.1 (7)°, and that between the benzene ring and the attached thiophene ring is 36.4 (8)°.

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## Comment

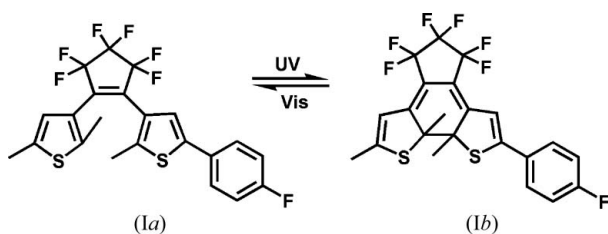
Photochromic diarylethene molecules have attracted much attention from both a fundamental as well as a practical point of view because of their potential applications as optical storage and optical switching devices (Uchida *et al.*, 2005; Irie, 2000; Tian & Yang, 2004). For further background information, see Pu, Yang & Wang & Xu (2005). This study presents the synthesis and crystal structure of the title diarylethene, (Ia).



In the hexafluorocyclopentene ring, the C7–C11 bond is clearly a double bond, being notably shorter than the other single bonds from atoms C7 and C11 (Table 1). The two planar thiophene ring systems have essentially identical geometries and the dihedral angles between the central hexafluorocyclopentene ring and the adjacent thiophene rings are 44.7 (7)° for S1/C2–C5 and 46.1 (7)° for S2/C13/C12/C15–C16. A *para*-substituted benzene ring is attached to one thiophene ring at the 5-position; the dihedral angle between this thiophene ring and the benzene ring is 36.4 (8)°. The two methyl groups are located on opposite sides of the C7=C11 double bond, as reflected by the C5–C4–C7=C11 and C7=C11–C12–C13 torsion angles (Table 1). The distance between the two reac-

tive C atoms, C5 and C13, is 3.572 (5) Å, which is short enough for the molecule to undergo a photocyclization reaction (Ramamurthy & Venkatesan, 1987; Kobatake *et al.*, 2002; Morimoto & Irie, 2006).

Upon irradiation with 254 nm light, a colorless single crystal turns red immediately and the color remains stable in the dark. On dissolving the red crystal in hexane, the solution shows a red color with the absorption maximum at 538 nm, consistent with the presence of the closed-ring isomer, (Ib), in which the methyl groups are *trans* with respect to the double bond. Upon irradiation with visible light of wavelength longer than 450 nm, the red crystal reverts to the initial colorless one, and the absorption spectrum of the hexane solution containing the colorless crystal is the same as that of a solution of the open-ring form, (Ia), with the absorption maximum at 293 nm.



## Experimental

The title diarylethene, (Ia), was prepared as outlined in the reaction scheme in the *Comment*. 3-Bromo-5-(4-fluorophenyl)-2-methylthiophene, (3) (2.7 g, 10.0 mmol), was prepared in 57% yield by reacting 3-bromo-2-methyl-5-thienylboronic acid, (2) (Pu *et al.*, 2006; Pu, Li & Wang & Zhao, 2005) (3.9 g, 17.7 mmol) with 4-bromo-1-fluorobenzene (3.1 g, 17.7 mmol) in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.7 g) and Na<sub>2</sub>CO<sub>3</sub> (2 mol l<sup>-1</sup>, 74.0 mmol) in THF (70 ml) for 12 h at 343 K. To a stirred THF solution (50 ml) of compound (3) (2.7 g, 10.0 mmol), an *n*-BuLi/hexane solution (4.0 ml, 2.5 mol l<sup>-1</sup>, 10.0 mmol) was added at 195 K under a nitrogen atmosphere. After 30 min, (2,5-dimethyl-3-thienyl)perfluorocyclopent-1-ene, (4) (Sun *et al.*, 2003) (2.9 g, 10.0 mmol), was added and the mixture was stirred for 2 h at this temperature. The reaction mixture was extracted with diethyl ether

and evaporated *in vacuo*, then purified by column chromatography (petroleum ether) to give the title compound (Ia) (2.5 g, 5.2 mmol) in 52% yield. The compound crystallized from chloroform at room temperature and produced crystals suitable for X-ray analysis. The structure of (Ia) was confirmed by melting point and NMR (m.p. 365.7 K).

## Crystal data

C <sub>22</sub> H <sub>15</sub> F <sub>7</sub> S <sub>2</sub>	<i>V</i> = 1074.1 (5) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 476.46	<i>Z</i> = 2
Triclinic, <i>P</i> $\bar{1}$	<i>D<sub>x</sub></i> = 1.473 Mg m <sup>-3</sup>
<i>a</i> = 8.602 (2) Å	Mo <i>K</i> α radiation
<i>b</i> = 11.709 (3) Å	<i>μ</i> = 0.31 mm <sup>-1</sup>
<i>c</i> = 11.984 (3) Å	<i>T</i> = 294 (2) K
<i>α</i> = 105.472 (4)°	Prism, colorless
<i>β</i> = 94.977 (4)°	0.24 × 0.22 × 0.20 mm
<i>γ</i> = 109.737 (4)°	

## Data collection

Bruker SMART CCD area-detector diffractometer	5439 measured reflections
<i>φ</i> and <i>ω</i> scans	3763 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2668 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>T<sub>min</sub></i> = 0.653, <i>T<sub>max</sub></i> = 1.000 (expected range = 0.613–0.939)	<i>R<sub>int</sub></i> = 0.017
	<i>θ<sub>max</sub></i> = 25.0°

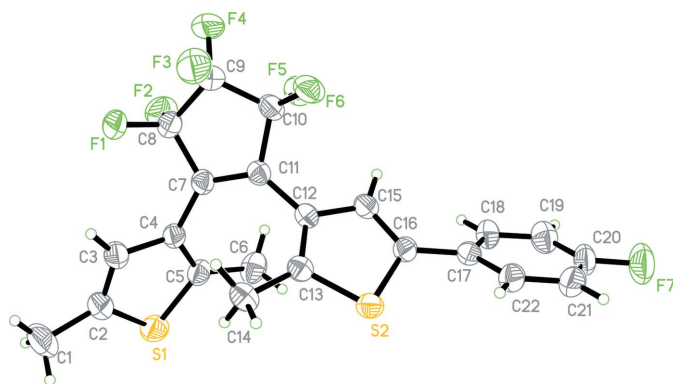
## Refinement

Refinement on <i>F</i> <sup>2</sup>	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F<sub>o</sub></i> <sup>2</sup> ) + (0.0679 <i>P</i> ) <sup>2</sup> + 0.5304 <i>P</i> ]
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.046	where <i>P</i> = ( <i>F<sub>o</sub></i> <sup>2</sup> + 2 <i>F<sub>c</sub></i> <sup>2</sup> )/3
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.147	(Δ/σ) <sub>max</sub> = 0.001
<i>S</i> = 1.07	Δρ <sub>max</sub> = 0.20 e Å <sup>-3</sup>
3763 reflections	Δρ <sub>min</sub> = -0.28 e Å <sup>-3</sup>
283 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

S1–C2	1.714 (4)	C7–C8	1.512 (5)
S1–C5	1.724 (3)	C8–C9	1.530 (5)
S2–C13	1.727 (3)	C9–C10	1.515 (5)
S2–C16	1.729 (3)	C10–C11	1.505 (4)
C7–C11	1.347 (4)		
C5–C4–C7–C11	-46.2 (5)	C8–C7–C11–C10	-5.5 (4)
C3–C4–C7–C8	-50.8 (5)	C9–C10–C11–C7	19.0 (4)
C7–C8–C9–C10	20.9 (4)	C7–C11–C12–C13	-42.8 (5)
C8–C9–C10–C11	-24.0 (3)	C15–C16–C17–C18	-37.9 (5)



**Figure 1**

The molecular structure of compound (Ia), showing 35% probability ellipsoids and the atomic numbering scheme. H atoms are shown as spheres of arbitrary radii.

All H atoms were placed in calculated positions, with C–H = 0.93 (aromatic) and 0.96 Å (CH<sub>3</sub>), and included in the refinement in the riding-model approximation, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(carrier atom) for aromatic and 1.5*U*<sub>eq</sub>(carrier) for methyl H 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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## References

- Bruker (1997). *SMART* (Version 5.0), *SAINTE* (Version 4.0) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Irie, M. (2000). *Chem. Rev.* **100**, 1685–1716.
- Kobatake, S., Uchida, K., Tsuchida, E. & Irie, M. (2002). *Chem. Commun.* pp. 2804–1805.
- Morimoto, M. & Irie, M. (2006). *Chem. Eur. J.* **12**, 4275–4282.
- Pu, S.-Z., Li, G.-Z., Wang, R.-J. & Zhao, J.-Q. (2005). *Acta Cryst.* **E61**, o4246–o4249.
- Pu, S.-Z., Li, G.-Z., Wang, R.-J. & Zhao, J.-Q. (2006). *Acta Cryst.* **E62**, o150–o152.
- Pu, S.-Z., Yang, T.-S., Wang, R.-J. & Xu, J.-K. (2005). *Acta Cryst.* **C61**, o568–o570.
- Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sun, F., Zhang, F.-S., Guo, H.-B., Zhou, X.-H., Wang, R.-J. & Zhao, F.-Q. (2003). *Tetrahedron*, **59**, 7615–7621.
- Tian, H. & Yang, S.-J. (2004). *Chem. Soc. Rev.* **33**, 85–97.
- Uchida, K., Saito, M., Murakami, A., Kobayashi, T., Nakamura, S. & Irie, M. (2005). *Chem. Eur. J.* **11**, 534–542.