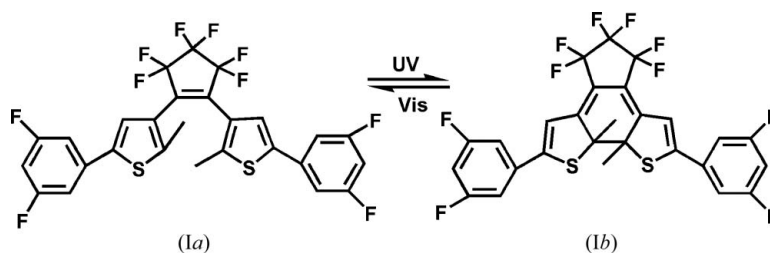


1,2-Bis[5-(3,5-difluorophenyl)-2-methyl-3-thienyl]-3,3,4,4,5,5-hexafluorocyclopent-1-ene: a new photochromic diarylethene compound**Gang Liu,^a Tong Zheng,^b
Shou-Zhi Pu^{a*} and Jing-Kun Xu^a**^aJiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China, and ^bDepartment of Technology, Guangzhou Exit and Entry Frontier Inspection General Station, Guangzhou 510660, People's Republic of ChinaCorrespondence e-mail:
pushouzhi@tsinghua.org.cn**Key indicators**Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.040
 wR factor = 0.112
Data-to-parameter ratio = 10.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{27}\text{H}_{14}\text{F}_{10}\text{S}_2$, is a new symmetrical photochromic diarylethene derivative which can be used potentially for optical recording media and other optoelectronic device materials. The distance between the two reactive C atoms is 3.571 (4) Å. The dihedral angles between the thiophene rings and the attached benzene rings are 15.2 (6) and 24.7 (7)°.

Received 7 June 2006
Accepted 12 June 2006**Comment**

The development of photochromic materials is an ever-growing field because of new potential applications of this type of materials (Guirado *et al.*, 2005). Of all the photochromic materials, diarylethenes are the most promising candidates owing to their good thermal stability and remarkable fatigue resistance (Irie, 2000; Tian & Yang, 2004). For further background information, see Pu *et al.* (2005). The present paper presents the synthesis and crystal structure of the title new photochromic diarylethene, (Ia), with two F atoms on both terminal benzene rings.



The molecular structure of (Ia) is shown in Fig. 1. Relevant bond lengths and torsion angles are given in Table 1. As shown in Fig. 1, the molecule has approximately local twofold rotation symmetry, with the two thiophene rings in a photoactive antiparallel conformation. The central perfluorocyclopentene ring adopts an envelope conformation, with the flap atom equally disordered over two sites (C14 and C14') and concomitant disorder of the attached F atoms (Fig. 2). The two methyl groups (C11 and C19) are located on different sides of the C9–C12=C16–C17 plane, reflected in the torsion angles C10–C9–C12=C16 and C12=C16–C17–C18 (Table 1). The dihedral angles between the thiophene rings and the adjacent benzene rings are 15.2 (6)° for C1–C6 and 24.7 (7)° for C22–C27. The distance between the two reactive C atoms (C10 and C18) is 3.571 (4) Å, suggesting that this crystal can undergo photochromism in the crystalline phase (Rama-murthy & Venkatesan, 1987; Kobatake *et al.*, 2004).

In fact, the crystal of (Ia) shows photochromism in accordance with the expected ring closure, to form (Ib). Upon

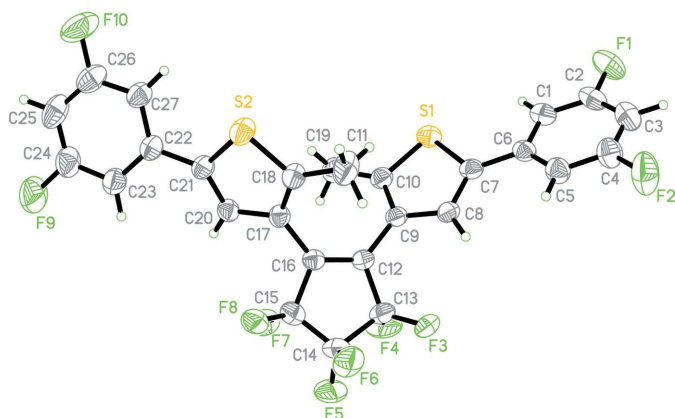


Figure 1
The structure of compound (1a), with 35% probability ellipsoids, showing the atomic numbering scheme. For clarity, only one component of the disordered cyclopentene ring is shown.

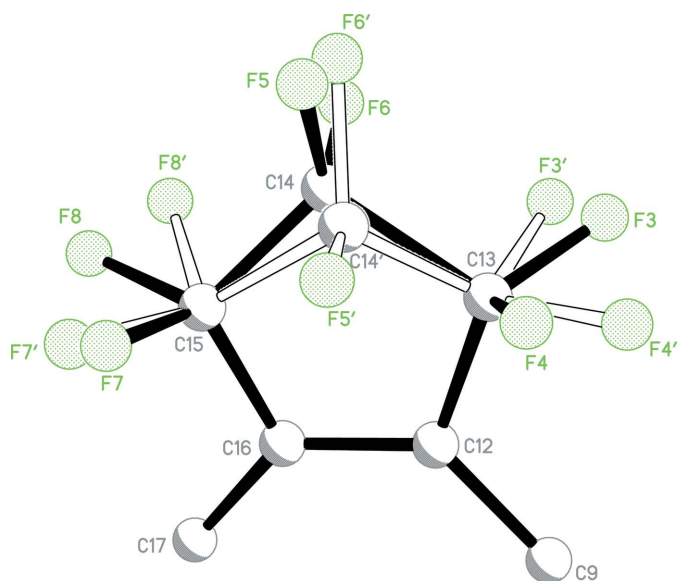


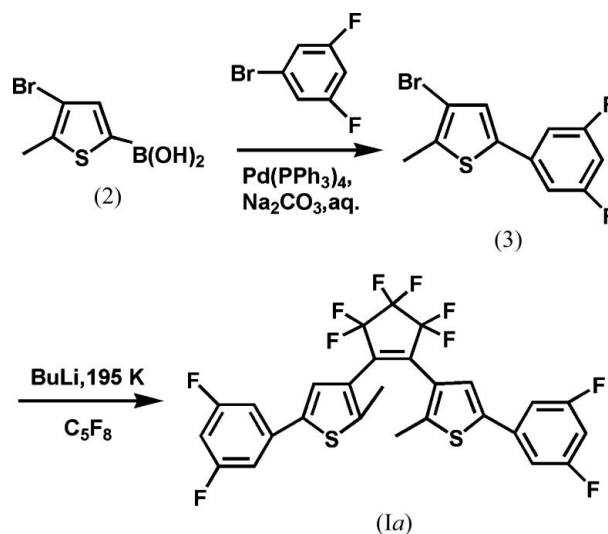
Figure 2
A ball-and-stick diagram, showing the disorder of the cyclopentene ring.

irradiation with 313 nm light, the colourless single crystal turned blue rapidly, and the colour remained stable in the dark. When the blue crystal was dissolved in hexane, the solution also showed a blue colour (absorption maximum at 581 nm). This phenomenon suggests that the title compound can undergo a photochromic reaction and produce the closed-ring molecule of (1b) in the single crystalline phase. Upon irradiation with visible light having a wavelength longer than 460 nm, the blue crystal can return to its initial colourless state, and the absorption spectrum of the hexane solution is the same as that of the open-ring form, (1a), with the absorption maximum at 293 nm.

Experimental

Compound (1a) was synthesized as follows. First, 3-bromo-2-methyl-5-(3,5-difluorophenyl)thiophene, (3) (2.74 g, 9.5 mmol), was prepared in 73% yield by reacting 3-bromo-2-methyl-5-thienylboronic acid (2)

(2.87 g, 13 mmol) (Ern *et al.*, 1999; Pu *et al.*, 2005) with 1,3-difluoro-5-bromobenzene (2.51 g, 13 mmol) in the presence of tetrakis(triphenylphosphine)palladium(0) (0.5 g) and Na_2CO_3 (5.3 g, 50 mmol) in THF (80 ml containing 10% water) for 16 h at 343 K. Under an argon gas atmosphere, compound (3) (2.31 g, 8 mmol) was dissolved in THF (55 ml) and *n*-butyl lithium hexane solution (3.2 ml of 2.5 mol l^{-1}) was added at 195 K. Stirring was continued for 30 min at this low temperature; octafluorocyclopentene (0.55 ml, 4 mmol) was added and the mixture was stirred for 2 h at this temperature. After extracting with diethyl ether and evaporation *in vacuo*, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to give (1a) (yield 0.97 g, 41%). Crystals suitable for X-ray analysis were grown from a chloroform solution by slow evaporation at room temperature (m.p. 430.4 K).



Crystal data

$\text{C}_{27}\text{H}_{14}\text{F}_{10}\text{S}_2$
 $M_r = 592.50$
Monoclinic, $P2_1/n$
 $a = 13.582(2) \text{ \AA}$
 $b = 11.552(2) \text{ \AA}$
 $c = 16.127(3) \text{ \AA}$
 $\beta = 99.019(3)^\circ$
 $V = 2499.1(8) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.575 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 0.30 \text{ mm}^{-1}$
 $T = 294(2) \text{ K}$
Prism, colourless
 $0.24 \times 0.20 \times 0.14 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.889$, $T_{\max} = 1.000$

12416 measured reflections
4401 independent reflections
2811 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.112$
 $S = 1.06$
4401 reflections
417 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.5704P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C14—C15	1.449 (9)	C12—C16	1.343 (3)
C14—C13	1.617 (9)	C12—C13	1.501 (4)
C14'—C13	1.434 (9)	C15—C16	1.493 (4)
C14'—C15	1.619 (9)		
C1—C6—C7—S1	−15.2 (3)	C13—C14'—C15—C16	19.7 (5)
C10—C9—C12—C16	−46.3 (4)	C13—C12—C16—C15	−5.5 (3)
C15—C14'—C13—C12	−23.1 (5)	C14—C15—C16—C12	20.7 (4)
C16—C12—C13—C14'	19.4 (4)	C14'—C15—C16—C12	−8.6 (4)
C16—C12—C13—C14	−9.9 (4)	C12—C16—C17—C18	−44.7 (4)
C15—C14—C13—C12	21.5 (5)	S2—C21—C22—C27	24.3 (3)
C13—C14—C15—C16	−25.0 (4)		

The C14 atom is disordered over two sites (C14 and C14'), correlated with F atoms F5/F6 and F5'/F6', corresponding to the two orientations of the cyclopentene ring in a C14-envelope conformation. The occupancy of each disordered atom is 0.5. Restraints were used to keep the C14—F, C14'—F and F···F separations in agreement with the C—F geometry at the C13 and C15 sites. 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 $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$ for aromatic or $1.5U_{\text{eq}}(\text{C})$ for methyl groups.

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*.

This work was partially supported by the Projects of the Natural Science Foundation of Jiangxi, China (grant No. 050017), and the Science Funds of the Education Office of Jiangxi, China (grant No. [2005] 140).

References

- Bruker (1997). *SMART* (Version 5.0), *SAINT* (Version 4.0) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Ern, J., Bens, A. T., Martin, H.-D., Mukamel, S., Schmid, D., Tretiak, S., Tsiper, E. & Krysch, C. (1999). *Chem. Phys.* **246**, 115–125.
- Guirado, G., Coudret, C., Hliwa, M. & Launay, J.-P. (2005). *J. Phys. Chem. B*, **109**, 17445–17459.
- Irie, M. (2000). *Chem. Rev.* **100**, 1685–1716.
- Kobatake, S., Kuma, S. & Irie, M. (2004). *Bull. Chem. Soc. Jpn.* **77**, 945–951.
- 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.
- Tian, H. & Yang, S.-J. (2004). *Chem. Soc. Rev.* **33**, 85–97.