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2-[5-(3-Cyanophenyl)-2-methyl-3-thienyl]-1-(2,5-dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene: a new photochromic diarylethene compound

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The title compound, $C_{23}H_{15}F_6NS_2$ is a new non-symmetric photochromic dithienylethene. The molecule adopts a photo-active antiparallel conformation, the distance between the two reactive C atoms being 3.552 (6) Å. The dihedral angles between the cyclopentene ring and the two thiophene rings are 44.0 (5) and 45.8 (5)°.

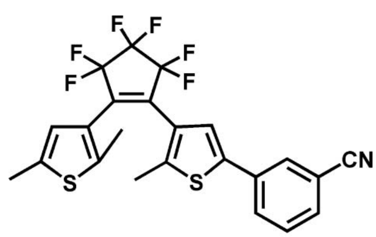
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.044
wR factor = 0.140
Data-to-parameter ratio = 11.4

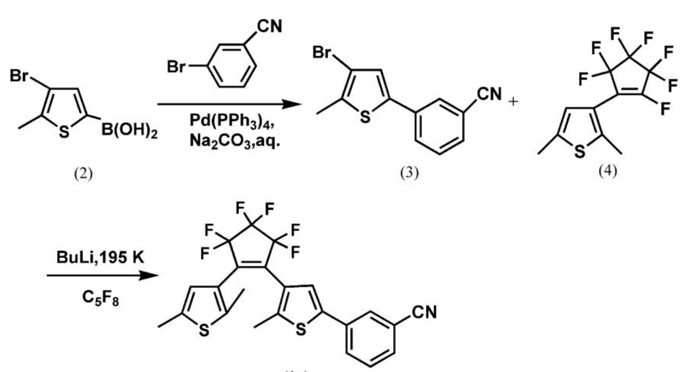
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The design and synthesis of new photochromic diarylethene compounds is an area of intense research because of their widespread potential application as optical memories and photoswitches (Pu, Li *et al.*, 2006; Pu, Yang *et al.*, 2006; Pu, Zheng *et al.*, 2006) and their good thermal stability and fatigue resistance (Irie, 2000; Tian & Yang, 2004; Morimoto *et al.*, 2006). For further background information, see Pu, Yang *et al.* (2005). We present here the structure of the title compound, (I) (Fig. 1). Some related compounds have been reported previously (Pu, Zheng *et al.*, 2006; Wen *et al.*, 2006).



(I)



In the cyclopent-1-ene ring of (I), the C7—C11 bond is clearly a double bond, being significantly shorter than the other single bonds from atoms C7 and C11 (Table 1). The two independent thiophene ring systems have essentially identical geometries and the dihedral angles between the cyclopentene ring and the adjacent thiophene rings are 45.8 (5)° for S1/C2–

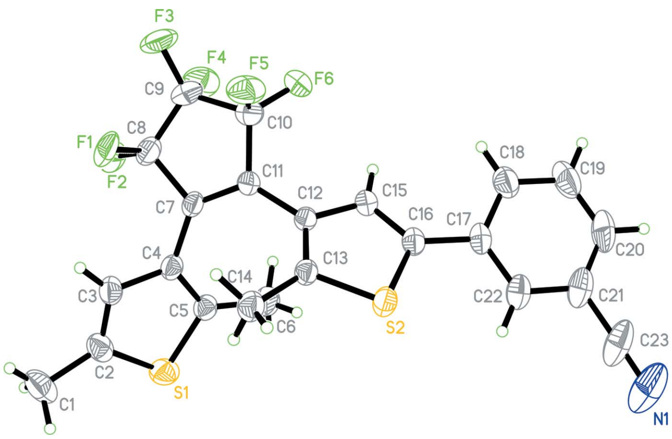


Figure 1
The molecular structure of (I), with 35% probability displacement ellipsoids, showing the atomic numbering scheme. The minor components of the disordered F atoms are not shown.

C5 and 44.0 (5)° for S2/C13/C12/C15/C16. A *meta*-cyanophenyl substituent is attached to one of the thiophene rings. The dihedral angle between the thiophene ring and the adjacent benzene ring is 24.4 (3)°.

In this molecule, the thiophene methyl substituents are located on opposite sides of the alkene plane, as reflected in the torsion angles (Table 1), and are *trans* with respect to the C7=C11 double bond. This conformation is crucial to the photochromic and photo-induced properties (Woodward & Hoffmann, 1970). The distance between the potentially photoactive methyl-substituted C atoms (C5···C13) is 3.552 (6) Å. It has been shown that photochromism similar to that described below is likely in the crystalline phase when this distance is < 4.2 Å and the molecule is packed in an anti-parallel manner in the crystalline phase (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).

Upon irradiation with 297 nm light, a colourless crystal of (I) rapidly turns red, and this colour remains stable in the dark. On dissolving the red crystal in hexane, the solution also shows a red colour, with an absorption maximum at 544 nm, suggesting the presence of a closed-ring isomer. Hence (I) undergoes a photochromic reaction to produce a closed-ring molecule in the crystalline phase. On irradiation at wavelengths longer than 450 nm, the red crystal reverts to colourless, with an absorption spectrum in hexane identical to that of the colourless crystals, indicating a return to the open-ring isomer, (I) (absorption maximum 294 nm).

Experimental

Compound (I) was prepared as outlined in the second scheme. 3-Bromo-2-methyl-5-(3-cyanophenyl)thiophene, (3) (5.5 g, 19.8 mmol), was prepared in 65% yield by reacting 3-bromo-2-methyl-5-thienylboronic acid, (2) (Pu, Li *et al.*, 2005; 2006) (6.8 g, 30.6 mmol), with 3-bromo-1-cyanobenzene (5.6 g, 30.6 mmol) in the presence of $Pd(PPh_3)_4$ (0.9 g) and aqueous Na_2CO_3 (2 *M*, 100.0 mmol) in tetrahydrofuran (THF; 90 ml) for 12 h at 343 K. To a stirred THF solution (50 ml) of compound (3) (1.5 g, 5.4 mmol), an *n*-BuLi–hexane solution (3.4 ml, 1.6 *M*, 5.4 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) (1.7 g, 5.4 mmol), was added and the mixture was stirred for 2 h at this temperature. The reaction mixture was extracted with ethyl ether and evaporated *in vacuo*, then purifed by column chromatography (silica, petroleum ether) to give the title compound, (I) (1*a* in the second scheme) (1.3 g, 2.6 mmol), in 49% yield. The compound was crystallized from chloroform at room temperature to produce crystals suitable for X-ray analysis. The structure of (I) was confirmed by melting point and NMR analysis (m.p. 411.8 K).

Crystal data

$C_{23}H_{15}F_6NS_2$
$M_r = 483.48$
Monoclinic, $P2_1/c$
$a = 16.598$ (4) Å
$b = 8.7178$ (18) Å
$c = 17.250$ (4) Å
$\beta = 116.899$ (4)°
$V = 2226.1$ (8) Å^3
$Z = 4$
$D_x = 1.443$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 294$ (2) K
Block, colourless
0.18 × 0.14 × 0.12 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.731$, $T_{max} = 1.000$
10978 measured reflections
3935 independent reflections
2197 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 25.0$°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.140$
$S = 1.02$
3935 reflections
346 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.2736P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.720 (4)	C7—C8	1.502 (4)
S1—C5	1.723 (3)	C8—C9	1.491 (5)
S2—C16	1.727 (4)	C9—C10	1.504 (5)
S2—C13	1.727 (3)	C10—C11	1.500 (5)
C7—C11	1.347 (4)		
C7—C4—C5—C6	2.2 (6)	C7—C11—C12—C13	−44.7 (5)
C5—C4—C7—C11	−44.3 (6)	C11—C12—C13—C14	−1.9 (5)
C4—C7—C11—C12	−7.1 (6)		

The F atoms are disordered over two possible sets of positions. Based on the anisotropic refinement, the site occupancies of atoms F1–F6 and F1′–F6′ were fixed at 0.6 and 0.4, respectively. All H atoms were placed in calculated positions, with C—H distances of 0.93 Å (aromatic) and 0.96 Å (CH_3). They were included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ 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*.

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