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Key indicators

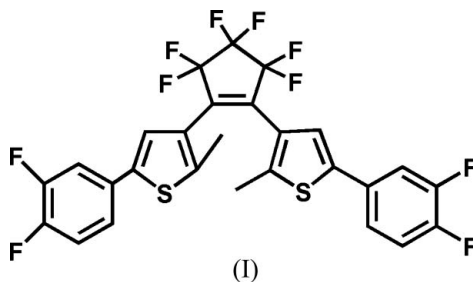
Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.052
 wR factor = 0.152
Data-to-parameter ratio = 12.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.1,2-Bis[5-(3,4-difluorophenyl)-2-methyl-3-thienyl]-
3,3,4,4,5,5-hexafluorocyclopent-1-ene

The title compound, $\text{C}_{27}\text{H}_{14}\text{F}_{10}\text{S}_2$, is a symmetrical photochromic diarylethene derivative and crystallizes with two independent molecules in the asymmetric unit. Both adopt a photoactive antiparallel conformation. The distances between the potentially photochemically active methyl-substituted C atoms on each thiophene ring in the two molecules are 3.556 (3) and 3.853 (3) Å. The photochromic behavior of the crystals is described.

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Comment

Photochromic dithienylethenes which undergo reversible photocyclization and cycloreversion reactions between open and closed-ring forms are regarded as promising materials for optical data storage and switches because of their good thermal stabilities and remarkable fatigue resistance (Irie, 2000; Tian & Yang, 2004; Jeong *et al.*, 2006). We present here the structure of the title compound, (I) (Fig. 1 and Table 1). Some related compounds have been reported previously (Pu *et al.* 2005; Liu, Xu *et al.*, 2006; Liu, Zheng *et al.*, 2006).



There are two unique molecules in the asymmetric unit; each comprises two thiophene rings substituted by two 3,4-difluorobenzene rings in an antiparallel conformation, with approximately twofold local molecular symmetry. The thiophene rings also bind to the alkene C atoms, C12, C16, C39 and C43, of the five-membered hexafluorocyclopentene rings (Table 1). In each 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 double bonds in both molecules. This conformation for (I) is crucial to its photochromic and photo-induced properties (Woodward & Hoffmann, 1970).

The two planar thiophene ring systems have similar geometry in each molecule, with dihedral angles between the cyclopentene ring and thiophene rings of 159.0 (7)° (S1/C7–C10) and 132.1 (7)° (S2/C18/C17/C20/C21) in one molecule and 120.1 (7)° (S3/C45/C44/C47/C48) and 93.3 (7)° (S4/C34–C37) in the other. The angles between the thiophene and

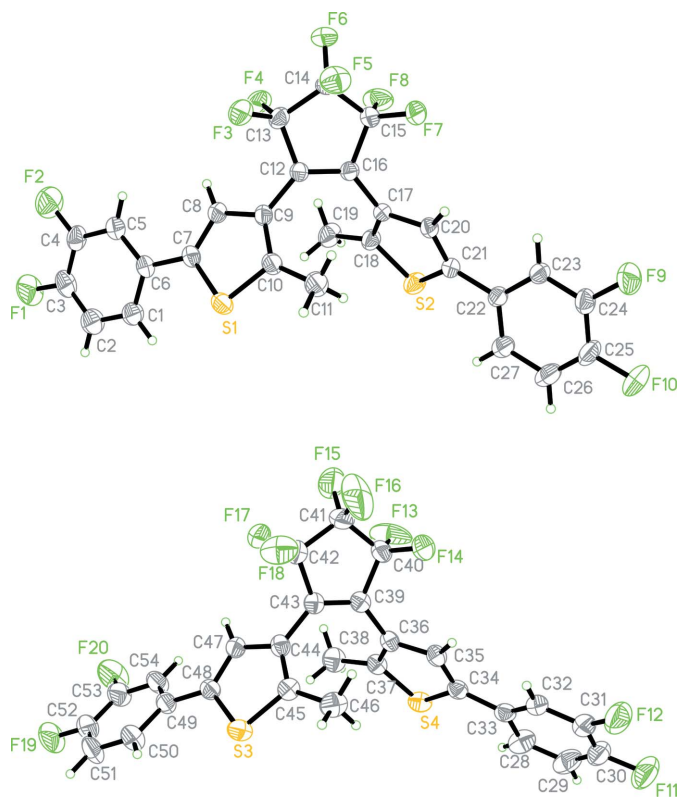


Figure 1
The structure of the two independent molecules in the asymmetric unit of (I), with 35% probability displacement ellipsoids, showing the atomic numbering scheme.

adjacent benzene rings are $51.9(7)^\circ$ (C1–C6), $28.1(7)^\circ$ (C22–C27), $26.5(7)^\circ$ (C49–C54) and $6.1(7)^\circ$ (C28–C33). The distances between the potentially photoactive methyl-substituted C atoms (C10...C18 and C37...C45) in each molecule are $3.556(3)$ and $3.853(3)$ Å, respectively. It has been shown that photochromism similar to that described below is likely in the crystalline phase when this distance is <4.2 Å (Ramarathu & Venkatesan, 1987; Kobatake *et al.*, 2004; Morimoto & Irie, 2006).

When (I) was irradiated with 254 nm light, the colorless crystals rapidly turned blue; this color remained stable in the dark. Dissolution in hexane gave a blue solution (absorption maximum 572 nm), consistent with the presence of the ring-closed isomer. Hence (I) undergoes a photochromic reaction to produce the ring-closed molecule in the crystalline phase. On irradiation at wavelengths greater than 500 nm, the blue crystal reverts to colorless, with an absorption spectrum in hexane identical to that of the colorless crystals, indicating a return to the open-ring form, (I) (absorption maximum 272 nm).

Experimental

The title compound, (I), was prepared in 25% total yield by literature methods (Liu, Xu *et al.*, 2006; Liu, Zheng *et al.*, 2006) using 1,2-difluoro-4-bromobenzene as the starting material. Crystals suitable for X-ray analysis were grown from a chloroform solution by slow evaporation at room temperature (m.p. 407 K).

Crystal data

$C_{27}H_{14}F_{10}S_2$
 $M_r = 592.50$
 Monoclinic, $P2_1/c$
 $a = 19.126(4)$ Å
 $b = 12.098(3)$ Å
 $c = 21.528(5)$ Å
 $\beta = 93.876(4)^\circ$
 $V = 4969.8(18)$ Å³

$Z = 8$
 $D_x = 1.584$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.31$ mm⁻¹
 $T = 294(2)$ K
 Prism, colorless
 $0.24 \times 0.22 \times 0.16$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.829$, $T_{\max} = 1.000$

24860 measured reflections
 8768 independent reflections
 5160 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.152$
 $S = 1.01$
 8768 reflections
 707 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 3.5743P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.78$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–C10	1.710 (4)	C12–C13	1.505 (5)
S1–C7	1.720 (4)	C13–C14	1.532 (5)
S2–C21	1.724 (4)	C14–C15	1.525 (5)
S2–C18	1.724 (4)	C15–C16	1.510 (5)
S3–C45	1.720 (4)	C39–C43	1.331 (5)
S3–C48	1.728 (4)	C39–C40	1.497 (5)
S4–C37	1.722 (4)	C40–C41	1.502 (6)
S4–C34	1.732 (4)	C41–C42	1.523 (6)
C12–C16	1.343 (5)	C42–C43	1.509 (5)
C8–C9–C10–S1	0.2 (4)	C12–C16–C17–C18	52.6 (6)
C10–C9–C12–C16	45.1 (6)	C37–C36–C39–C43	59.4 (6)
C10–C9–C12–C13	–140.1 (4)	C35–C36–C39–C40	58.4 (5)
C8–C9–C12–C13	42.4 (5)	C39–C40–C41–C42	–1.7 (5)
C16–C12–C13–C14	–18.5 (4)	C40–C41–C42–C43	1.8 (5)
C12–C13–C14–C15	24.5 (4)	C40–C39–C43–C44	–179.7 (4)
C13–C14–C15–C16	–22.2 (4)	C40–C39–C43–C42	0.2 (5)
C13–C12–C16–C15	4.1 (4)	C41–C42–C43–C39	–1.2 (5)
C14–C15–C16–C12	12.0 (4)	C39–C43–C44–C45	59.1 (6)

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 set equal to $1.2U_{\text{eq}}(\text{C})$ for aromatic and $1.5U_{\text{eq}}(\text{C})$ for CH₃ 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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