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

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.010 Å
Disorder in main residue
R factor = 0.067
wR factor = 0.156
Data-to-parameter ratio = 12.4

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

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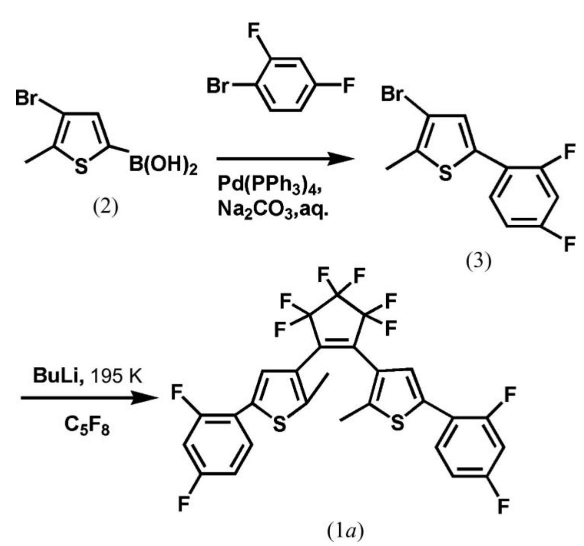
The title compound, $C_{27}H_{14}F_{10}S_2$, is a new symmetrical photochromic diarylethene derivative which can be used potentially for optical recording media and other optoelectronic device materials. There are two independent molecules in the asymmetric unit. Both adopt a photoactive antiparallel conformation. The distances between the reactive C atoms in the two molecules are 3.664 (7) and 3.621 (7) Å. For one molecule, the dihedral angles between the central cyclopentene ring and the thiophene rings are 46.4 (9) and 51.9 (9)°, and those between the thiophene rings and the adjacent benzene rings are 2.1 (8) and 18.9 (8)°. For the other molecule, the dihedral angles between the central cyclopentene ring and the thiophene rings are 134.5 (9) and 44.3 (9)°, and those between the thiophene rings and the adjacent benzene rings are 2.7 (8) and 27.7 (8)°.

Comment

Photochromic diarylethene crystals are very interesting not only in designing new materials for optical data storage, but also because the photoinduced molecular transformations might be used to gain control over other physical properties in the solid state (Kobatake & Irie, 2004; Chai *et al.*, 2005). To date, many diarylethenes have been reported (Irie, 2000; Matsuda & Irie, 2004; Tian & Yang, 2004; Pu, Li *et al.*, 2006; Pu, Yang *et al.*, 2006; Yang *et al.*, 2006). For further background information, see Pu, Yang *et al.* (2005). The present paper presents the crystal structure of the title compound, (1*a*).



The molecular structure of (1*a*) is shown in Fig. 1. Relevant bond lengths and torsion angles are given in Table 1. There are

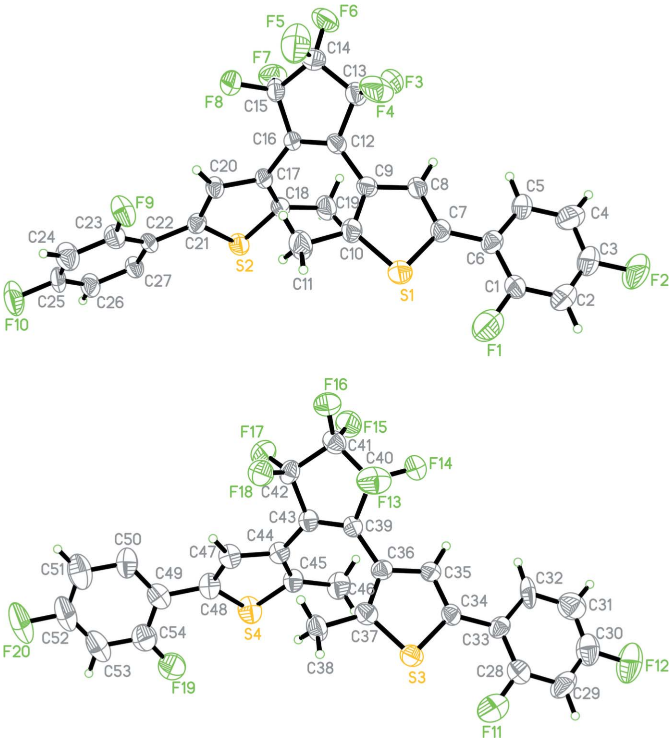


Figure 1
The structures of the two independent molecules in the asymmetric unit of (1*a*), with 35% probability displacement ellipsoids, showing the atomic numbering scheme. The minor components of disorder for F atoms are not shown.

two molecules in the asymmetric unit and both of them have a photoactive antiparallel conformation. The F atoms (F9 and F19) are disordered over one *ortho* position of one benzene ring of each molecule (Fig. 1). In the central cyclopentene ring of the two molecules, the C12═C16 and C39═C43 bonds are clearly double bonds and the other bonds to atoms C12, C16, C39 and C43 are clearly single bonds (Table 1).

For one molecule, the two methyl groups are located on different sides of the C12═C16 bond, reflected in the torsion angles C10—C9—C12═C16 and C12═C16—C17—C18, and are thus *trans* with respect to the double bond. Such a conformation is crucial to its photochromic and photoinduced properties (Woodward & Hoffmann, 1970). The two independent planar thiophene ring systems have essentially identical geometry, and the dihedral angles between the central cyclopentene ring and the thiophene rings are 46.4 (9)° for S1/C7–C10 and 51.9 (9)° for S2/C18/C17/C20/C21, while those between the thiophene rings and the adjacent benzene rings are 2.1 (8)° for C1–C6 and 18.9 (8)° for C22–C27. For the other molecule, the two methyl groups are also located on different sides of C12=C16 bond, reflected in the torsion angles C37—C36—C39═C43 and C39═C43—C44—C45. The dihedral angles between the central cyclopentene ring and the thiophene rings are 134.5 (9)° for S3/C34–C37 and 44.3 (9)° for S4/C45/C44/C47/C48, and those between the thiophene rings and the adjacent benzene rings are 2.7 (8)° for C28–C33 and 27.7 (8)° for C49–C54. The distances between the reactive C atoms (C10···C18 and C37···C45) in the two molecules are 3.664 (7) and 3.621 (7) Å. This distance demonstrates that this crystal can undergo photochromism in the crystalline phase (Ramamurthy & Venkatesan, 1987; Kobatake *et al.*, 2004).

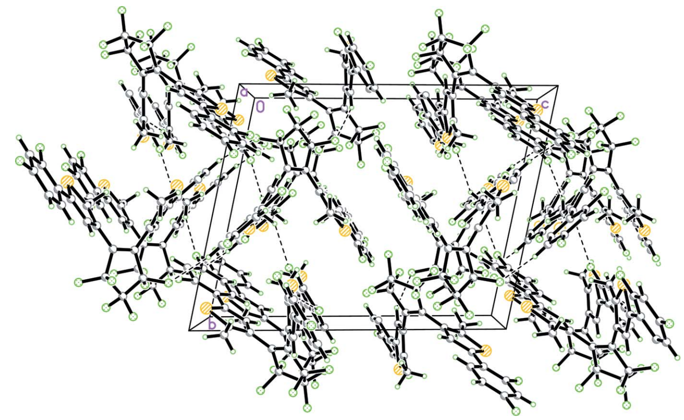


Figure 2
A packing diagram for (I*a*), viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

Experimental

Compound (1*a*) was derived originally from 2-methylthiophene. First, 3-bromo-2-methyl-5-(2,4-difluorophenyl)thiophene, (3) (2.65 g, 9.1 mmol), was prepared in 70% yield by reacting 2-bromo-2-methyl-5-thienylboronic acid (2) (2.87 g, 13 mmol) (Miyasaka *et al.*, 1997; Pu, Liu *et al.*, 2005) with 1,5-difluoro-2-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 (35 ml) and *n*-butyl lithium hexane solution (3.2 ml of 2.5 mol l^{-1}) was added at 273 K. Stirring was continued for 30 min at this low temperature, and then octafluorocyclopentene (0.55 ml, 4 mmol) was added and 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 (hexane) to give 0.95 g of the title compound in 40% yield. Crystals suitable for X-ray analysis were grown from a chloroform solution by slow evaporation at room temperature (m.p. 374 K).

Crystal data

$C_{27}H_{14}F_{10}S_2$	$V = 2525.6$ (18) Å^3
$M_r = 592.50$	$Z = 4$
Triclinic, $P\overline{1}$	$D_x = 1.558$ Mg m^{-3}
$a = 11.873$ (5) Å	Mo $K\alpha$ radiation
$b = 13.106$ (5) Å	$\mu = 0.30$ mm^{-1}
$c = 16.653$ (7) Å	$T = 294$ (2) K
$\alpha = 101.505$ (8)°	Prism, colorless
$\beta = 94.504$ (9)°	0.24 × 0.22 × 0.12 mm
$\gamma = 92.914$ (8)°	

Data collection

Bruker SMART CCD area-detector diffractometer	12920 measured reflections
φ and ω scans	8867 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3277 reflections with $I > 2\sigma(I)$
$T_{min} = 0.757$, $T_{max} = 1.000$	$R_{int} = 0.051$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 5P]$
$R[F^2 > 2\sigma(F^2)] = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.156$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.01$	$\Delta\rho_{max} = 0.75$ e Å^{-3}
8867 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
713 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—C10	1.717 (7)	C12—C13	1.500 (8)
S1—C7	1.729 (6)	C13—C14	1.532 (9)
S2—C18	1.725 (6)	C14—C15	1.520 (9)
S2—C21	1.737 (6)	C15—C16	1.501 (8)
S3—C37	1.707 (7)	C39—C43	1.355 (8)
S3—C34	1.732 (6)	C39—C40	1.524 (8)
S4—C45	1.713 (7)	C40—C41	1.523 (9)
S4—C48	1.734 (7)	C41—C42	1.540 (9)
C12—C16	1.345 (8)	C42—C43	1.508 (8)
C12—C9—C10—S1	−177.6 (5)	C12—C16—C17—C18	−53.3 (10)
C10—C9—C12—C16	−46.3 (11)	C37—C36—C39—C43	−47.9 (11)
C10—C9—C12—C13	135.1 (7)	C35—C36—C39—C40	−51.2 (9)
C8—C9—C12—C13	−41.9 (9)	C40—C41—C42—C43	−27.1 (7)
C16—C12—C13—C14	10.6 (8)	C40—C39—C43—C44	176.6 (6)
C13—C14—C15—C16	9.8 (8)	C41—C42—C43—C39	22.0 (7)
C13—C12—C16—C15	−4.4 (8)	C39—C43—C44—C45	−42.4 (11)
C14—C15—C16—C12	−3.7 (8)		

The F atoms at C23 and C54 were found to be disordered over two distinct conformations. From refinement (anisotropic), the site occupancies were fixed at 0.70:0.30 for these F atoms. 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 isotropic displacement parameters set equal to $1.2U_{eq}$ of the carrier atom for the aromatic H and $1.5U_{eq}$ of the carrier for CH_3.

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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