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Key indicators

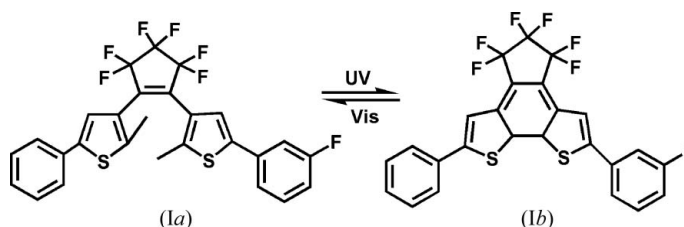
Single-crystal X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
Disorder in main residue
 R factor = 0.068
 wR factor = 0.143
Data-to-parameter ratio = 12.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

3,3,4,4,5,5-Hexafluoro-1-[5-(3-fluorophenyl)-2-methyl-3-thienyl]-2-(2-methyl-5-phenyl-3-thienyl)cyclopent-1-ene

In the crystal structure of the title compound, $\text{C}_{27}\text{H}_{17}\text{F}_7\text{S}_2$, there are two molecules in the asymmetric unit. In the two molecules, the distances between the two reactive C atoms, *i.e.* the ring C atoms to which the methyl groups are attached, are 3.553 (6) and 3.624 (6) Å. The dihedral angles between the thiophene ring and the adjacent benzene rings are 13.7 (1) and 20.9 (2)° in one molecule, and 28.2 (1) and 10.1 (1)° in the other.

Comment

Of all the photochromic compounds, diarylethenes are the most promising candidates because of their good thermal stability, high sensitivity, fast response and high fatigue resistance (Irie, 2000; Tian & Yang, 2004). For further background information, see Pu, Liu, Chen & Wang (2005) and Pu, Fan *et al.* (2005). A large number of diarylethene crystal structures and their properties have been reported (Kobatake & Irie, 2004), including some structures we have determined (Pu *et al.*, 2003, 2004; Pu, Fan *et al.*, 2005; Pu, Xu *et al.*, 2005; Pu, Xiao *et al.*, 2005; Pu, Yang, Wang & Xu, 2005; Pu, Liu & Yan, 2005; Pu, Yang & Yan, 2005). Many diarylethenes incorporating thienyl groups and a *para*-substituted benzene ring are known (Irie, 2000; Tian & Yang, 2004; Matsuda & Irie, 2004; Morimoto & Irie, 2005) but diarylethenes with a *meta*-substituted benzene ring are rare (Yamamoto *et al.*, 2003). In order to investigate the photochemical properties of a diarylethene with a *meta*-substituted benzene ring, we have synthesized the title compound, (Ia), and its structure is reported here.



The two independent molecules of (Ia) are shown in Figs. 1 and 2, and selected geometric parameters are given in Table 1. Both molecules show a photoactive antiparallel conformation *i.e.* the molecules have molecular C_2 symmetry. In the hexafluorocyclopentene rings of the two molecules, the $\text{C1}=\text{C2}$ and $\text{C28}=\text{C29}$ bonds are clearly double bonds, while the other bonds in the ring are single. The thiophene rings are linked by the $\text{C1}=\text{C2}$ and $\text{C28}=\text{C29}$ double bonds; the two methyl groups are located on different sides of the double bond and thus are *trans* with respect to the double bond. Such a

Received 21 November 2005

Accepted 5 December 2005

Online 10 December 2005

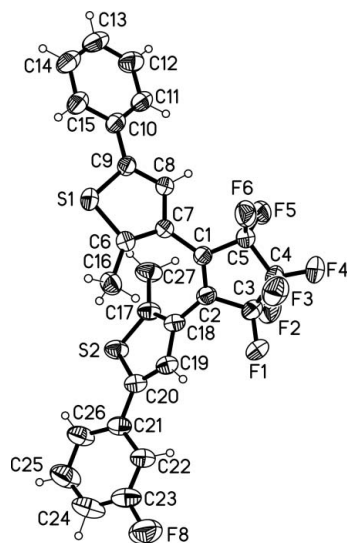


Figure 1

View of one independent molecule of the title compound, shown with 35% probability ellipsoids; H atoms are shown as spheres of arbitrary radii. Only one component of the disordered F atom is shown.

conformation is crucial for the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970).

In one independent molecule of (*Ia*), the dihedral angles between the least-squares plane of atoms of the central cyclopent-1-ene ring and those of the thiophene rings are $49.6 (2)^\circ$ for S1/C6–C9 and $47.7 (2)^\circ$ for S2/C17–C20, and those between the thiophene rings and the adjacent benzene rings are $13.7 (1)^\circ$ for C10–C15 and $20.9 (2)^\circ$ for C21–C26. The distance between the two reactive C atoms (C6...C17) is $3.553 (6) \text{ \AA}$ and this distance indicates that the crystal can undergo photochromism in the crystalline phase (Ramarathy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004). Similarly for the other independent molecule, the dihedral angles between the central cyclopent-1-ene ring and the thiophene rings are $45.1 (2)^\circ$ for S3/C33–C36 and $49.7 (2)^\circ$ for S4/C44–C47, and those between thiophene rings and the adjacent benzene rings are $28.2 (1)^\circ$ for C37–C42 and $10.1 (1)^\circ$ for C48–C53. This conformation leads to a C33...C44 separation of $3.624 (6) \text{ \AA}$, which again is less than 4.2 \AA , allowing photochromism.

When the title compound was irradiated with 313 nm light, the colorless single crystals turned to blue rapidly, and the blue color remained stable in the dark. When the blue crystals were dissolved in hexane, the solution also remained blue. The absorption maximum of this solution was observed at a wavelength of 577 nm, consistent with the presence of the closed-ring isomer, (*Ib*). This result suggests that the title compound undergoes a photochromic reaction to produce the closed-ring molecule of (*Ib*) in the single-crystal phase. We have not, so far, been able to determine the crystal structure of (*Ib*). Furthermore, upon irradiation with wavelengths greater than 450 nm, the blue crystal changes back to colourless, and the absorption spectrum of a hexane solution of the colourless

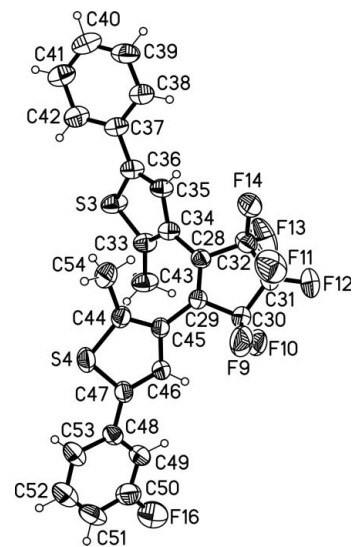


Figure 2

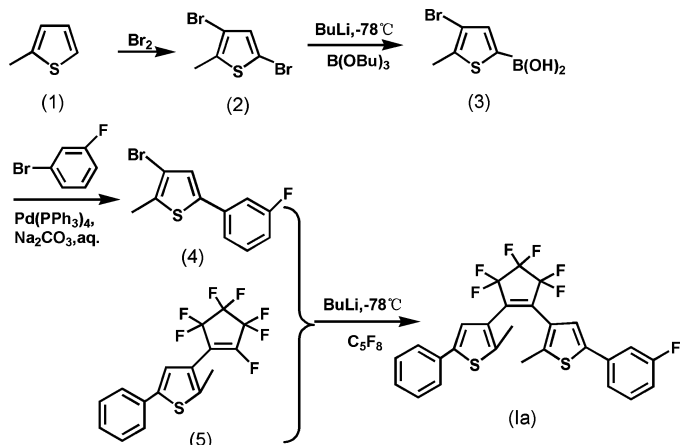
View of the second molecule of the title compound, shown with 35% probability ellipsoids; H atoms are shown as spheres of arbitrary radii. Only one component of the disordered F atom is shown.

crystals was the same as that of a solution of the open-ring form, (*Ia*), with the absorption maximum at 276 nm.

Experimental

The title compound was originally derived from 2-methylthiophene, (1). 3,5-Dibromo-2-methylthiophene, (2) (50.7 g, 198.1 mmol), in 81.2% yield was synthesized by brominating (1) (24.0 g, 244.8 mmol) in acetic acid at 273 K. 3-Bromo-2-methyl-5-thienylboronic acid, (3) (12.0 g, 54.3 mmol), was prepared in 85.5% yield in the presence of compound (2) (16.3 g, 63.7 mmol), *n*-BuLi/hexane solution (2.5 mol l^{-1} , 65 mmol) and tri-*n*-butyl borate (18.8 ml, 68.9 mmol) at 195 K under a nitrogen atmosphere. 3-Bromo-2-methyl-5-(3-fluorophenyl)thiophene, (4) (6.8 g, 25.1 mmol), was prepared in 82.5% yield by reacting compound (3) (6.7 g, 30.4 mmol) with 3-bromo-1-fluorobenzene (5.3 g, 30.4 mmol) in the presence of Pd(PPh₃)₄ (1.0 g) and Na₂CO₃ (2 mol l^{-1} , 114 mmol) in tetrahydrofuran (THF, 120 ml) for 15 h at 343 K. Finally, to a stirred THF solution (100 ml) of compound (4) (1.9 g, 7.0 mmol), *n*-BuLi/hexane solution (2.8 ml , 2.5 mol l^{-1} , 7.0 mmol) was added slowly at 195 K under a nitrogen atmosphere. 30 min later, (2-methyl-5-phenyl-3-thienyl)perfluorocyclopent-1-ene, (5) (Peters *et al.*, 2003) (2.6 g, 7.1 mmol), was added and the mixture was stirred for 2 h at this temperature. The reaction mixture was extracted with ether and evaporated *in vacuo*, then purified by column chromatography (petroleum ether) to give the title compound (*Ia*) (1.5 g, 2.8 mmol) in 40% yield. The compound crystallized from hexane at room temperature and produced crystals suitable for X-ray analysis. The structure of (*Ia*) was confirmed by melting point, element analysis, NMR and IR: m.p. 393.8–394.3 K. Analysis calculated for C₂₇H₁₇F₇S₂: C 60.22, H 3.18%; found: C 60.31, H 3.23%. ¹H NMR (400 MHz, CDCl₃, δ , p.p.m.): 1.965 (s, 3H), 1.969 (s, 3H), 6.977–7.015 (t, 1H, $J = 7.6 \text{ Hz}$, benz-H), 7.223 (s, 1H, thiophene-H), 7.278 (s, 1H, thiophene-H), 7.293–7.305 (d, 2H, $J = 4.8 \text{ Hz}$, benz-H), 7.324 (s, 1H, benz-H), 7.337–7.357 (t, 1H, $J = 7.6 \text{ Hz}$, benz-H), 7.370–7.408 (t, 2H, $J = 7.6 \text{ Hz}$, benz-H), 7.535–7.553 (d, 2H, $J = 7.2 \text{ Hz}$, benz-H); ¹⁹F NMR (400 MHz, CDCl₃, δ , p.p.m.): 110.01 (4F), 112.33 (1F), 131.79 (2F); IR

(KBr): ν (cm⁻¹) 759, 783, 821, 986, 1055, 1112, 1138, 1186, 1274, 1340, 1442, 1470, 1502, 1586, 1612.



Crystal data

C₂₇H₁₇F₇S₂
M_r = 538.53
Monoclinic, P2₁/c
a = 18.945 (2) Å
b = 11.7925 (19) Å
c = 21.876 (4) Å
β = 96.587 (12)°
V = 4855.1 (13) Å³
Z = 8

D_x = 1.473 Mg m⁻³
Mo Kα radiation
Cell parameters from 50 reflections
θ = 5.0–12.5°
μ = 0.29 mm⁻¹
T = 295 (2) K
Prism, colourless
0.6 × 0.5 × 0.2 mm

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: none
10367 measured reflections
8526 independent reflections
5532 reflections with I > 2σ(I)
R_{int} = 0.036

θ_{max} = 25.0°
h = -22 → 1
k = -1 → 14
l = -25 → 26
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.068
wR(F²) = 0.143
S = 1.01
8526 reflections
661 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.001P)² + 1P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.002
Δρ_{max} = 0.88 e Å⁻³
Δρ_{min} = -0.40 e Å⁻³

Table 1

Selected bond lengths (Å).

S1—C9	1.718 (4)	C1—C7	1.471 (5)
S1—C6	1.721 (4)	C1—C5	1.496 (6)
S2—C17	1.715 (5)	C2—C18	1.468 (6)
S2—C20	1.728 (4)	C2—C3	1.511 (6)
S3—C33	1.718 (5)	C3—C4	1.501 (7)
S3—C36	1.731 (4)	C4—C5	1.531 (6)
S4—C44	1.713 (4)	C28—C29	1.338 (5)
S4—C47	1.727 (5)	C28—C34	1.474 (6)
F7—C12	1.328 (5)	C28—C32	1.516 (6)
F8—C23	1.319 (4)	C29—C45	1.475 (5)
F15—C39	1.317 (5)	C29—C30	1.505 (6)
F16—C50	1.316 (5)	C30—C31	1.514 (7)
C1—C2	1.346 (5)	C31—C32	1.505 (7)

In each independent molecule, the *m*-substituted F atom of the benzene ring is disordered over the two *meta* positions of both rings but only one *meta* position in each ring is occupied by partial F atoms, the H atoms in these positions being equally disordered. The site occupancies of the disordered atoms F7/F8 and F15/F16 are 0.497 (5)/0.503 (5) and 0.481 (5)/0.519 (5), respectively. H atoms were positioned geometrically [0.93 (CH) and 0.96 Å (CH₃)] and constrained to ride on their parent atoms with U_{iso}(H) values of 1.2 or 1.5 (for methyl) times U_{eq}(C).

Data collection: XSCANS (Bruker, 1997); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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

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