

Shou-Zhi Pu,^{a*} Gui-Zhen Li,^{a,b,‡}
Ru-Ji Wang^c and Ji-Quan Zhao^b

^aJiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China, ^bSchool of Chemical Engineering, Hebei University of Technology, Tianjin 300130, People's Republic of China, and ^cDepartment of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

‡ Current address: Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, People's Republic of China.

Correspondence e-mail:
pushouzhi@tsinghua.org.cn

Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.007$ Å
Disorder in main residue
 R factor = 0.070
 wR factor = 0.145
Data-to-parameter ratio = 12.9

For 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-[2-methyl-5-(2-fluorophenyl)-3-thienyl]-2-(2-methyl-5-phenyl-3-thienyl)cyclopent-1-ene, a new photochromic dithienylethene

The title compound, $\text{C}_{27}\text{H}_{17}\text{F}_7\text{S}_2$, a new unsymmetrical photochromic dithienylethene with an *ortho*-fluorophenyl substituent, is one of the most promising candidates for photoelectronic applications, such as optical storage, photo-switches and waveguides. There are two molecules in the asymmetric unit. Both adopt a photoactive anti-parallel conformation. For one molecule, the distance between the two reactive C atoms is 3.572 (6) Å; the dihedral angles between the central cyclopentene ring and the thiophene rings are 49.7 (2) and 45.9 (2)°, and those between the thiophene rings and the adjacent benzene rings are 8.1 (2) and 25.5 (1)°. For the other molecule, the distance between the two reactive C atoms is 3.588 (6) Å; the dihedral angles between the central cyclopentene ring and the thiophene rings are 43.7 (2) and 46.8 (2)°, and those between the thiophene rings and the adjacent benzene rings are 27.5 (1) and 11.1 (2)°.

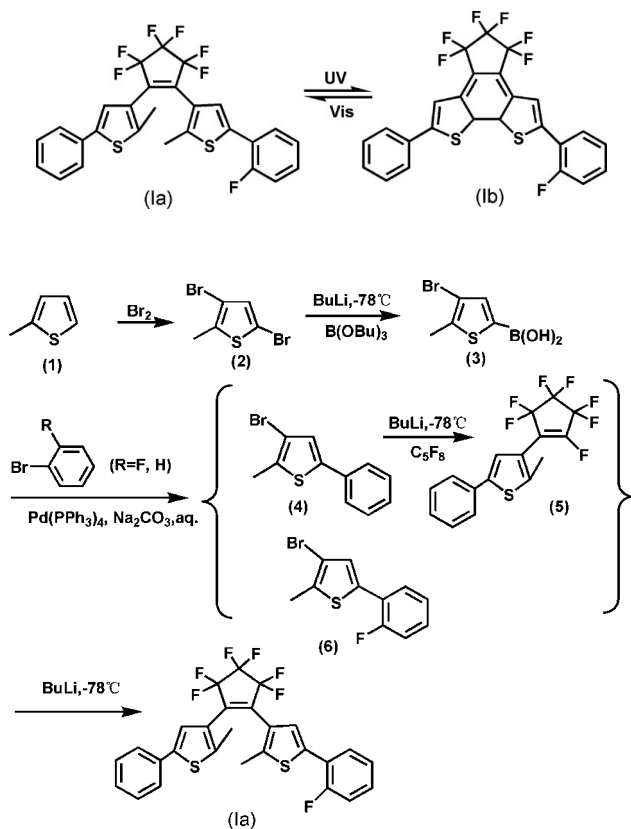
Received 3 November 2005
Accepted 18 November 2005
Online 23 November 2005

Comment

The design and synthesis of photochromic compounds have attracted much attention because of their possible widespread use in optoelectronic device applications, such as optical storage, photoswitches and waveguides (Fan *et al.*, 1999; Dürr & Bouas-Laurent, 1990). Among various photochromic compounds, photochromic dithienylethenes are the most promising organic photochromic compounds for photoelectronic devices because of the thermal non-interconversion of the two isomers and their high sensitivity, fast response and remarkable fatigue resistance (Irie, 2000; Matsuda & Irie, 2004; Tian & Yang, 2004).

In general, dithienylethenes have two conformations. One is an anti-parallel conformation with the aryl rings related by C_2 symmetry, and the other is a parallel conformation with the aryl rings related by mirror symmetry (Pu *et al.*, 2003). The two conformations can interconvert in solution, but there is no interconversion in single crystals (Li & Tian, 2005). Conrotatory cyclization can proceed only from the anti-parallel conformation, while the parallel conformation is photochemically inactive (Nakamura & Irie, 1988; Yamada *et al.*, 2000; Kobatake & Irie, 2004). Crystals of diarylethenes belong to a unique class of photochromic crystals because they have some characteristic properties, such as dichroism under polarized light, thermal stability, and fatigue-resistant photochromic performance (Morimoto *et al.*, 2004). Therefore, they are the most promising candidates for practical applications, such as high-density three-dimensional optical recording media (Kawata & Kawata, 2000), optical switches (Nakatani & Delaire, 1997) and photo-driven nano-scale actuators (Irie *et al.*, 2001).

To date, many dithienylethene derivatives and their properties have been reported (Irie, 2000; Matsuda & Irie, 2004; Tian & Yang, 2004), and we have also reported some perfluorocyclopentene derivatives that undergo single-crystal photochromism (Pu *et al.*, 2004; Pu, Xu *et al.*, 2005; Pu, Yang, Wang & Xu, 2005; Pu, Yang & Yan, 2005; Pu, Liu & Yan, 2005). In addition, dithienylethenes bearing terminal phenyl groups are of special interest, because the phenyl group can be substituted by many electron-donating or electron-withdrawing groups that influence the properties of the corresponding dithienylethenes (Pu, Yang, Xu *et al.*, 2005). Among the reported dithienylethenes bearing phenyl groups, all substituents are attached to the phenyl groups at the *para*- or *meta*-positions. In order to investigate the substituent effect at the *ortho*-position on the photochemical properties, we have now synthesized the title compound, (*Ia*), and its structure is presented in this paper. To the best of our knowledge, this is the first unsymmetrical dithienylethene compound with phenyl groups bearing an *ortho* substituent.



The molecular structure of (*Ia*) is shown in Fig. 1 and selected geometric parameters are given in Table 1. There are two molecules in the asymmetric unit and both of them have a photoactive anti-parallel conformation. The F atoms are disordered over one *ortho*-position of each benzene ring of each molecule (Fig. 1). In the hexafluorocyclopentene rings of the two molecules, the C1–C2 and C28–C29 bonds are clearly double bonds and the other bonds to atoms C1, C2, C28 and C29 are clearly single bonds (Table 1). The thiophene

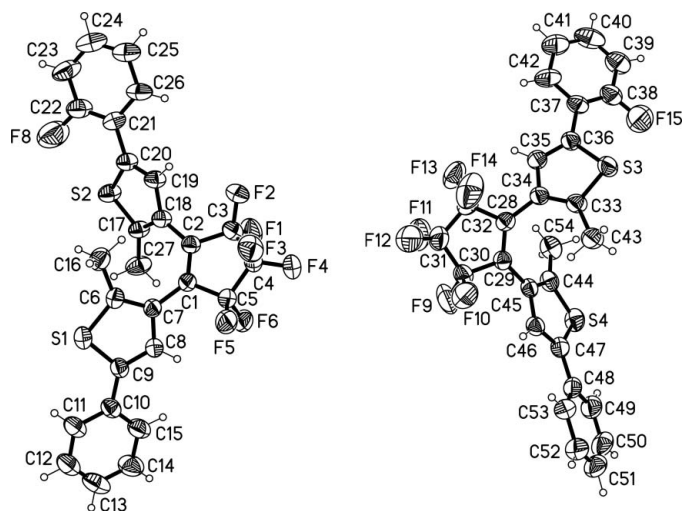


Figure 1
Views of the two independent molecules of (*Ia*), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. Only the major disorder component is shown for the *o*-fluorophenyl groups.

groups are linked by the C1=C2 and C28=C29 double bonds. The methyl groups are located on different sides of the double bond and mutually *trans* relative to the thiophene planes. This kind of conformation is crucial to photochromic and photo-induced properties (Woodward & Hoffmann, 1970).

For one molecule, the two independent planar thiophene ring systems have essentially identical geometry, and the dihedral angles between the central cyclopent-1-ene ring and the thiophene rings are 49.7 (2)° for S1/C6–C9 and 45.9 (2)° for S2/C17–C20, while those between the thiophene rings and the adjacent benzene rings are 8.1 (2)° for C10–C15 and 25.51 (1)° for C21–C26. The distance between the two reactive C atoms (C6 and C17) is 3.572 (6) Å. This distance indicates that the crystal can undergo photochromism (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004). Similarly, for the second molecule, the two independent planar thiophene ring systems have essentially identical geometry, and the dihedral angles between the central cyclopent-1-ene ring and the thiophene rings are 43.7 (2)° for S3/C33–C36 and 46.8 (2)° for S4/C44–C47, and those between the thiophene rings and the adjacent benzene rings are 27.5 (1)° for C37–C42 and 11.1 (2)° for C48–C53. The distance between the two reactive C atoms (C33 and C44) is 3.588 (6) Å.

Crystals of (*Ia*) show photochromism in accordance with the expected ring closure, to form (*Ib*). Upon irradiation with 313 nm light, the colourless single crystals rapidly turned blue, and the colour remained stable in the dark. A blue solution was obtained when the blue crystal was dissolved in hexane, and the absorption maximum was observed at 577 nm, consistent with the presence of the closed-ring isomer, (*Ib*). Unfortunately, we have not been able to establish the crystal structure of (*Ib*) following irradiation of crystals of (*Ia*). The possible reason is that (*Ib*) can return easily to (*Ia*) under these experimental conditions. The blue crystals returned to the initial colourless state upon irradiation with visible light

longer than 500 nm, and the absorption spectrum of the solution containing the colourless material was the same as that of solutions of the open-ring form, (Ia), with the absorption maximum at 274 nm.

Experimental

The new photochromic diarylethene, (Ia), was originally derived from 2-methylthiophene, (1), 3,5-Dibromo-2-methylthiophene, (2) (50.7 g, 198.1 mmol), was afforded in 81.2% yield by treatment of (1) (24.0 g, 244.8 mmol) in acetic acid with bromine (11.2 ml, 218.4 mmol) at 273 K. 3-Bromo-2-methyl-5-thienylboronic acid, (3) (12.0 g, 54.3 mmol), was prepared in 85.5% yield from compound (2) (16.3 g, 63.7 mmol), *n*-BuLi/hexane solution (2.5 M, 65 mmol) and tri-*n*-butylborate (18.8 ml, 68.9 mmol) at 195 K under a nitrogen atmosphere. 3-Bromo-2-methyl-5-phenylthiophene, (4) (6.3 g, 24.9 mmol), was prepared in 70% yield by reacting compound (3) (7.8 g, 35.3 mmol) with 1-bromobenzene (5.6 g, 35.7 mmol) in the presence of Pd(PPh₃)₄ (0.9 g) and Na₂CO₃ (2 M, 130 mmol) in tetrahydrofuran (THF; 120 ml) for 15 h at 343 K. To a stirred THF solution (80 ml) of compound (4) (3.1 g, 12.3 mmol) was slowly added an *n*-BuLi/hexane solution (4.9 ml, 2.5 M, 12.3 mmol) at 195 K under a nitrogen atmosphere. After 30 min, perfluorocyclopentene (1.7 ml, 12.5 mmol) was added quickly. The mixture was stirred for 3 h at this temperature. The reaction mixture was extracted with diethyl ether, dried with MgSO₄, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane) to give (2-methyl-5-phenyl-3-thienyl)perfluorocyclopent-1-ene, (5) (2.4 g, 6.5 mmol), in 53% yield. 3-Bromo-2-methyl-5-(2-fluorophenyl)thiophene, (6) (2.6 g, 9.6 mmol), was prepared in 55% yield by reacting compound (3) (3.8 g, 17.2 mmol) with 2-bromo-1-fluorobenzene (3.0 g, 17.2 mmol) by the same procedure as that used for (4) above. Finally, to a stirred THF solution (50 ml) of compound (6) (0.8 g, 3.0 mmol) was slowly added an *n*-BuLi/hexane solution (1.2 ml, 2.5 M, 3.0 mmol) at 195 K under a nitrogen atmosphere. After 30 min, compound (5) (1.1 g, 3.0 mmol) was added and the mixture was stirred for 2 h at this temperature. The reaction mixture was extracted with diethyl ether and evaporated *in vacuo*, then purified by column chromatography (petroleum ether) to give the title compound, (Ia) (0.6 g, 1.1 mmol), in 37% yield. The compound was crystallized from chloroform at room temperature. The structure of (Ia) was also confirmed by the melting point, elemental analysis and NMR spectroscopy: m. p. 384.9–385.8 K; analysis calculated for C₂₇H₁₇F₇S₂: C 60.22, H 3.18%; found: C 60.28, H 3.21. ¹H NMR (400 MHz, CDCl₃, δ, p.p.m.): 1.973 (*s*, 3H), 1.993 (*s*, 3H), 7.140–7.184 (*m*, 1H, *J* = 7.2 Hz, benzene-H), 7.275 (*s*, 2H, thiophene-H), 7.297–7.315 (*d*, 1H, *J* = 7.2 Hz, benzene-H), 7.363–7.401 (*t*, 2H, *J* = 7.6 Hz, benzene-H), 7.433 (*s*, 1H, benzene-H), 7.531–7.553 (*m*, 4H, *J* = 7.2 Hz, benzene-H); ¹⁹F NMR (400 MHz, CDCl₃, δ, p.p.m.): 110.04 (4 F), 113.62 (1 F), 131.84 (2 F).

Crystal data

C₂₇H₁₇F₇S₂
M_r = 538.53
 Triclinic, *P* $\bar{1}$
a = 11.8563 (15) Å
b = 13.7789 (18) Å
c = 15.281 (2) Å
 α = 81.368 (9)°
 β = 82.348 (9)°
 γ = 82.442 (9)°
V = 2430.2 (6) Å³

Z = 4
D_x = 1.472 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 48 reflections
 θ = 2.7–13.7°
 μ = 0.29 mm⁻¹
T = 295 (2) K
 Prism, blue
 0.6 × 0.5 × 0.4 mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: none
 9883 measured reflections
 8533 independent reflections
 5559 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.020

θ_{\max} = 25.0°
 h = -13 → 1
 k = -16 → 16
 l = -18 → 18
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.070
wR (*F*²) = 0.145
S = 1.04
 8533 reflections
 661 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 4.5P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.04 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond lengths (Å).

S1—C6	1.711 (4)	C1—C7	1.464 (5)
S1—C9	1.724 (4)	C1—C5	1.498 (6)
S2—C17	1.718 (4)	C2—C18	1.468 (6)
S2—C20	1.727 (4)	C2—C3	1.494 (6)
S3—C33	1.715 (5)	C3—C4	1.529 (7)
S3—C36	1.729 (4)	C4—C5	1.526 (6)
S4—C44	1.717 (5)	C28—C29	1.345 (6)
S4—C47	1.720 (5)	C28—C34	1.474 (6)
F7—C11	1.336 (3)	C28—C32	1.492 (6)
F8—C22	1.338 (3)	C29—C45	1.459 (6)
F15—C38	1.328 (3)	C29—C30	1.494 (6)
F16—C49	1.333 (3)	C30—C31	1.486 (7)
C1—C2	1.352 (5)	C31—C32	1.512 (7)

H atoms were positioned geometrically and refined using a riding model, with aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(aromatic C) or 1.5*U*_{eq}(methyl C). The highest residual electron-density peak is 1.56 Å from F12. The fluoro substituents were found to be disordered over one *ortho*-position of each benzene ring within each independent molecule, with refined occupancy factors of 0.776:0.224 (9) and 0.590:0.410 (10).

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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