

Tian-She Yang,^a Chun-Yan Xu,^b
Yuan-Ming Tu^a and
Shou-Zhi Pu^{a*}^aJiangxi Key Laboratory of Organic Chemistry,
Jiangxi Science and Technology Normal
University, Nanchang 330013, People's
Republic of China, and ^bCollege of Science,
Beijing University of Chemical Technology,
Beijing 100029, People's Republic of ChinaCorrespondence e-mail:
pushouzhi@tsinghua.org.cn

Key indicators

Single-crystal X-ray study
 $T = 294$ K
Mean $\sigma(C-C) = 0.005$ Å
Disorder in main residue
 R factor = 0.055
 wR factor = 0.168
Data-to-parameter ratio = 13.1For 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-bis[5-(3-methoxy-
phenyl)-3-methyl-2-thienyl]cyclopent-1-ene

The title compound, $C_{29}H_{28}F_6O_2S_2$, a new symmetrical photochromic dithienylethene with 3-methoxyphenyl substituents, may have applications in optoelectronic devices. In the crystal structure, the molecule adopts a photo-active anti-parallel conformation. The distance between the two reactive thiophene ring C atoms is 3.490 (5) Å.

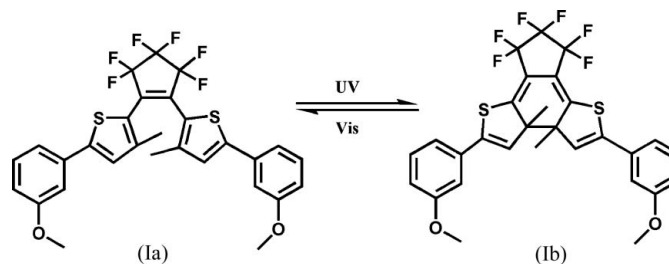
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Comment

Compounds that interconvert between two isomers with different absorption spectra when stimulated with an appropriate wavelength of light are referred to as photochromic and this process is named photochromism (Li & Tian, 2005). Various types of photochromic compounds, such as azobenzenes, spirobenzopyrans, fulgides, and diarylethenes, have hitherto been developed (Yamamoto *et al.*, 2003). Of all these compounds, diarylethene derivatives are the most promising materials for photoelectronic devices, such as high-density optical recording, photo-switches and color displays, because of the good thermally irreversible properties of the two isomers and their high sensitivity, fast response and remarkable fatigue resistance (Irie, 2000; Tian & Yang, 2004).

For diarylethene derivatives, the absorption spectra mainly depend on the substituents and the π conjugation length. Compared with the closed-ring form of di-3-thienylethene, where the π conjugation extends throughout the whole molecule, the π conjugation in the closed-ring form of di-2-thienylethene is localized in a cyclohexadiene structure, so that it has a shorter absorption wavelength (Sun *et al.*, 2003). For applications it is desirable to develop diarylethene compounds whose closed-ring forms show yellow or red colors (Takami & Irie, 2004). In order to realize this goal, an effective approach is to attach 2-thienyl rings to the ethylene unit of diarylethenes (Pu, Liu & Yan, 2005; Pu, Fan *et al.*, 2005; Uchida *et al.*, 1998). For further background information see Pu, Liu & Chen *et al.* (2005). In the present work, a new photochromic diarylethene, (Ia), was synthesized, and its crystal structure is presented here.



The molecule of (Ia) shows a photoactive antiparallel conformation (Fig. 1). The two thiophene groups are linked by

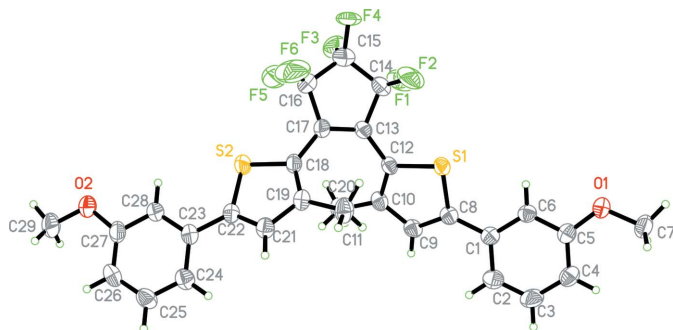


Figure 1

The structure of (*Ia*), with 35% probability displacement ellipsoids (arbitrary spheres for the H atoms), showing the atomic numbering scheme. The minor components of disorder for atoms F3 and F4 are not shown.

the C13=C17 double bond, with both of them attached to the ethylene group *via* the 2-position. The two methyl groups are located on different sides of the double bond, reflected in the torsion angles C10—C12—C13—C17 [39.2 (6)°] and C13—C17—C18—C19 [42.4 (6)°], and are thus *trans* with respect to the double bond. Such a conformation is crucial to the photochromic and photoinduced properties of such materials (Pu, Luo *et al.*, 2006; Pu, Li *et al.*, 2006).

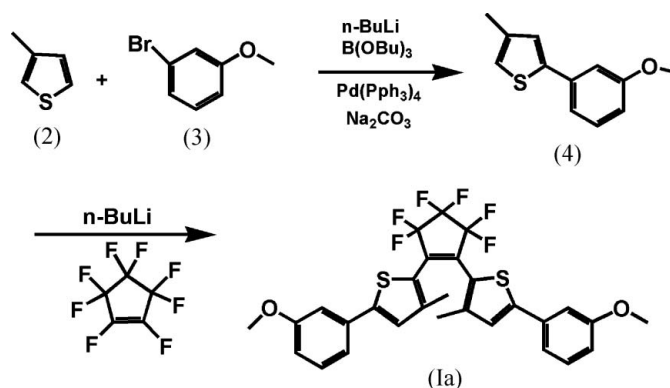
In the hexafluorocyclopentene ring of (*Ia*), C13=C17 is clearly a double bond, being significantly shorter than the other single bonds from atoms C13 and C17 (Table 1). The two independent planar thiophene ring systems have essentially identical geometries, and the dihedral angles between the least-squares plane of the central cyclopent-1-ene ring and those of the two thiophene rings, S1/C8—C10/C12 and S2/C18/C19/C21/C22, are 42.2 (3) and 137.4 (3)°, respectively. The dihedral angle between the thiophene and adjacent benzene ring is 21.3 (5)° for the C1—C6 benzene ring and 161.8 (5)° for the C23—C28 benzene ring. The distance between the two reactive C atoms (C10...C19) is 3.490 (5) Å, which is short enough, theoretically, for the ring-closure reaction to take place in the crystalline phase (Ramamurthy & Venkatesan, 1987).

The crystals of (*Ia*) showed photochromism in accordance with the expected ring closure, to form (*Ib*). Upon irradiation with 365 nm light, the yellowish single crystals turned yellow rapidly, and the color remained stable in the dark. When the yellow crystals were dissolved in hexane, the solution also showed a yellow color. The absorption maximum of this solution was observed at 446 nm, consistent with the presence of the closed-ring isomer, (*Ib*). This phenomenon suggested that a solid-state photochromic reaction can occur in (*Ia*) and generate the closed-ring molecule of (*Ib*) in the single crystalline phase. We have not, so far, been able to determine the crystal structure of (*Ib*) because of the limitations of the experimental conditions; the structure of the closed-ring isomer should be determined at a reduced temperature (Yamaguchi & Irie, 2005). Upon irradiation with light of wavelength greater than 420 nm, the yellow-colored crystal can return to the initial yellowish one, and the absorption

spectrum of the hexane solution containing the yellowish crystal was the same as that of solutions of the open-ring form, (*Ia*), with the absorption maximum at 373 nm.

Experimental

Compound (*Ia*) was prepared from 3-methylthiophene, (**2**) (see scheme below). First, a hexane solution of *n*-butyl lithium (12.2 ml of 2.5 mol l⁻¹) was gradually added to a diethyl ether solution (40 ml) containing 3-methylthiophene (3.0 g) at 273 K. The solution was heated for 1 h under reflux. After cooling the solution to 273 K, trimethyl borate (8.2 ml) was added. The solution was then stirred for 1 h at room temperature. 20% (*w/w*) Na₂CO₃ aqueous solution (30 ml), 1-bromo-3-methoxybenzene, (**3**) (5.7 g), and tetrakis(triphenylphosphine)palladium(0) (0.55 g) were added, and the mixture was heated for 5 h under reflux with vigorous stirring to give 5.7 g of 4-methyl-2-phenylthiophene, (**4**), in 91% yield. Under an argon gas atmosphere, compound (**4**) (3.42 g) was dissolved in diethyl ether (50 ml) and a hexane solution of *n*-butyl lithium (6.7 ml of 2.5 mol l⁻¹) was added at 273 K. After the mixture had been heated under reflux for 1 h, the reaction mixture was cooled to 273 K. Octafluorocyclopentene (1.1 ml) was added and stirred for 1 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 2.87 g of the title compound in 59% yield. The compound crystallized from hexane/chloroform (*v/v* 1:1) at room temperature and produced crystals suitable for X-ray analysis. M.p. 389.3 K.



Crystal data

C₂₉H₂₂F₆O₂S₂
M_r = 580.59
 Monoclinic, *P*2₁/*n*
a = 7.8013 (11) Å
b = 26.675 (4) Å
c = 12.9844 (18) Å
 β = 92.654 (3)°
V = 2699.2 (7) Å³

Z = 4
D_x = 1.429 Mg m⁻³
 Mo K α radiation
 μ = 0.27 mm⁻¹
T = 294 (2) K
 Prism, colorless
 0.42 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
T_{min} = 0.755, *T_{max}* = 1.000
 (expected range = 0.697–0.924)

13656 measured reflections
 4782 independent reflections
 3208 reflections with *I* > 2 σ (*I*)
R_{int} = 0.032
 θ_{max} = 25.0°

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.168$
 $S = 1.02$
 4782 reflections
 364 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0795P)^2 + 2.3881P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.003$
 $\Delta\rho_{\max} = 0.94 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C5—O1	1.360 (4)	C13—C17	1.358 (5)
C7—O1	1.415 (4)	C17—C18	1.450 (5)
C9—C10	1.407 (5)	C18—C19	1.372 (5)
C10—C12	1.373 (5)	C19—C21	1.409 (5)
C12—C13	1.448 (5)		
C7—O1—C5—C4	−1.5 (6)	C12—C13—C17—C16	−175.9 (4)
C11—C10—C12—C13	6.4 (6)	C15—C16—C17—C13	4.5 (5)
C10—C12—C13—C17	39.2 (6)	C15—C16—C17—C18	−179.0 (4)
S1—C12—C13—C17	−138.7 (4)	C13—C17—C18—C19	42.4 (6)
C13—C14—C15—C16	15.0 (5)	C29—O2—C27—C26	−7.4 (6)
C14—C15—C16—C17	−12.1 (5)		

Atoms F3 and F4 are disordered over two positions in a 0.60:0.40 ratio (determined by the initial refinement). All H atoms were placed in calculated positions ($C-H = 0.93-0.96 \text{ \AA}$) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$.

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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