

1-(2-Methyl-5-phenyl-3-thienyl)- 2-(3-methyl-5-phenyl-2-thienyl)- 3,3,4,4,5,5-hexafluorocyclopent-1-ene: a novel photochromic hybrid diarylethene

Shou-Zhi Pu,^{a*} Gang Liu,^a Bing Chen^a and Ru-Ji Wang^b

^aJiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, People's Republic of China, and ^bDepartment of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Correspondence e-mail: pushouzhi@tsinghua.org.cn

Received 22 August 2005

Accepted 7 September 2005

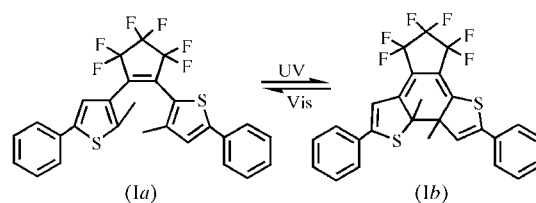
Online 17 September 2005

The title compound, C₂₇H₁₈F₆S₂, a novel photochromic hybrid diarylethene derivative containing 2- and 3-thienyl substituents, is one of the most promising photochromic candidates with shorter wavelength for optical storage and other optoelectronic devices. In the crystal structure, the molecule adopts a photoactive antiparallel conformation. The distance between the two reactive C atoms, *i.e.* the ring C atoms to which the methyl groups are attached, is 3.430 (4) Å. The dihedral angles between the thienyl and adjacent phenyl rings are 26.8 (2) and 33.98 (9)°.

Comment

Photochromism is described as a photoinduced reversible transformation of a chemical species between two isomeric forms having different absorption spectra (Brown, 1971; Dürr & Bouas-Laurent, 1990). Photochromic compounds have attracted much attention because of their potential uses for optical memory, and for photo-optical switching and display devices (Takami & Irie, 2004). Of all the photochromic compounds, diarylethene derivatives 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 application to a full color display and for increasing the optical storage density, it is indispensable to prepare diarylethene derivatives whose ring-closure isomers show red and yellow colours (Takami & Irie, 2004). One approach to shorten the absorption wavelength of diarylethene is to attach 2-thienyl rings to the ethylene moiety (Uchida *et al.*, 1998). For diarylethene, the absorption spectrum depends on the substituent and the π conjugation length. Compared with the closed-ring isomer of di-3-thienylethane, where the π conjugation extends throughout the whole molecule, the π conjugation in the closed-ring isomer of di-2-

thienylethane is localized in a cyclohexadiene structure, so that it has a shorter absorption wavelength (Sun *et al.*, 2003). Although many photochromic diarylethenes have been reported, they are mainly symmetric diarylethene derivatives with both aryl substituents attached through either their 2- or 3-positions (Irie, 2000; Tian & Yang, 2004; Pu *et al.*, 2004; Pu, Yang, Wang & Xu, 2005; Pu, Yang & Yan, 2005; Pu, Liu & Yan, 2005); diarylethenes with aryl substituents attached through a mixture of their 2- or 3-positions and which absorb at a short wavelength (400–500 nm) (Sun *et al.*, 2003; Takami & Irie, 2004) are very rare. Therefore, it is desirable to prepare diarylethene derivatives of this type for short wavelength memories. In the present paper, the structure of the title compound, *i.e.* 1-(2-methyl-5-phenyl-3-thienyl)-2-(3-methyl-5-phenyl-2-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene, (Ia), is presented.



The molecule of (Ia) shows a photoactive antiparallel conformation (Fig. 1). The two thiophene moieties are linked by the C1=C2 double bond, with the S1-containing thiophene ring attached to the ethylene moiety *via* the 2-position and the S2-containing thiophene ring attached *via* the 3-position. The two methyl groups are located on different sides of the double

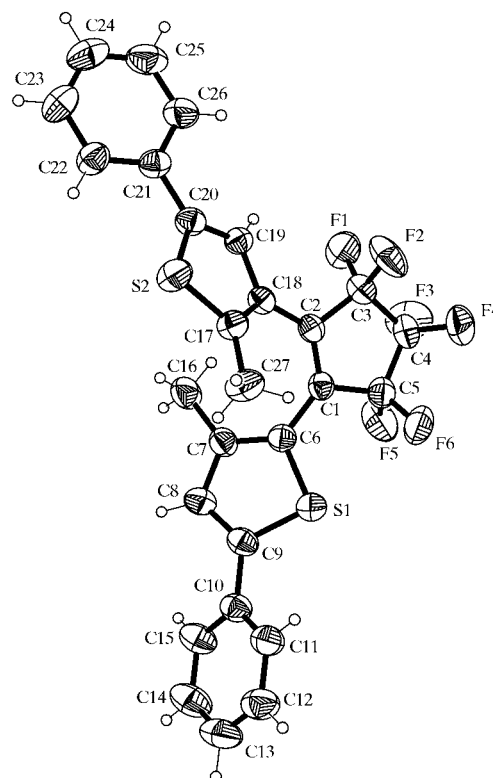


Figure 1

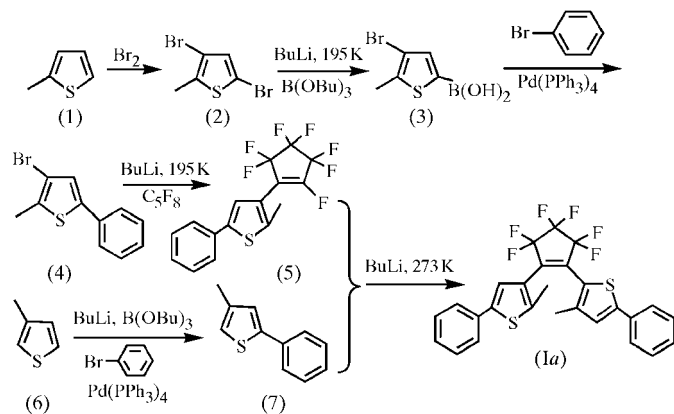
The structure of (Ia), drawn with 35% probability displacement ellipsoids, showing the atomic numbering scheme.

bond and are thus *trans* with respect to the double bond. Such a conformation is crucial for the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970). The dihedral angle between the thiophene and adjacent benzene ring is 33.98 (9)° for the C10–C15 benzene ring and 26.8 (2)° for the C21–C26 benzene ring. The distance between the two reactive C atoms (C7···C17) is 3.430 (4) Å, which is short enough, theoretically, for the ring-closure reaction to take place in the crystalline phase (Ramamurthy & Venkatesan, 1987).

In fact, the crystal of (Ia) undergoes a photochromic reaction in accordance with the expected ring closure, forming (Ib) (see scheme). Upon irradiation with light of wavelength 254 nm, the colourless crystal of (Ia) rapidly turned red. When observed under polarized light, the intensity of the red colour changed on rotation of the crystalline sample. This phenomenon suggested that the closed-ring isomers were regularly oriented in the crystal and that the photochromic reaction took place in the crystal lattice (Yamamoto *et al.*, 2003). When the red crystal was dissolved in hexane, the solution turned red and the absorption maximum was observed at 501 nm, as for the closed-ring isomer (Ib). The red colour of the crystal disappeared upon irradiation with either light of wavelength 500 nm or daylight, and the absorption spectrum of the solution containing the colourless crystal was the same as that of the open-ring isomer (Ia), with the maximum absorption at 292 nm.

Experimental

The novel title photochromic diarylethene (Ia) was derived originally from 2-methylthiophene, (1), and 3-methylthiophene, (6) (see reaction scheme below). The reaction was carried out in six steps: (i) 3,5-dibromo-2-methylthiophene, (2) (50.7 g, 198.1 mmol), was obtained in 81.2% yield by brominating (1) (24.0 g, 244.8 mmol) in acetic acid at 273 K; (ii) 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*-butylborate (18.8 ml, 68.9 mmol) at 195 K under a nitrogen atmosphere; (iii) 3-bromo-2-methyl-5-phenylthiophene, (4) (6.3 g, 24.9 mmol), was prepared in 70% yield



by reacting (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 mol l⁻¹, 130 mmol) in tetrahydrofuran (THF, 120 ml) for 15 h at 343 K; (iv) 1-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopent-1-ene,

(5) (2.4 g, 6.5 mmol), was synthesized in 53% yield according to the procedure of Peters *et al.* (2003) from (4) (3.1 g, 12.3 mmol), *n*-BuLi/hexane solution (2.5 mol l⁻¹, 12.3 mmol) and perfluorocyclopentene (1.7 ml, 12.5 mmol); (v) 4-methyl-2-phenylthiophene, (7) (4.6 g, 26.4 mmol), was prepared in 67% yield by reacting (6) (3.9 g, 39.7 mmol) with 1-bromobenzene (6.2 g, 39.7 mmol) according to the procedure of Pu, Liu & Yan (2005); (vi) 2.8 ml of *n*-BuLi/hexane solution (2.5 mol l⁻¹, 7.0 mmol) was added slowly at 273 K under a nitrogen atmosphere to a stirred THF solution (50 ml) containing compound (7) (1.2 g, 6.9 mmol). After 30 min, compound (5) (2.4 g, 6.5 mmol) was added and the mixture was stirred for 3 h at this temperature. The reaction mixture was extracted with ether, evaporated *in vacuo* and purified by column chromatography (hexane) to give the title compound (Ia) (1.9 g, 3.6 mmol) in 56% yield. Crystals of (Ia) were grown from a chloroform solution by slow evaporation (m.p. 403.2–403.5 K). Analysis calculated for C₂₇H₁₈F₆S₂ (%): C 62.30, H 3.49; found: C 62.44, H 3.57. ¹H NMR (400 MHz, CDCl₃): δ 1.794 (s, 3H), 2.014 (s, 3H), 7.073 (s, 1H, thiophene H), 7.284 (s, 1H, thiophene H), 7.301–7.341 (t, 2H, *J* = 8.0 Hz, phenyl H), 7.369–7.407 (t, 4H, *J* = 7.6 Hz, phenyl H), 7.543–7.587 (m, 4H, *J* = 8.8 Hz, phenyl H). ¹⁹F NMR (400 MHz, CDCl₃): δ 109.33 (2F), 109.50 (2F), 131.42 (2F).

Crystal data

C₂₇H₁₈F₆S₂
M_r = 520.53
 Monoclinic, *P*2₁/*c*
a = 11.5406 (12) Å
b = 9.2179 (7) Å
c = 22.432 (2) Å
 β = 90.263 (8)°
V = 2386.3 (4) Å³
Z = 4

D_x = 1.449 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 36 reflections
 θ = 5.1–12.6°
 μ = 0.28 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.6 × 0.5 × 0.4 mm

Data collection

Bruker *P4* diffractometer
 ω scans
 5525 measured reflections
 4201 independent reflections
 3121 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.028
 θ_{max} = 25.0°

h = -13 → 1
k = -10 → 1
l = -26 → 26
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.054
wR(*F*²) = 0.112
S = 1.02
 4201 reflections
 318 parameters
 H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.001)*P*]²
 + 2.7*P*
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.48 e Å⁻³
 Δρ_{min} = -0.34 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–C9	1.724 (3)	C4–C5	1.508 (5)
S1–C6	1.726 (3)	C6–C7	1.367 (4)
S2–C17	1.715 (3)	C7–C8	1.429 (4)
S2–C20	1.727 (3)	C7–C16	1.501 (5)
C1–C2	1.346 (4)	C8–C9	1.387 (4)
C1–C6	1.460 (4)	C17–C18	1.371 (4)
C1–C5	1.501 (4)	C17–C27	1.496 (4)
C2–C18	1.464 (4)	C18–C19	1.456 (4)
C2–C3	1.500 (4)	C19–C20	1.385 (4)
C3–C4	1.534 (5)		
C6–C1–C2–C18	10.5 (5)	C1–C2–C18–C17	38.9 (5)
C2–C1–C6–C7	43.7 (5)	S2–C20–C21–C22	-27.7 (5)
S1–C9–C10–C11	35.1 (4)		

Methyl H atoms were positioned geometrically (C–H = 0.96 Å) and refined as riding, with free rotation about the C–C bond and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Phenyl H atoms were also positioned geometrically (C–H = 0.93 Å) and were refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1244). Services for accessing these data are described at the back of the journal.

References

- Brown, G. H. (1971). *Photochromism*. New York: Wiley Interscience.
- Bruker (1997). *SHELXTL* (Version 5.10) and *XSCANS* (Version 2.2). Bruker AXS Inc., Madison, Wisconsin, USA.
- Dürr, H. & Bouas-Laurent, H. (1990). *Photochromic: Molecules and Systems*. Amsterdam: Elsevier.
- Irie, M. (2000). *Chem. Rev.* **100**, 1685–1716.
- Peters, A., Vitols, C., McDonald, R. & Branda, N. R. (2003). *Org. Lett.* **5**, 1183–1186.
- Pu, S.-Z., Liu, G. & Yan, L.-S. (2005). *Acta Cryst.* **E61**, o2856–o2858.
- Pu, S.-Z., Yang, T.-S., Wang, R.-J. & Xu, J.-K. (2005). *Acta Cryst.* **C61**, o568–o570.
- Pu, S.-Z., Yang, T.-S. & Yan, L.-S. (2005). *Acta Cryst.* **E61**, o2961–o2963.
- Pu, S.-Z., Zhang, F.-S., Wang, R.-J. & Liang, Q. (2004). *Acta Cryst.* **C60**, o305–o307.
- Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.
- Sun, F., Zhang, F.-S., Guo, H.-B., Zhou, X.-H., Wang, R.-J. & Zhao, F.-Q. (2003). *Tetrahedron*, **59**, 7615–7621.
- Takami, S. & Irie, M. (2004). *Tetrahedron*, **60**, 6155–6161.
- Tian, H. & Yang, S.-J. (2004). *Chem. Soc. Rev.* **33**, 85–97.
- Uchida, K., Kido, Y., Yamaguchi, T. & Irie, M. (1998). *Bull. Chem. Soc. Jpn.* **71**, 1101–1108.
- Woodward, R. B. & Hoffmann, R. (1970). *The Conservation of Orbital Symmetry*. Weinheim: Verlag Chemie GmbH.
- Yamamoto, S., Matsuda, K. & Irie, M. (2003). *Angew. Chem. Int. Ed.* **42**, 1636–1639.