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Key indicators

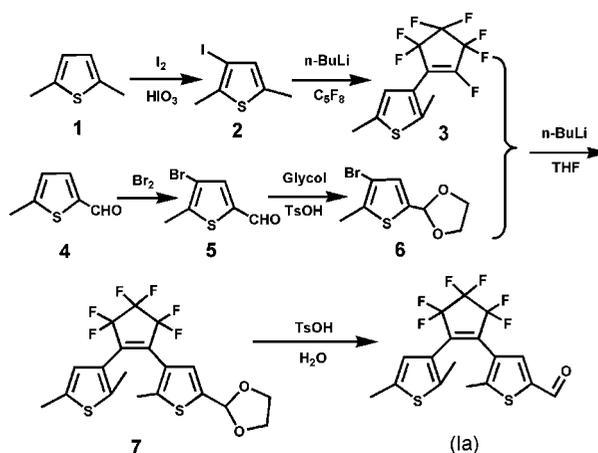
Single-crystal X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
Disorder in main residue
 R factor = 0.075
 wR factor = 0.162
Data-to-parameter ratio = 11.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1-(2,5-Dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluoro-2-(5-formyl-2-methyl-3-thienyl)cyclopent-1-ene: a new photochromic diarylethene compound

The title compound, $\text{C}_{17}\text{H}_{12}\text{F}_6\text{OS}_2$, is a new nonsymmetric photochromic diarylethene which contains 3-thienyl substituents. The distance between the two reactive C atoms in the molecule is 3.550 (7) Å. The dihedral angles between the central cyclopentene ring and two thiophene rings are 44.7 (3) and 43.6 (3)°.Received 17 January 2006
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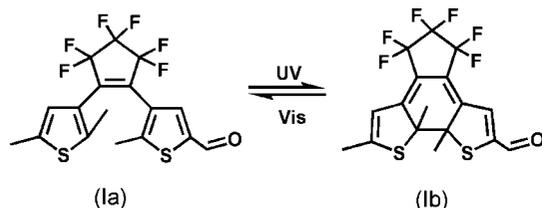
Comment

Photochromic compounds have attracted much attention from both fundamental and practical points of view because of their potential for application as photonic devices, such as optical memories and switches (Uchida *et al.*, 2005). Among the various types of photochromic compounds, diarylethenes are regarded as the most promising candidates for such applications because of their excellent thermal stability, fatigue-resistant character, rapid response and high reactivity in the solid state (Pu, Yang, Xu *et al.*, 2005; Pu, Liu *et al.*, 2005; Pu, Yang, Wang & Xu, 2005). Although the structures and properties of many diarylethenes have been reported (Irie, 2000; Tian & Yang, 2004; Matsuda & Irie, 2004; Morimoto & Irie, 2005; Pu, Fan *et al.*, 2005; Pu, Li *et al.*, 2005, 2006; Pu, Yang *et al.*, 2006), compounds which show strong photochromic reactivity in the crystalline phase are rare (Kobatake & Irie, 2004). Among the diarylethenes reported to date, compounds bearing formyl groups are interesting, because the formyl group can be easily displaced by many other functional groups by some simple reactions, and this is an effective method for the development of new diarylethene compounds (Pu, Yang & Yan, 2005; Pu, Xu *et al.*, 2005). The present paper presents the synthesis and crystal structure of the title new nonsymmetric diarylethene, (Ia), with one formyl group.



In the cyclopent-1-ene ring of (Ia), the C1—C2 bond is clearly a double bond, being significantly shorter than the

other single bonds from atoms C1 and C2 (Table 1). The two methyl groups attached to atoms C6 and C12 are located on different sides of the C1=C2 double bond, as reflected in the torsion angles C1–C2–C13–C12 [45.8 (9)°] and C2–C1–C7–C6 [43.3 (9)°] (Fig. 1). Such a conformation is crucial for the compound to exhibit photochromic and photoinduced properties (Woodward & Hoffmann, 1970). 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 adjacent thiophene rings, S1/C6–C9 and S2/C12–C15, are 44.7 (3) and 43.6 (3)°, respectively. The intramolecular distance between the two reactive C atoms (C6···C12) is 3.550 (7) Å. This distance indicates that the crystal can be expected to undergo photochromism to generate compound (Ib) (see scheme), because photochromic reactivity usually appears when the distance between the reactive C atoms is less than 4.2 Å (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).



The crystal of (Ia) shows photochromism to form (Ib) in accordance with the expected ring closure. Upon irradiation with light of wavelength 254 nm, the colourless single crystals turn rapidly to blue, and the colour remains stable in the dark. When these blue crystals are dissolved in dichloromethane, the resulting solution also shows a blue colour, with a maximum absorption at 585 nm, consistent with the presence of the closed-ring isomer, (Ib). This phenomenon suggests that the title compound can undergo a photochromic reaction to produce 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 visible light of wavelength >500 nm, the blue coloured crystal returns to the initial colourless crystal. The absorption spectrum of a dichloromethane solution of the colourless crystal shows an absorption maximum at 251 nm, *i.e.* it is a solution of the opening form, (Ia).

Experimental

Compound (Ia) was derived from 2,5-dimethylthiophene, (1), and 5-methylthiophene-2-carbaldehyde, (4). 1-(2,5-Dimethyl-3-thienyl)-perfluorocyclopent-1-ene, (3) (6.95 g, 22.84 mmol), was synthesized in 51.33% yield according to the procedure of Sun *et al.* (2003), from (1) (5.0 g, 44.64 mmol), *n*-BuLi–hexane solution (1.6 M, 24.0 ml) and octafluorocyclopentene (5.17 ml, 38.00 mmol). Dioxolane acetal, (6)

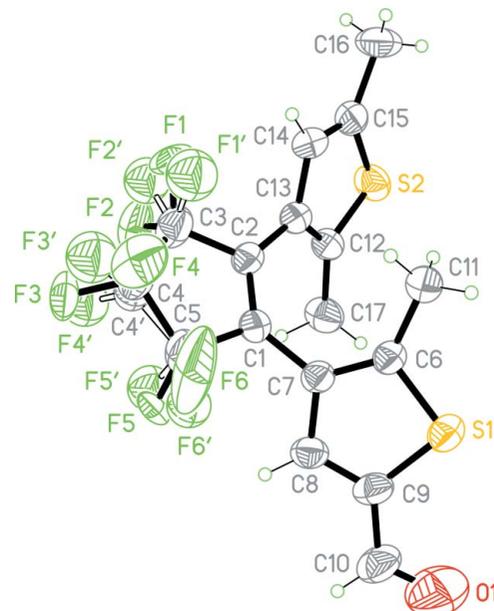


Figure 1

The molecular structure of (Ia), showing 35% probability ellipsoids and the atom-numbering scheme. Primed atoms indicate the minor disorder component.

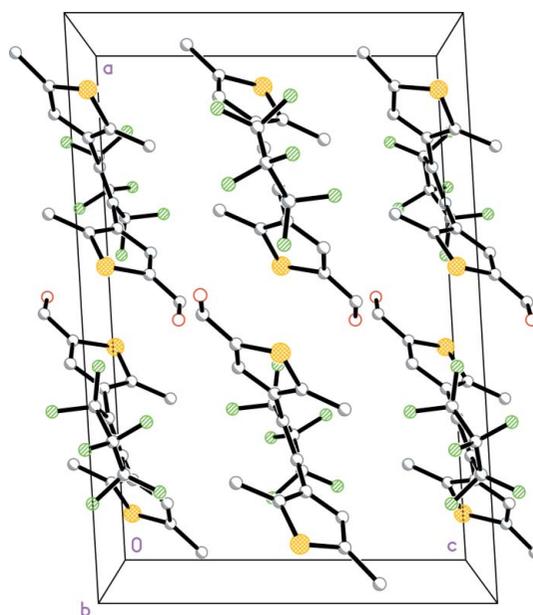


Figure 2

A packing diagram for (Ia), viewed down the *b* axis. H atoms and the minor disorder component have been omitted for clarity.

(4.15 g, 16.67 mmol), was prepared in 66.01% yield according to the procedure of Pu *et al.* (2002), from (4) (3.18 g, 25.25 mmol), glycol (6.0 ml) and *p*-toluenesulfonic acid (TsOH; 0.01 g, 0.05 mmol). To a stirred solution of (6) (4.15 g, 16.67 mmol) in tetrahydrofuran (THF; 50 ml) was added dropwise a 1.6 M *n*-BuLi solution in hexane (10.5 ml, 16.80 mmol) at 195 K under a nitrogen atmosphere. Stirring was continued for 30 min, and then (3) (5.07 g, 16.67 mmol) dissolved in THF (10.0 ml) was added to the reaction mixture, and the mixture was stirred for 5 h at 195 K. The reaction was quenched by the addition of water. After a series of routine operations, 3,3,4,4,5,5-hexafluoro-1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-[2-(1,3-dioxol-

ane)]-3-thienyl]-cyclopent-1-ene, (7) (3.62 g, 7.97 mmol), was obtained in 47.8% yield by column chromatography on SiO₂ using petroleum ether as the eluent. Finally, the title compound, (1a) (2.98 g, 7.26 mmol), was obtained in 91.1% yield by hydrolysing (7) (3.62 g, 7.97 mmol). The total yield for compounds (1) and (4) was 16.20%. Slow evaporation of a chloroform solution of crude (1a) gave colourless crystals of (1a) (m.p. 382.2 K). Analysis, calculated for C₁₇H₁₂F₆OS₂: C 49.75, H 2.95%; found: C 49.81, H 3.01%. Spectroscopic analysis: ¹H NMR (400 MHz, CDCl₃, δ, p.p.m.): 1.830 (s, -CH₃), 2.004 (s, -CH₃), 2.421 (s, -CH₃), 6.698 (s, 1H, thiophene-H), 7.746 (s, 1H, thiophene-H), 9.845 (s, 1H, -CHO); ¹⁹F NMR (376 MHz, CDCl₃, δ, p.p.m.): 109.92 (2F), 110.44 (2F), 131.85 (2F); ¹³C NMR (100 MHz, CDCl₃, δ, p.p.m.): 14.1, 14.3, 15.4, 124.1, 124.4, 126.8, 136.4, 138.5, 139.9, 141.7, 151.8, 182.1.

Crystal data

C₁₇H₁₂F₆OS₂
M_r = 410.39
 Monoclinic, *P*2₁/*c*
a = 17.1836 (15) Å
b = 8.8408 (8) Å
c = 11.6536 (16) Å
 β = 93.342 (9)°
V = 1767.4 (3) Å³
Z = 4
D_x = 1.542 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 47 reflections
 θ = 2.4–16.9°
 μ = 0.36 mm⁻¹
T = 295 (2) K
 Prism, colourless
 0.4 × 0.2 × 0.2 mm

Data collection

Bruker *P*4 diffractometer
 ω scans
 Absorption correction: none
 4094 measured reflections
 3107 independent reflections
 1421 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029
 θ_{max} = 25.0°
h = -20 → 20
k = -10 → 1
l = -1 → 13
 3 standard reflections every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.075
wR(*F*²) = 0.162
S = 1.02
 3107 reflections
 267 parameters
 H-atom parameters constrained
w = 1/[σ²(*F*_o²) + (0.001*P*)² + 5*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.51 e Å⁻³
 Δρ_{min} = -0.30 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—C9	1.712 (6)	C1—C2	1.338 (6)
S1—C6	1.725 (5)	C1—C7	1.478 (7)
S2—C15	1.712 (6)	C1—C5	1.513 (7)
S2—C12	1.709 (5)	C2—C13	1.466 (7)
O1—C10	1.194 (9)	C2—C3	1.507 (7)
C7—C1—C2—C13	6.8 (10)	C3—C4—C5—C1	16.3 (8)
C5—C1—C2—C3	5.5 (6)	C2—C1—C7—C6	43.3 (9)
F2—C3—C4—C5	102.2 (7)	C1—C2—C13—C12	45.8 (9)
C2—C1—C5—C4	-13.6 (7)		

Atom C4 and all F atoms of the hexafluorocyclopentene ring are disordered over two positions. The site occupancies were initially refined, and then fixed at 0.65 and 0.35 in the final refinement. The atoms with minor occupancy were refined isotropically to avoid abnormal deformation of the displacement ellipsoids. H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 (aromatic) and 0.96 Å (methyl), and with *U*_{iso}(H) = 1.2*U*_{eq}(aromatic C) or 1.5*U*_{eq}(methyl 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*.

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References

Bruker (1997). *XSCANS* (Version 2.2) and *SHELXTL* (Version 5.10). Bruker AXS Inc., Madison, Wisconsin, USA.
 Irie, M. (2000). *Chem. Rev.* **100**, 1685–1716.
 Kobatake, S. & Irie, M. (2004). *Bull. Chem. Soc. Jpn.* **77**, 195–210.
 Kobatake, S., Kuma, S. & Irie, M. (2004). *Bull. Chem. Soc. Jpn.* **77**, 945–951.
 Matsuda, K. & Irie, M. (2004). *J. Photochem. Photobiol. C* **5**, 169–182.
 Morimoto, M. & Irie, M. (2005). *Chem. Commun.* pp. 3895–3905.
 Pu, S.-Z., Fan, C.-B., Chen, B., Wang, R.-J. & Xu, J.-K. (2005). *Acta Cryst.* **E61**, o4369–o4371.
 Pu, S.-Z., Li, G.-Z., Wang, R.-J. & Zhao, J.-Q. (2005). *Acta Cryst.* **E61**, o4246–o4249.
 Pu, S.-Z., Li, G.-Z., Wang, R.-J. & Zhao, J.-Q. (2006). *Acta Cryst.* **E62**, o150–o152.
 Pu, S.-Z., Liu, G., Chen, B. & Wang, R.-J. (2005). *Acta Cryst.* **C61**, o599–o601.
 Pu, S.-Z., Xu, J.-K., Shen, L., Xiao, Q., Yang, T.-S. & Liu, G. (2005). *Tetrahedron Lett.* **46**, 871–875.
 Pu, S.-Z., Yang, T.-S., Chen, B. & Xu, J.-K. (2006). *Acta Cryst.* **E62**, o279–o281.
 Pu, S.-Z., Yang, T.-S., Wang, R.-J. & Xu, J.-K. (2005). *Acta Cryst.* **C61**, o568–o570.
 Pu, S.-Z., Yang, T.-S., Xu, J.-K., Shen, L., Li, G.-Z., Xiao, Q. & Chen, B. (2005). *Tetrahedron*, **61**, 6623–6629.
 Pu, S.-Z., Yang, T.-S. & Yan, L.-S. (2005). *Acta Cryst.* **E61**, o2961–o2963.
 Pu, S.-Z., Zhang, F.-S., Zhou, X.-H., Sun, F., Guo, H.-B., Chan, S.-K. & Wang, R.-J. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 413–414.
 Ramamurthy, V. & Venkatesan, K. (1987). *Chem. Rev.* **87**, 433–481.
 Shibata, K., Muto, K., Kobatake, S. & Irie, M. (2002). *J. Phys. Chem. A*, **106**, 209–214.
 Sun, F., Zhang, F.-S., Guo, H.-B., Zhou, X.-H., Wang, R.-J. & Zhao, F.-Q. (2003). *Tetrahedron*, **59**, 7615–7621.
 Tian, H. & Yang, S.-J. (2004). *Chem. Soc. Rev.* **33**, 85–97.
 Uchida, K., Saito, M., Murakami, A., Kobayashi, T., Nakamura, S. & Irie, M. (2005). *Chem. Eur. J.* **11**, 534–542.
 Woodward, R. B. & Hoffmann, R. (1970). *The Conservation of Orbital Symmetry*. Weinheim: Verlag Chemie GmbH.
 Yamaguchi, T. & Irie, M. (2005). *J. Org. Chem.* **70**, 10323–10328.