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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ (C–C) = 0.003 Å
Disorder in main residue
R factor = 0.040
wR factor = 0.114
Data-to-parameter ratio = 12.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

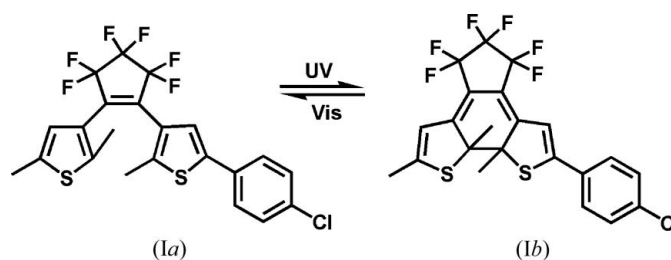
1-[5-(4-Chlorophenyl)-2-methyl-3-thienyl]-2-(2,5-dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene: a new photochromic diarylethene compound

The title compound, C₂₂H₁₅ClF₆S₂, is a new unsymmetrical photochromic diarylethene with a *para*-chlorophenyl substituent. It is a promising candidate for an optical recording medium and other optoelectronic device materials. The distance between the two reactive C atoms is 3.612 (6) Å; the dihedral angles between the cyclopentene ring and the thiophene rings are 40.9 (5) and 41.2 (5)°, and that between one thiophene ring and the adjacent benzene ring is 27.8 (4)°.

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Comment

Photochromic diarylethenes have attracted much attention because of their potential applicability to optoelectronic devices, such as photon-mode optical recording (Pu *et al.*, 2006), photoswitches (Yam *et al.*, 2004; Irie, 2000) and color displays (Higashiguchi *et al.*, 2005). For further background information, see Pu, Yang *et al.* (2005). The present paper presents the synthesis and crystal structure of compound (Ia).



A drawing of the asymmetric unit is shown in Fig. 1. Relevant bond lengths and torsion angles are given in Table 1. As shown in Fig. 1, the molecule adopts a photoactive antiparallel conformation. In the cyclopent-1-ene ring, C18–C22 is clearly a double bond, being significantly shorter than the other single bonds from atoms C18 and C22 (Table 1). The two methyl groups are located on different sides of this double bond, as is reflected in the torsion angles C5–C4–C18=C22 and C18=C22–C9–C8 (Table 1), and thus are *trans* with respect to the double bond. The two independent planar thiophene ring systems have essentially identical geometries, and the dihedral angles between the plane of the cyclopent-1-ene ring and the thiophene rings are 40.9 (5)° for S1/C2–C5 and 41.2 (5)° for S2/C8–C11. A *para*-chlorophenyl substituent is attached to one thiophene ring at the 5-position, and the dihedral angle between them is 27.8 (4)°. The distance between the two reactive C atoms, C5 and C8, is 3.612 (6) Å. If the molecule is fixed in an antiparallel mode and the distance between reacting C atoms on the aryl rings is less than 4.2 Å, the molecule undergoes a photocyclization reaction (Kobayashi *et al.*, 2002; Morimoto & Irie, 2006). Therefore, the title

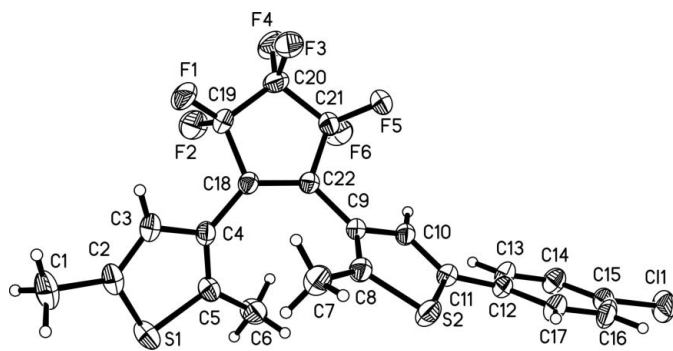


Figure 1

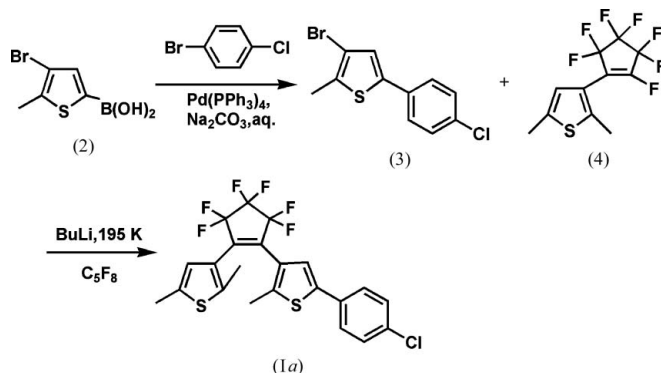
The structure of compound (1a) with 35% probability displacement ellipsoids, showing the atomic numbering scheme. For clarity, only the major disorder component is shown for the hexafluorocyclopentene ring.

compound can display photochromism in the crystalline phase.

Actually, crystals of (1a) showed photochromism in accordance with the expected ring closure, to form (1b). Upon irradiation with 254 nm light, the colorless crystals rapidly turned to red, and the color remained stable in the dark. When the red crystal was dissolved in hexane solution, the solution was also red in color. The maximum absorption of this solution was observed at 534 nm, consistent with the presence of the closed-ring isomer, (1b). Upon irradiation with longer than 450 nm visible light, the red crystal can return to the initial colorless one, and the absorption spectrum of the hexane solution containing the colorless crystal was the same as that of solutions of the open-ring form, (1a), with the maximum absorption at 293 nm.

Experimental

Compound (1a) was prepared as outlined in the reaction scheme.



3-Bromo-2-methyl-5-(4-chlorophenyl)thiophene, (3) (5.8 g, 20.3 mmol), was prepared in 89.7% yield by reacting 3-bromo-2-methyl-5-thienylboronic acid, (2) (Pu, Li *et al.*, 2005) (5.0 g, 22.6 mmol) with 4-bromo-1-chlorobenzene (4.3 g, 22.6 mmol) in the presence of Pd(PPh₃)₄ (0.8 g) and Na₂CO₃ (2 mol l⁻¹, 84.8 mmol) in THF (100 ml) for 12 h at 343 K. To a stirred THF solution (80 ml) of compound (3) (5.8 g, 20.3 mmol), an *n*-BuLi/hexane solution (8.1 ml, 2.5 mol l⁻¹, 20.3 mmol) was added at 195 K under a nitrogen atmosphere. 30 min later, (2,5-dimethyl-3-thienyl)perfluorocyclo-

pent-1-ene, (4) (Sun *et al.*, 2003) (6.2 g, 20.3 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 (1a) (5.5 g, 11.2 mmol) in 55% yield. The compound crystallized from hexane at room temperature and produced crystals suitable for X-ray analysis. The structure of (1a) was confirmed by melting point and NMR. M.p. 418 K; ¹H NMR (400 MHz, CDCl₃): δ 1.86 (s, 3H, -CH₃), 1.92 (s, 3H, -CH₃), 2.42 (s, 3H, -CH₃), 6.73 (s, 1H, thiophene-H), 7.23 (s, 1H, thiophene-H), 7.34–7.36 (d, 2H, *J* = 8.5 Hz, ben-H), 7.45–7.47 (d, 2H, *J* = 8.5 Hz, ben-H).

Crystal data

C ₂₂ H ₁₅ ClF ₆ S ₂	<i>Z</i> = 4
<i>M_r</i> = 492.91	<i>D_x</i> = 1.537 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 21.232 (3) Å	<i>μ</i> = 0.43 mm ⁻¹
<i>b</i> = 9.0912 (13) Å	<i>T</i> = 294 (2) K
<i>c</i> = 11.1534 (17) Å	Prism, colorless
<i>β</i> = 98.243 (2)°	0.24 × 0.22 × 0.20 mm
<i>V</i> = 2130.6 (5) Å ³	

Data collection

Bruker SMART CCD area-detector diffractometer	11640 measured reflections
<i>φ</i> and <i>ω</i> scans	4337 independent reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	2721 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.903, <i>T</i> _{max} = 0.918	<i>R</i> _{int} = 0.033
	<i>θ</i> _{max} = 26.4°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0534 <i>P</i>) ² + 0.3854 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.040	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.114	(Δ/ <i>σ</i>) _{max} = 0.001
<i>S</i> = 1.01	Δ <i>ρ</i> _{max} = 0.21 e Å ⁻³
4337 reflections	Δ <i>ρ</i> _{min} = -0.26 e Å ⁻³
340 parameters	H-atom parameters constrained

Table 1

Selected geometric parameters (Å, °).

S1—C2	1.718 (3)	C18—C19	1.502 (3)
S1—C5	1.719 (2)	C19—C20	1.506 (3)
S2—C8	1.722 (2)	C20—C21	1.512 (3)
S2—C11	1.724 (2)	C21—C22	1.496 (3)
C18—C22	1.350 (3)		
C2—C3—C4—C18	175.9 (2)	S2—C11—C12—C13	157.63 (19)
C3—C4—C5—C6	177.2 (2)	C11—C15—C16—C17	179.6 (2)
S2—C8—C9—C22	-174.46 (17)	C5—C4—C18—C22	-42.4 (4)
C22—C9—C10—C11	174.4 (2)	C8—C9—C22—C18	-40.8 (4)

The F atoms at C19, C20, C21 were found to be disordered over two distinct conformations. From refinement (anisotropic), the site occupancies were fixed at 0.63 (2):0.37 (2) for F atoms at C19, 0.64 (3):0.36 (3) for F atoms at C20 and 0.69 (3):0.31 (3) for F atoms at C21. All H atoms were placed in calculated positions, with C—H distances of 0.93 Å (aromatic) and 0.96 Å (CH₃). They were included in the refinement in the riding-model approximation with isotropic displacement parameters set equal to 1.2*U*_{eq} of the carrier atom for the aromatic H and 1.5*U*_{eq} of the carrier for CH₃.

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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