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1-[5-(2-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

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The title compound, $C_{22}H_{15}ClF_6S_2$, is a new asymmetric photochromic dithienylethene with an *ortho*-chlorophenyl substituent. The molecule adopts a photoactive antiparallel conformation, the distance between the two reactive C atoms being 3.582 (4) Å. The dihedral angles between the central cyclopentene ring and the two thiophene rings are 41.0 (5) and 52.1 (5)°, and that between one thiophene ring and the attached benzene ring is 39.9 (5)°.

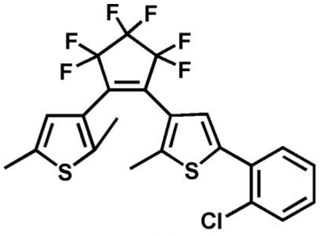
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.105
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In recent years, considerable effort has been expended towards the synthesis of photochromic diarylethenes, due to their potential capabilities for various optoelectronic devices, such as optical recording and photoswitches (Dinescu & Wang, 1999; Nakashima & Irie, 1999; Irie, 2000; Pu, Zhang *et al.*, 2006; Pu, Tang *et al.*, 2006). For further background information, see Pu *et al.* (2005). In the present work, the title photochromic diarylethene, (I) (Fig. 1), was synthesized. We have previously reported the structure of the 4-chloro-analogue, (II), of this compound (Pu, Zheng *et al.*, 2006). In order to investigate systematically the effect of the substituent position on the photochemical properties of diarylethenes, we have now determined the structure of (I).



(I)

In the hexafluorocyclopentene ring of (I), C7—C11 is clearly a double bond, being significantly shorter than the other bonds to atoms C7 and C11 (Table 1). The two methyl groups attached to atoms C5 and C13 are located on opposite sides of the alkene plane, as reflected in the torsion angles (Table 1), and are *cis* with respect to the C7═C11 double bond. The two independent thiophene ring systems have essentially identical geometries and the dihedral angles between the cyclopentene ring (major disorder component) and the attached thiophene rings are 41.0 (5)° for S1/C2–C5 and 52.1 (5)° for S2/C13/C12/C15/C16. An *ortho*-chlorophenyl substituent is attached to one of the thiophene rings. The dihedral angle between the thiophene ring and the attached benzene ring is 39.9 (5)°. The corresponding values in the 4-chloro-analogue, (II), are 40.9 (5), 41.2 (5) and 27.8 (4)°, respectively. This conformation leads to a C5···C13 separation of 3.582 (4) Å [compared with 3.612 (6) Å in (II)], which is short enough, theoretically, for a cyclization reaction to take place in the crystalline phase (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).

Crystals of (I) show a photochromic reaction, in accordance with the expected ring closure. Upon irradiation with 250 nm light, the colourless crystals rapidly turn red, and this colour remains stable in the dark. When a red crystal is dissolved in hexane, the solution also shows a red colour, with an absorption maximum at 531 nm, suggesting the presence of a closed-ring isomer. Hence (I) undergoes a photochromic reaction to produce the closed-ring molecule in the crystalline phase. On irradiation at wavelengths longer than 450 nm, the red crystal reverts to colourless, with an absorption spectrum in hexane identical to that of the colourless crystals, indicating a return to the open-ring isomer, (I) (absorption maximum 250 nm).

Experimental

The title compound, (I), was prepared in 29% total yield by literature methods (Pu, Zheng *et al.*, 2006) using 1-chloro-2-bromobenzene as the starting material. Crystals suitable for X-ray analysis were grown from a hexane solution by slow evaporation at room temperature (m.p. 354 K).

Crystal data

$C_{22}H_{15}ClF_6S_2$
$M_r = 492.91$
Monoclinic, $P2_1/n$
$a = 6.9539\ (12)$ Å
$b = 21.661\ (4)$ Å
$c = 14.543\ (2)$ Å
$\beta = 94.278\ (3)^\circ$
$V = 2184.5\ (6)$ Å^3

$Z = 4$
$D_x = 1.499$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.42$ mm^{-1}
$T = 294\ (2)$ K
Block, colourless
0.35 × 0.27 × 0.21 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.866$, $T_{\max} = 0.916$

10959 measured reflections
3841 independent reflections
2519 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 25.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.105$
$S = 1.02$
3841 reflections
311 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 0.7775P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C8—C7	1.5002 (19)	C10—C11	1.5000 (19)
C8—C9	1.537 (2)	C7—C11	1.3467 (18)
C9—C10	1.524 (2)		
C5—C4—C7—C11	43.4 (2)	C7—C11—C12—C13	49.6 (2)

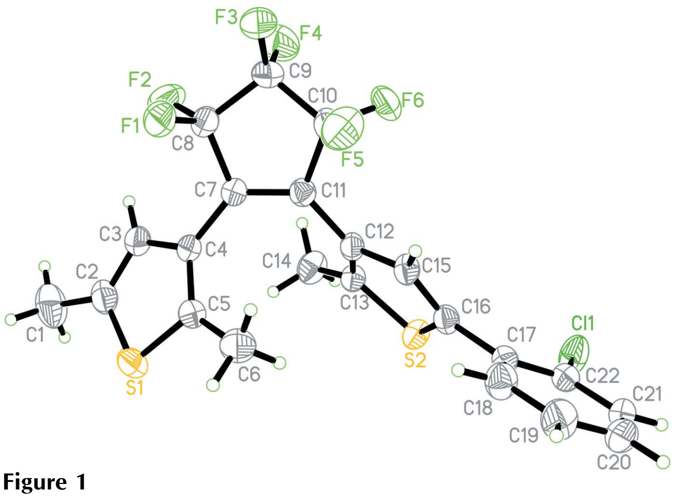


Figure 1
The molecular structure of (I), with 35% probability displacement ellipsoids, showing the atomic numbering scheme. The minor disorder component is not shown.

Electron-density maps showed that the CF_2 groups at C8, C9 and C10 were disordered, corresponding to two conformations of the cyclopentene ring. The site occupancies refined to 0.9036 (7):0.0964 (7). Corresponding atoms in the major and minor disorder components were assigned the same anistropic displacement parameters. All H atoms were placed in calculated positions, with C—H distances of 0.93 (aromatic) and 0.96 Å (CH_3). They were included in the refinement in the riding-model approximation, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for aromatic H or $1.5U_{\rm eq}({\rm C})$ for CH_3.

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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