

5,5'-Dimethyl-4,4'-(3,3,4,4,5,5-hexafluorocyclopentene-1,2-diyl)bis(thiophene-2-carboxylic acid) acetone 0.25-solvate

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Key indicators

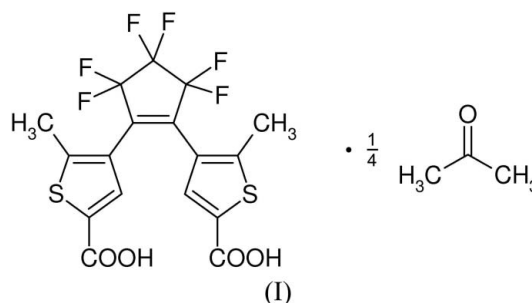
Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in solvent or counterion
 R factor = 0.060
 wR factor = 0.149
Data-to-parameter ratio = 12.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{17}\text{H}_{10}\text{F}_6\text{O}_4\text{S}_2 \cdot 0.25\text{C}_3\text{H}_6\text{O}$, there are two non-solvent molecules in the asymmetric unit, with different conformations. One is a photo-active antiparallel conformation in which the reactive C atoms are separated by 3.569 (6) Å. The other is a photo-inactive parallel conformation in which the reactive C atoms are separated by 4.541 (7) Å.

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Comment

Amongst photochromic compounds, the class of diarylethenes is often regarded as one of the most attractive because of the thermal stability of both isomers, together with good fatigue resistance and electronic properties (Irie, 2000; Fernandez-Asebes & Lehn, 1999). Diarylethene derivatives usually exhibit one of two conformations in the solid state, *viz.* parallel or antiparallel (Kobatake *et al.*, 1999).



The title compound (DTEC), (I), was synthesized from 1,2-bis(2-methyl-5-formylthien-3-yl)perfluorocyclopentene, which is a good intermediate for preparing novel diarylethenes. It attracted our attention on account of its potential for optical storage and optical switching. Unlike other diarylethene molecules, which commonly exhibit a single conformation in the solid state, DTEC adopts both the antiparallel (Fig. 1) and parallel (Fig. 2) conformations in the same crystal structure. In the antiparallel conformation, the distance between the reactive C atoms (C6 and C12) is 3.569 (6) Å, which is close enough for a photocyclization reaction. In the parallel conformation, the distance between the comparable atoms (C23 and C29) is 4.541 (7) Å, which is too long to allow photocyclization.

Experimental

The title compound was obtained by oxidation of 1,2-bis(2-methyl-5-formylthien-3-yl)perfluorocyclopentene, which was prepared according to the literature method of Pu *et al.* (2003). Jones reagent (15 ml) was added dropwise to a well stirred solution of (2-methyl-5-

formylthien-3-yl)perfluorocyclopentene (0.5 g, 1.18 mmol) in acetone (35 ml) at room temperature, and stirring was continued for 3 h. 2-Propanol (30 ml) was then added slowly and the resultant mixture was extracted with diethyl ether, and the combined organic extracts were dried over MgSO_4 . After removal of the solvent, column chromatography (silica gel, ethyl acetate) of the residue afforded the title compound (yield 0.78 g, 95%) as a white powder. Colorless single crystals were obtained from a 2:1 acetone/hexane solution (m.p. 428–429 K).

Crystal data

$\text{C}_{17}\text{H}_{10}\text{F}_6\text{O}_4\text{S}_2 \cdot 0.25\text{C}_3\text{H}_6\text{O}$
 $M_r = 470.89$
 Triclinic, $P\bar{1}$
 $a = 8.8885$ (11) Å
 $b = 15.1907$ (17) Å
 $c = 16.734$ (2) Å
 $\alpha = 68.855$ (8)°
 $\beta = 84.902$ (9)°
 $\gamma = 75.965$ (10)°

$V = 2044.5$ (4) Å³
 $Z = 4$
 $D_x = 1.530$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.34$ mm⁻¹
 $T = 295$ (2) K
 Prism, colorless
 $0.5 \times 0.3 \times 0.2$ mm

Data collection

Bruker *P4* diffractometer
 ω scans
 Absorption correction: none
 7484 measured reflections
 6969 independent reflections
 3915 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 25.0^\circ$
 3 standard reflections
 every 97 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.149$
 $S = 1.02$
 6969 reflections
 570 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 4P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.62$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2A}\cdots\text{O5}^{\text{i}}$	0.82	1.84	2.635 (3)	164
$\text{O4}-\text{H4A}\cdots\text{O7}^{\text{ii}}$	0.82	1.87	2.674 (3)	168
$\text{O6}-\text{H6A}\cdots\text{O1}^{\text{iii}}$	0.82	1.82	2.630 (3)	171
$\text{O8}-\text{H8B}\cdots\text{O3}^{\text{ii}}$	0.82	1.81	2.598 (3)	162

Symmetry codes: (i) $x + 2, y, z$; (ii) $-x + 1, -y + 2, -z$; (iii) $x - 2, y, z$.

H atoms bound to C atoms were placed in geometrically idealized positions, with $\text{C}-\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for Csp^2 , and $\text{C}-\text{H} = 0.96$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for Csp^3 . The methyl groups were allowed to rotate about their local threefold axes. The H atoms of the carboxyl groups were positioned geometrically, with $\text{O}-\text{H} = 0.82$ Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. For the acetone molecule, the $\text{C}=\text{O}$ bond was restrained to be 1.22 (1) Å, the two $\text{C}-\text{C}$ bonds were restrained to be 1.50 (1) Å, and the 1,3-distances were restrained to be 2.59 (5) and 2.38 (5) Å for $\text{C}\cdots\text{C}$ and $\text{C}\cdots\text{O}$, respectively. The $\text{C}=\text{O}$ bonds of the carboxylic acid groups were also restrained to be 1.22 (1) Å.

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*.

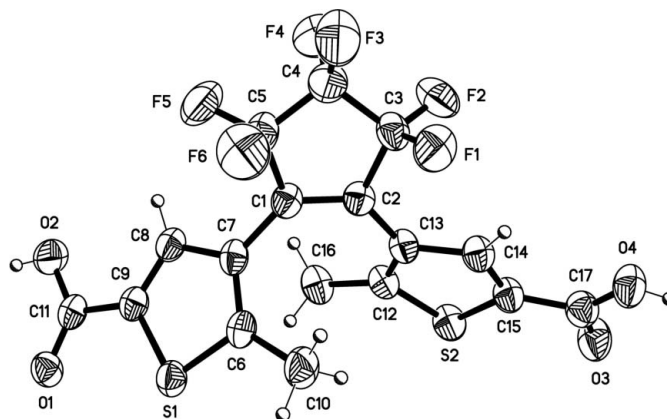


Figure 1

View of one of the DTEC molecules in the asymmetric unit, exhibiting a photo-active antiparallel conformation. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

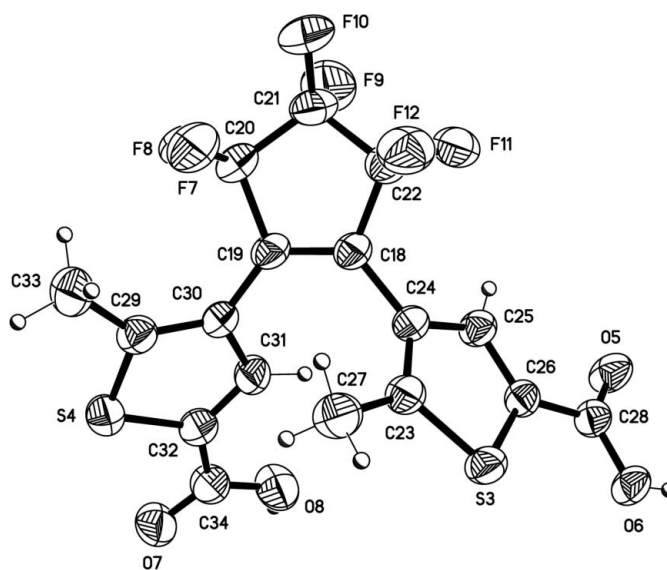


Figure 2

View of the other DTEC molecule in the asymmetric unit, exhibiting a photo-inactive parallel conformation. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

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