

3,3,4,4,5,5-Hexafluoro-1,2-bis(5-hydroxymethyl-2-methyl-3-thienyl)-cyclopent-1-ene

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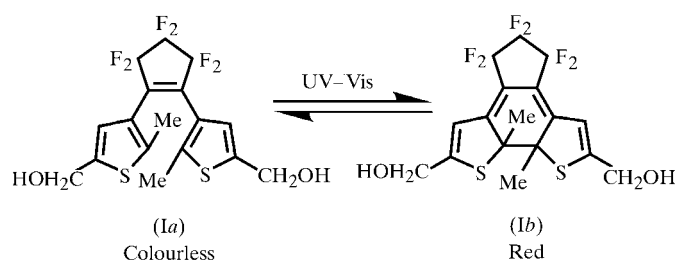
The title compound, $C_{17}H_{14}F_6O_2S_2$, a photochromic diarylethene, is one of the most promising materials for optical memories and other optoelectronic devices. The hexafluorocyclopentene group and the two thiophene rings are all planar, and the dihedral angles between the cyclopentene ring and the adjacent thiophene rings are 46.4 (1) and 49.5 (1)°.

Comment

Photochromic diarylethene derivatives have attracted much attention as the most promising materials for optical memories and other optoelectronic devices because of their good thermal stability, high sensitivity and multiplexed recording (Guo *et al.*, 2003; Irie, 2000). A diarylethene with five-membered heterocyclic rings can have one of two possible conformations, *viz.* with the two rings in mirror symmetry (parallel conformation) or in C_2 symmetry (antiparallel conformation; Irie & Mohri, 1988; Uchida *et al.*, 1990). According to the Woodward–Hoffmann rule, photoinduced cyclization and cycloreversion reactions can proceed in a conrotatory mode by alternate irradiation with UV and visible light only from the antiparallel conformation (Woodward & Hoffmann, 1970; Irie, 2000). In a previous paper, we have reported the allomorphy of a diarylethene compound and discussed its photochromic properties both in solution and in the single-crystal phase (Pu *et al.*, 2003). This compound is a good example for validating the rule exactly. In the present work, a novel photochromic diarylethene compound, (Ia), was synthesized in high yield by a simple method. The structure of this compound is presented here.

The molecular structure of (Ia) is shown in Fig. 1 and a packing diagram is shown in Fig. 2. Selected geometric

parameters are given in Table 1. In the hexafluorocyclopentene ring, the C1–C2 bond is clearly a double bond, being significantly shorter than the C1–C5 and C2–C3 single bonds. The distance between the reactive C atoms C6 and C12 is 3.596 (4) Å; this distance is short enough theoretically for the reaction to take place in the crystalline phase (Ramamurthy & Venkatesan, 1987). The dihedral angles between the hexafluorocyclopentene ring and the adjacent thiophene rings are 46.4 (1) and 49.5 (1)°, respectively. In addition, there exist intermolecular hydrogen-bonding interactions between molecules. There are two independent hydrogen bonds (Table 2); the O1–H···O2 interaction connects two molecules into a dimer, and the O2–H···O1 interaction enables the dimers to form two-dimensional layers parallel to the (100) plane.



The molecule has approximate C_2 symmetry (antiparallel conformation) and can therefore undergo a photocyclization reaction (Yamada *et al.*, 2000). The photochromism is shown in the scheme above. On irradiation with 254 nm UV light, the colorless single crystal of (Ia) turned red immediately. When observed under polarized light, the red color intensity changed on rotation of the crystal. This phenomenon suggests that the closed-ring isomers are packed regularly in the crystal. When the red crystal was dissolved in ethanol, the solution turned red; the absorption maximum was observed at 514 nm, as it is for the closed-ring form, (Ib), shown in the scheme above. Unfortunately, the single-crystal diffraction pattern of

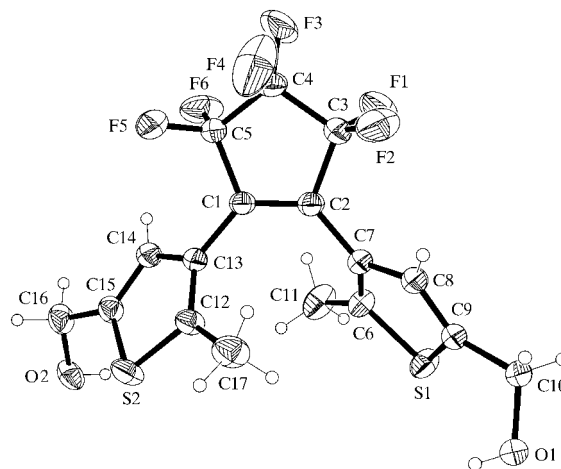


Figure 1

The structure of (Ia), showing 35% probability displacement ellipsoids and the atom-numbering scheme.

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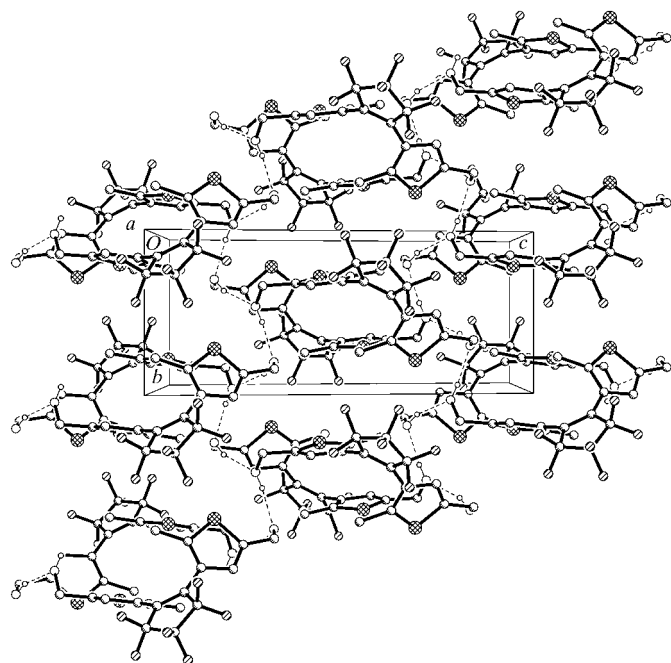
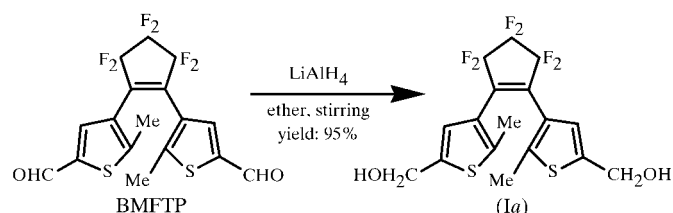


Figure 2
A packing view along the *a* direction, showing the hydrogen bonding.

(Ib) could not be obtained because it was very unstable under the experimental conditions. The red color disappeared rapidly upon irradiation with 450 nm light or daylight, and the absorption spectrum of the solution containing the colorless crystal is the same as that of the open-ring form (Ia).

Experimental

The novel diarylethene (Ia) was prepared by the reduction of 3,3,4,4,5,5-hexafluoro-1,2-bis(4-formyl-2-methyl-3-thienyl)cyclopentene (BMFTP; Gilat *et al.*, 1993; Pu *et al.*, 2002) with lithium aluminium hydride (see scheme below). A solution of BMFTP (0.8486 g, 2 mmol) in ether (20 ml) was added dropwise to a stirred solution of LiAlH₄ (0.1723 g, 4 mmol) in anhydrous ether (50 ml) at room temperature, and stirring was continued for 1 h at room temperature. Aqueous sodium potassium tartrate (30%, 5 ml) was then added. The mixture was filtered after stirring for a few minutes and dried over anhydrous MgSO₄. The solvent was removed, and column chromatography (silica gel, ethyl acetate/hexane 1:1) afforded (Ia) (0.8131 g, 95%) as colorless crystals. The structure of (Ia) was confirmed by its melting point, NMR analysis and mass spectrometry (m.p. 398 K). ¹H NMR (500 MHz, CDCl₃): δ 2.06 (s, 6H), 2.99 (s, 4H), 4.72 (s, 2H), 6.99 (s, 2H); MS *m/z* (*M*⁺): 428.



Crystal data

C₁₇H₁₄F₆O₂S₂
M_r = 428.40
 Monoclinic, *P*2₁/*c*
a = 13.5688 (10) Å
b = 7.5506 (6) Å
c = 18.0929 (14) Å
 β = 98.728 (2)°
V = 1832.2 (2) Å³
Z = 4
D_x = 1.553 Mg m⁻³

Data collection

Bruker SMART APEX CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
*T*_{min} = 0.79, *T*_{max} = 0.93
 14 143 measured reflections

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.063
wR (*F*²) = 0.118
S = 1.05
 5308 reflections
 254 parameters
 H atoms treated by a mixture of independent and constrained refinement

Mo *K*α radiation
 Cell parameters from 6248 reflections
 θ = 2.2–32.8°
 μ = 0.36 mm⁻¹
T = 296 (2) K
 Prism, colorless
 0.5 × 0.3 × 0.2 mm

5308 independent reflections
 4075 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.024
 θ_{max} = 30.0°
h = -19 → 19
k = -7 → 10
l = -25 → 25

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 2.5P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.75 e Å⁻³
 Δρ_{min} = -0.58 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1—C6	1.718 (2)	O1—C10	1.424 (3)
S1—C9	1.727 (3)	C12—C13	1.367 (3)
F1—C3	1.343 (4)	C12—C17	1.497 (3)
C6—S1—C9	92.73 (12)	F1—C3—C2	111.6 (2)
C2—C1—C13	130.4 (2)	C2—C3—C4	105.3 (2)
C2—C1—C5	111.15 (19)	C5—C4—C3	105.3 (2)
C13—C1—C5	118.43 (19)	C1—C5—C4	105.29 (19)
F2—C3—F1	105.9 (2)	C8—C9—C10	128.5 (2)
F2—C3—C2	113.7 (2)	O1—C10—C9	113.12 (19)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O2 ⁱ	0.78 (3)	2.00 (3)	2.738 (3)	159 (3)
O2—H2A...O1 ⁱⁱ	0.79 (3)	1.96 (3)	2.748 (3)	173 (3)

Symmetry codes: (i) 2 - *x*, 1 - *y*, 1 - *z*; (ii) *x*, ½ - *y*, ½ + *z*.

H atoms of the hydroxy groups were found in a difference Fourier map and were refined individually. The other H atoms were placed at idealized positions and treated as riding on their parent atoms, with C—H distances of 0.93 Å for aryl, 0.96 Å for methylene and 0.97 Å for methyl H atoms. The *U*_{iso}(H) values were set to 1.2*U*_{eq} of the parent atoms for aryl and methylene H atoms, and at 1.5*U*_{eq} for methyl atoms.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1446). Services for accessing these data are described at the back of the journal.

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