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Key indicators

Single-crystal X-ray study
T = 294 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.051
wR factor = 0.157
Data-to-parameter ratio = 14.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

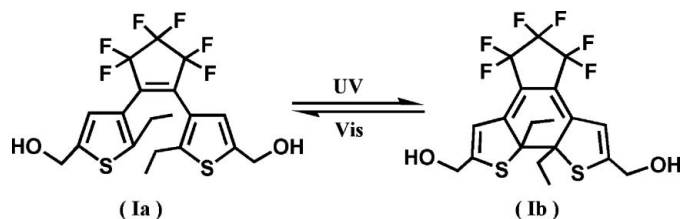
1,2-Bis(2-ethyl-5-hydroxymethyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene, a new photochromic diarylethene compound

The title compound, $\text{C}_{19}\text{H}_{18}\text{F}_6\text{O}_2\text{S}_2$, is one of the most promising materials for optical memories and other optoelectronic devices. The molecular structure has a photoactive antiparallel conformation. The dihedral angles between the cyclopentene ring and the attached thiophene rings are $52.12(1)$ and $52.70(1)^\circ$. The distance between the two reactive C atoms, *i.e.* the ring C atoms to which the ethyl groups are attached, is $3.596(4) \text{ \AA}$. A dichloromethane solution of the colorless crystals turns pink when exposed to UV radiation, with an absorption maximum of 542 nm.

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Comment

Photochromic compounds have attracted considerable attention because of their potential application to photonic devices, such as optical memories and switches (Dürr & Bouas-Laurent, 1990; Irie, 1994). Among the various types of photochromic compounds, diarylethene derivatives containing heterocyclic aryl rings are the most promising candidates for optoelectronic materials because of their excellent thermal stability, fatigue resistant character, rapid response and high reactivity in the solid state (Irie, 2000; Tian & Yang, 2004). In solution, diarylethene compounds containing thiophene heterocyclic rings have two possible conformations, namely, a parallel conformation with the two thiophene rings related by mirror symmetry and an antiparallel conformation with the two rings related by twofold symmetry. 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). So far, the crystal structures of several dithienylethene derivatives have been reported (Irie, 2000; Tian & Yang, 2004; Pu, Fan *et al.*, 2005; Pu, Li, Wang *et al.*, 2005, 2006; Pu, Liu, Chen *et al.*, 2005; Pu, Xu, Shen *et al.*, 2005; Pu, Yang, Chen *et al.*, 2006; Pu, Yang, Wang *et al.*, 2005; Pu, Yang & Yan, 2005) but compounds that show strong photochromic reactivity in the single-crystal phase are rare (Kobatake & Irie, 2004).



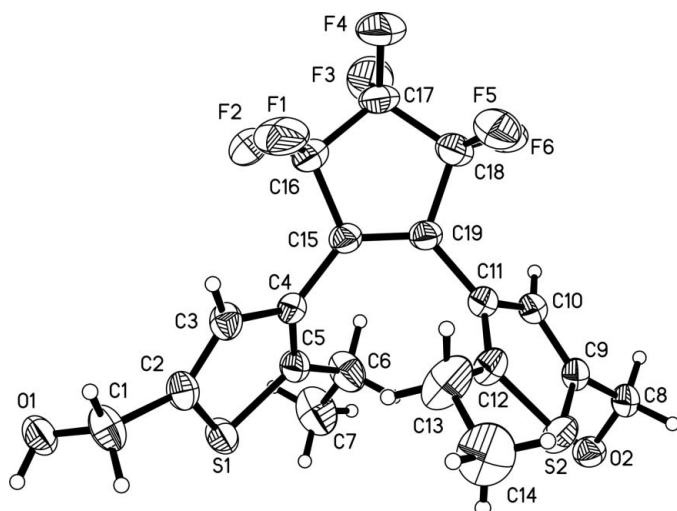


Figure 1
The molecular structure of the title compound, shown with 30% probability ellipsoids.

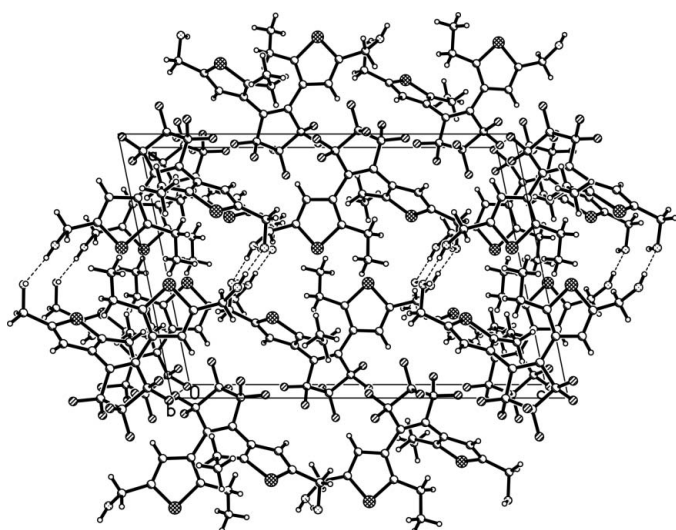


Figure 2
A view along the *b* direction, showing the O—H...O interactions in (Ia) (dashed lines).

report here the crystal structure of (Ia) as part of an investigation of the substituent effect at the 2-position of thiophene of diarylethenes on the photochemical properties. The 2-methyl and 2-ethyl analogs differ from each other not only in their crystal structures but also in their various photochemical properties, for example absorption maxima, ease of cyclization, cycloreversion quantum yield and oxidation–reduction potentials.

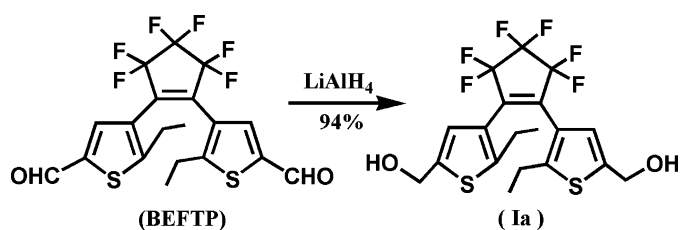
The molecular structure of (Ia) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Compound (Ia) has molecular twofold symmetry, with the two thiophene rings arranged in a photoactive antiparallel conformation, which is a prerequisite for a photocyclization reaction (Yamada *et al.*, 2000). In the hexafluorocyclopentene

ring, the C15=C19 bond is clearly a double bond, being significantly shorter than the other bonds in the ring; the two thiophene rings are linked by this double bond. The two ethyl groups are located on different sides of the double bond and are *trans* with respect to the thiophene rings. The orientations of the ethyl groups at C5 and C12 are defined by the torsion angles C4–C5–C6–C7 [–153.1 (5) Å] and C11–C12–C13–C14 [–163.2 (6) Å]. The dihedral angles between the central cyclopent-1-ene ring and the attached thiophene rings are 52.1 (1)° for S1/C2–C5 and 52.7 (1)° for S2/C9–C12. The corresponding values in the methyl analog, (II), are 46.4 (1) and 49.5 (1)°, respectively (Pu *et al.*, 2004). The distance between the two reactive C atoms (C5...C12) is 3.596 (4) Å, which is the same as that in (II) [3.596 (4) Å]. This distance indicates that the crystal can undergo photochromism in the crystalline phase to generate compound (Ib) as the photochromic reactivity depends on the distance between the reactive C atoms being less than 4.2 Å (Ramamurthy & Venkatesan, 1987). In the crystal structure, molecules are linked by O–H...O intermolecular hydrogen-bonding interactions to form a two-dimensional network perpendicular to the *a* axis (Fig. 2 and Table 2).

As predicted above, crystal (Ia) shows photochromic reactivity. Upon irradiation with 254 nm light, the colorless single crystal (Ia) turned pink. Although the crystal structures of ring-closed molecules have been determined (Yamaguchi & Irie, 2005), we have not, so far, been able to determine the crystal structure of the pink crystals [presumably (Ib)]. When the pink crystal was dissolved in dichloromethane, the solution turned pink and an absorption maximum was observed at 542 nm. The pink color disappeared on irradiation with light of wavelength longer than 510 nm, and the absorption spectrum of this solution corresponded to the spectrum of the open-ring isomer (Ia).

Experimental

Compound (Ia) was prepared by the reduction of 1,2-bis(2-ethyl-5-formyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (BEFTP) (Pu, Yang & Yan, 2005) with lithium aluminium hydride. A solution of BEFTP (0.0452 g, 0.1 mmol) in tetrahydrofuran (THF, 5 ml) was added dropwise to a stirred solution of LiAlH₄ (0.015 g, 0.47 mmol) in anhydrous THF (5 ml) at room temperature, and stirring was continued for 1 h. Aqueous sodium potassium tartrate (30%, 2 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) (0.043 g, 0.094 mmol) in 94% yield as colorless crystals. The structure of (Ia) was confirmed by its melting point, elemental analysis and NMR analysis (m.p. 399 K). Analysis calculated for C₁₉H₁₈F₆O₂S₂ (%): C 49.99, H 3.97%; found: C 50.06, H 3.99%; ¹⁹F NMR (376 MHz, CDCl₃): δ 110.46 (4F), 131.95 (2F); ¹H NMR (400 MHz, CDCl₃): δ 0.933–0.969 (*t*, 6H, *J* = 7.2 Hz, –CH₃), 2.222–2.278 (*q*, 4H, *J* = 5.6 Hz, –CH₂), 4.773 (*s*, 4H, –CH₂), 6.921 (*s*, 2H, thiophene-H); ¹³C NMR (100 MHz, CDCl₃): δ 14.112, 22.457–22.704, 29.373–29.714, 60.035, 116.049, 123.084, 124.842, 142.286, 149.894; IR (KBr): ν (cm^{–1}) 3295 (OH), 2938, 2879 (CH₂, CH₃), 1458, 1493, 1562 (thiophene), 1102, 1131 (CF₂).


Crystal data

$C_{19}H_{18}F_6O_2S_2$
 $M_r = 456.45$
 Monoclinic, $P2_1/c$
 $a = 12.902$ (2) Å
 $b = 8.6229$ (14) Å
 $c = 18.972$ (3) Å
 $\beta = 101.588$ (3)°
 $V = 2067.7$ (6) Å³
 $Z = 4$

$D_x = 1.466$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3152 reflections
 $\theta = 2.5$ – 24.1 °
 $\mu = 0.32$ mm⁻¹
 $T = 294$ (2) K
 Prism, colorless
 $0.22 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.932$, $T_{max} = 0.944$
 11247 measured reflections

4208 independent reflections
 2538 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.028$
 $\theta_{max} = 26.4$ °
 $h = -14 \rightarrow 16$
 $k = -8 \rightarrow 10$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.157$
 $S = 1.02$
 4208 reflections
 288 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 1.0406P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.43$ e Å⁻³
 $\Delta\rho_{min} = -0.34$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–C2	1.720 (3)	C15–C19	1.337 (4)
S1–C5	1.720 (3)	C15–C16	1.493 (4)
S2–C12	1.718 (3)	C16–C17	1.526 (5)
S2–C9	1.721 (3)	C17–C18	1.515 (5)
O1–C1	1.413 (4)	C18–C19	1.502 (5)
O2–C8	1.418 (4)		
O1–C1–C2–S1	–58.5 (4)	O2–C8–C9–S2	77.1 (4)
C4–C5–C6–C7	–153.1 (5)	C11–C12–C13–C14	–163.2 (6)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 ⁱ ⋯O2 ⁱ	0.82 (4)	1.93 (4)	2.745 (4)	171 (4)
O2–H2A ⁱ ⋯O1 ⁱⁱ	0.85 (5)	1.96 (5)	2.807 (4)	170 (4)

 Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

The C atoms of the ethyl groups are disordered and two distinct conformations were modeled. In the final refinement, the site occupancies were fixed at 0.80:0.20 for C6/C7 and at 0.65:0.35 for C13/C14 according to the results of refinement for site occupancies before. The distances between C6 and C7, C6' and C7', C13 and C14, C13' and C14' were restrained to be 1.54 (1) Å. H atoms bonded to C were placed in calculated positions, with C–H distances of 0.93 Å (aromatic), 0.96 Å (CH₃) and 0.97 Å (CH₂). They were included in the refinement in the riding-model approximation, with isotropic displacement parameters set equal to $1.2U_{eq}$ of the carrier atom for the aromatic H atoms, and $1.5U_{eq}$ of the carrier for CH₃. The H atoms of hydroxy groups were found in a difference Fourier map. The coordinates and isotropic displacement parameters were refined.

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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