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1,2-Bis(2-ethyl-5-formyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene

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The title compound, $C_{19}H_{14}F_6O_2S_2$, a novel photochromic diarylethene, is one of the most promising candidates for optoelectric devices such as optical memories, photo-switches and waveguides. It adopts a photoactive anti-parallel conformation in the crystalline phase.

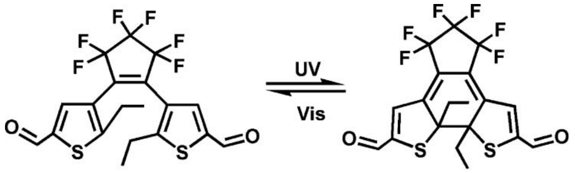
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
R factor = 0.069
wR factor = 0.141
Data-to-parameter ratio = 13.5

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

Comment

Photochromic materials have attracted much attention from both a fundamental as well as a practical point of view, because of their potential for applications in optoelectronic devices such as optical memories, photo-switches and waveguides, *etc* (Dürr & Bouas-Laurent, 1990). Among all photochromic systems, diarylethene derivatives are regarded as the best candidates because of the good thermal stability of the two isomers, high sensitivity, fast response, and high fatigue resistance (Irie, 2000; Tian & Yang, 2004).



(I*a*) (I*b*)

In solution, diarylethenes with thiophene rings have two interconverting conformations in almost equal amounts, *viz.*, anti-parallel and parallel conformations (Irie & Mohri, 1988; Uchida *et al.*, 1990); only anti-parallel conformations can undergo effective photocyclization reactions by a conrotatory mechanism, parallel conformations being photochemically inactive (Yamada *et al.*, 2000). However, there is no interconversion between the two conformers in the crystalline

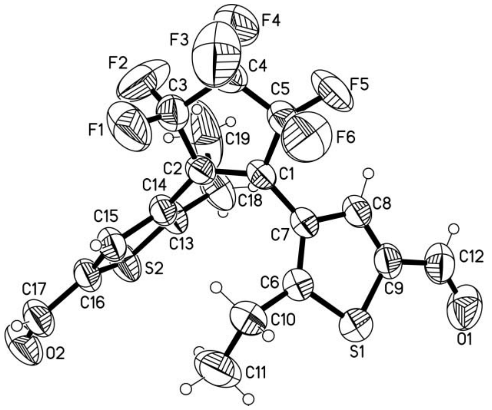


Figure 1
A view of the molecule of (I*a*), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

phase of diarylethenes. Although many diarylethene compounds have been reported so far (Irie, 2000; Tian & Yang, 2004; Sun *et al.*, 2003), compounds which show strong photochromic reactivity in the crystalline phase are rare (Kobatake & Irie, 2004). Diarylethenes bearing formyl groups are very interesting because the formyl group can be easily changed to many other functional groups by some simple reactions (Pu *et al.*, 2003, 2004, 2005). This is an effective method by which to increase rapidly the number of new diarylethene compounds. In this work, a new diarylethene with formyl groups, (I*a*), was synthesized, and its structure is presented here.

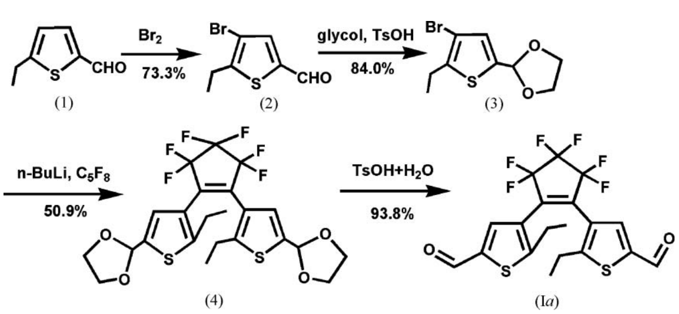
The molecular structure of (I*a*) is shown in Fig. 1 and a packing diagram is shown in Fig. 2. Selected geometric parameters are given in Table 1. As shown in Fig. 1, the molecule has approximately C_2 symmetry, and it packs in a photoactive anti-parallel conformation in the crystalline phase. In the hexafluorocyclopentene ring, the C1—C2 [1.333 (5) Å] bond is clearly a double bond, being significantly shorter than the C1—C5 [1.479 (6) Å] and C2—C3 [1.484 (6) Å] single bonds. The two thiophene moieties are linked by the C1═C2 double bond.

The two ethyl groups are located on different sides of the double bond and *trans* with respect to the thiophene planes. The dihedral angle between the hexafluorocyclopentene ring and the thiophene ring S1/C6–C9 is 55.2 (2)°, and that between the hexafluorocyclopentene ring and thiophene ring S2/C13—C16 is 65.1 (1)°. The distance between the two reactive C atoms (C6 and C15) is 3.893 (7) Å. This distance indicates that the crystal can undergo photochromism in the crystalline phase; the photochromic reactivity of crystals depends on the distance between the reactive carbon atoms (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).

Crystal (I*a*) shows a photochromic reaction, just as predicted by theoretical analysis. Upon irradiation with 254 nm light, the colorless crystal (I*a*) quickly turns blue. When observed under polarized light, the blue color intensity changes on rotation of the crystalline sample. This phenomenon suggests that the closed-ring isomers are regularly packed in the crystal. When the blue crystal is dissolved in hexane, the solution turns blue, and the absorption maximum is observed at 604 nm, as for the closed-ring isomer (I*b*). Unfortunately, the single-crystal diffraction pattern of (I*b*) could not be obtained because it reverts easily to the original isomer under experimental conditions. The blue color disappears upon irradiation with 600 nm light or daylight, and the absorption spectrum of the solution containing the colorless crystal is the same as that of the open-ring isomer (I*a*).

Experimental

The novel diarylethene (I*a*) was derived originally from 5-ethylthiophene-2-carbaldehyde (1). First, 4-bromo-5-ethylthiophene-2-carbaldehyde, (2) (2.28 g, 10.4 mmol), was obtained in 73.3% yield by bromination of compound (1) (2 g, 14.3 mmol) in acetic acid at room temperature. Then, the dioxolane acetal (3) (2.296 g, 8.73 mmol) was prepared in 84.0% yield by refluxing under Dean–Stark conditions in the presence of compound (2) (2.28 g, 10.4 mmol), glycol (2 ml, 58.5 mmol) and *p*-toluenesulfonic acid (TsOH) (0.05 g, 0.3 mmol) in benzene (200 ml). Finally, to a stirred solution of compound (3) (2.296 g, 8.73 mmol) in THF (50 ml) was added dropwise a 2.5 mol l^{-1} *n*-BuLi (3.5 ml, 8.75 mmol) at 195 K under a nitrogen atmosphere. Stirring was continued for 30 min, octafluorocyclopentene (0.59 ml, 4.36 mmol) was slowly added to the reaction mixture, and the mixture was stirred for 2.5 h at 195 K. The reaction was stopped by the addition of water. Through a series of routine operations, 3,3,4,4,5,5-hexafluoro-1,2-bis[5-(1,3-dioxolan-2-yl)-2-ethyl-3-thienyl]cyclopent-1-ene, (4) (1.2 g, 2.2 mmol), was obtained in 50.9% yield by column chromatography on SiO_2 using $CHCl_3$ as the eluent. Finally, the title compound was produced in 93% yield by hydrolysing compound (4), and colorless crystals were obtained by slow vapour diffusion of chloroform.



The structure of (I*a*) was confirmed by melting point, elemental analysis and NMR (m.p. 379.4–380.4 K). Analysis calculated for $C_{19}H_{14}F_6O_2S_2$ (%): C 50.44, H 3.12; found: C 50.57, H 3.19; ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.042–1.079 (*t*, 6H, J = 7.6 Hz, CH$_3$), 2.297–2.353 (*q*, 4H, J = 7.6 Hz, CH$_2$), 7.718 (*s*, 2H, thiophene-H), 9.869 (*s*, 2H, —CHO); ^{19}F NMR (400 MHz, CDCl$_3$): δ 110.56 (4 F), 131.82 (2 F).

Crystal data

$C_{19}H_{14}F_6O_2S_2$
M_r = 452.42
Monoclinic, $P2_1/n$
a = 11.2889 (11) Å
b = 13.4306 (13) Å
c = 13.4236 (12) Å
β = 96.816 (7)°
V = 2020.9 (3) Å^3
Z = 4

D_x = 1.487 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 51 reflections
θ = 3.0–14.7°
μ = 0.33 mm^{-1}
T = 295 (2) K
Prism, colorless
0.5 × 0.4 × 0.3 mm

Data collection

Bruker P4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.800, $T_{\max}$ = 0.906
4499 measured reflections
3548 independent reflections
2023 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 25.0°
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 15$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.141
S = 1.04
3548 reflections
262 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 3P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.31 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

S1—C6	1.709 (5)	C3—C4	1.502 (7)
S1—C9	1.718 (5)	C4—C5	1.493 (7)
F1—C3	1.338 (6)	C6—C7	1.378 (6)
F2—C3	1.307 (6)	C6—C10	1.520 (6)
O1—C12	1.215 (6)	C7—C8	1.409 (6)
C1—C2	1.333 (5)	C8—C9	1.360 (6)
C1—C7	1.464 (6)	C9—C12	1.439 (7)
C1—C5	1.497 (6)	C10—C11	1.453 (8)
C2—C3	1.484 (6)		
C6—S1—C9	92.3 (2)	C7—C6—C10	128.4 (4)
C2—C1—C7	129.8 (4)	C7—C6—S1	111.4 (3)
C2—C1—C5	110.1 (4)	C10—C6—S1	120.1 (4)
C7—C1—C5	120.1 (4)	C6—C7—C8	111.7 (4)
C1—C2—C3	111.4 (4)	C6—C7—C1	124.0 (4)
F2—C3—F1	106.8 (5)	C8—C7—C1	124.2 (4)
F2—C3—C2	112.7 (5)	C9—C8—C7	114.0 (4)
F1—C3—C2	111.7 (5)	C8—C9—C12	127.3 (5)
F2—C3—C4	111.4 (5)	C8—C9—S1	110.6 (4)
C2—C3—C4	105.8 (4)	C11—C10—C6	114.5 (5)
C5—C4—C3	105.9 (4)	O1—C12—C9	125.1 (6)
C4—C5—C1	106.3 (4)		

H atoms were positioned geometrically [C—H = 0.93 (CH), 0.97 (CH_2) and 0.96 Å (CH_3)] and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2 (1.5 for methyl) times U_{eq}(parent atom).

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*.

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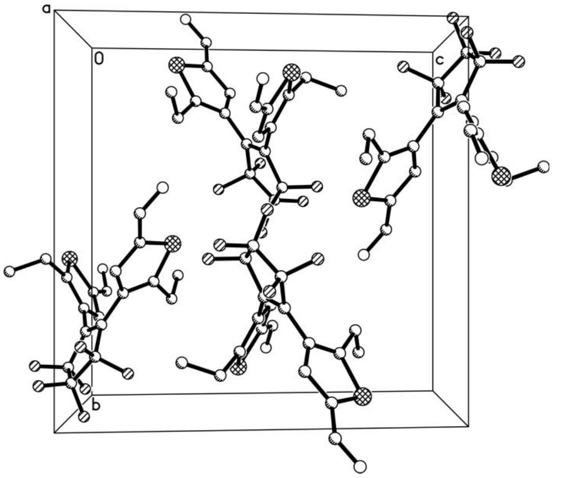

Figure 2
A packing diagram of (I*a*).

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