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

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The title compound, $C_{25}H_{14}N_4F_6S_2$, is a new symmetric photochromic diarylethene which can potentially be applied in optoelectronic devices, such as optical memories, photo switches, and color displays. In the crystalline phase, this molecule, which has crystallographic twofold rotation symmetry, adopts an antiparallel conformation that can undergo effective photocyclization reactions by a conrotatory mechanism. The distance between the two reactive C atoms is 3.642 (7) Å. The dihedral angle between the central cyclopentene ring and each thiophene ring is 48.0 (2)°. The colourless crystals turn green when exposed to UV radiation and the process is reversible when exposed to visible light of appropriate wavelength.

Comment

Photochromism is the result of reversible photo-isomerizaton between two forms that have remarkable differences not only in their absorption spectra, but also in various physical and chemical properties, such as refractive index, dielectric constant, oxidation-reduction potential, and geometric structure (Kobatake *et al.*, 2005). Photochromic compounds have attracted considerable attention from both fundamental and practical points of view, because of their potential application to optical memory media and optical switches (Feringa, 2001; Irie, 1994). Among the compounds, diarylethene derivatives are the most promising candidates for technological applications because of their thermal and photostability (Irie, 2000; Tian & Yang, 2004; Tanifuji *et al.*, 2005).

Generally, diarylethene compounds have two interconverting conformations in solution, *viz*. the antiparallel conformer and parallel conformer, in almost equal amounts. A photocyclization reaction proceeds in a conrotatory fashion only from the antiparallel conformer according to the Woodward–Hoffmann rule (Kobatake *et al.*, 1999). However, there is no interconversion between the two conformers in the crystalline phase of diarylethenes and the molecules are regularly oriented in a fixed conformation (Morimoto & Irie, 2005; Pu *et al.*, 2004; Pu, Liu *et al.*, 2005; Pu, Xiao *et al.*, 2005; Pu, Xu *et al.*, 2005; Pu, Yang & Yan, 2005), except for one example (Kobatake *et al.*, 2005), where there are two independent molecules with different conformations in the asymmetric unit. Photochromic diarylethene crystals with an antiparallel conformation can reversibly turn various colors from colorless, depending on their molecular structure, upon irradiation with UV and visible light of appropriate wavelength (Kobatake & Irie, 2004). These crystals also exhibit good thermal stability and fatigue resistance. Thus, crystals of diarylethenes with different absorption spectra in the antiparallel conformation are very promising for practical applications (Pu, Yang, Wang & Xu, 2005).

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To date, a large number of diarylethene compounds and their structures and properties have been reported (Irie, 2000; Kobatake & Irie, 2004). However, the absorption maxima of closed-ring forms of these diarylethenes are almost always less than 700 nm. Diarylethenes which absorb at a long wavelength (higher than 700 nm) are very rare. In order to use diarylethenes in full-color displays, it is essential to synthesize green-developing compounds for which the absorption maxima of closed-ring forms are longer than 700 nm. So far, the longest absorption band of the closed-ring form of a diarylethene is 828 nm, reported by Gilat *et al.* (1993, 1995).
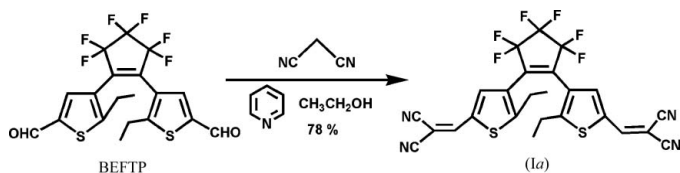
In the present work, we have synthesized the title compound, (I*a*), and its structure is presented here. This compound has a relatively long wavelength absorption spectrum, and the absorption maximum of its closed-ring form is 769 nm. To the best of our knowledge, this is the second longest absorption wavelength of closed-ring forms among all of the diarylethenes reported so far. Previously, we have reported the structure of the 2-methyl analog, (II), of this compound (Pu *et al.*, 2003). In order to investigate systematically the substituent effect at the 2-position of the thiophene of diarylethenes on their photochemical properties, we have now determined the structure of (I*a*). The 2-methyl and 2-ethyl compounds differ from each other, not only in their crystal structures, but also in their absorption maxima, ease of cyclization, cycloreversion quantum yield and oxidation–reduction potentials (Pu, Yang, Wang & Xu, 2005).
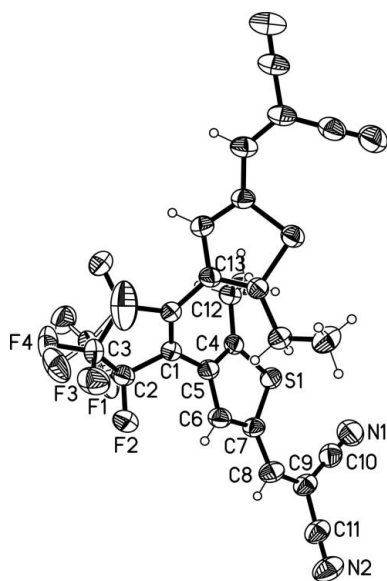

Figure 1
The structure of the title compound, shown with 35% probability ellipsoids. Both disorder components are shown. (Symmetry code for unlabeled atoms: $1 + x - y$, $2 - y$, $-z$.)

The molecular structure of (I*a*) is shown in Fig. 1. Selected geometric parameters are given in Table 1. As shown in Fig. 1, the molecule has twofold rotation symmetry, with the two thiophene rings in a photoactive antiparallel conformation. In the cyclopent-1-ene ring, the C1—C1^i bond is clearly a double bond, and the other bonds to C1 and C1^i (Table 1) are clearly single bonds. Atom C3 of this ring is disordered.

The two thiophene rings are essentially planar, with a mean deviation of 0.0092 Å. The two thiophene rings are linked by the C1═C1^i double bond. The two ethyl groups are located on different sides of the double bond and are directed *trans* relative to the thiophene planes. The orientations of the ethyl groups are defined by the torsion angle C5—C4—C12—C13 [$-153.8\,(5)°$]. This kind of conformation is crucial to the photochromic and photoinduced properties (Woodward & Hoffmann, 1970). The dihedral angle between the central cyclopent-1-ene ring and each adjacent thiophene ring is 48.0 (2)°. The corresponding values in the methyl analog, (II), are 44.9°. This conformation leads to a C4···C4^i separation of 3.642 (7) Å in (I) [compared with 3.589 Å in (II)]. This distance indicates that the crystal can undergo photochromism in the crystalline phase to generate compound (I*b*) (see scheme below), because the photochromic reactivity depends on the distance between the reactive C atoms (Ramamurthy & Venkatesan, 1987; Shibata *et al.*, 2002; Kobatake *et al.*, 2004).
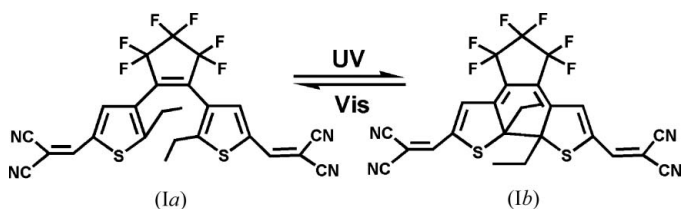
In fact, crystals of (I*a*) show photochromism in accordance with the expected ring closure, to form (I*b*). Upon irradiation with 365 nm light, the colorless single crystals turned green rapidly, and the color remained stable in the dark. When the green crystal was dissolved in dichloromethane, the solution also showed a green color, with an absorption maximum at 769 nm, consistent with the presence of the closed-ring isomer, (I*b*). This phenomenon suggests that the title compound can undergo a photochromic reaction and produce the closed-ring molecule of (I*b*) in the crystalline phase. Unfortunately, we have not been able to establish the crystal structure of (I*b*) under such experimental conditions. Upon irradiation with visible light longer than 550 nm, the green crystal can return to its initial colorless state, and the absorption spectrum of the dichloromethane solution containing the colorless material is the same as that of solutions of the open-ring form, (I*a*), with the absorption maximum at 362 nm.

Experimental

The title photochromic diarylethene, (I*a*), was synthesized by the Knoevenagel condensation reaction (Pu *et al.*, 2003) of 1,2-bis-(2-ethyl-5-formyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene

(BEFTP; Pu, Yang & Yan, 2005) with malonodinitrile. A very small quantity of piperidine was added dropwise at room temperature to a stirred solution of BEFTP (0.169 g, 0.374 mmol) and malonodinitrile (0.049 g, 0.748 mmol) in anhydrous ethanol (5 ml), which was refluxed for 15 h at 351 K. The reaction mixture was dried over anhydrous $MgSO_4$. The solvent was removed, and column chromatography (silica gel, chloroform) afforded the title compound (Ia) (0.160 g, 0.292 mmol) in 78% yield. The compound crystallized from chloroform:hexane (1:1) at room temperature and produced crystals suitable for X-ray analysis. The structure of (Ia) was confirmed also by melting point, element analysis and NMR (m.p. 438–4–39 K). Analysis calculated for $C_{25}H_{14}N_4F_6S_2$: C 54.74, H 2.57%; found: C 54.77, H 2.61%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.121–1.158 (t, 6H, $J = 7.6$ Hz, –CH$_3$), 2.392–2.448 (q, 4H, J = 7.6 Hz, –CH$_2$), 7.632 (s, 2H, thiophene H), 7.783 (s, 2H, –CH); ^{19}F NMR (400 MHz, CDCl$_3$): δ 110.42 (4F), 131.66 (2F); ^{13}C NMR (400 MHz, CDCl$_3$): δ 15.5, 23.5, 80.0, 112.5, 113.2, 125.1, 133.7, 137.5, 149.6, 160.7.

Crystal data

$C_{25}H_{14}F_6N_4S_2$	Mo $K\alpha$ radiation
$M_r = 548.52$	Cell parameters from 60
Hexagonal, $P6_522$	reflections
$a = 8.4786$ (7) Å	$\theta = 2.1–12.5°$
$c = 59.562$ (9) Å	$\mu = 0.28$ mm^{-1}
$V = 3708.0$ (7) Å^3	$T = 295$ (2) K
$Z = 6$	Prism, colorless
$D_x = 1.474$ Mg m^{-3}	$0.4 \times 0.4 \times 0.3$ mm

Data collection

Bruker P4 diffractometer	$\theta_{max} = 25.0°$
ω scans	$h = -1 \rightarrow 10$
Absorption correction: none	$k = -10 \rightarrow 1$
5982 measured reflections	$l = -1 \rightarrow 70$
2178 independent reflections	3 standard reflections
1542 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{int} = 0.064$	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$\Delta\rho_{max} = 0.18$ e Å^{-3}
$wR(F^2) = 0.118$	$\Delta\rho_{min} = -0.19$ e Å^{-3}
$S = 1.07$	Extinction correction: SHELXL97
2178 reflections	Extinction coefficient: 0.0026 (4)
182 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	725 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 4P]$	Flack parameter: -0.1 (2)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

S1—C4	1.713 (4)	C2—C3^i	1.476 (8)
S1—C7	1.725 (5)	C2—C3	1.555 (8)
N1—C10	1.143 (7)	C3—C2^i	1.476 (8)
N2—C11	1.146 (6)	C7—C8	1.419 (6)
C1—C1^i	1.351 (7)	C8—C9	1.348 (6)
C1—C5	1.468 (5)	C9—C10	1.417 (8)
C1—C2	1.511 (6)	C9—C11	1.427 (6)
C5—C1—C2—C3	170.8 (5)	C2—C1—C5—C6	−47.5 (6)
C2—C1—C5—C4	130.4 (5)	C6—C7—C8—C9	−175.5 (5)
C1^i—C1—C5—C6	134.0 (6)	C5—C4—C12—C13	−153.8 (5)

Symmetry code: (i) $x - y + 1$, $-y + 2$, $-z$.

The central CF$_2$ group is disordered across the twofold rotation axis, with equal occupancy for both components. All H atoms were placed in calculated positions, with C—H distances of 0.93 (aromatic), 0.96 (CH$_3$) and 0.97 Å (CH$_2$). They were included in the refinement in the riding-model approximation, with U_{iso}(H) = $1.2U_{eq}$(C) for aromatic H and CH$_2$, and $1.5U_{eq}$(C) for CH$_3$.

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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