

3,3,4,4,5,5-Hexafluoro-1-(2-methoxyphenyl)-2-[5-(4-methoxyphenyl)-2-methyl-3-thienyl]cyclopent-1-ene: a photochromic compound

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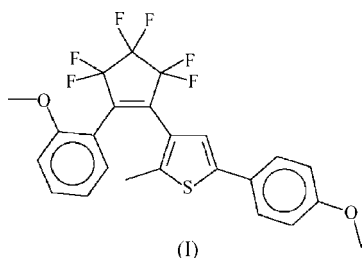
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The photochromic title compound, C₂₄H₁₈F₆O₂S, has thienyl and aryl substituents on the C=C double bond of the shallow half-chair-shaped cyclopentene ring. The planes of the two substituent rings are inclined to that of the cyclopentene ring, with dihedral angles between the mean plane of the cyclopentene ring and those of the phenylene and thienyl rings of 51.2 (1) and 51.3 (1)°, respectively. The molecule adopts an antiparallel conformation, with a distance between the two photoreactive C atoms of 3.717 (2) Å.

Comment

Photochromic diarylethenes find possible applications in optical memory-storage devices and as optical switches (Irie, 2000; Tian & Yang, 2004). In our own studies, we have found that central to photochromic activity of the class of perfluorocyclopentenenes is a pendant five-membered heterocyclic ring (Fan *et al.*, 2008), a feature that is displayed by the title compound, (I).



The cyclopentene ring has a shallow half-chair conformation twisted on C10–C11 (the r.m.s. deviation of the constituent C atoms is 0.08 Å) and has a substituent thienyl group

and an anisyl group on opposing ends of the C=C double bond (Fig. 1). Steric hindrance is avoided by the planes of the phenylene and thienyl rings being inclined to that of the cyclopentene ring by 51.2 (1) and 51.3 (1)°, respectively, but the avoidance of crowding places the aliphatic ring substituents on opposite sides of the mean cyclopentene plane. This configuration is crucial for the manifestation of photochromism and other photo-induced properties (Woodward & Hoffmann, 1970). More importantly, the C=C double bond of the cyclopentene ring can, theoretically, change to a C–C single bond. Such a reduction in bond order would accompany the formation of a new C–C bond between the C atom of the phenylene group bearing the methoxy unit and the C atom of the thienyl group bearing the methyl substituent (Fig. 2). As the distance between these two C atoms (C1...C13) is 3.717 (2) Å, the compound can be expected to exhibit photochromism (Fig. 2). It is known that photochromic activity in similar compounds is usually present when this distance is less than 4.2 Å (Kobatake & Irie, 2004; Ramamurthy & Venkatesan, 1987). We have been able to verify this experimentally. Upon irradiation with 365 nm radiation, the colorless crystals turned blue rapidly, but if the UV light was removed, the crystals became colorless immediately. In hexane, the irradiated compound showed an absorption maximum at 592 nm. Upon irradiation using a wavelength of more than 510 nm, the blue hexane solution was rendered colorless and showed an absorption maximum at 287 nm. In a poly(methyl methacrylate) amorphous film, the title diaryl-

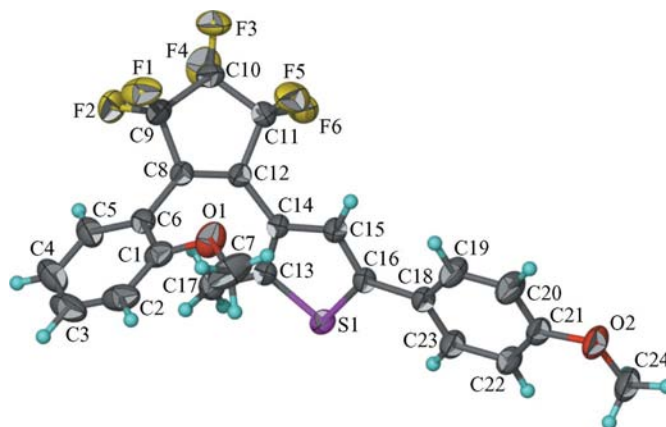


Figure 1

A displacement ellipsoid plot (Barbour, 2001) of (I). Ellipsoids are drawn at the 50% probability level.

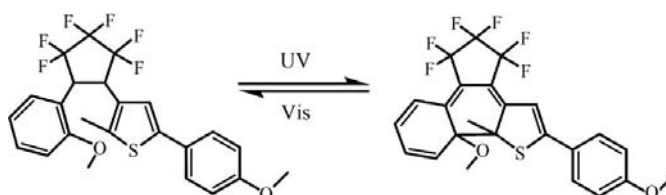


Figure 2

Photochromic interconversion of (I).

ethene also demonstrates photochromism. Yamamoto *et al.* (2003) have tested photocyclization of a photochromic diarylethene derivative in single crystals. The results showed a photogenerated closed-ring diarylethene whose occupancy was estimated to be roughly 9%. In order to prove that the diarylethene crystal structure is changed by UV light, we hope to design an experiment where a continually irradiated crystal can be subjected to X-ray crystallographic analysis to see if changes in the intensities and the unit cell can be observed and interpreted.

Experimental

To a tetrahydrofuran solution of 2-(bromomethoxy)benzene (0.94 g, 5 mmol) was added a hexane solution of *n*-butyllithium (2.0 ml, 5 mmol) at 195 K under a nitrogen atmosphere. The mixture was stirred for half an hour. An excess of octafluorocyclopentene (1.5 ml, 10 mmol) was added and stirring was continued for another 2 h at this temperature. The reaction was then quenched by the addition of water. The product, 1,3,3,4,4,5,5-heptafluoro-2-(methoxyphenyl)cyclopent-1-ene (1.43 g, 4.75 mmol), was collected and dried (yield 90%). This compound (1.43 g, 4.75 mmol) was reacted with 3-bromo-5-(4-methoxyphenyl)-2-methylthiophene (0.94 g, 5 mmol; Perters *et al.*, 2003) in the presence of *n*-butyllithium (2.0 ml, 5 mmol) at 195 K under a nitrogen atmosphere. After an hour, the reaction was quenched by the addition of water. The solid product was purified by column chromatography on silica using petroleum ether as the eluant to give the title compound (yield 1.50 g, 3.10 mmol, 65%; m.p. 384–390 K). Crystals suitable for analysis were obtained by slow evaporation of a solution in hexane. Analysis calculated for C₂₄H₁₈F₆O₂S: C 59.50, H 3.75%; found: C 59.22, H 3.80%. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.87 (*s*, 3H, –CH₃), 3.50 (*s*, 3H, –OCH₃), 3.84 (*s*, 3H, –OCH₃), 6.83, 6.85 (*d*, *J* = 8.0 Hz, 1H, aromatic H), 6.90, 6.92 (*d*, *J* = 8.0 Hz, 2H, aromatic H), 6.99 (*t*, *J* = 8.0 Hz, 1H, aromatic H), 7.11 (*s*, 1H, thienyl H), 7.37 (*t*, *J* = 8.0 Hz, 2H, aromatic H), 7.44, 7.46 (*d*, *J* = 8.0 Hz, 2H, aromatic H). ¹³C NMR (100 MHz, CDCl₃): δ 14.03, 55.22, 55.39, 111.48, 114.36, 117.50, 120.80, 121.92, 126.79, 129.97, 131.73, 138.76, 141.07, 157.13, 159.32.

Crystal data

C ₂₄ H ₁₈ F ₆ O ₂ S	$\gamma = 94.055 (1)^\circ$
<i>M_r</i> = 484.44	$V = 1103.7 (2) \text{ \AA}^3$
Triclinic, <i>P</i> $\bar{1}$	<i>Z</i> = 2
<i>a</i> = 9.477 (1) \AA	Mo <i>K</i> α radiation
<i>b</i> = 10.398 (1) \AA	$\mu = 0.22 \text{ mm}^{-1}$
<i>c</i> = 11.4573 (1) \AA	<i>T</i> = 291 K
$\alpha = 90.259 (1)^\circ$	0.43 × 0.35 × 0.27 mm
$\beta = 101.436 (1)^\circ$	

Data collection

Bruker SMART area-detector diffractometer	9784 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	4979 independent reflections
$T_{\min} = 0.913$, $T_{\max} = 0.944$	4028 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	301 parameters
$wR(F^2) = 0.135$	H-atom parameters constrained
<i>S</i> = 1.06	$\Delta\rho_{\max} = 0.42 \text{ e \AA}^{-3}$
4979 reflections	$\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$

All H atoms were positioned geometrically and treated as riding [methyl C–H = 0.96 \AA with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ or aromatic C–H = 0.93 \AA with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3103). Services for accessing these data are described at the back of the journal.

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