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5,5′-Dimethyl-4,4′-bis[2-(2-methyl-3-thienyl)-cyclopentenyl]-2,2′-bithiophene

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Key indicators

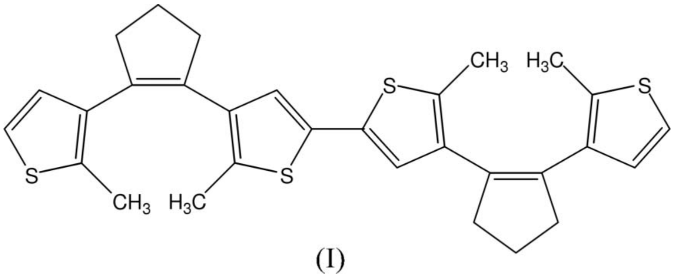
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.102
Data-to-parameter ratio = 16.1

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

The molecule of the title compound, $C_{30}H_{30}S_4$, is located on a centre of inversion. The cyclopentene ring is almost planar. The thiophene rings are twisted out of the plane of the cyclopentene ring by 47.41 (8) and 46.25 (9)°.

Comment

Dithienylethenes, as light-switchable frameworks, can adopt two different conformations, which can be addressed specifically by irradiation with either ultraviolet or visible light (Irie, 2000; Lucas *et al.*, 2003). In the open form, the thienyl rings are able to rotate freely around the C—C bond to the bridging cyclopentene ring. Upon irradiation with UV light, a 2,2′-bond formation between the thienyl groups occurs, which fixes the thienyl rings in space, separated from each other (Irie, 2000; Lucas, 2001; Matsuda & Irie, 2004). By irradiation with visible light, the ring closure can be reversed and the photochromic framework is able to change its conformation freely again. This switching process is thermally irreversible and fatigue-resistant (de Jong *et al.*, 2004; Irie, 2000; Irie *et al.*, 1999). Dithienylethenes have already been shown to be useful, acting as photochromic frameworks of self-assembled supramolecular systems, optical storage devices and photo-responsive host–guest systems, *e.g.* molecular tweezers for small organic molecules or alkali metal ions (Irie, 1993, 2000; Lucas *et al.*, 2000, 2001; Mulder *et al.*, 2004; Takeshita *et al.*, 1998). In contrast to single dithienylethenes, photochrome dimers can adopt three different conformations (open–open, open–closed and *vice versa*, or closed–closed), which are potentially characterized by three different colours (Peters & Branda, 2000). The title compound, (I), was isolated as a by-product in a Suzuki coupling of 1,2-bis(5′-dibutoxyboronyl-2′-methylthien-3′-yl)cyclopentene and *p*-bromophenylalanine-O^{t}Bu-nitrilotriacetic acid ester.



(I)

The molecular structure of the title compound is shown in Fig. 1. Most bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.28, November 2006 plus one update; Allen, 2002; *Mogul*, Version

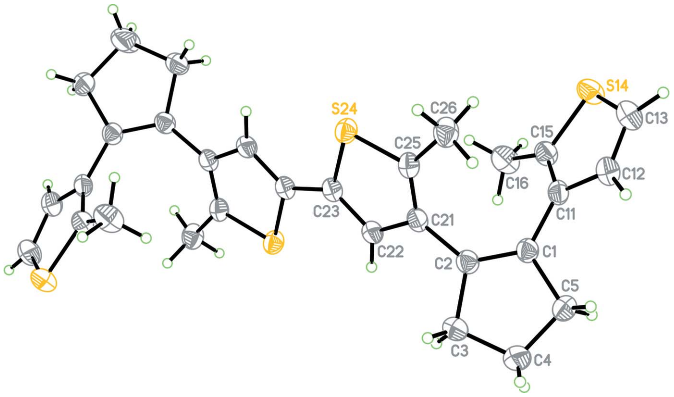


Figure 1
The molecular structure with the atom numbering; displacement ellipsoids are drawn at the 50% probability level. [Symmetry operator for unlabelled atoms ($2 - x, 1 - y, 1 - z$).]

1.1.1; Bruno *et al.*, 2004). The angles C1—C2—C21 and C2—C1—C11 are significantly widened (Table 1). Molecules of the title compound are located on centres of inversion. The cyclopentene ring is almost planar (r.m.s. deviation 0.011 Å). The thiophene rings are twisted out of the plane of the cyclopentene ring by 47.41 (8) and 46.25 (9)°.

Experimental

1,2-Bis(5′-chloro-2′-methylthien-3′-yl)cyclopentene (0.8 g, 2.5 mmol) (Wissler *et al.*, 2006) was dissolved in freshly distilled dry THF (50 ml) under an argon atmosphere. *n*-BuLi (2.7 *M* in heptane; 1.9 ml, 5.1 mmol) was added to the solution with a glass syringe and the solution was stirred for 5 min at room temperature. Tributyl borate (1.4 ml, 5.1 mmol) was added in one portion and the mixture stirred for 30 min at room temperature, giving 1,2-bis(5′-dibutoxyboronyl-2′-methylthien-3′-yl)cyclopentene. In a second flask, *p*-bromophenylalanine-O^{t}Bu-nitrilotriacetic acid ester (1.3 g, 2.5 mmol) and $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) were dissolved in THF (30 ml). The mixture was stirred for 15 min at room temperature and ethylene glycol (500 µl) and aqueous 2 *M* Na_2CO_3 (30 ml) were added. The reaction mixture was heated to 348 K under an argon atmosphere for 1 h. Freshly prepared 1,2-bis(5′-dibutoxyboronyl-2′-methylthien-3′-yl)cyclopentene (2.5 mmol) was now added without further purification in one portion and the mixture was refluxed for 2 h and then allowed to cool to room temperature. Diethyl ether (30 ml) and H_2O (40 ml) were added and the aqueous phase was washed three times with diethyl ether. The organic layers were combined and dried over $MgSO_4$. The organic solvent was evaporated under reduced pressure and the residue purified by silica column chromatography (cyclohexane/ethyl acetate 15:1) to give a yellow oil containing mainly 1-[5′-(*p*-phenyl-O^{t}Bu-nitrilotriacetic acid ester)-2′-methylthien-3′-yl)-2-(5′′-1*H*-2′′-methylthien-3′′-yl)cyclopentene from which the title compound was crystallized in the dark as light-pink blocks.

Crystal data

$C_{30}H_{30}S_4$
$M_r = 518.78$
Monoclinic, $P2_1/n$
$a = 9.3105\ (7)$ Å
$b = 14.0233\ (14)$ Å
$c = 10.2143\ (8)$ Å
$\beta = 96.901\ (6)°$
$V = 1324.0\ (2)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.38$ mm^{-1}
$T = 173\ (2)$ K
0.34 × 0.28 × 0.22 mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
$T_{\min} = 0.883$, $T_{\max} = 0.922$
15093 measured reflections
2516 independent reflections
2247 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.067$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.102$
$S = 1.06$
2516 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected bond angles (°).

C2—C1—C11	128.59 (15)	C1—C2—C21	128.82 (15)

H atoms bonded to C were refined with fixed individual displacement parameters [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C_{methyl}})$] using a riding model with C—H ranging from 0.95 to 0.99 Å. The methyl groups were allowed to rotate but not to tip.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97* and *PLATON*.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruno, I. J., Cole, J. C., Kessler, M., Luo, J., Motherwell, W. D. S., Purkis, L. H., Smith, B. R., Taylor, R., Cooper, R. I., Harris, S. E. & Orpen, A. G. (2004). *J. Chem. Inf. Comput. Sci.* **44**, 2133–2144.
Irie, M. (1993). *Mol. Cryst. Liq. Cryst.* **227**, 263–270.
Irie, M. (2000). *Chem. Rev.* **100**, 1685–1716.
Irie, M., Lifka, T., Uchida, K., Kobatake, S. & Shindo, Y. (1999). *Chem. Commun.* pp. 747–748.
Jong, J. J. D. de, Lucas, L. N., Kellogg, R. M., van Esch, J. H. & Feringa, B. L. (2004). *Science*, **304**, 278–281.
Lucas, L. N. (2001). PhD thesis, Ruiksuniversiteit Groningen, The Netherlands.
Lucas, L. N., de Jong, J. J. D., van Esch, J. H., Kellogg, R. M. & Feringa, B. L. (2003). *Eur. J. Org. Chem.* pp. 155–166.
Lucas, L. N., van Esch, J. H., Kellogg, R. M. & Feringa, B. L. (2000). *Abstr. Pap. Am. Chem. Soc.* **220**, U116.
Lucas, L. N., van Esch, J., Kellogg, R. M. & Feringa, B. L. (2001). *Chem. Commun.* pp. 759–760.
Matsuda, K. & Irie, M. (2004). *J. Photochem. Photobiol. Photochem. Rev.* **5**, 169–182.
Mulder, A., Huskens, J. & Reinhoudt, D. N. (2004). *Org. Biomol. Chem.* **2**, 3409–3424.
Peters, A. & Branda, N. R. (2000). *Adv. Mater. Opt. Electron.* **10**, 245–249.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Takeshita, M., Soong, C. F. & Irie, M. (1998). *Tetrahedron Lett.* **39**, 7717–7720.
Wissler, J., Mulder, A., Tampé, R. & Bolte, M. (2006). *Acta Cryst.* E**62**, o5649–o5650.

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