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1,2-Bis(5-chloro-2-methyl-3-thienyl)cyclopentene

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.070
Data-to-parameter ratio = 21.4

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

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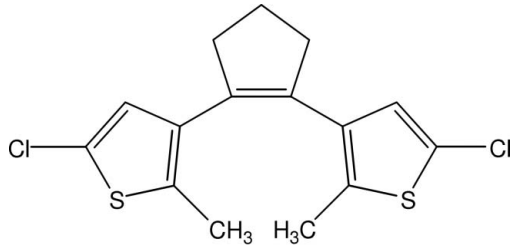
The cyclopentene ring of the title compound, $C_{15}H_{14}Cl_2S_2$, is almost planar. The two thiophene rings are twisted out of the mean plane of the cyclopentene ring by 39.97 (5) and 50.84 (5)°.

Comment

The title compound, (I), is a basic photochromic platform from which many light-switchable supramolecular structures have been synthesized. The suitability of the title compound, and of dithienylethenes in general, as light-switchable frameworks stems from their ability to 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 linking C—C bonds to the bridging cyclopentene ring. Upon irradiation with UV light, a 2,2′-bond formation reaction involving the thienyl rings 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 as photochromic frameworks of self-assembled supramolecular systems, optical storage devices or photoresponsive 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). Many dithienylethenes and related molecular devices are synthesized either directly or indirectly from the title compound.



(I)

A perspective view of (I) is shown in Fig. 1. Most bond lengths and angles can be regarded as normal (Cambridge Structural Database, Version 5.27, November 2005 plus two updates; *MOGUL* Version 1.1; Allen, 2002). The central cyclopentene ring is almost planar (r.m.s. deviation from the mean plane for the C1–C5 ring = 0.064 Å). The dihedral angles between the cyclopentene ring and the thiophene rings are

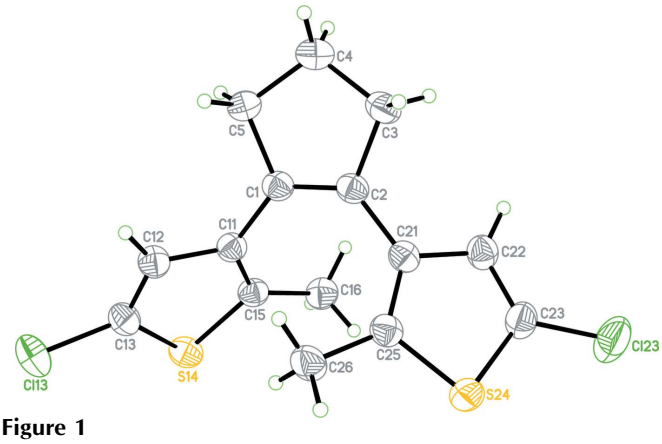


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms).

39.97 (5) and 50.84 (5)° for the S24 and S14 rings, respectively. The methyl group of one thiophene ring is located above and the other below the plane of the cyclopentene ring. The Cl atoms point away from the molecule in different directions. Due to strain, the C1—C2—C21 and C2—C1—C11 angles are significantly widened compared with the C5—C1—C11 and C3—C2—C21 angles (Table 1).

No short C—H···S or C—H···Cl contacts could be found when analysing the packing of (I).

Experimental

The synthesis of (I) was performed according to a modification of the procedure of Lucas *et al.* (2003). Zinc dust (4.6 g, 70 mmol) was suspended in freshly distilled tetrahydrofuran (THF; 100 ml). $TiCl_4$ (5 ml) was cautiously added with a glass syringe and the suspension stirred at reflux for 30 min. The mixture was allowed to cool to room temperature and a solution of 1,5-bis(5-chloro-2-methylthiophen-3-yl)pentane-1,5-dione (18.1 g, 50 mmol) in THF (50 ml) was added dropwise over a period of 2 h, followed by stirring at reflux overnight. The reaction mixture was cooled down to room temperature and quenched with 2*M* K_2CO_3 (25 ml). The suspension was filtered over a glass filter of pore size 3 and extracted with diethyl ether (3 × 75 ml). The organic layers were washed with water (2 × 10 ml) and then dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography (cyclohexane). Fractions containing the desired product were combined, the solvent removed under reduced pressure and the residue recrystallized from cyclohexane as yellow crystals of (I) in 76% yield (12.5 g, 38 mmol).

Crystal data

$C_{15}H_{14}Cl_2S_2$
M_r = 329.28
Monoclinic, $P2_1/c$
a = 8.7555 (12) Å
b = 12.2720 (14) Å
c = 14.256 (2) Å
β = 101.513 (12)°
V = 1501.0 (3) Å^3
Z = 4
D_x = 1.457 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 173 (2) K
Block, colourless
0.45 × 0.38 × 0.36 mm

Data collection

Stoe IPDS II two-circle diffractometer
ω scans
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)
T_{min} = 0.746, T_{max} = 0.788
7653 measured reflections
3724 independent reflections
2750 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 28.7°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.070
S = 0.87
3724 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected bond angles (°).

C2—C1—C11	128.50 (13)	C21—C2—C3	119.51 (12)
C11—C1—C5	119.89 (12)	C13—S14—C15	91.29 (7)
C1—C2—C21	128.88 (13)	C23—S24—C25	91.47 (7)

The H atoms were located in a difference map and relocated in idealized positions, with C—H = 0.95–0.99 Å, and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C), or 1.5 U_{eq}(methyl C). 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* (Spek, 2003).

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