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1,4-Diphenyl-2,3-dithien-3-ylcyclopentadien-1-one

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Key indicators

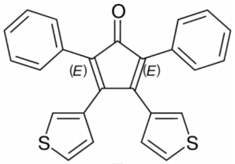
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.052
wR factor = 0.132
Data-to-parameter ratio = 16.9

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

The title compound, $C_{25}H_{16}OS_2$, (I), was synthesized *via* the alkali-catalysed condensation of 3,3′-thenil and 1,3-diphenyl-2-propanone in absolute ethanol. Both 3-thienyl rings in (I) exhibit an 18.89% flip disorder. Thienyl-ring flip disorders are often observed with molecules having unsubstituted terminal 3-thienyl rings [Crundwell *et al.* (2002). *Acta Cryst.* E**58**, o668–o670.

Comment

Since the molecular volumes of thiophene and benzene are nearly identical, guest molecules that contain 2- or 3-thienyl rings are ideal probes for investigating the host–guest interactions during crystal growth of analogous phenyl-containing host species (Vaida *et al.*, 1988). Thienyl-based guests have shown preferential inclusion into the host by keeping thienyl-ring S atoms pointed away from the face of growing crystals, possibly to avoid unfavorable electrostatic interactions between sulfur lone pairs coplanar with the thiophene ring and molecules already incorporated into the growing crystal face (Shimon *et al.*, 1993). Research in our laboratory has centered on the synthesis of new 2- and 3-thienyl analogs to dope into phenyl-based hosts (Crundwell *et al.*, 2003). Crystal structures of thienyl-containing molecules have shown that unsubstituted, terminal 2- and 3-thienyl rings often exhibit ring flip disorder (Crundwell *et al.*, 2002; 2003). These types of thienyl ring flip disorders are common, occurring in about one third of Cambridge Structural Database (Allen, 2002) entries containing terminal unsubstituted thienyl rings (Crundwell *et al.*, 2002).



(I)

Initially, least-squares refinement of the crystal structure of (I) was carried out using a simple model. The model contained four disordered atoms, S1*B*, C21*B*, S2*B*, and C25*B*, to account for disorder of each flipped thienyl ring. The following constraints were applied: (i) the positions of S1 and C21*B*, C21 and S1*B*, S2 and C25*B*, and C25 and S2*B* were equal; (ii) the anisotropic displacement parameters of S1 and S1*B*, C21 and C21*B*, S2 and S2*B*, and C25 and C25*B* were equal; (iii) the percentage of thienyl ring flip was determined by refining a single occupancy variable for atoms S1, C21, S2, and C25 and their flipped analogs S1*B*, C21*B*, S2*B*, and C25*B*.

The resulting model had a 19.5 (3)% ring-flip disorder which led to unrealistic S—C bond lengths [*e.g.* S1—C18 and

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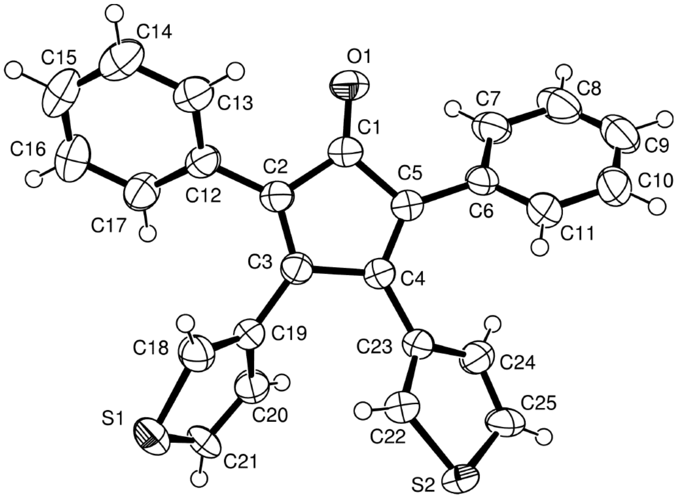

Figure 1
A view of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level. The ring flip disorder of each thienyl ring has been omitted for clarity.

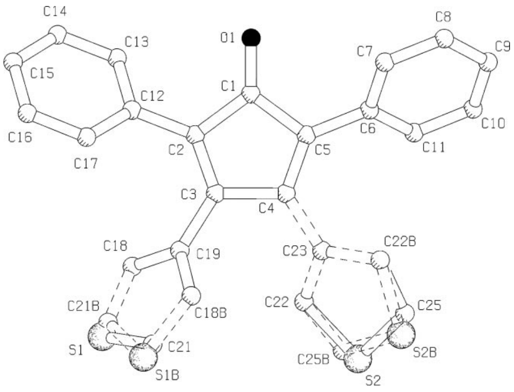

Figure 2
Molecules of (I) exhibit an 18.89% thienyl ring flip disorder (Spek, 1990). Dashed lines show the minor ring component. H atoms have been removed for clarity.

S1—C25 bond lengths of 1.6492 (17) Å and 1.731 (3) Å, respectively]. The model had 255 parameters for 4511 observed reflections utilizing four restraints, and the refinement converged to $R = 0.059$ and $Rw = 0.134$. (The CIF for this refinement as well as a scattering factor file are available as supplementary materials.)

The disorder model presented in this paper has two complete flipped thienyl rings (additional atoms S1*B* and C18*B*–C21*B* and S2*B* and C22*B*–C25*B*) and the following constraints were applied: (i) the positions for three of the four C atoms in each flipped thienyl ring were equal (*viz.* C18 and C20*B*, C19 and C19*B*, C20 and C18*B*, C22 and C24*B*, C23 and C23*B*, and C24 and C22*B*); (ii) the anisotropic displacement parameters of S1 and S1*B*, C21 and C21*B*, S2 and S2*B*, and C25 and C25*B* were equal; (iii) distances for every S—C bond were constrained to 1.710 (2) Å; (iv) a single occupancy variable was refined for both flipped rings.

The percentage occupancy of the ring disorder refined to 18.89 (19)%. The total number of parameters in this model was 267 for 4511 observed reflections with 68 restraints. This refinement converged to an $R = 0.052$ and $Rw = 0.118$.

In 1965, Hamilton published a paper concerning significance tests on crystallographic *R* factors that provided crystallographers with equations for testing whether or not the addition of parameters during refinement significantly improved the model (Hamilton, 1965). The application of Hamilton's test to our refinements indicated that there was a significant reduction in the *R* value upon increasing the parameters, even at the strictest level (0.005) of the statistical test. The choice to increase the number of parameters also led to a more meaningful and physically significant structure solution, since the simplified disorder model masked overlapping thienyl fragments to give unrealistic S—C bond lengths. With the increased use of crystallographic databases to extract bond lengths and angles, need for realistic disorder models with reasonable geometry is important.

Experimental

The title compound, (I), is a 3-thienyl derivative of tetraphenylcyclopentadienone. It can be prepared in adequate yields by reacting equimolar amounts of 3,3′-thenil and 1,3-diphenyl-2-propanone in absolute ethanol and potassium hydroxide, in an identical manner to that used for the synthesis of tetraphenylcyclopentadienone (Pavia *et al.*, 1998). The yield for the above reaction is 38%. Low yields of 32% were reported for the analogous dithien-2-yl species using this reaction scheme (Oda *et al.*, 1994). Recrystallization from a warmed 50/50 mixture of ethanol and toluene afforded flat, deep purple needles (m.p. 454 K). [^{1}H NMR ($CDCl_3$, δ): 7.260 (*m*, 10H), 7.195 (*dd*, 2H), 6.842 (*d*, 2H), 6.705 (*d*, 2H); analysis, found: C 75.57, H 3.93%; calculated for $C_{25}H_{16}OS_2$: C 75.72, H 4.07%.

Crystal data

$C_{25}H_{16}OS_2$
$M_r = 396.50$
Monoclinic, $P2_1/c$
$a = 21.2902$ (19) Å
$b = 10.4773$ (9) Å
$c = 8.8835$ (8) Å
$\beta = 94.325$ (3)°
$V = 1975.9$ (3) Å^3
$Z = 4$

$D_x = 1.333$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17631 reflections
$\theta = 2.4$–28.5°
$\mu = 0.28$ mm^{-1}
$T = 293$ (2) K
Plate, purple
0.40 × 0.35 × 0.25 mm

Data collection

Bruker SMART *P*3/512 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.891$, $T_{\max} = 0.932$
17124 measured reflections

4511 independent reflections
3274 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 28.4°$
$h = -26 \rightarrow 26$
$k = -13 \rightarrow 13$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.132$
$S = 1.03$
4511 reflections
267 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 1.0401P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0098 (11)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.214 (3)	C12—C13	1.401 (3)
C1—C2	1.513 (3)	C13—C14	1.395 (3)
C1—C5	1.514 (3)	C14—C15	1.379 (4)
C2—C3	1.353 (3)	C15—C16	1.381 (4)
C2—C12	1.483 (3)	C16—C17	1.391 (3)
C3—C19	1.474 (3)	S1—C18	1.7071 (16)
C3—C4	1.533 (3)	S1—C21	1.7225 (19)
C4—C5	1.351 (3)	C18—C19	1.377 (3)
C4—C23	1.477 (3)	C19—C20	1.420 (3)
C5—C6	1.480 (3)	C20—C21	1.358 (3)
C6—C7	1.392 (3)	S2—C22	1.7130 (16)
C6—C11	1.400 (3)	S2—C25	1.7254 (18)
C7—C8	1.393 (4)	C22—C23	1.387 (3)
C8—C9	1.378 (5)	C23—C24	1.424 (3)
C9—C10	1.387 (5)	C24—C25	1.315 (4)
C10—C11	1.387 (4)	S1*B*—C21*B*	1.712 (2)
C12—C17	1.397 (3)	S2*B*—C25*B*	1.710 (2)
C2—C1—C5	106.95 (17)	C14—C15—C16	119.8 (2)
C3—C2—C1	106.94 (18)	C15—C16—C17	120.5 (3)
C2—C3—C4	109.51 (18)	C16—C17—C12	120.5 (2)
C5—C4—C3	109.30 (18)	C18—S1—C21	90.31 (13)
C4—C5—C1	107.18 (18)	C19—C18—S1	112.95 (16)
C7—C6—C11	118.5 (2)	C18—C19—C20	111.75 (18)
C6—C7—C8	120.5 (3)	C21—C20—C19	111.7 (2)
C9—C8—C7	120.3 (3)	C20—C21—S1	113.29 (19)
C8—C9—C10	120.0 (3)	C22—S2—C25	90.83 (15)
C9—C10—C11	120.0 (3)	C23—C22—S2	111.82 (16)
C10—C11—C6	120.8 (3)	C22—C23—C24	110.74 (18)
C17—C12—C13	118.5 (2)	C25—C24—C23	113.9 (2)
C14—C13—C12	120.3 (2)	C24—C25—S2	112.7 (2)
C15—C14—C13	120.5 (3)		

All H atoms were included in calculated positions with a C—H distance of 0.93 Å and were included in the refinement in riding-motion approximation with $U_{\rm iso} = 1.2U_{\rm eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *SHELXTL* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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