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# 1,2-Di-3-thienyl-2-hydroxyethanone (3,3′-thenoin)

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**Key indicators**

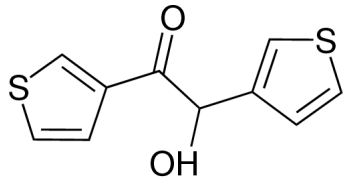
Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(C–C) = 0.006 Å
Disorder in main residue
$R$ factor = 0.063
$wR$ factor = 0.194
Data-to-parameter ratio = 12.7

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

The title compound, $C_{10}H_8O_2S_2$, is the 3-thienyl symmetric analog of benzoin. 3,3′-Thenoin can be synthesized in good yield utilizing the benzoin condensation reaction (starting with 3-thiophenecarboxaldehyde). The crystal structure of 3,3′-thenoin has been determined at room temperature. There are two independent molecules per asymmetric unit and each has a thienyl ring flip disorder involving one of the two rings in each molecule.

## Comment

There are two molecules per asymmetric unit of the title compound, (I) (Fig. 1), and both are disordered. The first molecule has a thienyl ring connected to the keto C atom that has a flip disorder of 11%; in contrast, the second molecule has a disordered thienyl ring attached to the C atom bearing the hydroxy group and has a 15% disorder.




(I)

## Experimental

3,3′-Thenoin is a symmetrically substituted thienyl analog of benzoin (Cardon & Lankelma, 1948). It can be prepared in adequate yield using the benzoin condensation reaction commonly encountered in undergraduate organic laboratory texts (Pavia *et al.*, 1998). Recrystallization from boiling ethanol afforded colorless flat needles of 3,3′-thenoin (m.p. 381–382 K). IR (Fluoromac, cm$^{-1}$): 3400 (*s* and *b*), 3100 (*m*), 2950 (*m*), 2850 (*m*); IR (Nujol, cm$^{-1}$): 1700 (*s*), 1450 (*m*), 1380 (*s*), 1070 (*s*); $^1$H NMR ($CDCl_3$, $\delta$, p.p.m.): 8.03 (*m*, 2H), 7.49 (*m*, 2H), 6.98 (*m*, 2H), 5.82 (*s*, 1H), 4.31 (*s*, 1H).

### Compound (I)

*Crystal data*

$C_{10}H_8O_2S_2$
$M_r$ = 224.28
Monoclinic, $P2_1/c$
$a$ = 8.2503 (17) Å
$b$ = 16.421 (3) Å
$c$ = 15.041 (3) Å
$\beta$ = 100.86 (3)°
$V$ = 2001.2 (7) Å$^3$
$Z$ = 8
$D_x$ = 1.489 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 12182 reflections
$\theta$ = 1.9–24.7°
$\mu$ = 0.50 mm$^{-1}$
$T$ = 293 (2) K
Needle, colorless
0.30 × 0.10 × 0.05 mm

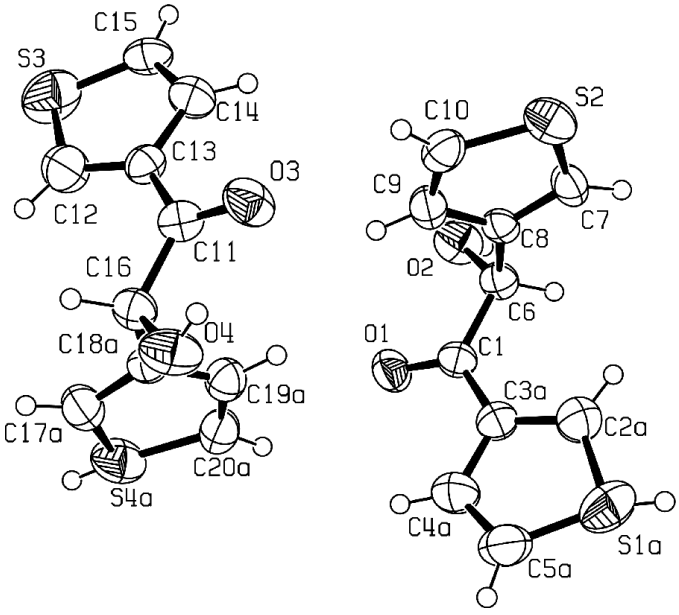



**Figure 1**
The molecular structure of the asymmetric unit of 3,3′-thenoin, showing 50% probability displacement ellipsoids. For clarity, only the major disorder components of the rings are depicted.

*Data collection*

| | |
|---|---|
| Siemens SMART P3/512 CCD diffractometer | $R_{int}$ = 0.059 |
| $\omega$ scans | $\theta_{max}$ = 24.7° |
| 11 939 measured reflections | $h = -9 \rightarrow 9$ |
| 3412 independent reflections | $k = -19 \rightarrow 19$ |
| 2086 reflections with $I > 2\,s(I)$ | $l = -17 \rightarrow 17$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.063 | $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.194 | $(\Delta/\sigma)_{max}$ = 0.007 |
| $S$ = 1.14 | $\Delta\rho_{max}$ = 0.34 e Å$^{-3}$ |
| 3412 reflections | $\Delta\rho_{min}$ = −0.35 e Å$^{-3}$ |
| 269 parameters | |

**Table 1**
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| S1*A*—C5*A* | 1.707 (9) | C6—C8 | 1.501 (5) |
| S1*A*—C2*A* | 1.683 (5) | S2—C7 | 1.697 (4) |
| C2*A*—C3A | 1.370 (5) | S2—C10 | 1.708 (4) |
| C3*A*—C4*A* | 1.403 (5) | C7—C8 | 1.358 (5) |
| C3*A*—C1 | 1.461 (5) | C8—C9 | 1.434 (5) |
| C4*A*—C5*A* | 1.362 (10) | C9—C10 | 1.352 (6) |
| S4*A*—C17*A* | 1.698 (5) | C11—O3 | 1.214 (5) |
| S4*A*—C20*A* | 1.731 (8) | C11—C13 | 1.471 (5) |
| C17*A*—C18*A* | 1.366 (5) | C11—C16 | 1.529 (5) |
| C18*A*—C19*A* | 1.410 (5) | S3—C12 | 1.681 (5) |
| C18*A*—C16 | 1.492 (5) | S3—C15 | 1.699 (4) |
| C19*A*—C20*A* | 1.366 (9) | C12—C13 | 1.357 (6) |
| C1—O1 | 1.223 (4) | C13—C14 | 1.422 (6) |
| C1—C6 | 1.515 (5) | C14—C15 | 1.386 (5) |
| C6—O2 | 1.433 (4) | C16—O4 | 1.418 (5) |
| | | | |
| C5*A*—S1*A*—C2*A* | 92.0 (4) | C7—S2—C10 | 91.9 (2) |
| C3*A*—C2*A*—S1*A* | 112.2 (3) | C8—C7—S2 | 112.6 (3) |
| C2*A*—C3*A*—C4*A* | 111.8 (4) | C7—C8—C9 | 111.1 (4) |
| C2*A*—C3*A*—C1 | 125.6 (4) | C7—C8—C6 | 125.2 (4) |
| C4*A*—C3*A*—C1 | 122.5 (4) | C9—C8—C6 | 123.7 (3) |
| C5*A*—C4*A*—C3*A* | 112.7 (6) | C10—C9—C8 | 112.9 (4) |
| C4*A*—C5*A*—S1*A* | 111.2 (6) | C9—C10—S2 | 111.5 (3) |
| C17*A*—S4*A*—C20*A* | 92.5 (3) | O3—C11—C13 | 121.6 (4) |
| C18*A*—C17*A*—S4*A* | 112.2 (3) | O3—C11—C16 | 119.4 (4) |
| C17*A*—C18*A*—C19*A* | 111.3 (4) | C13—C11—C16 | 119.0 (4) |
| C17*A*—C18*A*—C16 | 123.6 (3) | C12—S3—C15 | 93.5 (2) |
| C19*A*—C18*A*—C16 | 125.0 (4) | C13—C12—S3 | 112.3 (4) |
| C20*A*—C19*A*—C18*A* | 114.7 (5) | C12—C13—C14 | 111.5 (4) |
| C19*A*—C20*A*—S4*A* | 109.2 (6) | C12—C13—C11 | 125.9 (4) |
| O1—C1—C3*A* | 122.0 (4) | C14—C13—C11 | 122.5 (4) |
| O1—C1—C6 | 118.5 (4) | C15—C14—C13 | 113.1 (4) |
| C3*A*—C1—C6 | 119.5 (3) | C14—C15—S3 | 109.6 (3) |
| O2—C6—C8 | 109.6 (3) | O4—C16—C18*A* | 110.4 (3) |
| O2—C6—C1 | 109.3 (3) | O4—C16—C11 | 109.8 (3) |
| C8—C6—C1 | 110.4 (3) | C18*A*—C16—C11 | 109.3 (3) |

During the initial anisotropic refinement, including H atoms ($R_1$ = 7.47%), there were indications that rotational thienyl disorder around bonds C1—C3 and C16—C18 was possible. There was residual electron density close to atoms C5 and C20, and the bond lengths C4—C5 and C19—C20 were much longer (1.437 and 1.466 Å) than the chemically equivalent C9—C10 and C14—C15 bonds

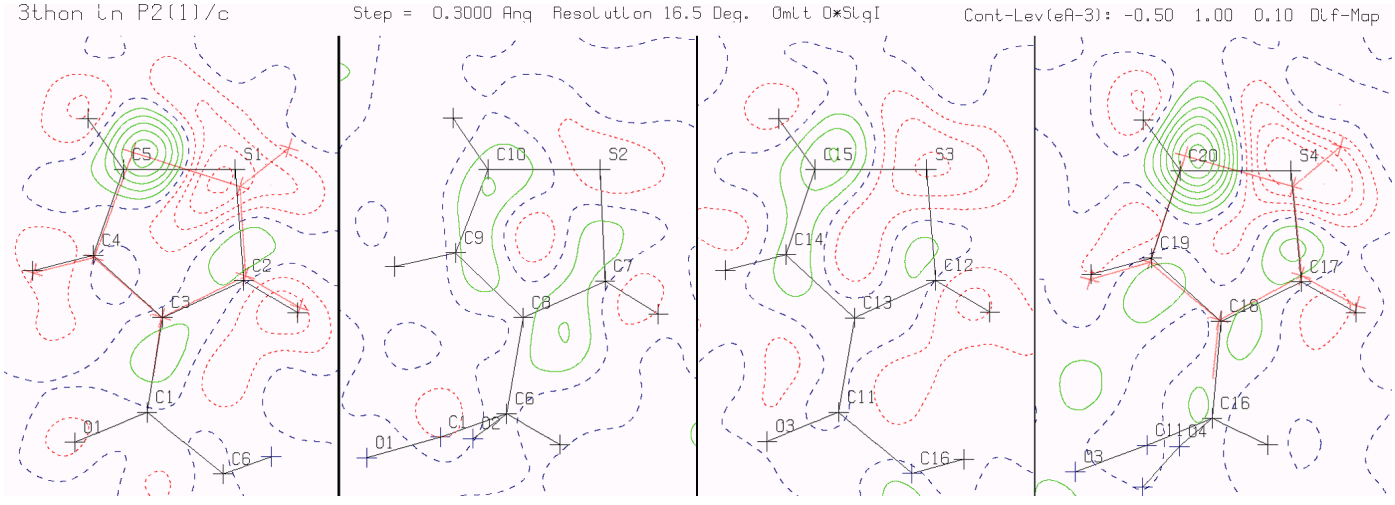



**Figure 2**
Initial refinement yielded these difference maps (generated using *PLATON*; Spek, 1990). The first and last rings (S1—C2—C3—C4—C5 and S4—C17—C18—C19—C20, respectively) show residual electron density, indicating a thienyl ring flip disorder. Ideal thienyl flip positions are overlaid in light red.

(1.350 Å and 1.384 Å). Difference maps were generated using *PLATON* (Spek, 1990) and these are shown in Fig. 2. The maps clearly showed that a thienyl rotational disorder would account for bond lengthening in the C4—C5 and C19—C20 bonds, since atoms C5 and C20 would be displaced from their ideal positions to account for the electron density generated by the flipped thienyl-ring S atoms. A search of the Cambridge Structural Database (Version 1.3 of October 2001; Allen & Kennard, 1993) revealed seven structures having terminal unsubstituted thienyl rings bound only at the 3-position. Of these seven, three have rotationally disordered thienyl rings. Based on this, a new refinement strategy was in order.

The final model was generated with the following restraints. Atoms in disordered rings that shared atomic positions were linked by positional and anisotropic displacement parameters (*e.g.* C4*A* and C2*B*, C3*A* and C3*B*, and C2*A* and C4*B* for the disordered ring in the first molecule). To allow for refinement of the site occupancies, the displacement parameters for all other disordered atoms that did not share sites were made equivalent with their disordered counterpart (*e.g.* the displacement parameters for C5*A* and C5*B* were linked). Finally 1,2- and 1,3-distances in the disordered thienyl rings were restrained to be equal. At the end of the refinement, the first thienyl ring (S1—C2—C3—C4—C5) had an 11% thienyl ring flip disorder, whereas the second ring (S4—C17—C18—C19—C20) had a 15% flip disorder. (Due to rounding during generation of the CIF file, occupancy sums for each ring disorder site are slightly higher than 1.000.)

It is interesting to point out that the disorder could be applied to all thienyl rings. We have chosen to model the two rings that (i) had the most anomalous C—C bond distances and (ii) gave clear regions of unaccounted electron density from difference maps.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL-Plus* (Sheldrick, 1990); 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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## References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Cardon, S. Z. & Lankelma, H. P. (1948). *J. Am. Chem. Soc.* **70**, 4248–4249.
Pavia, D. L., Lampman, G. M., Kris, G. S. & Engel, R. G. (1998). *Organic Laboratory Techniques: A Microscale Approach*, 2nd ed. New York: Saunders College Publishing.
Sheldrick, G. M. (1990). *SHELXTL-Plus.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta.* Cyst. A**46**, C-34.