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# 4,5-Dihydrocyclopenta[*b*]thiophen-6-one

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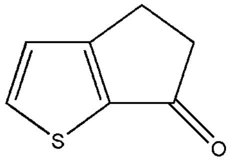
The title compound crystallizes with two unique but closely similar molecules, 1 and 2, in the asymmetric unit. Both molecules are planar with r.m.s. deviations of only 0.0193 and 0.0107 Å for the planes through the nine non-hydrogen atoms of molecules 1 and 2 respectively. In the crystal structure, $\pi-\pi$ and C–H$\cdots\pi$ contacts stack the molecules into columns in an inverse fashion along the *b* axis. An extensive series of C–H$\cdots$O hydrogen bonds links the columns generating an extended network structure.

**Keywords: thiophenes; hydrogen bonding**

## Chemical context

The title compound is a key intermediate in the synthesis of many conjugated thiophene vinylene oligomers for low bandgap and fluorescent applications with applications in nonlinear optics and LED devices. (Blanchard *et al.*, 1997, 1998*a*,*b*, 2006). This is because the ethylene bridge in the resulting vinylene system flattens the ring and increases the conjugation between the neighbouring thiophene groups. This technique can also be used to control the bandgap in the corresponding polymers (Roncali *et al.*, 1994).



## Structural commentary

The asymmetric unit of the triclinic unit cell of the title compound contains two unique molecules, 1 and 2, Fig. 1. These are closely similar and overlay almost perfectly with an r.m.s. deviation of only 0.024 Å (Macrae *et al.*, 2008). The molecules are approximately planar with r.m.s. deviations of 0.0193 and 0.0107 Å from the best fit planes through the nine non-hydrogen atoms in each of the two molecules. This is further illustrated by the fact that the thiophene and cyclopentadienone ring planes are inclined at 2.40 (13)° in molecule 1 and 0.64 (13)° in molecule 2. Bond distances in the molecule are normal (Allen *et al.*, 1987) and similar to those observed in related molecules such as *trans*-4,5-diphenyl-4,5-dihydro-6*H*-cyclopenta[*b*]thiophen-6-one (Chang *et al.*, 2004) or ethyl 5-hydroxy-6-oxo-4-phenyl-5,6-dihydro-4*H*-cyclopenta[*b*]thiophene-5-carboxylate (McAdam *et al.*, 2011).

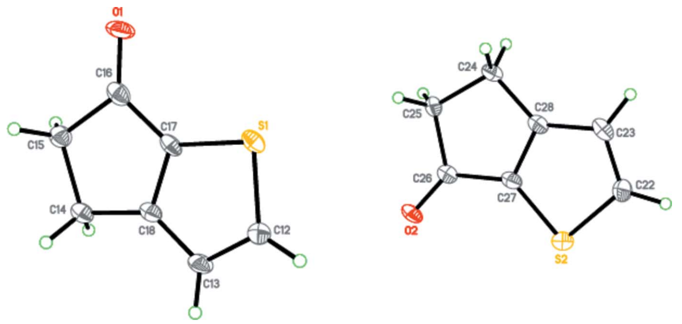


**Figure 1**
The asymmetric unit with ellipsoids drawn at the 50% probability level.

## Supramolecular features

In the crystal structure, molecules 1 and 2 are linked by C15–H15*A*$\cdots\pi$ and C25–H25*B*$\cdots\pi$ contacts into dimers. $\pi$–$\pi$ contacts of 3.6542 (17) Å, between the centroids of the thio-

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_7H_6OS$ |
| $M_r$ | 138.18 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 92 |
| *a*, *b*, *c* (Å) | 6.6133 (9), 7.4894 (11), 13.3213 (16) |
| $\alpha$, $\beta$, $\gamma$ (°) | 83.247 (8), 86.097 (7), 71.363 (8) |
| *V* (Å$^3$) | 620.54 (14) |
| *Z* | 4 |
| Radiation type | Mo *K*$\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.095 |
| Crystal size | 0.55 × 0.28 × 0.02 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD area detector |
| Absorption correction | Multi-scan |
| $T_{min}$, $T_{max}$ | 0.617, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 5251, 1522, 1264 |
| $R_{int}$ | 0.040 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.529 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.040, 0.119, 1.11 |
| No. of reflections | 1522 |
| No. of parameters | 163 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.30, −0.34 |

Computer programs used: *APEX2*, *SADABS* and *SAINT* (Bruker 2011), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008), *TITAN* (Hunter & Simpson, 1999), *Mercury* (Macrae *et al.*, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *publCIF* (Westrip 2010).

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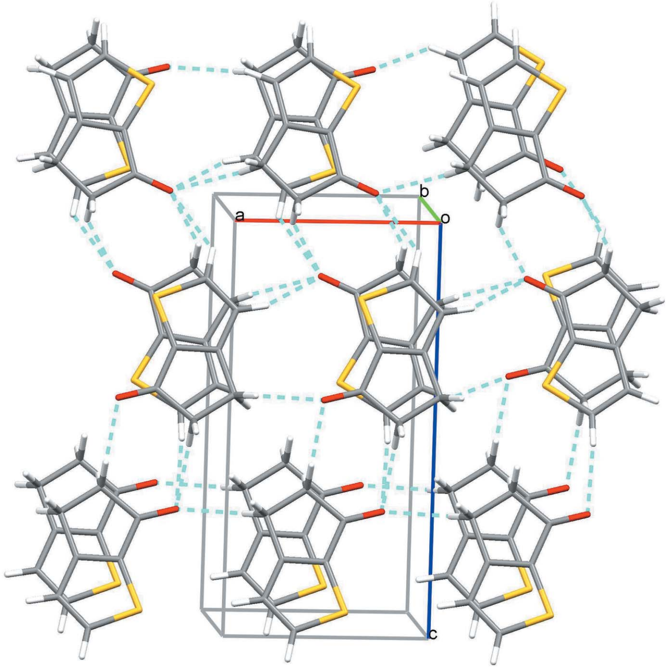

**Figure 2**
A general view of the crystal packing for the title compound along the *b* axis with hydrogen bonds drawn as dashed lines.

phene rings of molecules 1 and 2, link these dimers, forming columns along the *b* axis, Fig. 1*S*. An extensive series of C—H···O hydrogen bonds involving the carbonyl O atoms from both molecules join the columns into an extended network, Fig. 2. Interestingly the S atoms are not involved in any close intermolecular interactions.

## Synthesis and crystallization

The starting material methyl 6-oxo-5,6-dihydro-4*H*-cyclopenta-[*b*]thiophene-5-carboxylate was prepared by literature methods (Cai *et al.* 2002; More & Finney, 2002; Yang, 2009) and 124 mg, 0.63 mmol was dissolved in KOH (0.5 *M*) solution ($H_2O$/EtOH, *v*/*v* = 1) and refluxed for 4 h. The solution was cooled to room temperature, extracted with EtOAc (3× 20 ml), then the combined organic layers were washed with water (2× 50 ml) and dried over $MgSO_4$. The solvent was evaporated *in vacuo* to yield transparent gold crystals (52.3 mg, 0.38 mmol) 60% yield. $^1$H NMR ($\delta$ p.p.m., $CDCl_3$, 300 Hz): 7.896–7.884 (1*H*, *d*, *J* = 3.6 Hz, $C_4\mathbf{H_2}S$), 7.051–7.039 (1*H*, *d*, *J* = 3.6 Hz, $C_4\mathbf{H_2}S$), 3.049–2.974 (4*H*, *m*, $\mathbf{CH_2}CH_2$).

## Refinement

All H-atoms were refined using a riding model with d(C—H) = 0.95 Å, for aromatic and 0.99 Å, for $CH_2$ H atoms with $U_{iso} = 1.2U_{eq}$(C). Crystals were very weakly diffracting and data of reasonable intensity could not be obtained beyond $\theta = 22°$. This also contributes to the relatively poor data/parameter ratio observed for this refinement.

**Table 2**
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*4 are the centroids of the S1, C12, C13, C17, C18 and S2, C22, C23, C27, C28 thiophene rings, respectively.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C14—H14$A$···O1$^{i}$ | 0.99 | 2.52 | 3.473 (4) | 160 |
| C15—H15$B$···O1$^{ii}$ | 0.99 | 2.59 | 3.489 (3) | 151 |
| C12—H12···O2$^{iii}$ | 0.95 | 2.43 | 3.370 (4) | 168 |
| C13—H13···O2$^{iv}$ | 0.95 | 2.65 | 3.275 (4) | 124 |
| C23—H23···O1$^{v}$ | 0.95 | 2.62 | 3.425 (4) | 143 |
| C24—H24$A$···O2$^{vi}$ | 0.99 | 2.52 | 3.480 (4) | 164 |
| C25—H25$A$···O2$^{vii}$ | 0.99 | 2.71 | 3.704 (3) | 180 |
| C25—H25$B$···$Cg$1$^{viii}$ | 0.99 | 2.79 | 3.561 (3) | 135 |
| C15—H15$A$···$Cg$4$^{iii}$ | 0.99 | 2.84 | 3.571 (3) | 131 |

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+1, -z+2$; (iii) $x, y+1, z$; (iv) $-x+2, -y, -z+1$; (v) $-x, -y+1, -z+1$; (vi) $x-1, y, z$; (vii) $-x+1, -y, -z+1$; (viii) $x, y-1, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: zzyy05). Services for accessing these data are described at the back of the journal.

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