



Crystal structure of a new polymorph of di(thiophen-3-yl) ketone

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Received 16 September 2017

Accepted 19 September 2017

Edited by P. McArdle, National University of Ireland, Ireland

Keywords: crystal structure; di(thiophen-3-yl) ketone; polymorphism; C—H...O hydrogen bonding; C—H... π interaction.

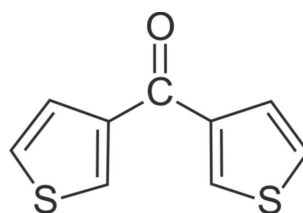
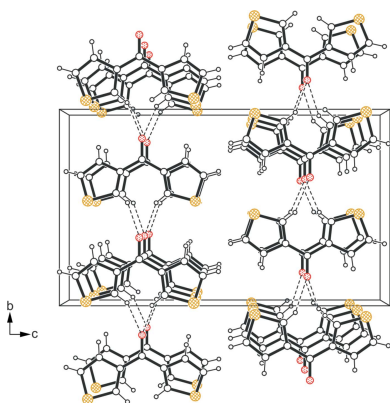
CCDC reference: 1575296

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The crystal structure of the title compound, C₉H₆OS₂, represents a new polymorph. The crystal structure was solved in the orthorhombic space group *Pbcn* with one half of the molecule in the asymmetric unit. The thiophene rings are perfectly planar and twisted with respect to each other, showing the molecule to be in an *S,O-trans/S,O-trans* conformation. In the crystal, C—H...O hydrogen bonds connect the molecules into layers extending parallel to the *ab* plane. The crystal structure also features π – π interactions.

1. Chemical context

With reference to the principle of bioisosterism (Lima & Barreiro, 2005), thiophene is an important structural moiety replacing benzene rings in drugs and biomolecules. Moreover, thiophene is a highly polarizable group due to the presence of the π -electrons and the sulfur atom available in the ring, making it a structural unit worthy of investigation related to crystal engineering (Desiraju *et al.*, 2012). This involves potential π -stacking (Tiekink & Zukerman-Schpector, 2012) and C—H... π (Nishio *et al.*, 2009) interactions, as well as other contacts including a chalcogen atom such as sulfur (Gleiter *et al.*, 2003). From this point of view, the title compound is likely to be an interesting study object. However, searching in the literature shows its crystal structure being already described twice (Sheldrick *et al.*, 1978; Benassi *et al.*, 1989). On the other hand, a polymorph resulted from our work, the structure of which is reported here and comparatively discussed in connection with the previous findings, bearing in mind the attention currently attracted by the field of polymorphism in molecular crystals (Bernstein, 2002; Cabri *et al.*, 2007; Braga *et al.*, 2009).



2. Structural commentary

The title compound crystallizes in the space group *Pbcn* with one half of the molecule in the asymmetric unit, *i.e.* the molecule is located on the twofold symmetry axis. A perspective

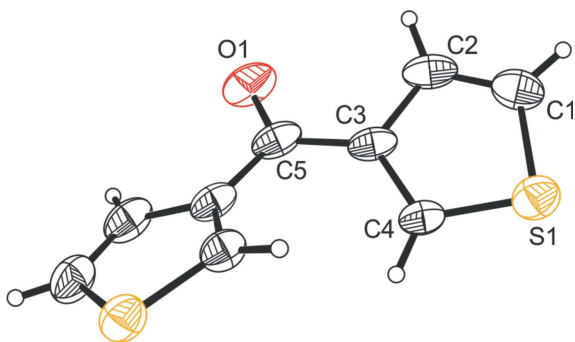


Figure 1
Perspective view of the molecular structure of the title compound. Anisotropic displacement ellipsoids are drawn at the 30% probability level.

view of the molecular structure of the title compound is presented in Fig. 1. The bond distances within the molecule agree with those found in the reported crystal structures of the polymorphs of this compound (Sheldrick *et al.*, 1978; Benassi *et al.*, 1989). Taking into account experimental error, the thiophene rings are perfectly planar. The heteroatom of the ring is always on the opposite side with respect to C=O, showing the molecule to be in an *S,O-trans/S,O-trans* conformation, as was predicted to be the more stable conformation for the compound (Benassi *et al.*, 1989). The torsion angle along the atomic sequence O1—C5—C3—C4 is $-155.2(3)^\circ$ and corresponds to an interplanar angle of $42.3(1)^\circ$ between the thiophene rings, being ascribed to steric hindrance between the H atoms on C4 and C4'.

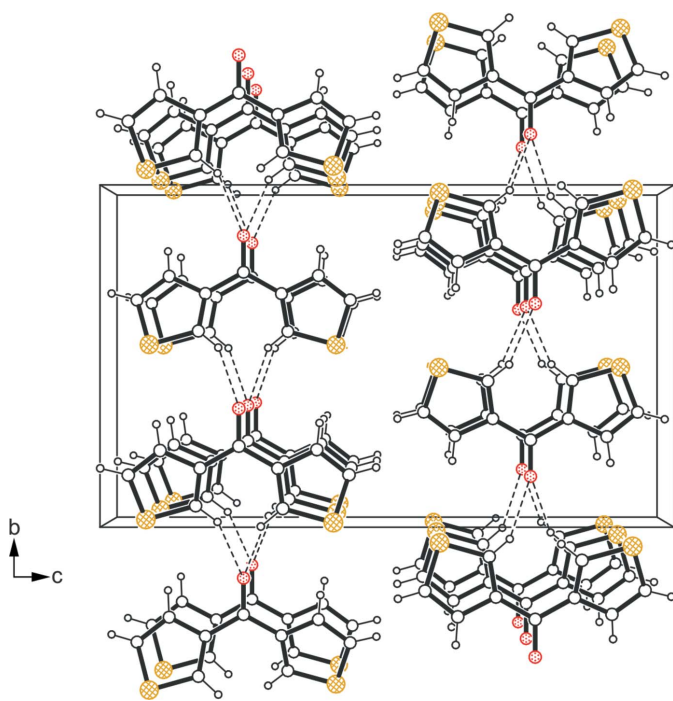


Figure 2
Packing diagram of the title compound viewed down the *a* axis. Dashed lines represent hydrogen-bonding interactions.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C4-H4\cdots O1^i$	0.93	2.42	3.261 (4)	151

Symmetry code: (i) $x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

3. Supramolecular features

The crystal structure is composed of molecular layers extending parallel to the *ab* plane (Table 1, Fig. 2). Within a given layer the molecules are connected *via* C—H \cdots O hydrogen bonds (Desiraju & Steiner, 1999) in which the oxygen atom acts as a bifurcated acceptor. Moreover, the layer structure features π – π stacking (Tiekink & Zukerman-Schpector, 2012) with a centroid \cdots centroid distance of $3.946(2) \text{\AA}$ and a slippage of 1.473\AA between the interacting thiophene rings. No directed non-covalent bonding is observed between the molecules of consecutive layers, so that the crystal structure appears to be stabilized only by van der Waals forces in the stacking direction of the molecular layers.

4. Database survey

A search in the Cambridge Structural Database (CSD, Version 5.38, update February 2017; Groom *et al.* 2016) revealed two crystal structures of the title compound [Refcodes DTHKET (Sheldrick *et al.*, 1978) and DTHKET01 (Benassi *et al.*, 1989)]. In these polymorphs (space group: $P2_1/c$, $P2_1/n$, $Z = 4$) the molecules show slight conformational differences and one of their thiophene rings is disordered over two positions. It is

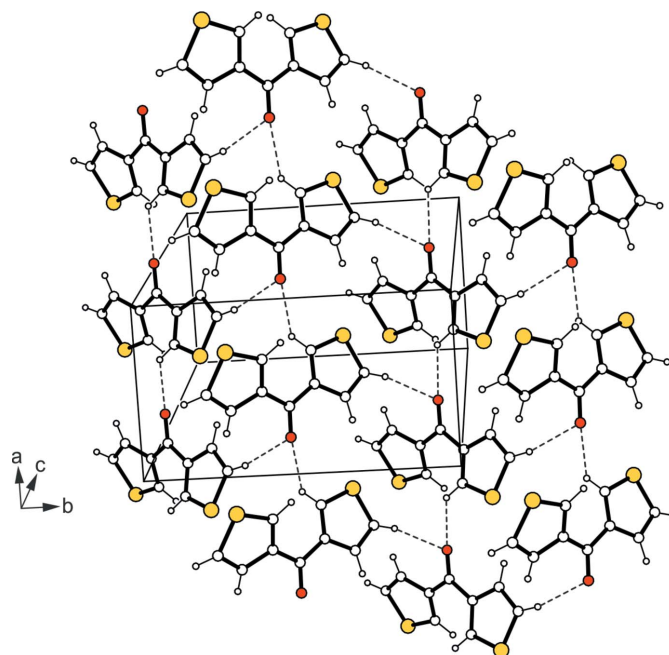


Figure 3
Packing excerpt of the previously reported polymorph (Benassi *et al.*, 1989). Hydrogen-bonding interactions are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₉ H ₆ OS ₂
<i>M_r</i>	194.26
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.9464 (2), 11.5015 (5), 19.2970 (9)
<i>V</i> (Å ³)	875.88 (7)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.55
Crystal size (mm)	0.53 × 0.15 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.759, 0.937
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	6469, 972, 667
<i>R_{int}</i>	0.033
(sin θ/λ) _{max} (Å ⁻¹)	0.643
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.161, 1.13
No. of reflections	972
No. of parameters	56
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.35, -0.22

Computer programs: *APEX2* (and *SAINT* (Bruker, 2008), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* (Farrugia, 2012).

obvious that crystallization from different solvents may have a fundamental influence on the molecular assembly in the solid-state structure, thus giving rise to polymorphism (Bernstein, 2002; Cabri *et al.*, 2007; Braga *et al.*, 2009). Unfortunately, the previous reports do not include information about the solvent used for crystallization of the compound and thus it is not possible to engage in a more qualified discussion of the facts. In the structures of the reported polymorphs, C—H...O hydrogen bonds connect the molecules into undulating sheets, in which the oxygen atom acts as a bifurcated acceptor (Fig. 3). Intersheet association is accomplished by C—H...π contacts, resulting in a three-dimensional supramolecular architecture. In summary, the structures of the two polymorphs differ basically in the molecular assembly.

5. Synthesis and crystallization

The synthesis of the title compound has been reported by different groups and following different procedures (Gronowitz & Erickson, 1963; Pittman & Hanes, 1977; Lucas *et al.*, 2000). We used the method of Lucas *et al.*, reacting thiophen-3-yl lithium (prepared from 3-bromothiophene and *n*-BuLi in dry diethyl ether/*n*-hexane at 195 K under argon) with *N,N*-dimethylcarbamoyl chloride. Column chromatography on SiO₂ with *n*-hexane/ethyl acetate (10:1) followed by recrystallization from methanol yielded the title compound as

colourless crystals, m.p. 353 K. Previous values for the m.p. are 345–346 K (Gronowitz & Erickson, 1963) and 346 K (Lucas *et al.*, 2000) pointing to polymorphic structures of the previously and presently isolated crystals.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms were positioned geometrically and refined isotropically using the riding model with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Funding information

We acknowledge the financial support within the Cluster of Excellence 'Structure Design of Novel High-Performance Materials via Atomic Design and Defect Engineering (ADDE)' provided to us by the European Union (European Regional Development Fund) and by the Ministry of Science and Art of Saxony (SMWK) as well as the Deutsche Forschungsgemeinschaft (DFG Priority Program 1362 'Porous Metal–Organic Frameworks').

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supporting information

Acta Cryst. (2017). E73, 1560-1562 [https://doi.org/10.1107/S2056989017013342]

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Bis(thiophen-3-yl)methanone

Crystal data

$C_9H_6OS_2$

$M_r = 194.26$

Orthorhombic, *Pbcn*

$a = 3.9464$ (2) Å

$b = 11.5015$ (5) Å

$c = 19.2970$ (9) Å

$V = 875.88$ (7) Å³

$Z = 4$

$F(000) = 400$

$D_x = 1.473$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1847 reflections

$\theta = 3.2\text{--}24.5^\circ$

$\mu = 0.55$ mm⁻¹

$T = 296$ K

Plate, colourless

$0.53 \times 0.15 \times 0.12$ mm

Data collection

Bruker APEXII CCD area detector
diffractometer

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2008)

$T_{\min} = 0.759$, $T_{\max} = 0.937$

6469 measured reflections

972 independent reflections

667 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.2^\circ$, $\theta_{\min} = 3.5^\circ$

$h = -4 \rightarrow 5$

$k = -14 \rightarrow 14$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.161$

$S = 1.13$

972 reflections

56 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.649P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.35$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.1430 (3)	0.46670 (8)	0.08955 (5)	0.0781 (4)
O1	0.0000	0.1486 (3)	0.2500	0.1066 (15)
C1	-0.0185 (11)	0.3364 (3)	0.0641 (2)	0.0791 (11)
H1	-0.0650	0.3163	0.0184	0.095*
C2	-0.0701 (9)	0.2660 (3)	0.1189 (2)	0.0755 (10)
H2	-0.1562	0.1910	0.1148	0.091*
C3	0.0202 (8)	0.3174 (2)	0.18397 (18)	0.0608 (8)
C4	0.1397 (8)	0.4274 (2)	0.17415 (17)	0.0604 (8)
H4	0.2116	0.4755	0.2100	0.073*
C5	0.0000	0.2550 (3)	0.2500	0.0672 (13)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0824 (8)	0.0643 (6)	0.0875 (7)	-0.0016 (4)	0.0059 (5)	-0.0061 (4)
O1	0.136 (4)	0.0338 (15)	0.150 (4)	0.000	0.023 (3)	0.000
C1	0.077 (2)	0.072 (2)	0.088 (2)	0.005 (2)	-0.004 (2)	-0.029 (2)
C2	0.064 (2)	0.0496 (16)	0.113 (3)	-0.0041 (15)	-0.002 (2)	-0.0277 (18)
C3	0.0486 (17)	0.0383 (13)	0.096 (2)	0.0003 (12)	-0.0013 (16)	-0.0127 (13)
C4	0.0570 (19)	0.0442 (14)	0.080 (2)	-0.0043 (13)	-0.0023 (15)	-0.0085 (14)
C5	0.054 (2)	0.0367 (19)	0.111 (4)	0.000	0.005 (3)	0.000

Geometric parameters (\AA , $^\circ$)

S1—C4	1.694 (3)	C2—H2	0.9300
S1—C1	1.701 (4)	C3—C4	1.363 (4)
O1—C5	1.225 (5)	C3—C5	1.464 (4)
C1—C2	1.347 (6)	C4—H4	0.9300
C1—H1	0.9300	C5—C3 ⁱ	1.464 (4)
C2—C3	1.434 (5)		
C4—S1—C1	92.30 (18)	C4—C3—C5	126.5 (3)
C2—C1—S1	111.1 (3)	C2—C3—C5	123.1 (3)
C2—C1—H1	124.5	C3—C4—S1	112.6 (2)
S1—C1—H1	124.5	C3—C4—H4	123.7
C1—C2—C3	113.7 (3)	S1—C4—H4	123.7
C1—C2—H2	123.2	O1—C5—C3 ⁱ	119.34 (17)
C3—C2—H2	123.2	O1—C5—C3	119.34 (17)
C4—C3—C2	110.3 (3)	C3 ⁱ —C5—C3	121.3 (3)

C4—S1—C1—C2	-0.3 (3)	C1—S1—C4—C3	0.2 (3)
S1—C1—C2—C3	0.3 (4)	C4—C3—C5—O1	-155.2 (3)
C1—C2—C3—C4	-0.2 (4)	C2—C3—C5—O1	21.2 (3)
C1—C2—C3—C5	-177.1 (3)	C4—C3—C5—C3 ⁱ	24.8 (3)
C2—C3—C4—S1	-0.1 (4)	C2—C3—C5—C3 ⁱ	-158.8 (3)
C5—C3—C4—S1	176.8 (2)		

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4 \cdots O1 ⁱⁱ	0.93	2.42	3.261 (4)	151

Symmetry code: (ii) $x+1/2, y+1/2, -z+1/2$.