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## Structure Reports

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## 5-(Methoxycarbonyl)thiophene-2-carboxylic acid

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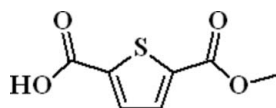
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.041;  $wR$  factor = 0.108; data-to-parameter ratio = 12.7.

In the title compound,  $\text{C}_7\text{H}_6\text{O}_4\text{S}$ , a monoester derivative of 2,5-thiophenedicarboxylic acid, the carboxylic acid and the carboxylic acid ester groups are approximately coplanar with thiophene ring, making a dihedral angle of 3.1 (4) and 3.6 (4)°, respectively. In the crystal structure, molecules are connected by classical intermolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds, forming centrosymmetric dimers.

## Related literature

For a related structure, see: Zhao *et al.* (2009).

## Experimental

## Crystal data

$\text{C}_7\text{H}_6\text{O}_4\text{S}$   
 $M_r = 186.19$

Monoclinic,  $P2_1/c$   
 $a = 18.2813$  (18) Å

$b = 5.9833$  (6) Å  
 $c = 7.3446$  (8) Å  
 $\beta = 99.081$  (1)°  
 $V = 793.30$  (14) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.38$  mm<sup>-1</sup>  
 $T = 298$  K  
 $0.40 \times 0.28 \times 0.12$  mm

## Data collection

Siemens SMART APEX CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.864$ ,  $T_{\max} = 0.956$

3914 measured reflections  
1398 independent reflections  
958 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.108$   
 $S = 0.96$   
1398 reflections

110 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.26$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4}\cdots\text{O3}^i$	0.82	1.82	2.639 (2)	173

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

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2181).

## References

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Zhao, L., Liang, J., Yue, G., Deng, X. & He, Y. (2009). *Acta Cryst.* **E65**, m722.

## supporting information

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## 5-(Methoxycarbonyl)thiophene-2-carboxylic acid

Guang-Ming Xia, Mu-Wei Ji, Ping Lu, Guo-Xin Sun and Wen-Fang Xu

### S1. Comment

The derivatives of thiophene have been viewed as significant compounds for application in many fields, such as photo-material, electronic luminescence material (Zhao *et al.*, (2009)). Many simple structures containing thiophene ring were synthesized for their derivatives. When substituted with different active function groups, a series of valuable derivatives of thiophene can be obtained. It may be used as a source to synthesize compounds which has more complex structures. The title compound was synthesized as a promising compound with biological activities and a precursor for the synthesis of various functional compounds for its delocalized structure.

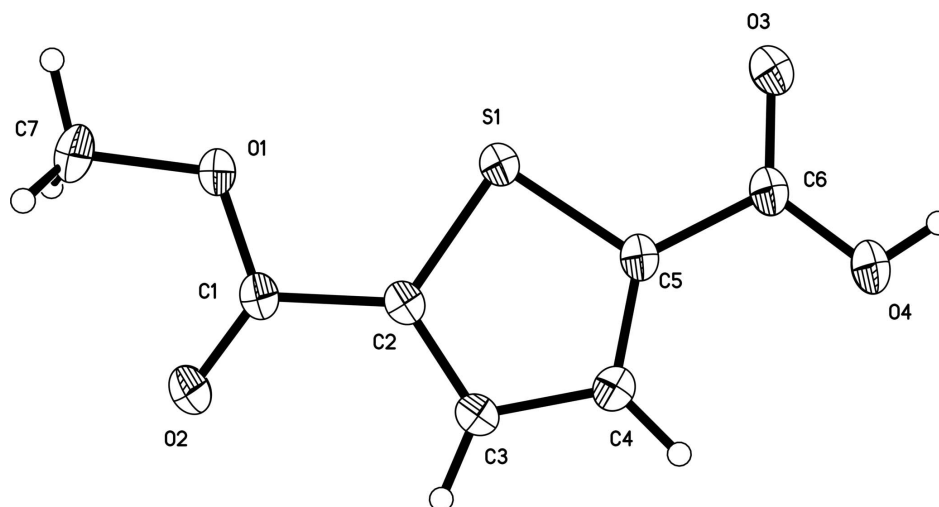
In the structure of the title compound (Fig. 1), the carboxylate groups are approximately coplanar with thiophene ring. The co-plane connection makes the  $\pi$ -conjugation expanded in a larger range. In the crystal structure, molecules are connected by intermolecular O4—H4 $\cdots$ O3' hydrogen-bonding interactions (Table 1) forming a dimer (Fig. 2). Symmetry code: (i)  $-x, -y+1, -z+1$ .

### S2. Experimental

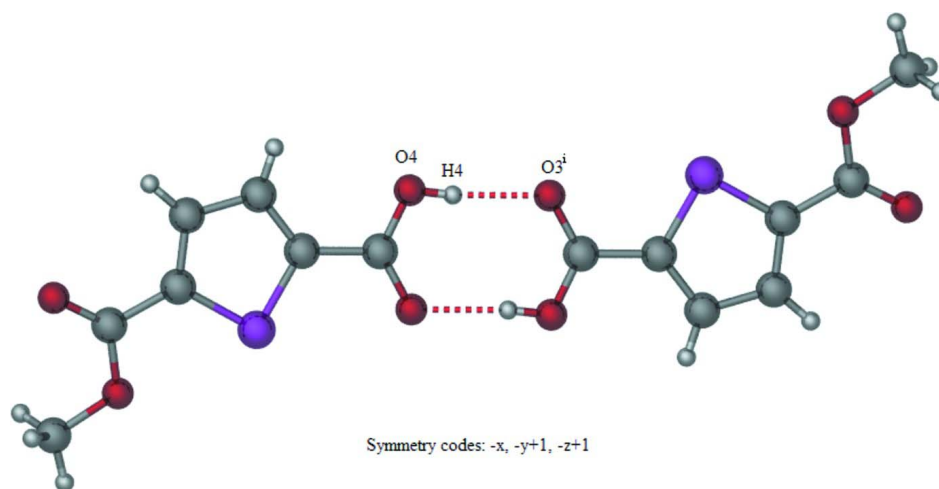
Sodium (230 mg, 10 mmol) was dissolved in 40 ml of absolute methanol, the resulting solution was adopted into a solution of dimethylthiophen-2,5-dicarboxylate (2000 mg, 10 mmol) in 60 ml of absolute methanol. The resulting mixture was heated at 343 K for 5 h, cooled, and the filtrated. The filtrate was acidified with HCl (6 mol.L<sup>-1</sup>) to pH about 5. As the HCl being adopted, the product was formed as colourless solid (yield: 152 mg, 82%). Recrystallized with methanol at room temperature afforded colourless crystal. IR-spectrum (KBr):  $\nu = 3097, 1728, 1712$  cm<sup>-1</sup>.

### S3. Refinement

All H atoms were geometrically fixed and allowed to ride on their attached atoms, which C—H = 0.93–0.96 Å and  $U_{iso}(H) = 1.2–1.5U_{eq}(C)$  and O—H = 0.82 Å and  $U_{iso}(H) = 1.2U_{eq}(O)$ .

**Figure 1**

Molecular structure of title compound with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level. H atoms are presented as a small spheres of arbitrary radius.

**Figure 2**

The centrosymmetrical H-bonded dimer. Hydrogen bonds presented by dashed lines. Symmetry code: (i)  $-x, -y+1, -z+1$ .

### 5-(Methoxycarbonyl)thiophene-2-carboxylic acid

#### Crystal data

$C_7H_6O_4S$

$M_r = 186.19$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P 2_1/c$

$a = 18.2813 (18) \text{ \AA}$

$b = 5.9833 (6) \text{ \AA}$

$c = 7.3446 (8) \text{ \AA}$

$\beta = 99.081 (1)^\circ$

$V = 793.30 (14) \text{ \AA}^3$

$Z = 4$

$F(000) = 384$

$D_x = 1.559 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 978 reflections

$\theta = 2.3\text{--}25.7^\circ$

$\mu = 0.38 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Block, colourless

$0.40 \times 0.28 \times 0.12 \text{ mm}$

*Data collection*

Siemens SMART APEX CCD area-detector diffractometer	3914 measured reflections
Radiation source: fine-focus sealed tube	1398 independent reflections
Graphite monochromator	958 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.035$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 2.3^\circ$
$T_{\text{min}} = 0.864$ , $T_{\text{max}} = 0.956$	$h = -17 \rightarrow 21$
	$k = -6 \rightarrow 7$
	$l = -8 \rightarrow 8$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2]$
$S = 0.96$	where $P = (F_o^2 + 2F_c^2)/3$
1398 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
110 parameters	$\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

*Special details*

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.36617 (8)	0.4062 (3)	1.0635 (2)	0.0477 (5)
O2	0.40524 (9)	0.7617 (3)	1.0853 (3)	0.0579 (5)
O3	0.07899 (9)	0.3919 (3)	0.6150 (2)	0.0593 (6)
O4	0.04479 (9)	0.7517 (3)	0.5849 (3)	0.0609 (6)
H4	0.0068	0.6974	0.5278	0.091*
S1	0.22488 (3)	0.47279 (11)	0.83803 (9)	0.0437 (3)
C1	0.35915 (12)	0.6246 (4)	1.0321 (3)	0.0398 (6)
C2	0.28593 (12)	0.6776 (4)	0.9231 (3)	0.0381 (6)
C3	0.25867 (13)	0.8855 (4)	0.8830 (3)	0.0419 (6)
H3	0.2847	1.0162	0.9174	0.050*
C4	0.18615 (13)	0.8808 (4)	0.7830 (3)	0.0421 (7)
H4A	0.1586	1.0079	0.7455	0.050*
C5	0.16150 (12)	0.6693 (4)	0.7481 (3)	0.0400 (6)
C6	0.09006 (13)	0.5956 (4)	0.6426 (3)	0.0432 (6)
C7	0.43390 (14)	0.3361 (5)	1.1788 (4)	0.0597 (8)
H7A	0.4753	0.3679	1.1174	0.090*

H7B	0.4318	0.1784	1.2017	0.090*
H7C	0.4395	0.4154	1.2938	0.090*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0345 (9)	0.0390 (11)	0.0619 (11)	0.0014 (8)	-0.0158 (8)	0.0037 (9)
O2	0.0401 (11)	0.0461 (12)	0.0783 (13)	-0.0098 (9)	-0.0190 (9)	0.0037 (10)
O3	0.0426 (11)	0.0456 (12)	0.0809 (14)	-0.0054 (9)	-0.0171 (9)	-0.0026 (10)
O4	0.0361 (10)	0.0523 (13)	0.0839 (13)	0.0006 (9)	-0.0226 (9)	-0.0035 (10)
S1	0.0357 (4)	0.0333 (4)	0.0563 (4)	-0.0016 (3)	-0.0105 (3)	-0.0007 (3)
C1	0.0310 (13)	0.0406 (16)	0.0446 (14)	-0.0017 (12)	-0.0045 (11)	0.0013 (12)
C2	0.0326 (13)	0.0355 (14)	0.0433 (14)	-0.0035 (10)	-0.0029 (11)	-0.0009 (11)
C3	0.0380 (14)	0.0327 (15)	0.0511 (15)	-0.0046 (12)	-0.0048 (11)	-0.0020 (12)
C4	0.0380 (14)	0.0349 (15)	0.0500 (15)	0.0040 (12)	-0.0034 (12)	0.0000 (12)
C5	0.0312 (14)	0.0393 (15)	0.0455 (14)	0.0007 (11)	-0.0063 (11)	0.0000 (12)
C6	0.0314 (13)	0.0434 (16)	0.0503 (15)	-0.0001 (13)	-0.0074 (11)	-0.0016 (13)
C7	0.0444 (16)	0.057 (2)	0.0694 (18)	0.0104 (14)	-0.0173 (13)	0.0124 (15)

*Geometric parameters (Å, °)*

O1—C1	1.330 (3)	C2—C3	1.355 (3)
O1—C7	1.447 (3)	C3—C4	1.411 (3)
O2—C1	1.196 (3)	C3—H3	0.9300
O3—C6	1.247 (3)	C4—C5	1.354 (3)
O4—C6	1.275 (3)	C4—H4A	0.9300
O4—H4	0.8200	C5—C6	1.477 (3)
S1—C2	1.708 (2)	C7—H7A	0.9600
S1—C5	1.709 (2)	C7—H7B	0.9600
C1—C2	1.482 (3)	C7—H7C	0.9600
C1—O1—C7	115.88 (19)	C3—C4—H4A	124.0
C6—O4—H4	109.5	C4—C5—C6	128.2 (2)
C2—S1—C5	90.67 (12)	C4—C5—S1	112.63 (16)
O2—C1—O1	125.0 (2)	C6—C5—S1	119.13 (18)
O2—C1—C2	124.0 (2)	O3—C6—O4	125.6 (2)
O1—C1—C2	111.00 (19)	O3—C6—C5	119.0 (2)
C3—C2—C1	125.7 (2)	O4—C6—C5	115.4 (2)
C3—C2—S1	112.49 (17)	O1—C7—H7A	109.5
C1—C2—S1	121.8 (2)	O1—C7—H7B	109.5
C2—C3—C4	112.2 (2)	H7A—C7—H7B	109.5
C2—C3—H3	123.9	O1—C7—H7C	109.5
C4—C3—H3	123.9	H7A—C7—H7C	109.5
C5—C4—C3	112.0 (2)	H7B—C7—H7C	109.5
C5—C4—H4A	124.0		
C7—O1—C1—O2	3.1 (4)	C2—C3—C4—C5	-1.0 (3)
C7—O1—C1—C2	-176.3 (2)	C3—C4—C5—C6	-177.8 (2)

O2—C1—C2—C3	-6.1 (4)	C3—C4—C5—S1	0.8 (3)
O1—C1—C2—C3	173.3 (2)	C2—S1—C5—C4	-0.3 (2)
O2—C1—C2—S1	175.6 (2)	C2—S1—C5—C6	178.4 (2)
O1—C1—C2—S1	-5.0 (3)	C4—C5—C6—O3	175.4 (3)
C5—S1—C2—C3	-0.3 (2)	S1—C5—C6—O3	-3.1 (3)
C5—S1—C2—C1	178.2 (2)	C4—C5—C6—O4	-3.6 (4)
C1—C2—C3—C4	-177.6 (2)	S1—C5—C6—O4	177.90 (19)
S1—C2—C3—C4	0.8 (3)		

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O4—H4 $\cdots$ O3 <sup>i</sup>	0.82	1.82	2.639 (2)	173

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