

## 2-(1,3-Dithiol-2-ylidene)-1,3-dithiole-4-carbaldehyde

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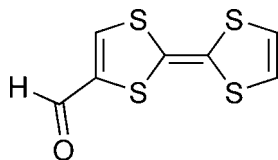
Received 13 June 2013; accepted 20 June 2013

 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.024;  $wR$  factor = 0.057; data-to-parameter ratio = 25.1.

The structure of the title compound,  $\text{C}_7\text{H}_4\text{OS}_4$ , at 100 K has orthorhombic symmetry. In the crystal, tetrathiafulvalene molecules form  $\pi$ -stacks along the  $a$  axis, with a stacking distance of 3.4736 (6) Å. Along the  $b$  axis, parallel stacks are interconnected with each other through a network of weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds and short  $\text{S}\cdots\text{S}$  contacts [3.4813 (7) Å]. Additional short  $\text{S}\cdots\text{S}$  contacts [3.4980 (9) Å] join parallel stacks along the  $c$  axis.

### Related literature

For tetrathiafulvalene derivatives and their applications, see: Yamada & Sugimoto (2004); Segura & Martín (2001). For a review on synthetic chemistry of tetrathiafulvalenes, see: Fabre (2004). For a previous synthesis of the title compound, see: Garín *et al.* (1994). For reviews on 'weak' non-classical hydrogen bonding, see: Steiner (2002); Desiraju (2005). For reviews on halogen-halogen contacts, see: Metrangolo *et al.* (2008).



### Experimental

#### Crystal data

 $\text{C}_7\text{H}_4\text{OS}_4$ 
 $M_r = 232.34$ 

 Orthorhombic,  $P2_12_12_1$ 
 $a = 3.8466$  (3) Å

 $b = 7.4052$  (7) Å

 $c = 30.577$  (3) Å

 $V = 870.99$  (13) Å<sup>3</sup>
 $Z = 4$ 

 Mo  $K\alpha$  radiation

 $\mu = 1.03$  mm<sup>-1</sup>
 $T = 100$  K

 $0.50 \times 0.21 \times 0.13$  mm

#### Data collection

Bruker SMART APEX CCD diffractometer

Absorption correction: multi-scan (SADABS in APEX2; Bruker,

 2012)  
 $T_{\min} = 0.675$ ,  $T_{\max} = 0.746$   
 6998 measured reflections

 2734 independent reflections  
 2663 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$ 

#### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.024$ 
 $wR(F^2) = 0.057$ 
 $S = 1.13$ 

2734 reflections

109 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.45$  e Å<sup>-3</sup>
 $\Delta\rho_{\min} = -0.25$  e Å<sup>-3</sup>

 Absolute structure: Flack  $x$  determined using 985 quotients [( $I^+$ )-( $I^-$ )]/[( $I^+$ )+( $I^-$ )] (Parsons & Flack, 2004), 1024 Friedel pairs

Flack parameter: 0.01 (4)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C1}-\text{H1}\cdots\text{O1}^i$	0.95	2.38	3.228 (3)	149
$\text{C3}-\text{H3}\cdots\text{O1}^i$	0.95	2.69	3.445 (3)	137

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

Data collection: APEX2 (Bruker, 2012); cell refinement: SAINT (Bruker, 2012); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2013) and SHELXLE (Hübschle *et al.*, 2011); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: publCIF (Westrip, 2010) and enCIFer (Allen *et al.*, 2004).

The authors are grateful to Dr C. Vande Velde (Karel de Grote University College, Antwerp, Belgium) for helpful discussions. The X-ray diffractometer (MZ) was funded by NSF grant No. 0087210, Ohio Board of Regents grant CAP-491 and Youngstown State University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2488).

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## supplementary materials

*Acta Cryst.* (2013). E69, o1157 [doi:10.1107/S160053681301711X]

**2-(1,3-Dithiol-2-ylidene)-1,3-dithiole-4-carbaldehyde****Matthias Zeller and Vladimir A. Azov****Comment**

The title compound, commonly known as 4-formyltetrathiafulvalene, was prepared from tetrathiafulvalene (TTF) and can serve as an intermediate for the synthesis of 4-(hydroxymethyl)tetrathiafulvalene by reduction with NaBH<sub>4</sub>, of conjugated TTF derivatives by means of Wittig reaction (Garín *et al.*, 1994), of TTF imines by reaction with amines, and of other functional tetrathiafulvalenes (Yamada & Sugimoto, 2004; Fabre, 2004).

The molecular structure of the title compound with atom numbering scheme is shown in Fig. 1. Bond lengths and angles may be considered normal. The molecular framework excluding the carbonyl group is essentially planar, with a maximum deviation of fitted atoms from the least-square plane, defined by the heavy atoms of the TTF backbone, of 0.042 (2) Å for C6. Atoms of the carbonyl group show more substantial out of plane deviation of 0.128 (2) Å for C1 and of 0.2393 (19) Å for O1, respectively.

Details of the packing interactions are given in the Tables. Molecules of the 4-formyltetrathiafulvalene form  $\pi$ -stacks along the *a* axis with a distance of 3.4736 (6) Å between the least-square planes defined by the S1, S2, S3, and S4 atoms (Figs. 1 & 2). Parallel  $\pi$ -stacks are interconnected with each other along the *b* axis by C1—H1 $\cdots$ O1<sup>i</sup> and C3—H3 $\cdots$ O1<sup>i</sup> (symmetry code: (i)  $-x, y + 1/2, -z + 1/2$ ) short contacts, which can be classified as non-classical hydrogen bonds. Additionally, two S $\cdots$ S short contacts, which may be similar in nature to halogen bonds (Metrangolo *et al.*, 2008), are observed in the crystal structure. The shorter S2 $\cdots$ S4<sup>iv</sup> (3.4813 (7) Å) contacts (symmetry code: (iv)  $x, 1 + y, z$ ) are observed along the *b* axis. The longer (3.4980 (9) Å) S3 $\cdots$ S3<sup>iii</sup> contacts (symmetry codes: (ii)  $-1/2 + x, 1/2 - y, -z$ ; (iii)  $1/2 + x, 1/2 - y, -z$ ) bind parallel  $\pi$ -stacks with each other along the *c* axis.

**Experimental**

The title compound was prepared as described by Garín *et al.* (1994) by treatment of monolithio-TTF with *N*-methyl-*N*-phenylformamide in dry Et<sub>2</sub>O. The product was obtained as a deep red microcrystalline solid. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in benzene/cyclohexane. Mp: 382–383 K; Lit: 382–383 K (Garín *et al.*, 1994). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  6.33 (d, *J* = 6.5 Hz, 1 H), 6.36 (d, *J* = 6.2 Hz, 1 H), 7.42 (s, 1 H), 9.48 (s, 1 H).

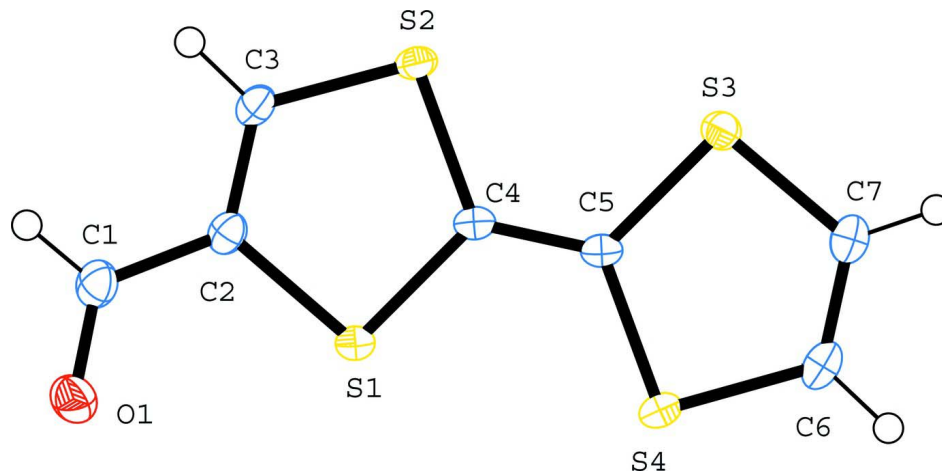
**Refinement**

Hydrogen atoms were included at calculated positions using a riding model with aromatic and formyl C—H = 0.95. The *U*<sub>iso</sub>(H) values were fixed at 1.2 × *U*<sub>eq</sub>(C) of the parent C atom.

**Computing details**

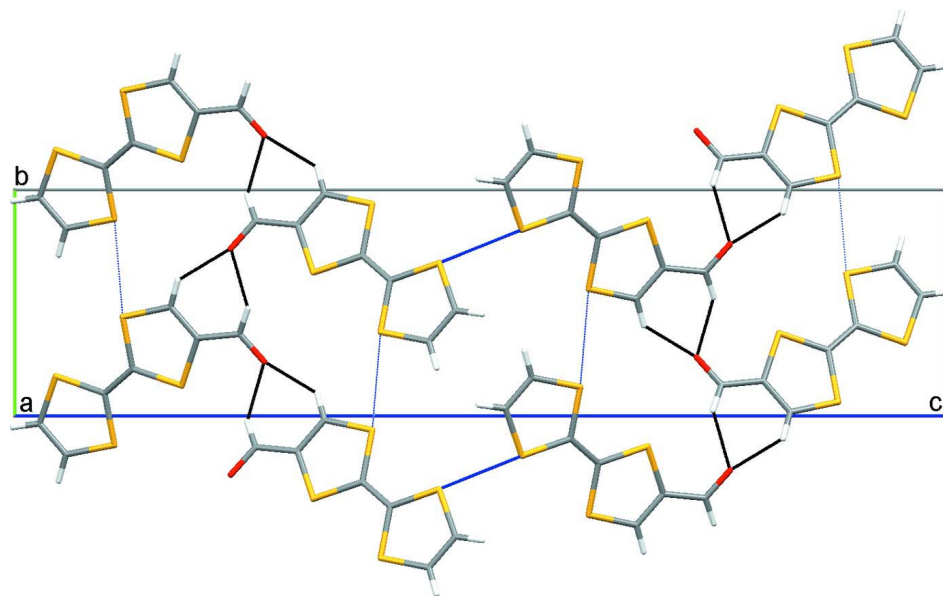
Data collection: *APEX2* (Bruker, 2012); cell refinement: *APEX2* (Bruker, 2012); data reduction: *APEX2* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2013) and *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012)

and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *enCIFer* (Allen *et al.*, 2004).



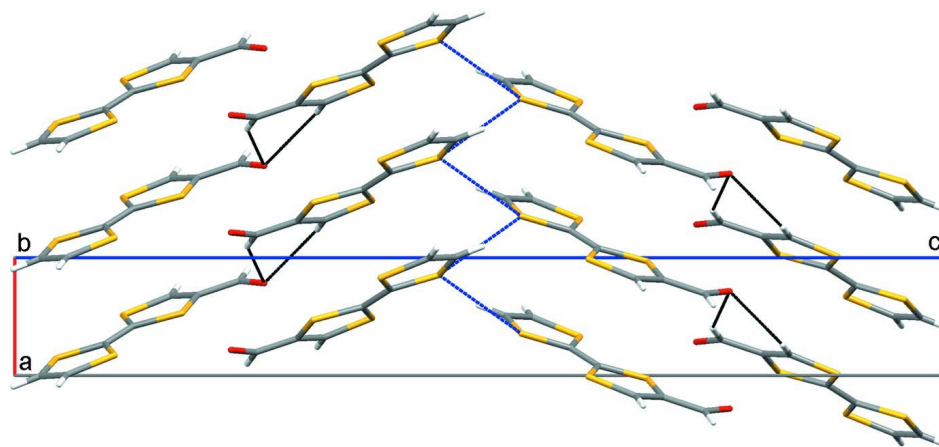
**Figure 1**

*ORTEP*-3 plot of the title molecule with the atom numbering scheme. Displacement ellipsoids are represented at 50% probability levels. H atoms are presented as a small spheres of arbitrary radius.



**Figure 2**

Crystal packing of the title compound viewed along the *a* axis. Hydrogen bonds are shown as solid black lines, short S3...S3 contacts are shown as solid blue lines, and short S2...S4 contacts are represented as dotted blue lines.

**Figure 3**

Crystal packing of the title compound viewed along the *b* axis. Hydrogen bonds are shown as solid black lines, short S3...S3 contacts are shown as solid blue lines.

## 2-(1,3-Dithiol-2-ylidene)-1,3-dithiole-4-carbaldehyde

### Crystal data

$C_7H_4OS_4$

$M_r = 232.34$

Orthorhombic,  $P2_12_12_1$

$a = 3.8466$  (3) Å

$b = 7.4052$  (7) Å

$c = 30.577$  (3) Å

$V = 870.99$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 472$

$D_x = 1.772$  Mg m<sup>-3</sup>

Melting point: 383 K

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

Cell parameters from 4789 reflections

$\theta = 2.8$ – $31.4^\circ$

$\mu = 1.03$  mm<sup>-1</sup>

$T = 100$  K

Plate, red

$0.50 \times 0.21 \times 0.13$  mm

### Data collection

Bruker SMART APEX CCD  
diffractometer

Radiation source: fine focus sealed tube

$\omega$  and  $\varphi$  scans

Absorption correction: multi-scan  
(*SADABS* in *APEX2*; Bruker, 2012)

$T_{\min} = 0.675$ ,  $T_{\max} = 0.746$

6998 measured reflections

2734 independent reflections

2663 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$

$\theta_{\max} = 31.9^\circ$ ,  $\theta_{\min} = 1.3^\circ$

$h = -5 \rightarrow 5$

$k = -10 \rightarrow 10$

$l = -42 \rightarrow 44$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.057$

$S = 1.13$

2734 reflections

109 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 0.4121P]$

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

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

$\Delta\rho_{\max} = 0.45$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.25$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using  
985 quotients  $[(I^+)-(I^-)]/[(I^+)+(I^-)]$  (Parsons &  
Flack, 2004), 1024 Friedel pairs.

Flack parameter: 0.01 (4)

*Special details*

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1960 (6)	0.3626 (3)	0.24133 (7)	0.0229 (4)
H1	0.0987	0.4745	0.2504	0.027*
C2	0.3148 (6)	0.3446 (3)	0.19636 (7)	0.0178 (4)
C3	0.3234 (6)	0.4823 (3)	0.16743 (7)	0.0188 (4)
H3	0.2417	0.5992	0.1751	0.023*
C4	0.5823 (5)	0.2086 (3)	0.12667 (7)	0.0154 (4)
C5	0.7332 (5)	0.1004 (3)	0.09665 (7)	0.0154 (4)
C6	0.9971 (6)	-0.1700 (3)	0.05523 (7)	0.0213 (4)
H6	1.0784	-0.2866	0.0473	0.026*
C7	1.0078 (7)	-0.0331 (3)	0.02682 (7)	0.0213 (4)
H7	1.0959	-0.0492	-0.0019	0.026*
O1	0.2158 (5)	0.2405 (2)	0.26790 (5)	0.0275 (4)
S1	0.47171 (14)	0.13395 (6)	0.17941 (2)	0.01732 (10)
S2	0.48840 (15)	0.43791 (6)	0.11609 (2)	0.01750 (10)
S3	0.85438 (14)	0.17653 (7)	0.04434 (2)	0.01774 (11)
S4	0.82962 (14)	-0.12822 (7)	0.10718 (2)	0.01786 (11)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0258 (11)	0.0227 (9)	0.0202 (10)	0.0009 (9)	-0.0027 (8)	-0.0048 (8)
C2	0.0168 (9)	0.0174 (9)	0.0190 (9)	0.0009 (8)	-0.0026 (7)	-0.0033 (7)
C3	0.0204 (10)	0.0154 (8)	0.0206 (10)	0.0022 (8)	-0.0014 (9)	-0.0033 (7)
C4	0.0151 (9)	0.0134 (8)	0.0177 (9)	-0.0006 (6)	-0.0023 (7)	0.0024 (6)
C5	0.0150 (9)	0.0132 (8)	0.0180 (9)	-0.0011 (6)	-0.0020 (7)	0.0027 (7)
C6	0.0193 (9)	0.0186 (9)	0.0260 (10)	0.0023 (9)	-0.0008 (9)	-0.0069 (7)
C7	0.0201 (10)	0.0217 (9)	0.0221 (10)	0.0006 (9)	0.0005 (9)	-0.0056 (7)
O1	0.0359 (10)	0.0274 (8)	0.0192 (7)	-0.0016 (8)	-0.0012 (7)	-0.0002 (6)
S1	0.0208 (2)	0.01368 (19)	0.0175 (2)	0.00034 (19)	0.00125 (19)	0.00193 (17)
S2	0.0205 (2)	0.01230 (18)	0.0197 (2)	0.00120 (19)	-0.0006 (2)	0.00242 (16)
S3	0.0183 (2)	0.0181 (2)	0.0169 (2)	0.00035 (19)	0.00033 (19)	0.00149 (17)
S4	0.0192 (2)	0.01267 (19)	0.0217 (2)	0.00182 (19)	-0.00120 (19)	0.00094 (17)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C1—O1	1.218 (3)	C4—S2	1.7661 (19)
C1—C2	1.455 (3)	C5—S3	1.759 (2)
C1—H1	0.9500	C5—S4	1.763 (2)
C2—C3	1.350 (3)	C6—C7	1.336 (3)
C2—S1	1.751 (2)	C6—S4	1.742 (2)
C3—S2	1.725 (2)	C6—H6	0.9500

C3—H3	0.9500	C7—S3	1.745 (2)
C4—C5	1.349 (3)	C7—H7	0.9500
C4—S1	1.757 (2)		
O1—C1—C2	122.9 (2)	C4—C5—S4	122.44 (15)
O1—C1—H1	118.6	S3—C5—S4	114.71 (12)
C2—C1—H1	118.6	C7—C6—S4	118.03 (16)
C3—C2—C1	123.9 (2)	C7—C6—H6	121.0
C3—C2—S1	118.05 (16)	S4—C6—H6	121.0
C1—C2—S1	118.02 (16)	C6—C7—S3	117.70 (17)
C2—C3—S2	117.48 (16)	C6—C7—H7	121.1
C2—C3—H3	121.3	S3—C7—H7	121.1
S2—C3—H3	121.3	C2—S1—C4	94.30 (10)
C5—C4—S1	122.80 (15)	C3—S2—C4	95.26 (10)
C5—C4—S2	122.29 (15)	C7—S3—C5	94.82 (10)
S1—C4—S2	114.90 (11)	C6—S4—C5	94.69 (10)
C4—C5—S3	122.85 (15)		
O1—C1—C2—C3	-174.0 (2)	C5—C4—S1—C2	178.23 (18)
O1—C1—C2—S1	3.4 (3)	S2—C4—S1—C2	-0.66 (13)
C1—C2—C3—S2	177.51 (17)	C2—C3—S2—C4	-0.5 (2)
S1—C2—C3—S2	0.1 (3)	C5—C4—S2—C3	-178.19 (18)
S1—C4—C5—S3	-178.29 (12)	S1—C4—S2—C3	0.71 (13)
S2—C4—C5—S3	0.5 (3)	C6—C7—S3—C5	-1.6 (2)
S1—C4—C5—S4	0.8 (3)	C4—C5—S3—C7	-178.51 (18)
S2—C4—C5—S4	179.63 (12)	S4—C5—S3—C7	2.32 (14)
S4—C6—C7—S3	0.3 (3)	C7—C6—S4—C5	1.2 (2)
C3—C2—S1—C4	0.3 (2)	C4—C5—S4—C6	178.61 (18)
C1—C2—S1—C4	-177.22 (18)	S3—C5—S4—C6	-2.21 (14)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1 $\cdots$ O1 <sup>i</sup>	0.95	2.38	3.228 (3)	149
C3—H3 $\cdots$ O1 <sup>i</sup>	0.95	2.69	3.445 (3)	137

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

Sulfur-sulfur short contacts ( $\text{\AA}$ ) of the title compound

System S $\cdots$ S	S $\cdots$ S	Symmetry code
S3 $\cdots$ S3 <sup>ii</sup>	3.4980 (9)	(ii) $-1/2+x, 1/2-y, -z$
S3 $\cdots$ S3 <sup>iii</sup>	3.4980 (9)	(iii) $1/2+x, 1/2-y, -z$
S2 $\cdots$ S4 <sup>iv</sup>	3.4813 (7)	(iv) $x, 1+y, z$