Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-[(Ethoxycarbonothioyl)sulfanyl]acetic acid

Shude Xiao, Renpeng Gu and Paul A. Charpentier*

Department of Chemical and Biochemical Engineering, Faculty of Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9
Correspondence e-mail: pcharpentier@eng.uwo.ca

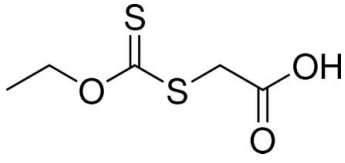
Received 28 March 2011; accepted 10 May 2011

Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.111; data-to-parameter ratio = 38.5.

In the title compound, $C_5H_8O_3S_2$, the C—S and C—O bonds in the xanthate unit are shorter than those linked to it. In the crystal, inversion dimers linked by pairs of O—H···O hydrogen bonds occur.

Related literature

For general background to the synthesis and applications of the title compound, see: Stenzel *et al.* (2003); Moad *et al.* (2005, 2008). For its applications in polymerization, see: Coote & Radom (2004); Simms *et al.* (2005); Russum *et al.* (2005); Assem *et al.* (2007); Wang *et al.* (2010). For similar structures, see: Xiao & Charpentier (2010, 2011).



Experimental

Crystal data

$C_5H_8O_3S_2$
M_r = 180.23
Monoclinic, $P2_1/n$
a = 4.7387 (2) Å
b = 14.7836 (8) Å
c = 11.9013 (6) Å
β = 100.845 (3)°
V = 818.86 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.60 mm^{-1}
T = 150 K
0.08 × 0.03 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.952, T_{max} = 0.982
39762 measured reflections
3582 independent reflections
2343 reflections with $I > 2\sigma(I)$
R_{int} = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.111
S = 1.01
3582 reflections
93 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3^{i}	0.84	1.81	2.645 (2)	175

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); 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*.

This work was supported by the Canadian Natural Sciences and Engineering Research Council (NSERC) Idea to Innovation (I2I) Program. The authors are grateful to Aneta Borecki and Dr Guerman Popov in the Department of Chemistry of the University of Western Ontario for the XRD data acquisition and interpretation.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5142).

References

Assem, Y., Chaffey-Millar, H., Barner-Kowollik, C., Wegner, G. & Agarwal, S. (2007). *Macromolecules*, **40**, 3907–3913.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Coote, M. L. & Radom, L. (2004). *Macromolecules*, **37**, 590–596.
Moad, G., Rizzardo, E. & Thang, S. H. (2005). *Aust. J. Chem.* **58**, 379–410.
Moad, G., Rizzardo, E. & Thang, S. H. (2008). *Polymer*, **49**, 1079–1131.
Russum, J. P., Barbre, N. D., Jones, C. W. & Schork, F. J. (2005). *J. Polym. Sci. Part A Polym. Chem.* **43**, 2188–2193.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Simms, R. W., Davis, T. P. & Cunningham, M. F. (2005). *Macromol. Rapid Commun.* **26**, 592–596.
Stenzel, M. H., Cummins, L., Roberts, G. E., Davis, T. P., Vana, P. & Barner-Kowollik, C. (2003). *Macromol. Chem. Phys.* **204**, 1160–1168.
Wang, W., Wang, D., Li, B. & Zhu, S. (2010). CN Patent 101693749.
Xiao, S. & Charpentier, P. A. (2010). *Acta Cryst.* E**66**, o3103.
Xiao, S. & Charpentier, P. A. (2011). *Acta Cryst.* E**67**, o575.

supporting information

Acta Cryst. (2011). E**67**, o1442 [doi:10.1107/S1600536811017703]

2-[(Ethoxycarbonothioyl)sulfanyl]acetic acid

Shude Xiao, Renpeng Gu and Paul A. Charpentier

S1. Comment

Reversible-deactivation radical polymerization (RDRP) of vinyl acetate (VAc) has been a challenge. Methyl 2-(ethoxycarbonothioylthio)acetate was investigated for reversible addition-fragmentation chain transfer (RAFT) polymerization of VAc (Moad *et al.*, 2005, 2008; Stenzel *et al.*, 2003; Coote & Radom, 2004), and was successfully applied in emulsion polymerizations (Simms *et al.*, 2005; Russum *et al.*, 2005). Thanks to the similarity of the molecular structures, 2-(ethoxycarbonothioylthio)acetic acid not only provides a carboxylic acid functionality but also works as the RAFT-CTA for VAc in RDRP. This RAFT-CTA has also found applications in the RAFT polymerization of other monomers (Assem *et al.*, 2007; Wang *et al.*, 2010). Compounds of similar structures were reported previously (Xiao & Charpentier, 2010, 2011).

S2. Experimental

Potassium *O*-ethyl dithiocarbonate 13.6 g was dissolved in THF 50 ml, and then mixed with 2-bromoacetic acid 6.9 g / THF 20 ml. The reaction was carried out at room temperature for 2 days. Excess hexanes was applied to the mixture and the precipitates were filtered off, followed by evaporating the solvents using a rotary evaporator. The light yellow oil was further purified by extraction and recrystallization with hexanes, and colorless crystals were obtained. m.p.: 56.4 °C(DSC). MS: 179.9917.

S3. Refinement

The structure was solved and refined using the Bruker *SHELXTL* Software Package, using the space group P 1 21/n 1, with $Z = 4$ for the formula unit, $C_5H_8O_3S_2$. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. The final anisotropic full-matrix least-squares refinement on F^2 with 93 variables converged at R1 = 4.54%, for the observed data and wR2 = 11.08% for all data. The goodness-of-fit was 1.005. The largest peak in the final difference electron density synthesis was 0.309 $e^-/Å^3$ and the largest hole was -0.368 $e^-/Å^3$ with an RMS deviation of 0.077 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.462 g/cm^3 and F(000), 376 e^-.

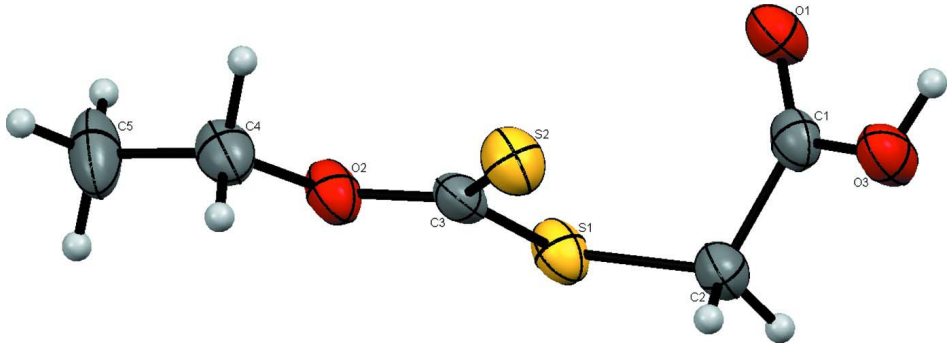


Figure 1

View of the title compound (50% probability displacement ellipsoids).

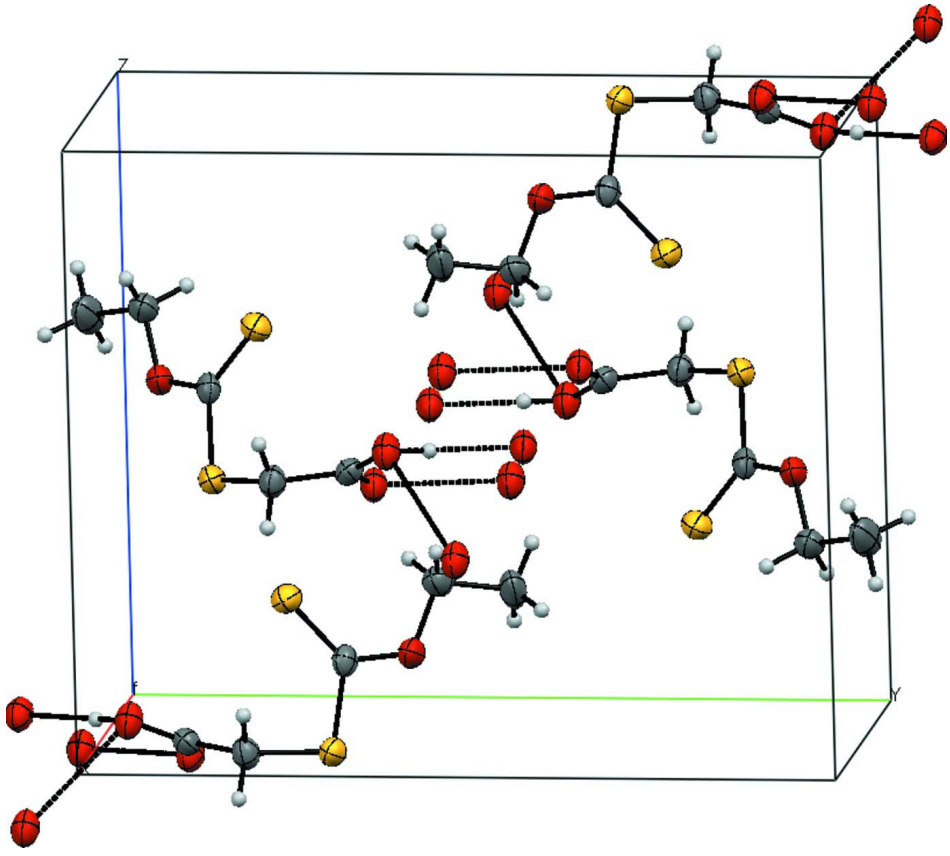


Figure 2

Packing diagram of the structure with H-bonds.

2-[(Ethoxycarbonothioyl)sulfanyl]acetic acid

Crystal data

$C_5H_8O_3S_2$
M_r = 180.23
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 4.7387 (2) Å
b = 14.7836 (8) Å
c = 11.9013 (6) Å
β = 100.845 (3)°
V = 818.86 (7) Å^3
Z = 4
F(000) = 376
D_x = 1.462 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4468 reflections
θ = 2.2–25.6°
μ = 0.60 mm^{-1}
T = 150 K
Cube, colourless
0.08 × 0.03 × 0.03 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.952, T_{max} = 0.982
39762 measured reflections
3582 independent reflections
2343 reflections with $I > 2\sigma(I)$
R_{int} = 0.092
θ_{max} = 35.0°, θ_{min} = 2.2°
h = −7→7
k = −23→23
l = −19→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.111
S = 1.01
3582 reflections
93 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
$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2 + 0.6076P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
S1	−0.08173 (11)	0.19417 (3)	1.01439 (4)	0.02745 (11)
S2	−0.03755 (11)	0.25308 (3)	0.77468 (4)	0.03030 (12)
O1	0.1868 (3)	0.10724 (9)	0.88947 (11)	0.0300 (3)
O2	−0.3267 (3)	0.44372 (9)	0.93538 (13)	0.0329 (3)
H2	−0.2443	0.4941	0.9464	0.049*
O3	0.0854 (3)	0.39432 (9)	1.04203 (12)	0.0306 (3)
C1	0.4719 (6)	−0.00588 (15)	0.8227 (2)	0.0510 (6)
H1A	0.6206	0.0051	0.8906	0.077*
H1B	0.5624	−0.0255	0.7592	0.077*
H1C	0.3409	−0.0531	0.8396	0.077*
C2	0.3067 (5)	0.07965 (13)	0.79013 (17)	0.0327 (4)
H2A	0.4352	0.1273	0.7699	0.039*

H2B	0.1508	0.0690	0.7234	0.039*
C3	0.0329 (4)	0.18315 (11)	0.88283 (14)	0.0236 (3)
C4	−0.3109 (4)	0.29105 (12)	0.98778 (16)	0.0276 (3)
H4A	−0.4369	0.2837	0.9120	0.033*
H4B	−0.4359	0.2923	1.0457	0.033*
C5	−0.1604 (4)	0.38094 (12)	0.98990 (14)	0.0239 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0365 (2)	0.02475 (19)	0.02263 (19)	−0.00361 (17)	0.00955 (16)	0.00040 (15)
S2	0.0354 (3)	0.0337 (2)	0.02195 (19)	−0.00021 (19)	0.00584 (17)	0.00340 (16)
O1	0.0375 (7)	0.0262 (6)	0.0284 (6)	0.0002 (5)	0.0118 (5)	0.0004 (5)
O2	0.0272 (7)	0.0267 (6)	0.0423 (8)	0.0001 (5)	0.0000 (6)	−0.0006 (6)
O3	0.0266 (6)	0.0272 (6)	0.0356 (7)	−0.0025 (5)	−0.0001 (5)	0.0014 (5)
C1	0.0734 (18)	0.0294 (10)	0.0603 (15)	0.0068 (11)	0.0385 (14)	−0.0004 (10)
C2	0.0384 (11)	0.0299 (9)	0.0332 (9)	−0.0048 (8)	0.0151 (8)	−0.0068 (7)
C3	0.0242 (8)	0.0242 (7)	0.0228 (7)	−0.0060 (6)	0.0050 (6)	−0.0028 (6)
C4	0.0259 (8)	0.0298 (9)	0.0289 (8)	−0.0038 (7)	0.0098 (7)	−0.0011 (7)
C5	0.0237 (8)	0.0269 (8)	0.0223 (7)	−0.0011 (6)	0.0075 (6)	−0.0020 (6)

Geometric parameters (Å, º)

S1—C3	1.7588 (17)	C1—H1A	0.9800
S1—C4	1.789 (2)	C1—H1B	0.9800
S2—C3	1.6356 (18)	C1—H1C	0.9800
O1—C3	1.332 (2)	C2—H2A	0.9900
O1—C2	1.463 (2)	C2—H2B	0.9900
O2—C5	1.308 (2)	C4—C5	1.506 (2)
O2—H2	0.8400	C4—H4A	0.9900
O3—C5	1.228 (2)	C4—H4B	0.9900
C1—C2	1.499 (3)		
C3—S1—C4	101.27 (9)	H2A—C2—H2B	108.6
C3—O1—C2	118.58 (14)	O1—C3—S2	127.40 (13)
C5—O2—H2	109.5	O1—C3—S1	106.40 (12)
C2—C1—H1A	109.5	S2—C3—S1	126.20 (11)
C2—C1—H1B	109.5	C5—C4—S1	115.70 (13)
H1A—C1—H1B	109.5	C5—C4—H4A	108.4
C2—C1—H1C	109.5	S1—C4—H4A	108.4
H1A—C1—H1C	109.5	C5—C4—H4B	108.4
H1B—C1—H1C	109.5	S1—C4—H4B	108.4
O1—C2—C1	106.83 (17)	H4A—C4—H4B	107.4
O1—C2—H2A	110.4	O3—C5—O2	124.18 (16)
C1—C2—H2A	110.4	O3—C5—C4	123.47 (16)
O1—C2—H2B	110.4	O2—C5—C4	112.25 (15)
C1—C2—H2B	110.4		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3^{i}	0.84	1.81	2.645 (2)	175

Symmetry code: (i) −*x*, −*y*+1, −*z*+2.