



Crystal structure of *O*-ethyl *N*-(ethoxy-carbonyl)thiocarbamate

Matthew J. Henley, Alex M. Schrader, Victor G. Young Jr and George Barany*

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA.

*Correspondence e-mail: barany@umn.edu

Received 26 July 2015; accepted 10 September 2015

Edited by S. V. Lindeman, Marquette University, USA

The title compound, $C_6H_{11}NO_3S$, provides entries to novel carbamoyl disulfanes and related compounds of interest to our laboratory. The atoms of the central $O(C=S)N(C=O)O$ fragment have an r.m.s. deviation of 0.1077 Å from the respective least-squares plane. While several conformational orientations are conceivable, the crystal structure shows only the one in which the carbonyl and the thiocarbonyl moieties are *anti* to each other across the central conjugated $C-N-C$ moiety. Pairs of 2.54 Å $N-H \cdots S=C$ hydrogen bonds between adjacent molecules form centrosymmetric dimers in the crystal.

Keywords: crystal structure; thiocarbamate; hydrogen bonding.

CCDC reference: 1423537

1. Related literature

A variety of methods to prepare the title compound and/or similar structures have been reported; see Delitsch (1874); Atkins *et al.* (1973); Barany (1977, and references therein); Vallejos *et al.* (2009, and references therein); Barany *et al.* (2015, and references therein). For closely related structures, see CSD (Groom & Allen, 2014) refcodes: BORBOA (Vallejos *et al.*, 2009); GAPPAQ (Kang *et al.*, 2012). For applications of the title compound in interesting chemistry, see: Atkins *et al.* (1973); Barany & Merrifield (1977); Shen *et al.* (1998, and references therein); Barany *et al.* (2006, 2015); Vallejos *et al.* (2009).



2. Experimental

2.1. Crystal data

$C_6H_{11}NO_3S$	$\gamma = 102.360 (5)^\circ$
$M_r = 177.22$	$V = 433.3 (3) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 4.1782 (17) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.236 (4) \text{ \AA}$	$\mu = 0.34 \text{ mm}^{-1}$
$c = 11.820 (5) \text{ \AA}$	$T = 173 \text{ K}$
$\alpha = 98.190 (5)^\circ$	$0.50 \times 0.10 \times 0.05 \text{ mm}$
$\beta = 98.571 (5)^\circ$	

2.2. Data collection

Siemens SMART Platform CCD diffractometer	4216 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2001)	1518 independent reflections
$T_{\min} = 0.851$, $T_{\max} = 0.984$	1194 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.037$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	102 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\max} = 0.25 \text{ e \AA}^{-3}$
1518 reflections	$\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots S1^i$	0.88	2.54	3.388 (2)	161

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

Acknowledgements

We thank the University of Minnesota CHEM 5755 class and X-Ray Crystallographic Laboratory for assistance with this structure determination.

Supporting information for this paper is available from the IUCr electronic archives (Reference: LD2135).

References

- Atkins, P. R., Glue, S. E. J. & Kay, I. T. (1973). *J. Chem. Soc. Perkin Trans. 1*, pp. 2644–2646.
- Barany, G. (1977). PhD thesis, The Rockefeller University, New York, USA.
- Barany, G., Britton, D., Chen, L., Hammer, R. P., Henley, M. J., Schrader, A. M. & Young, V. G. (2015). *J. Org. Chem.* **80**. Submitted.
- Barany, M. J., Corey, M. M., Hanson, M. C., Majerle, R. S., Hammer, R. P. & Barany, G. (2006). *Understanding Biology Using Peptides. Proceedings of the Nineteenth American Peptide Symposium*, edited by S. E. Blondelle, pp. 196–197. Berlin: Springer.
- Barany, G. & Merrifield, R. B. (1977). *J. Am. Chem. Soc.* **99**, 7363–7365.
- Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2007). *SMART and SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Delitsch, G. (1874). *J. Prakt. Chem.* **10**, 116–128.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Kang, S. K., Cho, N. S. & Jeon, M. K. (2012). *Acta Cryst.* **E68**, o300.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Shen, W. Z., Fornasiero, D. & Ralston, J. (1998). *Miner. Eng.* **11**, 145–158.
- Vallejos, S. T., Erben, M. F., Piro, O. E., Castellano, E. E. & Védova, C. O. D. (2009). *Polyhedron*, **28**, 937–946.

supporting information

Acta Cryst. (2015). E71, o782–o783 [doi:10.1107/S2056989015016989]

Crystal structure of *O*-ethyl *N*-(ethoxycarbonyl)thiocarbamate

Matthew J. Henley, Alex M. Schrader, Víctor G. Young and George Barany

S1. Structural commentary

The title compound, *O*-ethyl *N*-(ethoxycarbonyl)thiocarbamate (**1**), C₆H₁₁NO₃S, CAS registry # 5585-23-9, also known as (*N*-ethoxythiocarbonyl)urethane, was of interest to a multifaceted organosulfur research program that includes among its goals the development of amino protecting groups removable under mild conditions (Barany, 1977; Barany & Merrifield; 1977; Barany *et al.*, 2006, Barany *et al.*, 2015). Specifically, we have shown that reaction of **1** with (chlorocarbonyl)-sulfonyl chloride gives rise to the novel (chlorocarbonyl)(*N*-ethoxycarbonylcarbamoyl)disulfane, rather than the expected putative *N*-ethoxycarbonyl-1,2,4-dithiazolidine-3,5-dione (Barany *et al.*, 2015). Variations in reaction conditions and/or the nature of sulfonyl chlorides that react with **1** result in additional unusual structures which model previously uncharacterized intermediates in the mechanisms of reactions that successfully elaborate *N*-alkyl-1,2,4-dithiazolidine-3,5-dione heterocycles. Thiocarbamate **1** is also useful as an entry to pharmaceutically relevant heterocycles (Atkins *et al.*, 1973), as an additive in the purification of pyrite (Shen *et al.*, 1998), and as a precursor to compounds of interest to the agrochemical industry (Vallejos *et al.*, 2009).

X-ray quality crystals of **1** were readily obtained after bulk purification (recrystallization from hot hexane, about 7 mL/g).

All molecular parameters of **1** are within expected ranges. Ignoring the ethyl groups, the central fragment of **1** has a r.m.s. deviation of 0.1077 Å from the least squares plane [i.e., the plane consisting of atoms O1, C1, S1, N1, C2, O2, O3]. The largest deviation of any torsion angle from 0 or 180° is 11.5 (3)° for C2—N1—C1—O1. Although there are multiple theoretically stable conformations of **1** (Vallejos *et al.*, 2009), the molecule uniquely assumes the conformation where the carbonyl and the thiocarbonyl moieties are *anti* to each other across the central C—N—C moiety.

In the crystal, pairs of intermolecular N—H⋯S=C hydrogen bonds between two adjacent molecules form centrosymmetric dimers (see Figure 2).

A search of the Cambridge Structural Database (CSD; Version 5.36, update of November 2014; Groom & Allen, 2014) revealed two similar structures, *O*-benzyl *N*-(ethoxycarbonyl)thiocarbamate (**2**) (Kang *et al.*, 2012) [i.e., BnO(C=S)NH(C=O)OEt], and *O*-ethyl *N*-(methoxycarbonyl)thiocarbamate (**3**) (Vallejos *et al.*, 2009) [i.e., EtO(C=S)NH(C=O)OMe]. Interestingly, both **2** and **3** assume the same conformation as **1**, where the thiocarbonyl and carbonyl moieties are *anti* to each other across the C—N—C moiety. In all three structures, similar length N—H⋯S=C hydrogen bonds form between adjacent molecules.

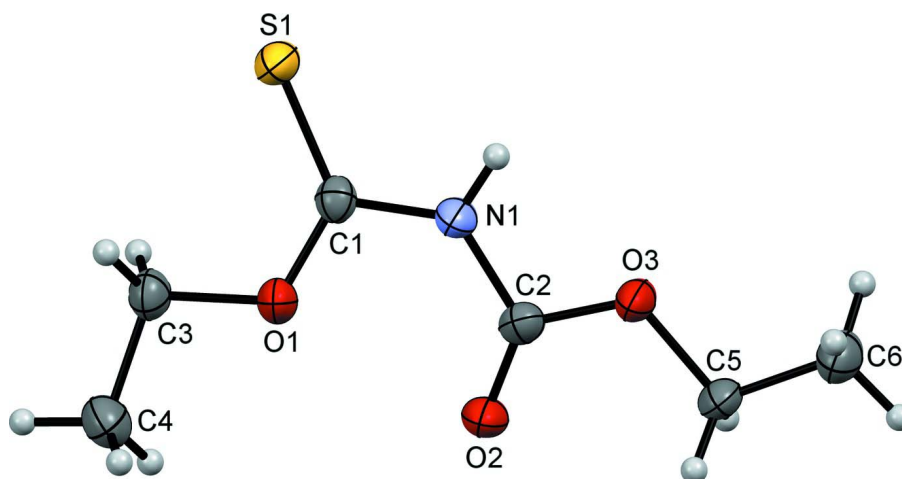
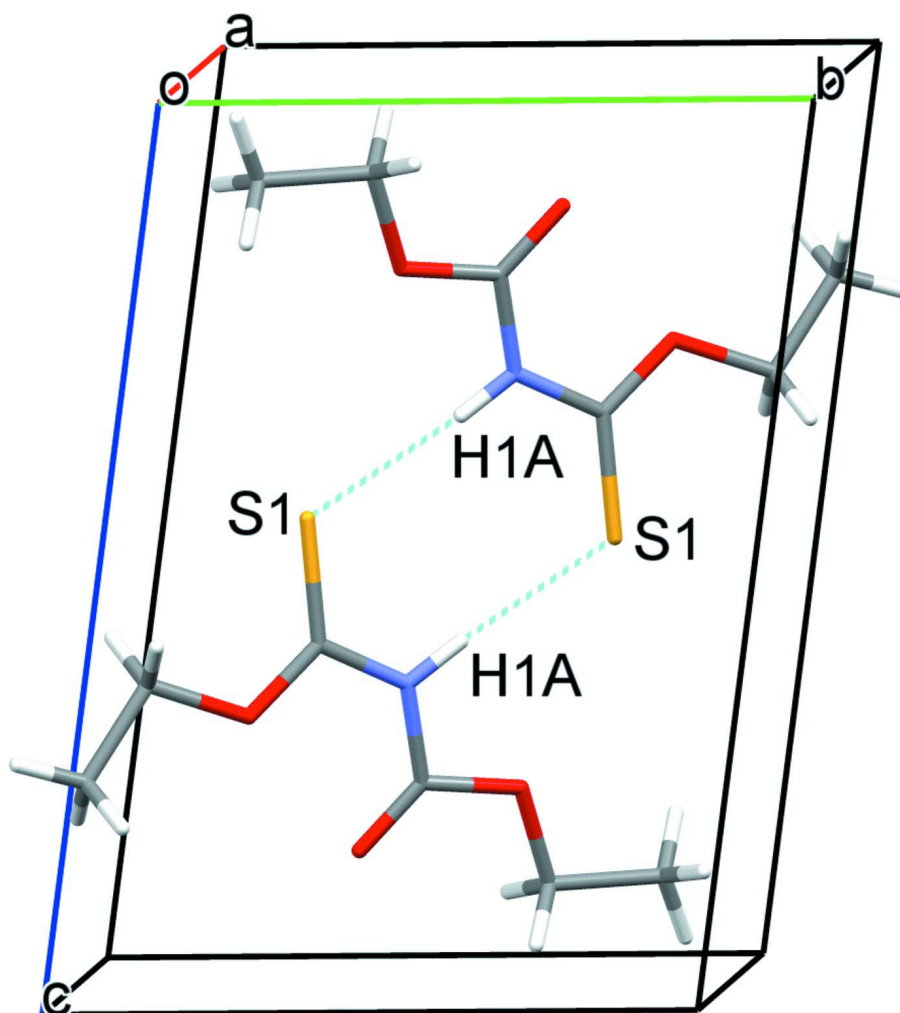


Figure 1

Crystallographic structure of *O*-ethyl *N*-(ethoxycarbonyl)thiocarbamate (**1**) showing 50% probability displacement ellipsoids with all non-hydrogen atoms labeled and numbered.

**Figure 2**

View of crystal packing down the *a*-axis, with hydrogen bonds highlighted and atoms involved in hydrogen bonding labeled and numbered.

O-Ethyl *N*-(ethoxycarbonyl)thiocarbamate

Crystal data

$C_6H_{11}NO_3S$

$M_r = 177.22$

Triclinic, $P\bar{1}$

$a = 4.1782$ (17) Å

$b = 9.236$ (4) Å

$c = 11.820$ (5) Å

$\alpha = 98.190$ (5)°

$\beta = 98.571$ (5)°

$\gamma = 102.360$ (5)°

$V = 433.3$ (3) Å³

$Z = 2$

$F(000) = 188$

$D_x = 1.358$ Mg m⁻³

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

Cell parameters from 1518 reflections

$\theta = 2.3$ – 25.1 °

$\mu = 0.34$ mm⁻¹

$T = 173$ K

Thin plates, colorless

$0.50 \times 0.10 \times 0.05$ mm

Data collection

Siemens SMART Platform CCD
diffractometer
Radiation source: normal-focus sealed tube
Graphite monochromator
area detector, ω scans per phi
Absorption correction: multi-scan
(*SADABS*; Bruker, 2001)
 $T_{\min} = 0.851$, $T_{\max} = 0.984$

4216 measured reflections
1518 independent reflections
1194 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\max} = 25.1^\circ$, $\theta_{\min} = 1.8^\circ$
 $h = -4 \rightarrow 4$
 $k = -10 \rightarrow 11$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.087$
 $S = 1.07$
1518 reflections
102 parameters
0 restraints

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.149P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

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.

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	0.08610 (15)	0.30032 (7)	0.46293 (5)	0.0321 (2)
O1	0.0371 (4)	0.25383 (16)	0.67694 (13)	0.0305 (4)
O2	0.5131 (4)	0.40638 (17)	0.85405 (13)	0.0346 (4)
O3	0.8025 (4)	0.61521 (17)	0.80409 (13)	0.0331 (4)
N1	0.4306 (5)	0.4541 (2)	0.66587 (16)	0.0300 (5)
H1A	0.5091	0.5211	0.6247	0.036*
C1	0.1822 (5)	0.3340 (2)	0.60663 (19)	0.0254 (5)
C2	0.5755 (6)	0.4835 (3)	0.78377 (19)	0.0273 (5)
C3	-0.2164 (6)	0.1158 (2)	0.6252 (2)	0.0304 (6)
H3A	-0.1188	0.0435	0.5797	0.037*
H3B	-0.4004	0.1381	0.5728	0.037*
C4	-0.3422 (6)	0.0515 (3)	0.7242 (2)	0.0402 (6)
H4A	-0.5151	-0.0417	0.6936	0.060*
H4B	-0.4363	0.1245	0.7687	0.060*
H4C	-0.1576	0.0295	0.7750	0.060*
C5	0.9980 (6)	0.6597 (3)	0.92221 (18)	0.0301 (6)
H5A	1.1317	0.5862	0.9389	0.036*
H5B	0.8494	0.6647	0.9798	0.036*
C6	1.2223 (7)	0.8123 (3)	0.9279 (2)	0.0413 (7)
H6A	1.3678	0.8447	1.0045	0.062*
H6B	1.0865	0.8850	0.9153	0.062*

H6C 1.3588 0.8068 0.8675 0.062*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0366 (4)	0.0312 (4)	0.0232 (3)	0.0006 (3)	-0.0001 (2)	0.0045 (2)
O1	0.0307 (9)	0.0285 (9)	0.0258 (9)	-0.0040 (7)	0.0025 (7)	0.0037 (7)
O2	0.0404 (10)	0.0341 (9)	0.0241 (9)	-0.0032 (8)	0.0031 (7)	0.0103 (8)
O3	0.0388 (10)	0.0286 (9)	0.0228 (8)	-0.0064 (8)	-0.0022 (7)	0.0054 (7)
N1	0.0348 (11)	0.0271 (10)	0.0229 (10)	-0.0034 (9)	0.0018 (9)	0.0082 (8)
C1	0.0242 (12)	0.0229 (12)	0.0281 (12)	0.0053 (10)	0.0024 (10)	0.0048 (10)
C2	0.0302 (13)	0.0290 (13)	0.0222 (12)	0.0064 (11)	0.0056 (10)	0.0037 (10)
C3	0.0296 (13)	0.0245 (12)	0.0325 (13)	0.0004 (10)	0.0023 (11)	0.0027 (10)
C4	0.0386 (15)	0.0377 (15)	0.0406 (15)	-0.0014 (12)	0.0064 (12)	0.0121 (12)
C5	0.0317 (13)	0.0327 (13)	0.0202 (12)	0.0004 (11)	-0.0021 (10)	0.0047 (10)
C6	0.0447 (15)	0.0356 (15)	0.0337 (14)	-0.0040 (12)	-0.0033 (12)	0.0055 (11)

Geometric parameters (Å, °)

S1—C1	1.654 (2)	C3—H3B	0.9900
O1—C1	1.319 (3)	C4—H4A	0.9800
O1—C3	1.459 (3)	C4—H4B	0.9800
O2—C2	1.191 (3)	C4—H4C	0.9800
O3—C2	1.338 (3)	C5—C6	1.503 (3)
O3—C5	1.462 (3)	C5—H5A	0.9900
N1—C1	1.366 (3)	C5—H5B	0.9900
N1—C2	1.397 (3)	C6—H6A	0.9800
N1—H1A	0.8800	C6—H6B	0.9800
C3—C4	1.498 (3)	C6—H6C	0.9800
C3—H3A	0.9900		
C1—O1—C3	118.15 (17)	C3—C4—H4B	109.5
C2—O3—C5	115.13 (16)	H4A—C4—H4B	109.5
C1—N1—C2	128.02 (19)	C3—C4—H4C	109.5
C1—N1—H1A	116.0	H4A—C4—H4C	109.5
C2—N1—H1A	116.0	H4B—C4—H4C	109.5
O1—C1—N1	112.26 (19)	O3—C5—C6	106.43 (18)
O1—C1—S1	126.16 (16)	O3—C5—H5A	110.4
N1—C1—S1	121.57 (17)	C6—C5—H5A	110.4
O2—C2—O3	125.7 (2)	O3—C5—H5B	110.4
O2—C2—N1	127.0 (2)	C6—C5—H5B	110.4
O3—C2—N1	107.34 (18)	H5A—C5—H5B	108.6
O1—C3—C4	106.44 (18)	C5—C6—H6A	109.5
O1—C3—H3A	110.4	C5—C6—H6B	109.5
C4—C3—H3A	110.4	H6A—C6—H6B	109.5
O1—C3—H3B	110.4	C5—C6—H6C	109.5
C4—C3—H3B	110.4	H6A—C6—H6C	109.5
H3A—C3—H3B	108.6	H6B—C6—H6C	109.5

C3—C4—H4A	109.5		
C3—O1—C1—N1	-175.56 (18)	C5—O3—C2—N1	-175.86 (18)
C3—O1—C1—S1	4.8 (3)	C1—N1—C2—O2	2.0 (4)
C2—N1—C1—O1	11.6 (3)	C1—N1—C2—O3	-178.5 (2)
C2—N1—C1—S1	-168.77 (18)	C1—O1—C3—C4	-178.52 (19)
C5—O3—C2—O2	3.6 (3)	C2—O3—C5—C6	-177.19 (19)

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>
N1—H1A \cdots S1 ⁱ	0.88	2.54	3.388 (2)	161

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