



CRYSTAL STRUCTURE OF 4-ETHYL-1,3-OXAZOLIDINE-2-THIONE

Hisako Okumura^{[a]*}, Soh-ichi Kitoh^[b], Mitsuhiro Suda^[b], Mitsunori Honda^[b] and Ko-Ki Kunimoto^[b]

Keywords: Crystal structure; Hydrogen-bond; Oxazolidine thione; Thioamide; X-ray diffraction.

The crystal structure of 4-ethyl-1,3-oxazolidine-2-thione, C₅H₉NOS, has been determined from single crystal X-ray diffraction. This compound crystallizes in the monoclinic system, space group *P*2₁/*c* with the unit cell parameters: *a* = 8.4988(17) Å, *b* = 10.2300(15) Å, *c* = 7.5192(19) Å, β = 96.8299(11) ° and four molecules in the unit cell. In the crystals, a pair of enantiomeric (*R*)- and (*S*)-molecules is connected *via* intermolecular N1–H···S1 hydrogen bonds of the neighboring thioamide moieties to form a centrosymmetric dimer with an *R*²₂(8) graph-set motif.

* Corresponding Author

Fax: +81-258-34-9256

E-Mail: okumura@nagaoka-ct.ac.jp

[a] Department of Materials Engineering, National Institute of Technology, Nagaoka College, 888 Nishikata-kai-machi, Nagaoka-shi, Niigata 940-8532, Japan

[b] Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa-shi, Ishikawa 920-1192, Japan

INTRODUCTION

Substituted 1,3-oxazolidin-2-one derivatives and their sulfur analogs, 1,3-oxazolidine-2-thione derivatives represent an important class of 5-membered heterocyclic compounds due to a range of potential applications in pharmacology, biochemistry and organic synthesis.^{1,2}

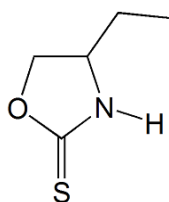


Figure 1. Chemical structure of the title compound.

Furthermore, these derivatives contain an amide or a thioamide group in the oxazolidine ring which may be involved in hydrogen-bonds. They can also act as ligands in coordination complexes. These structural features lead to capability of various hydrogen-bonding patterns and offer wide opportunities in crystal engineering.^{3,4}

We have been studying crystal structures and hydrogen-bonding patterns of several 5-membered heterocyclic compounds containing the amide and/or thioamide group.⁵⁻¹¹ As an extension of our research, the present paper reports the crystal structure and hydrogen-bonding pattern of the title compound, 4-ethyl-1,3-oxazolidine-2-thione, C₅H₉NOS (Figure 1), determined from single crystal X-ray diffraction data analysis.

EXPERIMENTAL

Synthesis and Crystallization

The title compound was prepared by the reaction of hydrogen peroxide with a mixture of *DL*-2-amino-1-butanol, carbon disulfide and base in ethanol according to a reported procedure.¹² Single crystals suitable for X-ray diffraction were obtained from a mixed diethylether and hexane solution.

X-ray Data Collection, Structure Solution and Refinement

X-ray diffraction data was collected at 133(2) K by the ω scan technique on a Rigaku/MSC Mercury CCD diffractometer equipped with graphite monochromated MoK α radiation ($\lambda = 0.71070$ Å) and processed using *CrystalClear*.¹³ The data were corrected for Lorentz-polarization and absorption effects.¹⁴

These structures were solved by direct methods using *SIR2008* program¹⁵ and refined by a full-matrix least-squares calculation on *F*² using *SHELXL-97*.¹⁶ All calculations were performed using *CrystalStructure* software package.¹⁷ Non-hydrogen atoms were refined anisotropically. The hydrogen atom bonded to nitrogen atom was located in a difference map and refined freely. The remaining hydrogen atoms were positioned geometrically (C–H = 0.98–1.00 Å) and refined using a riding model, with $U_{iso}(H) = 1.2 U_{eq}(C)$. Structures were visualized using *ORTEP-3 for windows*¹⁸ and *Mercury*.¹⁹

Crystallographic data for the title compound have been deposited with the Cambridge Crystallographic Data Centre [Deposition No. CCDC-1027326]. The data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.; e-mail: data_request@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Table 1 shows the crystal data, data collection and structure refinement parameters of the title compound. Figure 2 shows the molecular structure and atom-labeling scheme determined from single crystal X-ray diffraction analysis. Table 2 summarizes the selected geometric parameters. Figure 4 shows the crystal packing and hydrogen-bonding pattern.

As given in Table 1, the title compound crystallizes in the monoclinic system, space group $P2_1/c$ with the unit cell parameters: $a = 8.4988(17)$ Å, $b = 10.2300(15)$ Å, $c = 7.5192(19)$ Å, $\beta = 96.8299(11)^\circ$ and four molecules in the unit cell.

Table 1. Crystal data, data collection and structure refinement.

Crystal data	
Empirical formula	C ₅ H ₉ NOS
Formula weight	131.19
Crystal color, Habit	Colorless, Prism
Crystal dimensions	0.15 × 0.15 × 0.08 mm ³
Crystal system, Space group	Monoclinic, $P2_1/c$ (No. 14)
Unit cell dimensions	$a = 8.4988(17)$ Å $b = 10.2300(15)$ Å $c = 7.5192(19)$ Å $\beta = 96.8299(11)^\circ$
Volume, Z	649.1(2) Å ³ , 4
Density (calcd.)	1.342 g cm ⁻³
$F(0,0,0)$	280
Absorption coefficient (MoK α)	0.399 mm ⁻¹
Data collection	
Diffractometer	Rigaku/MSC Mercury CCD
Radiation	MoK α (0.71070 Å)
Temperature	133(2) K
Theta range for data collection	2.41 to 27.47 °
Index ranges	$-11 \leq h \leq 10$ $-13 \leq k \leq 10$ $-9 \leq l \leq 9$
Reflections collected	5774
Independent reflections	1396 [$R_{int} = 0.0184$]
Completeness to theta = 27.47 °	94.3 %
Absorption correction	Multi-scan ¹⁴
Structure solution and refinement	
Structure solution	Direct methods using <i>SIR2008</i> ¹⁵
Refinement method	Full-matrix least-squares on F^2 using <i>SHELXL-97</i> ¹⁶
Data / Restraints / Parameters	1396 / 0 / 78
Final R indices [$I > 2$ sigma(I)]	$R_1 = 0.0277$, $wR_2 = 0.0657$
R indices (all data)	$R_1 = 0.0317$, $wR_2 = 0.0674$
Goodness-of-fit on F^2	1.094
Largest diff. peak and hole	0.240 and -0.200 e Å ⁻³

As shown in Table 2 and Figure 2, the bond lengths and angles are normal, and comparable to those observed in 1,3-oxazolidine-2-thiones reported in the Cambridge Structural Database²⁰ Ver. 5.35. The 1,3-oxazolidine-2-thione moiety (O1/C1/S1/N1/C2/C3) is nearly planar, with maximum deviations of $-0.0595(14)$ Å for C2 atom and $0.0448(14)$ Å for C3 atom.

Table 2. Selected geometric parameters (Å, °).

Bond lengths			
S1–C1	1.671(2)	O1–C1	1.340(2)
O1–C3	1.463(2)	N1–C1	1.318(2)
N1–C2	1.468(2)	C2–C3	1.538(2)
C2–C4	1.520(2)		
Bond angles			
C1–O1–C3	109.14(9)	C1–N1–C2	113.50(10)
S1–C1–O1	120.63(8)	S1–C1–N1	128.20(10)
O1–C1–N1	111.16(11)	N1–C2–C3	99.90(9)
N1–C2–C4	112.05(10)	C3–C2–C4	113.68(10)
O1–C3–C2	105.60(10)		
Torsion angles			
C1–O1–C3–C2	$-6.75(11)$	C3–O1–C1–S1	$-178.63(8)$
C3–O1–C1–N1	2.30(12)	C1–N1–C2–C3	$-7.28(12)$
C1–N1–C2–C4	113.43(10)	C2–N1–C1–S1	$-175.42(9)$
C2–N1–C1–O1	3.57(13)	N1–C2–C3–O1	7.96(10)
N1–C2–C4–C5	68.29(12)	C3–C2–C4–C5	$-179.36(9)$
C4–C2–C3–O1	$-111.56(11)$		

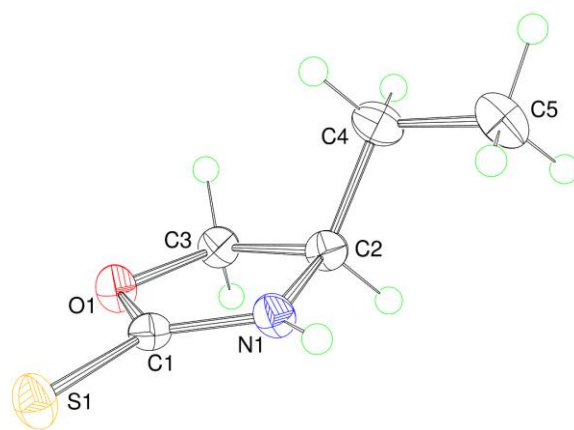


Figure 2. Molecular structure of the title compound. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

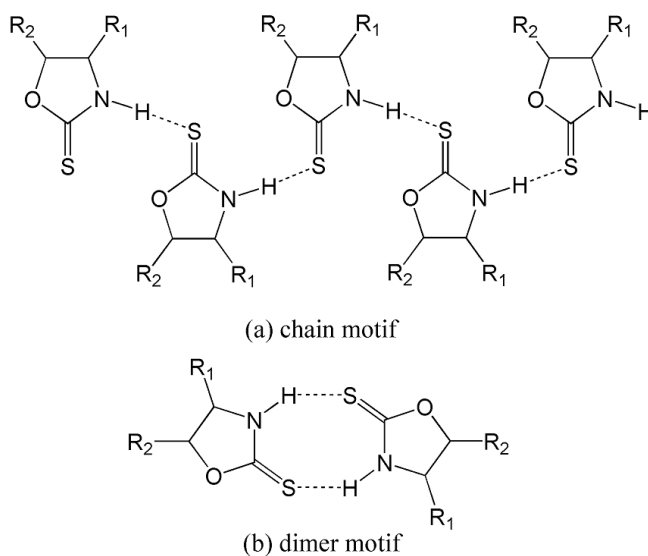


Figure 3. Possible hydrogen-bonding patterns of substituted 1,3-oxazolidine-2-thiones. Hydrogen-bonds are shown as dashed lines.

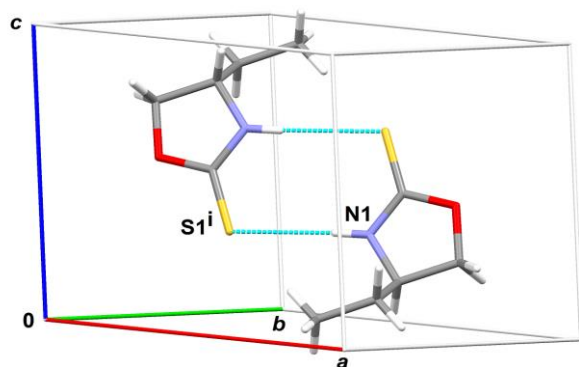


Figure 4. Crystal packing of the title compound. Hydrogen-bonds are shown as dashed cyan lines.

The Cambridge Structural Database survey indicates that substituted 1,3-oxazolidine-2-thiones form mainly two possible hydrogen-bonding patterns of the chain motif or the dimer motif (Figure 3).^{5,6,21,22} In the crystals of the title compound (Figure 4), a pair of enantiomeric (*R*)- and (*S*)-molecules is connected *via* intermolecular N1–H···S1 hydrogen bonds between the neighboring thioamide moieties to form a centrosymmetric dimer with an $R^2_2(8)$ graph-set motif²³ [N1···S1ⁱ 3.3593(14) Å, N1–H···S1ⁱ 177.0(15) °; symmetry code: (i) 1 – x, 1 – y, 1 – z].

Acknowledgement

We thank and acknowledge the technical assistance of Fukui Research Laboratory, Rengo Co., Ltd., 1-8-10 Jiyugaoka Awara-shi, Fukui 919-0604, Japan.

References

- ¹Kaur, D., Sharma, R., *Struct. Chem.*, **2014**, 25, 1111.
- ²Roux, M. V., Temprado, M., Jimenez, P., Foces-Foces, C., Notario, R., Parameswar, A. R., Demchenko, A. V., Chickos, J. S., Deakyn, C. A., Ludden, A. K., Liebman, J. F., *J. Phys. Chem. A*, **2009**, 113, 10772.

- ³Saxena, A., Pike, R. D., *J. Chem. Crystallogr.*, **2007**, 37, 755.
- ⁴Tan, Y. S., Halim, S. N. A., Tiekink, E. R. T., *Z. Kristallogr. NCS*, **2014**, 229, 55.
- ⁵Kitoh, S., Kunimoto, K.-K., Funaki, N., Senda, H., Kuwae, A., Hanai, K., *J. Chem. Crystallogr.*, **2002**, 32, 547.
- ⁶Kitoh, S., Senda, H., Kunimoto, K.-K., *Anal. Sci.: X-ray Struct. Anal. Online*, **2003**, 19, x15.
- ⁷Kunimoto, K.-K., Ichitani, M., Ogawa, T., Kitoh, S., Kuwae, A., Hanai, K., *Spectrosc. Lett.*, **2009**, 42, 73.
- ⁸Ichitani, M., Kitoh, S., Fujinami, S., Suda, M., Honda, M., Kunimoto, K.-K., *Acta Cryst. E*, **2013**, 69, o953.
- ⁹Kitoh, S., Feng, Y., Fujinami, S., Ichitani, M., Honda, M., Kunimoto, K.-K., *Acta Cryst. E*, **2013**, 69, o1699.
- ¹⁰Ichitani, M., Kitoh, S., Tanaka, K., Fujinami, S., Suda, M., Honda, M., Kuwae, A., Hanai, K., Kunimoto, K.-K., *Eur. J. Chem.*, **2013**, 4, 350.
- ¹¹Ichitani, M., Kitoh, S., Tanaka, K., Fujinami, S., Suda, M., Honda, M., Kunimoto, K.-K., *Eur. J. Chem.*, **2014**, 5, 6.
- ¹²Li, G., Ohtani, T., *Heterocycles*, **1997**, 45, 2471.
- ¹³Rigaku, *CrystalClear*, Rigaku Corporation, Tokyo, Japan, **2006**.
- ¹⁴Rigaku, *REQAB*, Rigaku Corporation, Tokyo, Japan, **1998**.
- ¹⁵Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D., Spagna, R., *J. Appl. Cryst.*, **2007**, 40, 609.
- ¹⁶Sheldrick, G. M., *Acta Cryst. A*, **2008**, 64, 112.
- ¹⁷Rigaku, *CrystalStructure*, Rigaku Corporation, Tokyo, Japan, **2010**.
- ¹⁸Farrugia, L. J., *J. Appl. Cryst.*, **2012**, 45, 849.
- ¹⁹Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M., van de Streek, J., *J. Appl. Cryst.*, **2006**, 39, 453.
- ²⁰Allen, F. H., *Acta Cryst. B*, **2002**, 58, 380.
- ²¹Li, L., Zhong, H., *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **1986**, 5, 52.
- ²²Gray, T., Laplaza, C. E., Staples, R. J., *Z. Kristallogr. NCS*, **1999**, 214, 230.
- ²³Etter, M. C., *Acc. Chem. Res.*, **1990**, 23, 120.

Received: 07.10.2014.
Accepted: 31.10.2014.