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

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The crystal structure of 4-ethyl-1,3-oxazolidine-2-thione, C_5H_9NOS, has been determined from single crystal X-ray diffraction. This 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, 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* intermoleculer N1−H···S1 hydrogen bonds of the neighboring thioamide moieties to form a centrosymmetric dimer with an $R^2_2(8)$ graph-set motif.

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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]

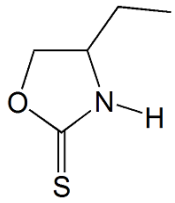

Figure 1. Chemical structure of the title compound.

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, C_5H_9NOS (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 (λ = 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* program[15] 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, β = 96.8299(11) ° and four molecules in the unit cell.

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

Crystal data	
Empirical formula	C_5H_9NOS
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
	β = 96.8299(11) °
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	$-11 \le h \le 10$
	$-13 \le k \le 10$
	$-9 \le l \le 9$
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 *SIR2008*[15]
Refinement method	Full-matrix least-squares on F^2 using *SHELXL-97*[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 A^{-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 Database[20] 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)		

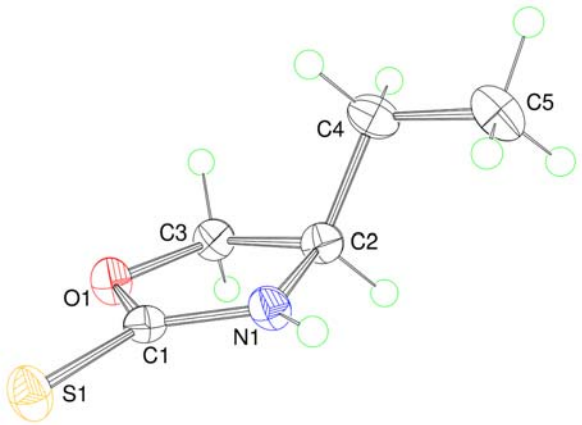

Figure 2. Molecular structure of the title compound. Anisotropic displacement ellipsoids are drawn at the 50% probability level.

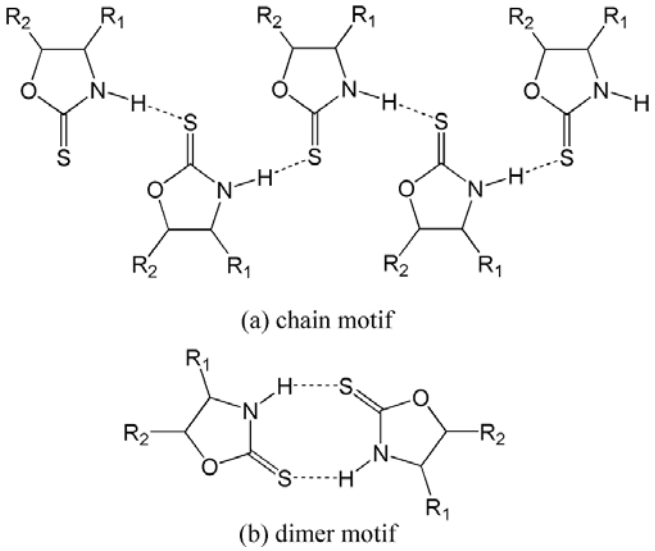

Figure 3. Possible hydrogen-bonding patterns of substituted 1,3-oxazolidine-2-thiones. Hydrogen-bonds are shown as dashed lines.

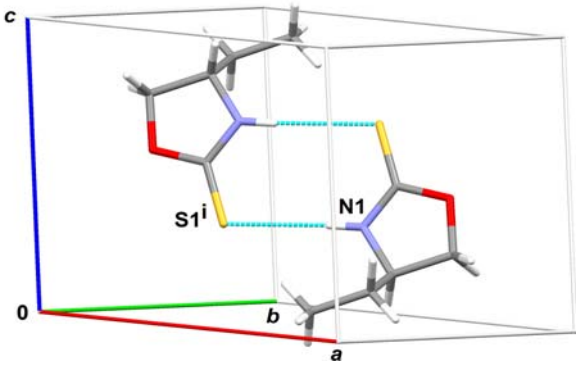

Figure 4. Crystal packing of the title compound. Hydrogen-bonds are shown as dashed cyan lines.

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* intermoleculer N1−H···S1 hydrogen bonds between the neighboring thioamide moieties to form a centrosymmetric dimer with an $R^2_2(8)$ graph-set motif[23] [N1···S1^i 3.3593(14) Å, N1−H···S1^i 177.0(15) °; symmetry code: (i) 1 − x, 1 − y, 1 − z].

Acknowledgement

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