

Structure of 2-Oxo-4-thiazolidinecarboxylic Acid

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Abstract. $C_4H_5NO_3S$, $M_r = 147.15$, orthorhombic, $P2_12_12_1$, $a = 5.968$ (3), $b = 17.945$ (3), $c = 5.387$ (3) Å, $V = 576.9$ (4) Å³, $Z = 4$, $D_x = 1.69$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.63$ cm⁻¹, $F(000) = 304$, $T = 296$ K, $R = 0.034$ for 730 reflections with $I > 2.50\sigma(I)$. Hydrogen bonds $NH\cdots O=C(\text{carboxyl})$ 2.96 and $OH\cdots O=C(\text{carbonyl})$ 2.62 Å afford a sheet structure. A signal 4.4 times that of quartz is observed in an optical second-harmonic test.

Introduction. The methyl ester of the title compound was prepared as an intermediate in the total synthesis of latrunculin A (White & Kawasaki, 1990). The hydrolyzed ester contains a high density of chromophores of interest for optical frequency conversion at short wavelengths and so crystals were grown to determine the structure and efficiency of second-harmonic generation.

Experimental. The compound was obtained by acid hydrolysis of the corresponding methyl ester following a known procedure (Maclaren, 1968). Crystals were grown by slow evaporation of an aqueous solution. A block of dimensions $0.25 \times 0.30 \times 0.25$ mm was mounted on a glass fiber and used for collection of data on a Rigaku AFC6R diffractometer. Unit-cell parameters were refined by least-squares analysis of the angle settings of 16 reflections in the range $30.5 < 2\theta < 36^\circ$. Intensity data were collected with the ω - 2θ -scan technique; the intensities of three standard reflections monitored throughout data collection exhibited an average fluctuation of 1.4%. An absorption correction was not applied. From 822 reflections measured to $(\sin\theta/\lambda)_{\text{max}} = 0.650$ Å⁻¹ over the range of indices $0 < h \leq 7$, $0 \leq k \leq 15$, $0 \leq l \leq 6$, 730 reflections with $I > 2.5\sigma(I)$ were obtained.

All calculations were performed on a MicroVAX II computer with programs from the TEXSAN crystallographic software package (Molecular Structure Corporation, 1989). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic positions were obtained

using the direct-methods program MITHRIL (Gilmore, 1984). H atoms bound to C atoms were placed in calculated positions ($C-H = 0.95$ Å) and assigned isotropic thermal parameters of $1.5 \times B_{\text{eq}}$ of the associated C atom. The remaining H atoms were located in a difference electron density map. Positional parameters and the isotropic thermal parameter were subsequently refined for each of these H atoms. Minimization of the function $\sum w(F_o - F_c)^2$ [where $w = 1/\sigma^2(F_o)$] with those data having $I > 2.5\sigma(I)$ using 90 variables and 730 observations affords the residuals $R = 0.034$, $wR = 0.045$ and the indicator $S = 1.79$. In the final cycle of refinement $\Delta/\sigma = 0.01$. The maximum feature in the final difference electron density map was 0.21 e Å⁻³. The enantiomorphs are indistinguishable from the X-ray data. Fractional atomic coordinates and isotropic temperature coefficients are given in Table 1.*

Discussion. Interatomic distances and angles are listed in Table 2. A drawing of the structure appears in Fig. 1. The chirality of the molecule originates with L-cysteine. Because the preparative method precludes racemization, the chiral center has an (*R*) absolute configuration.

Deviation from planarity of the amide linkage is observed from the torsion angle $S-C4-N1-C2$, -14.7 (3)°. The relative orientation of groups on either side of the linkage may be inferred from the torsion angles $C4-N1-C2-C1$, 158.3 (3)°, and $N1-C2-C1-O1$, 19.6 (4)°. The plane of atoms $N1-C4-O3$ is rotated by 17.6° relative to the plane of atoms $O1-C1-O2$.

Atoms $H4(N1)$ and $H5(O2)$ participate in intermolecular hydrogen bonding as indicated by the distances $N1\cdots O1$, 2.961 (3) Å, and $O2\cdots O3$, 2.622 (3) Å. The hydrogen bonds afford a sheet structure that extends in the *ac* plane (Fig. 2).

* Lists of anisotropic thermal parameters, H-atom positions and thermal parameters, bond lengths and angles involving H atoms, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53744 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and equivalent isotropic temperature factors

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
S	0.8942 (1)	0.05515 (4)	0.3841 (2)	2.98 (3)
O1	1.1319 (4)	0.2096 (1)	1.0774 (4)	3.0 (1)
O2	1.3854 (4)	0.1216 (1)	0.9841 (4)	3.3 (1)
O3	0.5833 (4)	0.1610 (1)	0.3984 (5)	3.8 (1)
N	0.8821 (4)	0.1719 (1)	0.6588 (5)	2.5 (1)
C1	1.2054 (5)	0.1626 (2)	0.9411 (6)	2.4 (1)
C2	1.1100 (5)	0.1453 (1)	0.6880 (5)	2.1 (1)
C3	1.0995 (5)	0.0625 (2)	0.6283 (6)	3.1 (1)
C4	0.7629 (5)	0.1385 (2)	0.4823 (6)	2.5 (1)

Table 2. Intramolecular interatomic distances (Å) and angles (°)

S—C3	1.803 (3)	N1—C2	1.450 (4)
S—C4	1.770 (3)	N1—C4	1.330 (4)
O1—C1	1.201 (4)	C1—C2	1.510 (4)
O2—C1	1.322 (3)	C2—C3	1.521 (4)
O3—C4	1.231 (4)		
C3—S—C4	91.2 (1)	S—C3—C2	104.7 (2)
C2—N1—C4	115.6 (3)	S—C4—O3	123.5 (3)
O1—C1—O2	125.4 (3)	S—C4—N1	110.9 (2)
O1—C1—C2	124.0 (3)	O3—C4—N1	125.5 (3)
O2—C1—C2	110.5 (3)	N1—C2—C3	105.1 (2)
N1—C2—C1	112.6 (3)		

A measurement of the efficiency of second-harmonic generation was made by examining a collection of crystals of maximum dimension 100 μm by the Kurtz method with an Nd:YAG laser. A signal 4.4 times greater than that of the quartz standard was observed. The magnitude of the signal compares with those of the common frequency converter KDP (potassium dihydrogen phosphate), formates (Vizgert, Davydov, Kotovshchikow & Starodubtseva, 1982), and certain derivatives of L-arginine that also contain the carboxyl chromophore and exhibit strong signals (Monaco, Davis, Velsko, Wang & Eimerl, 1987). The relatively strong signal observed probably arises from a constructive intramolecular summation of certain hyperpolarizability coefficients associated with the alignment and near coplanarity of the carboxyl and amide groups as well as their skewed orientations relative to the binary crystallographic axes. Crystallization of the material in point group 222, however, precludes the observation of noncritical phase matching.

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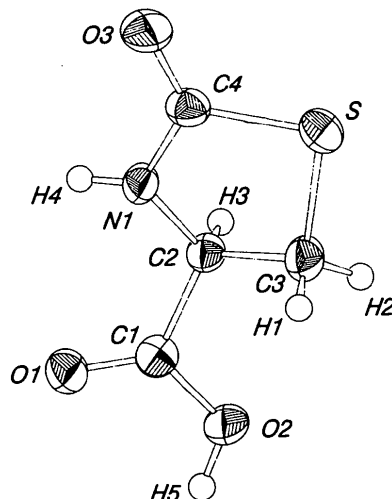


Fig. 1. Drawing of the structure of 2-oxo-4-thiazolidinecarboxylic acid.

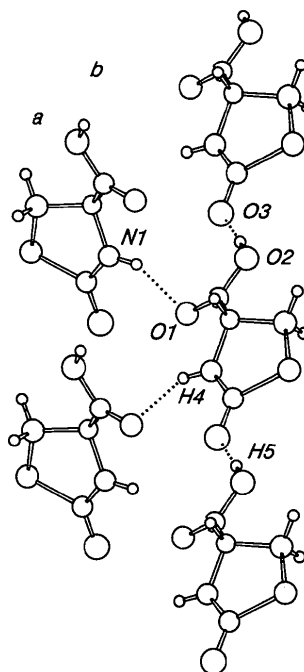


Fig. 2. Packing diagram for 2-oxo-4-thiazolidinecarboxylic acid. Hydrogen bonds are indicated by dashed lines.

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