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## Structure of DL-Lanthionine Monohydrate: Hydrogen-Bonding Patterns in Amino Acid Crystal Structures

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**Abstract.** C<sub>6</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>S.H<sub>2</sub>O, *M<sub>r</sub>* = 226.1, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.645 (2), *b* = 8.099 (1), *c* = 8.441 (1) Å, β = 91.64 (1)°, *V* = 932.4 (4) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.6, *D<sub>x</sub>* = 1.61 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 30.8 cm<sup>-1</sup>, *F*(000) = 512, *T* = 294 K. Final *R* = 0.029 for 1580 reflections >3σ. The S atom is synclinal to the N atom and the two carboxyl groups have slightly different twists about the Cα–C bond. A carboxyl O has a contact with S of 3.238 (1) Å and it approaches Sγ as a nucleophile, nearly in the sulfide plane and at the back of the Cβ(2)–Sγ bond. The hydrogen-bonding patterns of amino acids are compared to the pattern for DL-lanthionine. This structure exhibits two bifurcated hydrogen bonds involving the two amino groups.

**Introduction.** Lanthionine (3,3'-thiodialanine) is a rare, naturally occurring amino acid, the sulfide analog of cystine. We have determined earlier the crystal structure of *meso*-lanthionine dihydrochloride (Rosenfield & Parthasarathy, 1974) and found an interesting intermolecular S...S contact of 3.251 (2) Å that prompted us to carry out our studies on non-bonded atomic contacts with divalent sulfur (Rosenfield, Parthasarathy & Dunitz, 1977; Guru Row & Parthasarathy, 1981). This study forms part of our program on non-bonded atomic contacts with divalent sulfur. In this study, we have crystallized lanthionine in the zwitterionic form and find that this crystal structure contains an interesting intermolecular S...O interaction that follows

the pattern of the direction of approach of nucleophile to sulfide.

**Experimental.** A mixture of DL- and *meso*-lanthionine (Sigma) crystallized from water to yield needle-like crystals and also, on further evaporation, several badly shaped and significantly smaller crystals. One needle-like crystal of dimensions 0.1 × 0.17 × 0.30 mm was chosen for study; needle-like crystals turned out to correspond to DL-lanthionine; density measured using bromoform/benzene; three-dimensional data on a CAD-4 diffractometer to the limit 2θ = 154° for Cu Kα; 4128 reflections collected and averaged to yield a unique set of data of 1967 reflections (*R*<sub>int</sub> = 0.02) with 1580 >3σ; range of *hkl*: -17 to 17, 0 to 10 and -10 to 10; ω/2θ scan widths calculated using expression (0.50 + 0.15 tan θ)°, aperture widths using equation (4.0 + 1.2 tan θ) mm; maximum time spent on any reflection measurement 100s, faster scan used for strong reflections. Unit-cell constants from 25 reflections with 8 < θ < 25°. Intensities of three reflections ( $\bar{4}10$ , 424 and  $\bar{2}23$ ) monitored after every hour of exposure, variation in intensity <2% during data collection; orientation matrix checked every 100 reflections. Lorentz and polarization corrections applied; intensities of three reflections at χ ~ 90° measured for all values of φ from 0 to 360° and resultant curve of transmission as a function of φ used to calculate the anisotropy of absorption for all reflections, average transmission factor 0.95. Structure solved by direct methods using *MULTAN* (Germain Main & Woolfson, 1971). H atoms located from

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electron density difference maps and their positional parameters included in least-squares refinement. Refinement using full-matrix least-squares method with anisotropic thermal factors for non-H atoms and isotropic thermal factors for H atoms led to  $R = 0.029$  for 1590 reflections,  $wR = 0.048$ ,  $S = 1.51$ ; quantity minimized  $\sum w(|F_o| - |F_c|)^2$  where  $w = 4|F_o|^2 / \sigma(|F_o|^2)^2$  and  $\sigma(|F_o|^2) = [\sigma(I)^2 + 0.05I^2]^{1/2} / Lp$  where  $\sigma(I)$  is the standard deviation of intensity  $I$  based on counting statistics and  $k$  is the scale factor;  $(\Delta/\sigma)_{\max} 0.15$ ; final  $\Delta\rho$  excursions  $< 10.3 | e \text{ \AA}^{-3}$ . Programs and atomic scattering factors as in Enraf-Nonius (1979) *SDP*; torsion-angle program by Dr S. T. Rao and *ORTEP* by Johnson (1965).

Table 1. Positional parameters and their e.s.d.'s

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameters defined as:  $\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\gamma B(1,2) + a\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$ .

	x	y	z	$B_{\text{eq}}/B(\text{\AA}^2)$
Sy	0.42874 (2)	0.19258 (4)	0.19922 (4)	1.920 (6)
O(11)	0.36434 (9)	0.7900 (1)	0.1355 (1)	2.70 (2)
O(12)	0.51724 (9)	0.7492 (2)	0.2286 (2)	3.15 (2)
O(21)	0.7311 (1)	-0.0136 (2)	0.4396 (2)	3.60 (3)
O(22)	0.73137 (9)	0.2572 (2)	0.4825 (1)	3.04 (2)
OW	0.82703 (9)	0.1520 (2)	0.0791 (2)	3.12 (2)
N(1)	0.29545 (9)	0.5164 (2)	0.2660 (2)	1.93 (2)
N(2)	0.63601 (9)	0.0236 (2)	0.1505 (1)	1.86 (2)
C(1)	0.4299 (1)	0.7077 (2)	0.2045 (2)	1.87 (3)
Ca(1)	0.4032 (1)	0.5329 (2)	0.2622 (2)	1.69 (2)
Cβ(1)	0.4448 (1)	0.4063 (2)	0.1481 (2)	1.87 (2)
C(2)	0.7053 (1)	0.1303 (2)	0.4095 (2)	2.08 (3)
Ca(2)	0.6305 (1)	0.1578 (2)	0.2718 (2)	1.80 (2)
Cβ(2)	0.5286 (1)	0.1617 (2)	0.3404 (2)	2.15 (3)
H1(OW)	0.870 (2)	0.155 (4)	0.159 (4)	9.1 (9)*
H2(OW)	0.809 (2)	0.250 (4)	0.072 (3)	6.6 (7)*
H1(N1)	0.270 (1)	0.593 (3)	0.324 (2)	3.4 (5)*
H2(N1)	0.266 (1)	0.527 (3)	0.165 (2)	2.7 (4)*
H3(N1)	0.280 (1)	0.422 (3)	0.312 (2)	3.4 (4)*
H1(N2)	0.696 (1)	-0.013 (2)	0.142 (2)	2.2 (4)*
H2(N2)	0.598 (1)	-0.065 (2)	0.177 (2)	2.8 (4)*
H3(N2)	0.617 (1)	0.067 (2)	0.055 (2)	2.1 (4)*
H(Cα1)	0.429 (1)	0.521 (2)	0.374 (2)	1.7 (3)*
H(Cα2)	0.650 (1)	0.261 (3)	0.220 (2)	2.6 (4)*
H1(Cβ1)	0.516 (1)	0.438 (3)	0.140 (2)	3.4 (4)*
H2(Cβ1)	0.412 (1)	0.417 (3)	0.049 (2)	2.7 (4)*
H1(Cβ2)	0.515 (2)	0.047 (3)	0.390 (3)	3.5 (5)*
H2(Cβ2)	0.526 (2)	0.245 (3)	0.413 (2)	3.9 (5)*

Table 2. Covalent bond distances (Å) and angles (°)

	$i = 1$	$i = 2$
C(i)—O(i1)	1.247 (2)	1.242 (2)
C(i)—O(i2)	1.249 (2)	1.245 (2)
C(i)—Ca(i)	1.544 (2)	1.541 (2)
Ca(i)—Cβ(i)	1.527 (2)	1.521 (2)
Cβ(i)—Sy	1.798 (1)	1.802 (1)
Ca(i)—N(i)	1.478 (2)	1.497 (2)
O(i1)—C(i)—O(i2)	126.9 (2)	126.7 (2)
O(i1)—C(i)—Ca(i)	117.7 (2)	117.9 (2)
O(i2)—C(i)—Ca(i)	115.4 (2)	115.4 (2)
C(i)—Ca(i)—Cβ(i)	108.8 (1)	108.0 (2)
Ca(i)—Cβ(i)—Sy	116.5 (1)	115.7 (1)
Cβ(i)—Sy—Cβ(j)*	101.4 (1)	
C(i)—Ca(i)—N(i)	109.5 (1)	111.5 (1)
Cβ(i)—Ca(i)—N(i)	109.9 (1)	109.9 (1)

\*  $i = 1, j = 2$ .

**Discussion.** The final positional parameters for all atoms are given in Table 1 and atom labeling is shown in Fig. 1.\* The distances and angles (Table 2) in both halves of the molecules agree with each other very well ( $< 3\sigma$ ) except the two Cα—N distances that differ by 0.019 Å ( $\sim 10\sigma$ ) and the C'—Ca—N angles that differ by 2° ( $10\sigma$ ). No apparent explanation seems to be available for these differences. The values found in this structure are similar to those reported for *meso*-lanthionine hydrochloride and for other structures of amino acids containing sulfur, if the differences in protonation of the carboxyl group are taken into account. The S atom is  $-$ synclinal to the N atom  $\{\chi^1[\text{Sy}-\text{C}\beta(i)-\text{Ca}(i)-\text{N}(i)] = -63.8 (2)^\circ$  for  $i = 1$  and  $-58.1 (2)^\circ$  for  $i = 2\}$  for the molecule with two L-alanines whereas for *meso*-lanthionine with an L- and D-alanine,  $\chi^1$  values are 54° for the D-half and  $-58^\circ$  for the L-half. Although similar conformations have been found in related structures studied in our laboratory (Rosenfield & Parthasarathy, 1974), it has been found that most commonly Sy is  $+$ synclinal to N and  $-$ synclinal to C (Lakshminarayanan, Sasisekharan & Ramachandran, 1967). The  $\chi^2$  values  $\{\chi^2[\text{C}\beta(i)-\text{Sy}-\text{C}\beta(j)-\text{Ca}(j)] = -81.9 (1)^\circ$  for  $i = 1, j = 2$  and  $-63.8 (2)^\circ$  for  $i = 2, j = 1\}$  for the two halves differ from each other and also from the values found in *meso*-lanthionine ( $\chi^2 = 85^\circ$  for the D-half and  $100^\circ$  for the L-half). The two carboxyls have slightly different twists about Cα—C  $\{\psi[\text{N}(i)-\text{Ca}(i)-\text{C}(i)-\text{O}(i1)] = -17.0 (2)^\circ$  for  $i = 1$  and  $-27.1 (2)^\circ$  for  $i = 2\}$  and differ only slightly as compared to *meso*-lanthionine ( $\psi = 147$  and  $-13^\circ$  for D- and L-halves respectively).

\* Lists of structure factors, anisotropic thermal parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42701 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

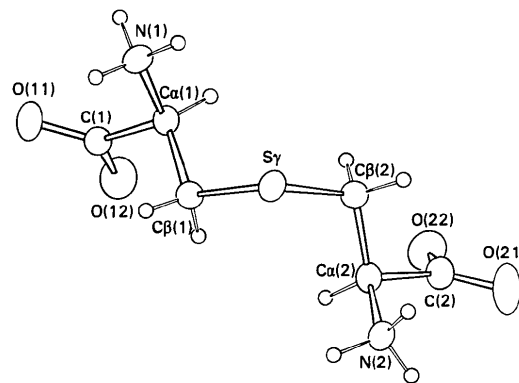


Fig. 1. View of the L-lanthionine molecule in the DL-structure. The coordinates given in Table 1 correspond to the L-molecule.

The hydrogen bonding in this structure is summarized in Table 3. A noteworthy feature is the bifurcated hydrogen interactions for H1(N1) and H1(N2) with H1(N1) involving an intermolecular N—H...S contact. Similar bifurcated hydrogen bonds have been discussed by us earlier (Parthasarathy, 1969; Koetzle, Hamilton & Parthasarathy, 1972; Rosenfield & Parthasarathy, 1974). Sulfur makes an intermolecular contact with O(22) at  $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$  of 3.238 (1) Å. This oxygen approaches S $\gamma$  nearly in the sulfide plane ( $\theta=84^\circ$ ) and along the back of the C $\beta$ (2)—S $\gamma$  bond ( $\varphi=131^\circ$ ), exactly as predicted for the approach of nucleophiles to sulfides (Rosenfield *et al.*, 1977). This structure does not contain any short S...S contacts, as observed in the crystal structure of *meso*-lanthionine dihydrochloride. The packing and hydrogen bonding in this structure are shown in Fig. 2.

#### Hydrogen-bonding patterns in crystal structures of amino acids

Lanthionine belongs to the class of amino acids containing the same number of hydrogen donor groups (amino) as acceptor groups (carboxyl). All of these amino acids (Ala, Gly, Ile, Leu, Met, Phe, Val) exist in the crystal as zwitterions and form very similar hydrogen-bonding patterns, almost identical for both enantiomeric and racemic forms (Benedetti, Pedone & Sirigu, 1973). The similarity in packing may be due to the same chemical nature and the same ratio of acceptor to donor (H) atoms of 2/3. There are two types of hydrogen-bonding systems, *A* and *B*, in the crystals of these zwitterionic amino acids. These systems can be described by a set of numbers that enumerates all of the hydrogen-bonding contacts of the receiver atoms and the hydrogen-bonding contacts of the H atoms that participate in hydrogen bonding. In these amino acids there are two receiving atoms, namely the two carboxyl O atoms, for the three amino H atoms that participate in hydrogen bonding. If all H atoms participate in an equal number of hydrogen bonds, then one of the O atoms must receive two hydrogen bonds — since the total number of donor contacts and receiver contacts must be the same. This leads to type *A* [(2 + 1)/(1 + 1 + 1)] where the numerator sums all the contacts of the receiving atoms and the denominator sums up all the contacts of the participating H atoms. If, on the other hand, the O atoms develop a tendency to receive an equal number of hydrogen contacts, there is an asymmetry in the number of contacts of the H atoms, since there are an odd number of H atoms. This leads to type *B* [(2 + 2)/(2 + 1 + 1)] where each O atom receives two hydrogen-bonding contacts and one H atom participates in a bifurcated hydrogen bond (for a definition of this bifurcated hydrogen bonding, see Parthasarathy, 1969). The situation in which each O atom receives only one hydrogen contact will leave one H atom with no

hydrogen bond {*B*[(1 + 1)/(1 + 1 + 0)]} and is, hence, unfavorable energetically. If a contact cannot be characterized as a hydrogen bond with certainty, then the classification *A* or *B* also becomes uncertain.

In real crystals of amino acids [NH $_3^+$ —CH(R)—COO $^-$ ] mentioned earlier, it is seen from an examination of the literature that type *B* seems to be preferred ( $\alpha$ -glycine: Jönsson & Kwick, 1972;  $\beta$ -glycine: Iitaka, 1960; L-isoleucine: Torii & Iitaka, 1971; DL-isoleucine: Benedetti *et al.*, 1973; L-methionine and L-norleucine: Torii & Iitaka, 1973; L-valine: Torii & Iitaka, 1970) though type *A* [(2 + 1)/(1 + 1 + 1)] also

Table 3. Hydrogen-bonding distances and angles

D—H...A	D—H (Å)	D...A (Å)	H...A (Å)	D—H...A (°)
OW—H1(OW)...O(12 <sup>b</sup> )	0.88 (3)	2.752 (2)	1.94 (4)	152 (3)
OW—H2(OW)...O(21 <sup>ii</sup> )	0.83 (3)	2.825 (2)	1.99 (3)	178 (2)
OW—H3(OW)...O(22 <sup>iii</sup> )	0.86 (2)	2.837 (1)	2.04 (2)	153 (2)*
N(1)—H1(N1)...S <sup>iv</sup>		3.396 (1)	2.83 (2)	124 (2)
N(1)—H2(N1)...O(21 <sup>v</sup> )	0.94 (2)	2.867 (2)	1.95 (2)	166 (2)
N(1)—H3(N1)...O(11 <sup>vi</sup> )	0.88 (2)	2.985 (2)	2.30 (2)	135 (2)†
N(2)—H1(N2)...O(22 <sup>vii</sup> )	0.88 (2)	3.050 (2)	2.37 (2)	135 (2)‡
N(2)—H2(N2)...OW <sup>viii</sup>		2.886 (2)	2.31 (2)	124 (2)
N(2)—H3(N2)...O(12 <sup>ix</sup> )	0.92 (2)	2.839 (2)	1.92 (2)	179 (2)
N(2)—H3(N2)...O(11 <sup>x</sup> )	0.91 (2)	2.847 (1)	2.00 (2)	153 (2)

Symmetry code: (i)  $\frac{1}{2} - x, -\frac{3}{2} + y, -\frac{1}{2} - z$ ; (ii)  $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $-\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ; (v)  $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (vi)  $-\frac{1}{2} - x, -\frac{3}{2} + y, -\frac{1}{2} - z$ ; (vii)  $x, y, z$ ; (viii)  $x, -1 + y, z$ ; (ix)  $1 - x, 1 - y, z$ .

\* Bifurcated hydrogen bond; O(22)...H1(N1)...S $\gamma$ , 81 (2)°; sum of angle around H1(N1), 359°.

† H3(N1) has two additional contacts, to OW of 2.41 (2) Å and to S of 2.92 (2) Å, possibly forming a trifurcated hydrogen bond.

‡ Bifurcated hydrogen interactions; O(22)...H1(N2)...OW, 91 (2)°; sum of angle around H1(N2), 350°.

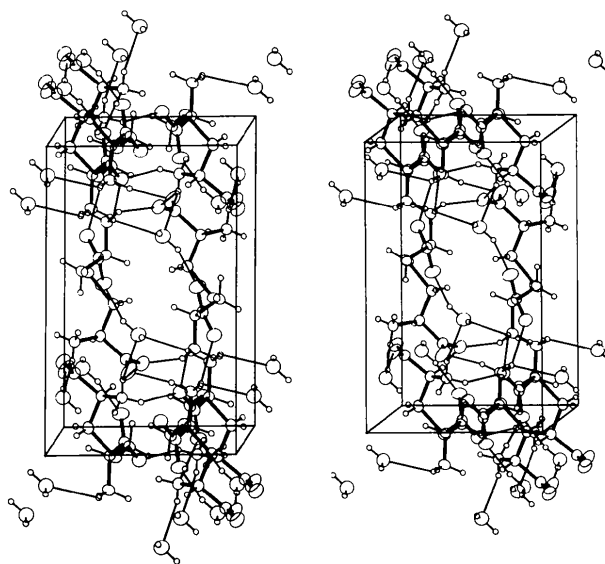


Fig. 2. A stereoview of the packing and hydrogen bonding along *b*.

occurs frequently (L-alanine: Lehmann, Koetzle & Hamilton, 1972; DL-alanine: Donohue, 1950;  $\gamma$ -glycine: Iitaka, 1961; L-leucine: Harding & Howieson, 1976; DL-methionine: Mathieson, 1952; DL-norleucine: Mathieson, 1953; DL-valine: Mallikarjunan & Rao, 1969).

In the present crystal, the hydrogen-bonding pattern is different because the acceptor/donor ratio has been changed from 2/3 to 5/8 by the presence of water in this crystal structure. Each O atom accepts two hydrogen bonds. As there are only eight H atoms (six from two  $\text{NH}_3^+$  groups and two from  $\text{H}_2\text{O}$ ) able to form hydrogen bonding, two of these bonds must be bifurcated. The hydrogen-bonding pattern can be described as  $[(2 + 2 + 2 + 2)/(2 + 2 + 1 + 1 + 1 + 1 + 1)]$ . The bifurcated hydrogen bonds are weaker ( $\text{H}\cdots\text{O}$  distances are 2.3 to 2.4 Å) than others (1.9 to 2.05 Å) and one of them involves the water O atom (Table 3). This hydrogen-bond system can be classified as *B* under the assumption of 'equal' O atoms (type *A* = 'equal' H atoms).

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## Structure of 5-Methoxysalicylaldehyde 4-Phenylthiosemicarbazone–Methanol (1/1)\*

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**Abstract.**  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2\text{S}\cdot\text{CH}_4\text{O}$ ,  $\text{MeOPhSNO}$ ,  $M_r = 333.4$ , monoclinic,  $P2_1/c$ ,  $a = 10.543$  (2),  $b = 9.863$  (4),  $c = 17.977$  (6) Å,  $\beta = 103.38$  (2)°,  $V = 1819$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.22$  Mg m<sup>-3</sup>,  $\text{Mo K}\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.185$  mm<sup>-1</sup>,  $F(000) = 704$ ,  $T = 293$  K, final  $R = 0.089$  for 1696 reflections. The S atom is *trans* to the N atom of the hydrazine group. The angle between the normals to the planes of the phenyl ring and salicylidene group is 72.0 (11)°. There is no strong

interaction between the phenyl ring and the thioureide group. The molecular packing is dominated by a three-dimensional hydrogen-bonding system.

**Introduction.** Semicarbazides, thiosemicarbazides and their derivatives have been used as drugs whose action is attributed to their ability to form metal complexes (Petering & Van Giessen, 1965). Several metal complexes of semicarbazide and thiosemicarbazide have been the subject of chemical and structural studies (Ablov & Gerbeleu, 1965; Ryabova, Ponomarev, Zelentsov & Atovmyan, 1981; Biyushkin, Gerasimov

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