absence of marked intermolecular binding in that direction.

The numerical calculations were carried out on an IBM 7070 computer (Centro de Cálculo Electrónico del C.S.I.C. Spain) with the use of programs of the Crystallography Laboratory of Pittsburg University. We wish to express our thanks to Professor G. A. Jeffrey for allowing us to use these programs. Part of this work forms part of the Ph.D. thesis of one of us (A.P.).

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# The Crystal Structure of DL-Acetylleucine N-Methylamide, C9H18O2N2

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The crystal structure of DL-acetylleucine N-methylamide (ALNMA) has been determined by the symbolic addition procedure. The crystals are monoclinic, space group $P2_1/a$ with four molecules in a cell with the dimensions; $a = 8·46$, $b = 17·33$, $c = 8·24$ Å, and $\beta = 113·5°$. Full-matrix least-squares refinement with anisotropic temperature factors yielded the final $R$ value of 0·15. The main chain of the molecule containing two *trans* planar peptide groups takes a nearly extended conformation, but the chain is puckered at the $\alpha$-carbon atom as in the pleated-sheet $\beta$-structure of protein, the dihedral angle between the two peptide planes being 108·4° and the torsion angles, $\varphi$ and $\psi$ (defined by Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, *J. Mol. Biol.* (1966, **15**, 339), are 86·2° and −41·4° respectively, for the L-molecules. Within the crystal, two kinds of chains of molecules, each consisting of D- and L-molecules, are joined together alternately through N–H···O hydrogen bonds in the b direction to form a sheet structure. The leucyl side chains are nearly perpendicular to the sheet and form a hydrophobic region between adjacent sheets.

## Introduction

In the course of a study on near-infrared spectra of compounds containing two peptide groups, Mizushima, Shimanouchi, Tsuboi, Kuratani, Sugita, Mataga & Souda (1953) suggested that the molecules of acetylleucine N-methylamide (ALNMA) in the crystalline state take an extended form and are associated through double hydrogen bonds (Fig.1). Since this substance can be taken as a simple model compound of the polypeptides, it may be of interest to confirm this suggestion and to determine the accurate molecular conformation. An X-ray analysis of the crystal structure of DL-ALNMA has, therefore, been carried out.

## Experimental

The crystals of ALNMA were grown from ethyl acetate solution. They were colourless plates elongated along the b axis with easy cleavage on (001). The lattice dimensions were measured on precession photographs taken with Cu Kα radiation.

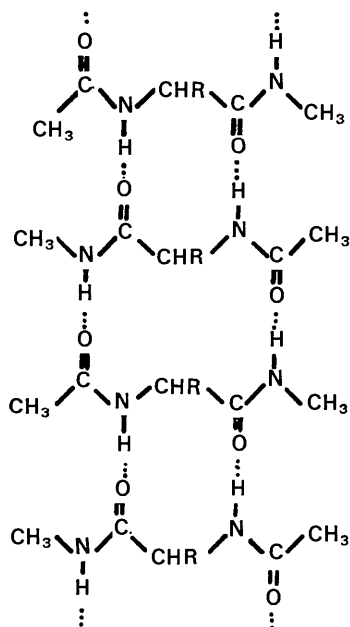Three-dimensional intensity data were collected from equi-inclination Weissenberg photographs, taken with

## Crystal data

DL-Acetylleucine N-methylamide, C9H18O2N2

| Crystal system | Monoclinic |
|---|---|
| $a$ | $8·46 \pm 0·01$ Å |
| $b$ | $17·33 \pm 0·02$ |
| $c$ | $8·24 \pm 0·01$ |
| $\beta$ | $113·5 \pm 0·2°$ |
| $U$ | $1101·8$ Å³ |
| $U$/mole | $275·5$ Å³ |
| Systematic absences | $h0l$ when $h = 2n$ |
| | $0k0$ when $k = 2n$ |
| Space group | $P2_1/a$ |
| $Z$ | 4 |

Cu Kα radiation on multiple-film packs. Intensities were measured visually with a calibrated intensity scale and corrected for Lorentz, polarization and spot-shape (Phillips, 1954) factors. Because of the low linear absorption coefficient [$\mu$(Cu Kα) = 7·46 cm⁻¹] and the small cross-sections of the crystals, no absorption correction was applied. These intensity data were scaled by correlating various layers and the mean temperature factor was calculated by Wilson's (1942) method.

*Intensity data*

b axis   0 and 1st layer
c axis   0 to 6th layer



R = $-$ CH$_2$CH(CH$_3$)$_2$ : leucyl side chain

Fig. 1. Structure of associated molecules of acetylamino acid
N-methylamide proposed on the basis of the infrared study
(after Mizushima, Shimanouchi, Tsuboi, Kuratani, Sugita,
Mataga & Souda, 1953).

Total number of independent observed reflexions,
1249

Total number of possible reflexions within 1·7 reciprocal lattice units, 1500

Mean temperature factor by Wilson's method,
3·79 Å$^2$.

Table 1. *Starting reflexions for the phase calculation*

| h | k | l | $|E|$ | Sign |
|---|---|---|------|------|
| $\bar{2}$ | 17 | 1 | 3·02 | + |
| 2 | 13 | 2 | 2·99 | + |
| $\bar{1}$ | 2 | 2 | 2·13 | + |
| 4 | 13 | 1 | 3·20 | a |
| 3 | 14 | 0 | 2·65 | b |
| $\bar{7}$ | 2 | 4 | 2·99 | c |

### Determination of the structure

The data collection and the preliminary data processing were carried out in 1962, but attempts at a solution of the structure from the Patterson maps were given up after many unsuccessful trials. The structure was finally solved by the symbolic addition method (Karle & Karle, 1966).

An absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's statistical method. The normalized structure factors $E_h$, were computed by the equation

$$E_h^2 = F_h^2/\varepsilon \sum_{j=1}^{N} f_{jh}^2 ,$$

Table 2. *Atomic parameters and their standard deviations*

Temperature factors are of the form:
$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right].$$
Standard deviations are listed in parentheses denoting the least significant digits.

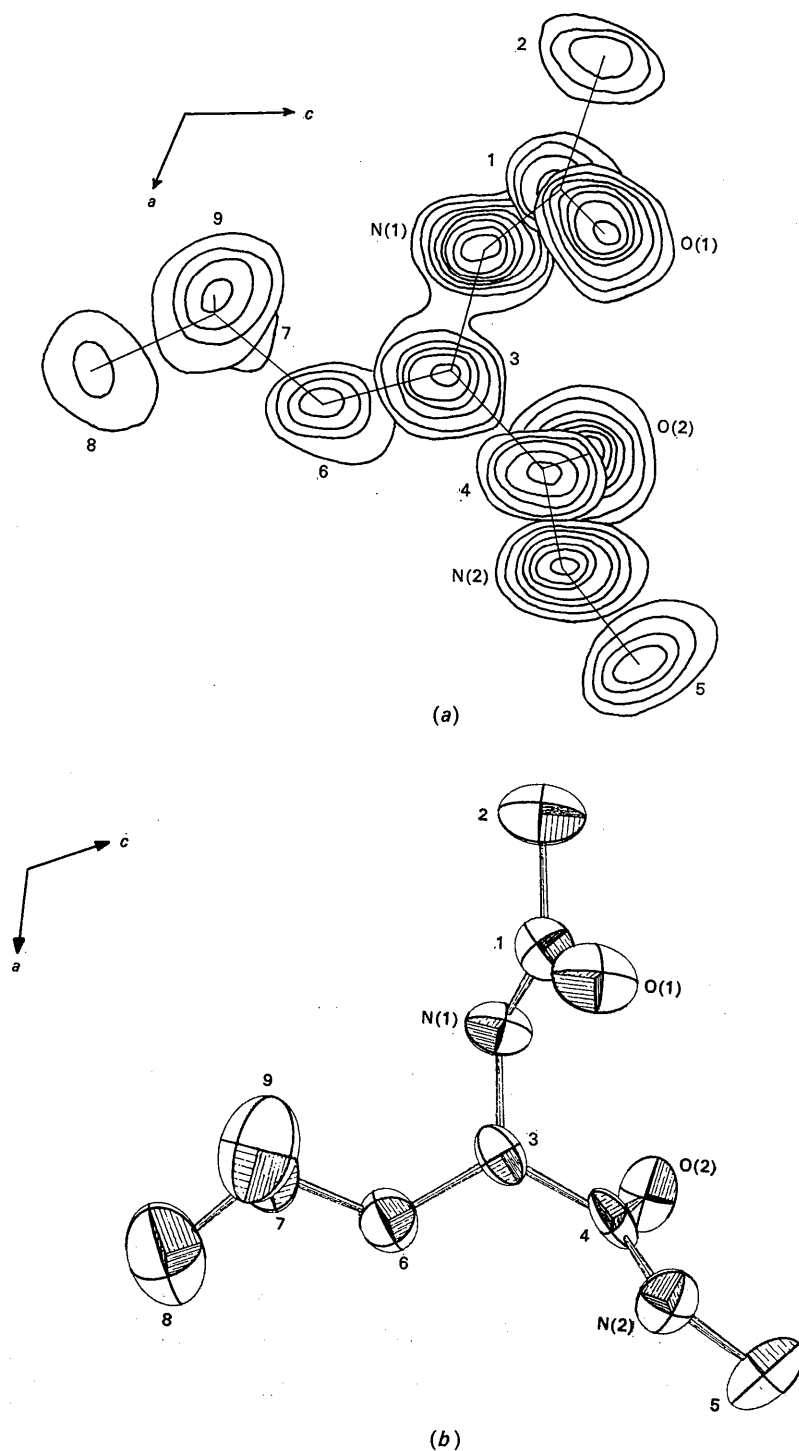| | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | −0·0801 | 0·2815 | 0·1019 | 0·0233 | 0·0026 | 0·0331 | −0·0001 | 0·0149 | 0·0044 |
| | (7) | (3) | (8) | (11) | (2) | (17) | (4) | (11) | (4) |
| O(2) | 0·2351 | 0·4745 | 0·2098 | 0·0220 | 0·0017 | 0·0146 | 0·0016 | 0·0037 | −0·0006 |
| | (6) | (2) | (6) | (10) | (1) | (11) | (3) | (8) | (3) |
| N(1) | −0·0539 | 0·3907 | −0·0288 | 0·0141 | 0·0022 | 0·0202 | 0·0002 | 0·0090 | 0·0008 |
| | (7) | (3) | (8) | (10) | (2) | (15) | (3) | (10) | (4) |
| N(2) | 0·3896 | 0·3649 | 0·2537 | 0·0167 | 0·0027 | 0·0168 | 0·0014 | 0·0043 | −0·0001 |
| | (7) | (3) | (8) | (12) | (2) | (14) | (4) | (10) | (4)) |
| C(1) | −0·1409 | 0·3435 | 0·0265 | 0·0177 | 0·0023 | 0·0163 | −0·0013 | 0·0081 | −0·0012 |
| | (9) | (4) | (10) | (14) | (2) | (16) | (4) | (11) | (5) |
| C(2) | −0·3238 | 0·3714 | 0·0031 | 0·0183 | 0·0038 | 0·0336 | 0·0004 | 0·0129 | −0·0004 |
| | (10) | (5) | (13) | (16) | (3) | (27) | (5) | (17) | (7) |
| C(3) | 0·1190 | 0·3728 | −0·0071 | 0·0180 | 0·0017 | 0·0129 | −0·0001 | 0·0096 | −0·0002 |
| | (8) | (3) | (9) | (13) | (2) | (16) | (4) | (11) | (4) |
| C(4) | 0·2537 | 0·4080 | 0·1638 | 0·0195 | 0·0028 | 0·0122 | 0·0009 | 0·0118 | 0·0019 |
| | (9) | (4) | (9) | (14) | (2) | (15) | (4) | (11) | (4) |
| C(5) | 0·5299 | 0·3956 | 0·4057 | 0·0158 | 0·0045 | 0·0233 | 0·0002 | −0·0018 | −0·0003 |
| | (10) | (5) | (13) | (15) | (3) | (21) | (6) | (13) | (6) |
| C(6) | 0·1593 | 0·4035 | −0·1593 | 0·0186 | 0·0039 | 0·0156 | −0·0016 | 0·0079 | −0·0006 |
| | (10) | (5) | (10) | (15) | (3) | (18) | (5) | (13) | (5) |
| C(7) | 0·0370 | 0·3753 | −0·3421 | 0·0334 | 0·0049 | 0·0193 | −0·0025 | 0·0125 | −0·0006 |
| | (13) | (6) | (12) | (24) | (4) | (23) | (8) | (19) | (7) |
| C(8) | 0·1094 | 0·4056 | −0·4748 | 0·0478 | 0·0130 | 0·0289 | −0·0035 | 0·0190 | 0·0002 |
| | (20) | (12) | (19) | (41) | (11) | (35) | (17) | (31) | (14) |
| C(9) | 0·0067 | 0·2886 | −0·3562 | 0·0437 | 0·0056 | 0·0280 | −0·0028 | 0·0069 | −0·0050 |
| | (17) | (7) | (15) | (34) | (5) | (30) | (10) | (25) | (9) |

Fig. 2. (a) Composite drawing of the final electron density map viewed along the $b$ axis. (b) Perspective drawing of the L-molecule viewed along the $b$ axis. The atoms are represented by ellipsoids of thermal vibration, with 50% probability that the atoms lie within the ellipsoids.

Table 3. *Observed and calculated structure factors*

| H | K | L | |F(OBS)| | F(CAL) |
|---|---|---|---|---|

Table 3 (cont.)

[Table of observed and calculated structure factors; columns of h k l, $F_o$, $F_c$ values]

where $\varepsilon$ is unity for all reflexions other than $h0l$ and $0k0$ for which $\varepsilon = 2\cdot0$. $N$ is the number of atoms in the unit cell and the $F_h$'s are on an absolute scale and corrected for thermal motion. Only those normalized structure factors greater than $1\cdot2$ were used in the phase determination.

A program originally written by Bednowitz (1965) and modified by one of the authors (T.I.) was used to facilitate the determination of signs and the application of the $\Sigma_2$ relationship. The six assignments listed in Table 1 were used to calculate 66 phases with $|E| > 2\cdot0$.

From inspection of the interactions among the signs and symbols, it was decided that the symbols $a$ and $b$ were probably both minus and $c$ was probably plus. When this assignment was made, the signs of 417 reflexions with $E$'s greater than $1\cdot2$ could be determined. An $E$ map was then calculated which revealed the whole structure except the terminal C(8) atom. The location of C(8) was easily determined from the subsequent electron density map. Refinement of the structure

was at first carried out by the block-matrix least-squares method with isotropic thermal parameters and then with anisotropic thermal parameters to an $R$ value of 0·16. Finally, by full-matrix least-squares calculations with anisotropic thermal parameters using the program by Busing, Martin & Levy (1962) the $R$ factor was reduced to 0·15. The weighting system adopted in the latter calculation was,

$$\sqrt{w} = F_o/6\cdot0 \quad \text{when } F_o \leq 6\cdot0,$$
$$\sqrt{w} = 6\cdot0/F_o \quad \text{when } 6\cdot0 < F_o \leq 50\cdot0,$$
$$\sqrt{w} = 300\cdot0/F_o^2 \quad \text{when } 50\cdot0 < F_o.$$

A composite projection of the final electron density map is shown in Fig. 2(a). The final atomic parameters and their standard deviations are listed in Table 2. A list of observed and calculated structure factors is given in Table 3. Throughout the present study, the atomic scattering factors given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry Veenendaal (1955) were used for the carbon, oxygen and nitrogen atoms.

Table 4. *Bond lengths and their estimated standard deviations*

| | DL-ALNMA | | L-Leucine HBr (Subramanian, 1967) | Peptide model (Pauling & Corey, 1953) |
|---|---|---|---|---|
| O(1)–C(1) | 1·246 Å | (0·008) Å | | 1·24 Å |
| O(2)–C(4) | 1·243 | (0·008) | | 1·24 |
| N(1)–C(1) | 1·298 | (0·010) | | 1·32 |
| N(1)–C(3) | 1·435 | (0·009) | | 1·47 |
| N(2)–C(4) | 1·322 | (0·008) | | 1·32 |
| N(2)–C(5) | 1·440 | (0·009) | | 1·47 |
| C(1)–C(2) | 1·558 | (0·012) | | 1·53 |
| C(3)–C(4) | 1·540 | (0·008) | | 1·53 |
| C(3)–C(6) | 1·520 | (0·012) | 1·51 ± 0·04 Å | |
| C(6)–C(7) | 1·527 | (0·011) | 1·51 | |
| C(7)–C(8) | 1·542 | (0·023) | 1·49 | |
| C(7)–C(9) | 1·521 | (0·016) | 1·53 | |

Table 5. *Bond angles and their estimated standard deviations*

| | DL-ALNMA | | L-Leucine HBr (Subramanian, 1967) | Peptide model (Pauling & Corey, 1953) |
|---|---|---|---|---|
| C(1)–N(1)–C(3) | 120·8° | (0·6°) | | 123° |
| C(4)–N(2)–C(5) | 120·6 | (0·7) | | 123 |
| C(2)–C(1)–O(1) | 121·4 | (0·7) | | 121 |
| C(2)–C(1)–N(1) | 115·8 | (0·7) | | 114 |
| O(1)–C(1)–N(1) | 122·7 | (0·7) | | 125 |
| C(4)–C(3)–N(1) | 112·0 | (0·6) | | 110 |
| C(4)–C(3)–C(6) | 106·8 | (0·6) | 113 ± 4° | |
| N(1)–C(3)–C(6) | 112·0 | (0·6) | 108 | |
| C(7)–C(6)–C(3) | 114·5 | (0·7) | 119 | |
| C(8)–C(7)–C(6) | 106·6 | (1·0) | 114 | |
| C(8)–C(7)–C(9) | 112·6 | (1·1) | 112 | |
| C(6)–C(7)–C(9) | 114·7 | (0·9) | 111 | |
| O(2)–C(4)–N(2) | 122·8 | (0·7) | | 125 |
| O(2)–C(4)–C(3) | 120·5 | (0·6) | | 121 |
| N(2)–C(4)–C(3) | 116·7 | (0·6) | | 114 |

Table 6. *Best planes through various groups of atoms*

The equations of the planes are expressed in the form: $AX + BY + CZ = D$, where $X$, $Y$ and $Z$ are the coordinates (measured in Å) referred to the orthogonal axes, $X \| a^*$, $Y \| b$ and $Z \| c$, respectively, and $D$ is the origin-to-plane distance.

| Plane | Atom | Deviation | $A$ | $B$ | $C$ | $D$ |
|---|---|---|---|---|---|---|
| Peptide group | O(1) | 0·004 Å | 0·369 | 0·451 | 0·812 | 2·995 |
| Plane 1 | N(1) | −0·012 | | | | |
| | C(1) | −0·023 | | | | |
| | C(2) | 0·016 | | | | |
| | C(3) | 0·015 | | | | |
| Peptide group | O(2) | 0·004 | −0·462 | −0·379 | 0·802 | −9·501 |
| Plane 2 | N(2) | 0·043 | | | | |
| | C(3) | −0·031 | | | | |
| | C(4) | 0·021 | | | | |
| | C(5) | −0·037 | | | | |
| Aliphatic group | C(3) | 0·036 | 0·561 | −0·817 | −0·132 | 0·059 |
| Plane 3 | C(4) | −0·001 | | | | |
| | C(6) | −0·040 | | | | |
| | C(7) | −0·029 | | | | |
| | C(8) | 0·033 | | | | |

Dihedral angle between:

plane 1 and plane 2 = 108·4°,
plane 1 and plane 3 = 74·6°,
plane 2 and plane 3 = 86·9°.

## Description and discussion of the structure

The bond lengths and angles calculated from the final atomic parameters are shown in Fig. 3; interatomic distances in the molecule less than 3·5 Å are also shown in Fig. 3(*a*). In Tables 4 and 5 are listed the bond lengths and angles together with the standard values for peptide groups (Pauling & Corey, 1953) and the values found in L-leucine hydrobromide (Subramanian, 1967). It is seen that the values obtained in the present determination are in good agreement with the standard values. The average of the six single-bond C–C distances is 1·54 Å which is in agreement with the value 1·54 Å usually assigned to the C–C single bond.

The molecule of ALNMA is composed of three planes which intersect at angles of about 120° to each other at the α-carbon atom when viewed along the *b* axis (Fig. 3). The equations of the least-squares planes of the two peptide groups, and of the aliphatic chain [excluding C(9)] are given in Table 6 together with the deviations of individual atoms from each plane. None of these deviations seems to be so significant.

The conformation of the polypeptide chain is described by defining the two parameters, $\varphi(N–C_\alpha)$ and $\psi(C_\alpha–C')$ which denote the torsion angles around the N–C$_\alpha$ and C$_\alpha$–C' bonds, respectively. The angles $\varphi$ and $\psi$ are defined according to the standard conventions and nomenclature (Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga, 1966). The internal rotation angles (definition of this angle is given in the footnote of Table 7) are calculated for the L-ALNMA molecule and listed in Table 7, from which the values of $\varphi$ and $\psi$ are calculated to be $\varphi(N–C_\alpha) = 86·2°$ and $\psi(C_\alpha–C') = -41·4°$. These values are plotted on the $\varphi–\psi$ chart (Ramakrishnan & Ramachandran, 1965; Leach, Némethy & Scheraga, 1966) and shown in Fig. 4. Standard values of $\varphi$ and $\psi$, found in the poly-

peptide chains in the normal α-helix, fully extended and parallel- and antiparallel-chain pleated-sheets are also plotted on the same Figure.

(*a*)

### Table 7. *Internal rotation angles*

|  | L-ALNMA | L-Leucine HBr (Subramanian, 1967) |
|---|---|---|
| C(2)–C(1)–N(1)–C(3) | 177·2° |  |
| C(1)–N(1)–C(3)–C(4) | −93·8 |  |
| C(1)–N(1)–C(3)–C(6) | 146·3 |  |
| O(1)–C(1)–N(1)–C(3) | 0·8 |  |
| N(1)–C(3)–C(6)–C(7) | −56·6 | −172·2° |
| N(1)–C(3)–C(4)–O(2) | −41·4 | −15·2 |
| N(1)–C(3)–C(4)–N(2) | 140·4 |  |
| C(3)–C(4)–N(2)–C(5) | 174·1 |  |
| C(3)–C(6)–C(7)–C(8) | −174·3 | −175·5 |
| C(3)–C(6)–C(7)–C(9) | −48·9 | 56·6 |
| C(4)–C(3)–C(6)–C(7) | −179·5 | 71·9 |
| O(2)–C(4)–N(2)–C(5) | −4·0 |  |
| O(2)–C(4)–C(3)–C(6) | 81·4 | 102·7 |
| N(2)–C(4)–C(3)–C(6) | −96·7 |  |

The internal rotation angle $\tau$ of *A–B–C–D* in this Table is defined as the angle between projection of *A–B* and that of *C–D*, when the projection is taken along the *B–C* bond. The positive $\tau$ is taken in the same sense as that of the turning direction of a right handed screw advancing along the *B–C* bond.
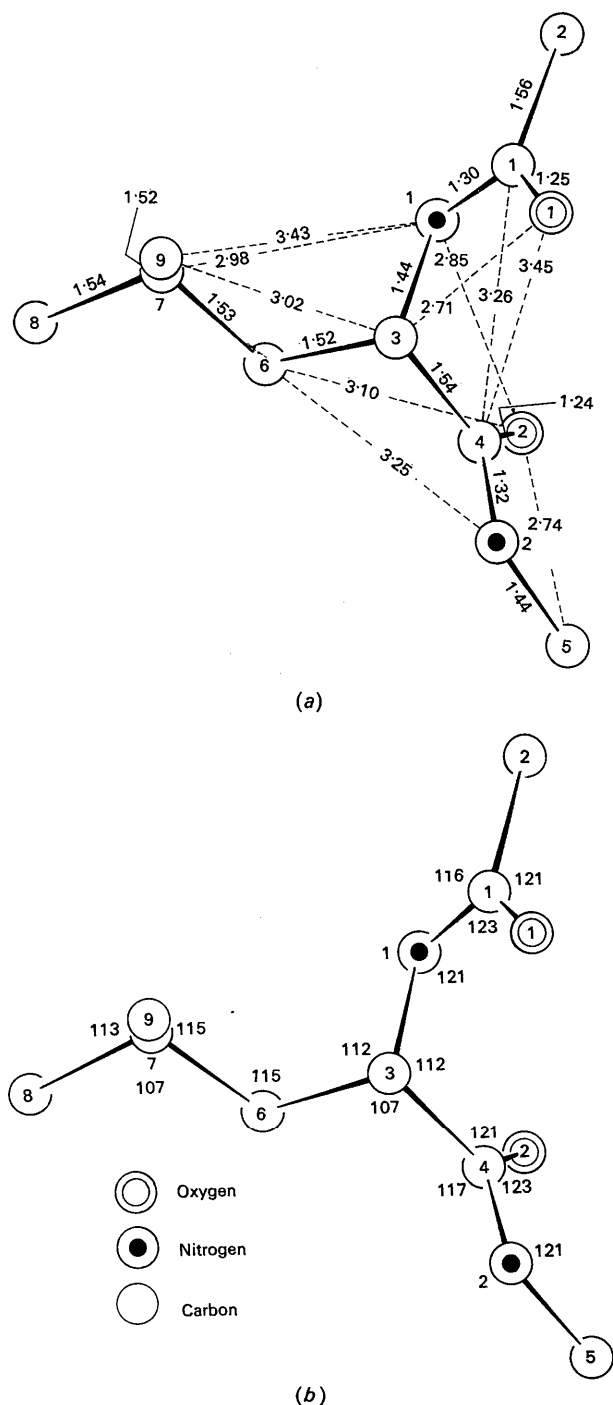
(*b*)

Fig. 3. The molecular structure of ALNMA viewed along the *b* axis. (*a*) Bond lengths (Å). Intramolecular short distances less than 3·5 Å are also shown in the Figure. (*b*) Bond angles (°).

The solid lines enclose the regions outside which unacceptable van der Waals contacts occur. It is seen that the conformation of the L-ALNMA molecule found in the present crystal lies just between those of the parallel and antiparallel-chain pleated-sheet structures.

Of interest is the comparison of the conformation of the leucyl side chains in L-leucine hydrobromide and ALNMA. As shown in Table 7, a great difference in the internal rotation angles, C(4)–C(3)–C(6)–C(7), is found among the two compounds. The $\gamma$-carbon atom in L-leucine hydrobromide is situated in the *trans* position to the amino nitrogen atom, while in ALNMA, it is *gauche* to the amide nitrogen atom or *trans* to the carbonyl carbon atom. Although the energy difference between the two $\gamma$-carbon positions is considered to be small (Lakshminarayanan, Sasisekharan & Ramachandran, 1967; Ichikawa & Iitaka, 1968), it is not easy to understand where this difference in conformation originates. The terminal methyl group of C(9) in ALNMA is in the *cis* position with respect to the C(3)–H bond. A similar conformation is also found in L-leucine hydrobromide.

Fig.5($a$) shows the projection of the structure along the $c$ axis. The molecules related to the molecule whose coordinates are listed in Table 2 by the symmetry

operations $(1+x,y,z)$, $(\frac{1}{2}+x,\frac{1}{2}-y,z)$ and $(1-x,1-y, 1-z)$, are designated I, II and III respectively. The distances and angles involving hydrogen bonds are listed in Table 8. The values are close to those found in glycylphenylalanylglycine (Marsh & Glusker, 1961) and in other peptides. Each molecule of ALNMA is fixed by four hydrogen bonds. An L-molecule, for example, is bound to the two D-molecules, related to the first by a glide plane, through two hydrogen bonds of length 2·89 Å. The other two hydrogen bonds (2·86 Å) connect the L- and D-molecules across the centre of symmetry. The molecules are arranged head-to-tail along the $a$ axis to form a chain. There are four stacks of the two kinds of such chains in the unit cell, each consisting of D- and L-molecules, and they are joined together in the **b** direction, through the hydrogen bonds, to form a sheet of molecules.

It is interesting that a hydrogen-bond system similar to that found in the antiparallel-chain pleated sheet is observed in the present structure between the molecular stacks, across the centres of symmetry, while that similar to the system found in parallel-chain pleated sheet is observed between those stacks related by the $a$-glide planes. However, since the stacking of the molecular chains in the present crystal is such that the D and L molecules stack together alternately, the leucyl side chains in the neighbouring molecular chains ought to lie either in the same direction, for the parallel-chain arrangement, or in the opposite direction, for the antiparallel-chain arrangement. Strong repulsions among the leucyl side chains would exist if the D- and L-molecules were arranged in a parallel-chain fashion. In the present structure, however, such repulsions are much relieved by sliding one kind of molecular chain along the $a$ axis through a distance of $a/2$ relative to the other. It has been suggested that in the $\beta$-structure of protein, where only L-residues are involved, repulsions amongst the side chains in adjacent peptide chains might cause the peptide chains to fold, resulting in the pleated-sheet structure. These kinds of repulsions are not observed in the present structure. Nevertheless, the peptide chains are creased, and as a result, the leucyl side chains lie nearly perpendicular to the molecular sheet. The dihedral angles at the $\alpha$-carbon atom between the two peptide planes is 108·4° which is close to the proposed value of 117·8° for the parallel-chain pleated sheet (Pauling & Corey, 1953). A reason for the puckering of the peptide chain at the $\alpha$-carbon atom may, therefore, be the interactions between the atoms of the main chain and the $\beta$-carbon atom (Scott & Scheraga, 1966).



Fig.4. $\varphi-\psi$ chart showing the allowed conformations for dipeptides with two $C_\delta$ atoms in the side chain as in Gly-L-Leu (after Leach, Némethy & Scheraga, 1966). The $\varphi$ and $\psi$ values for FA (flat-sheet structure), PCP (parallel-chain pleated sheet structure) and APA (antiparallel-chain pleated sheet structure) are plotted on the chart for comparison.

Table 8. *Hydrogen bond distances and angles*

| N···O distances | | Angles at N | |
|---|---|---|---|
| N(1)–H···O(2) | $2·864 \pm 0·006$ Å | C(1)–N(1)···O(2) | $115·9 \pm 0·6°$ |
| | | C(3)–N(1)···O(2) | $123·3 \pm 0·6$ |
| N(2)–H···O(1) | $2·885 \pm 0·008$ | C(4)–N(2)···O(1) | $117·5 \pm 0·7$ |
| | | C(5)–N(2)···O(1) | $121·2 \pm 0·7$ |

The projection of the structure along the $b$ axis is shown in Fig.5($b$). It is seen that the sheets of molecules are arranged nearly parallel to the (001) plane, and the leucyl side chains extend from the sheets to form hydrophobic regions between them. The N-terminal methyl groups also project into the same region. Close intermolecular contacts between the atoms are shown in Figs.4 and 5.

The magnitudes and angles which define the principal axes of the ellipsoids of atomic thermal vibrations are given in Table 9 where the $\alpha_{ij}$'s are the angles between the $j$th principal axis and the axes of the unit cell. In Fig.3 a perspective drawing of the molecule viewed along the $b$ axis is shown, in which the atoms are represented by ellipsoids of thermal vibration. This was drawn on a Calcomp Plotter using the *ORTEP* program of Johnson (1965). The directions of the principal axes of the thermal ellipsoids nearly coincide with those expected on the basis of the geometry of the molecule and the intermolecular packing. Thus most of the largest components of vibration for the atoms in the peptide groups are directed nearly perpendicular-

ly to the planes of the peptide groups, or to the direction of the hydrogen bonds. Those of the atoms in the leucyl side chain are nearly perpendicular to the chain or parallel to the molecular sheets.

Table 9. *Magnitudes and direction cosines of the vibration ellipsoids*

| | | (r.m.s.)ⱼ (Å) | cos α₁ⱼ | cos α₂ⱼ | cos α₃ⱼ |
|---|---|---|---|---|---|
| O(1) | 1 | 0·144 | −0·351 | −0·860 | 0·368 |
| | 2 | 0·256 | −0·936 | 0·331 | −0·119 |
| | 3 | 0·328 | −0·019 | −0·386 | −0·921 |
| O(2) | 1 | 0·148 | 0·219 | −0·967 | −0·126 |
| | 2 | 0·203 | −0·202 | 0·081 | −0·975 |
| | 3 | 0·286 | −0·954 | −0·239 | 0·177 |
| N(1) | 1 | 0·177 | −0·375 | −0·894 | 0·241 |
| | 2 | 0·192 | −0·914 | 0·399 | 0·058 |
| | 3 | 0·244 | −0·148 | −0·198 | −0·968 |
| N(2) | 1 | 0·188 | −0·487 | 0·844 | −0·221 |
| | 2 | 0·215 | 0·231 | 0·369 | 0·899 |
| | 3 | 0·256 | 0·842 | 0·387 | −0·375 |
| C(2) | 1 | 0·173 | 0·182 | 0·913 | 0·364 |
| | 2 | 0·243 | −0·354 | −0·932 | −0·072 |
| | 3 | 0·312 | 0·013 | 0·072 | −0·997 |
| | 1 | 0·159 | −0·435 | 0·671 | 0·599 |





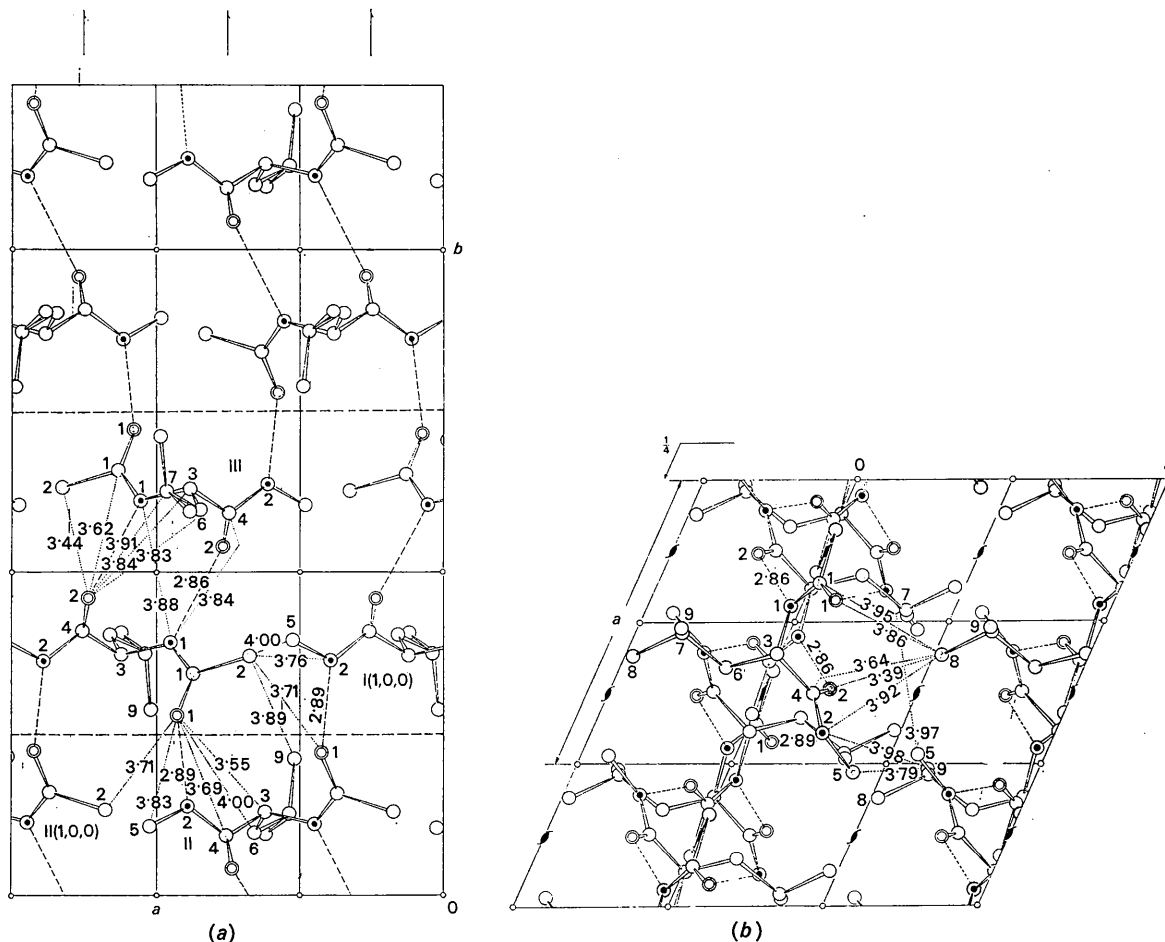(a)                                    (b)

Fig. 5. The crystal structure of ALNMA in projection along (a) the $c$-axis, (b) the $b$-axis. Hydrogen bonds are indicated by broken lines and intermolecular short contacts less than or equal to 4·0 Å, by dotted lines. Oxygen atoms are indicated by double circles, nitrogen by circles enclosing a black circle and carbon by single circles.

## Table 9 *(cont.)*

| | | (r.m.s.) (Å) | $\cos\alpha_{1j}$ | $\cos\alpha_{2j}$ | $\cos\alpha_{3j}$ |
|---|---|---|---|---|---|
| C(3) | 2 | 0·163 | 0·424 | 0·740 | −0·520 |
|      | 3 | 0·238 | 0·793 | −0·027 | 0·607 |
|      | 1 | 0·116 | −0·562 | −0·309 | 0·766 |
| C(4) | 2 | 0·205 | −0·478 | 0·878 | 0·004 |
|      | 3 | 0·257 | 0·674 | 0·364 | 0·642 |
|      | 1 | 0·189 | −0·667 | 0·000 | −0·744 |
| C(5) | 2 | 0·260 | 0·052 | −0·997 | −0·046 |
|      | 3 | 0·327 | 0·742 | 0·070 | −0·666 |
|      | 1 | 0·204 | −0·544 | −0·148 | 0·825 |
| C(6) | 2 | 0·217 | 0·585 | 0·637 | 0·500 |
|      | 3 | 0·263 | −0·600 | 0·755 | −0·259 |
|      | 1 | 0·223 | 0·356 | 0·097 | −0·929 |
| C(7) | 2 | 0·257 | −0·375 | −0·895 | −0·238 |
|      | 3 | 0·332 | 0·855 | −0·433 | 0·282 |
|      | 1 | 0·268 | 0·402 | 0·091 | −0·910 |
| C(8) | 2 | 0·369 | −0·842 | −0·351 | −0·407 |
|      | 3 | 0·455 | 0·357 | −0·931 | 0·064 |
|      | 1 | 0·219 | 0·126 | 0·673 | 0·727 |
| C(9) | 2 | 0·340 | −0·104 | 0·738 | −0·665 |
|      | 3 | 0·395 | 0·986 | −0·008 | −0·164 |

The root-mean-square displacement (r.m.s.)$_j$ is directed along the *j*th axes of the ellipsoid where $\alpha_{1j}$, $\alpha_{2j}$ and $\alpha_{3j}$ are the angles between the *j*th axis and the *a*, *b* and *c*\* axes, respectively.

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# The Crystal and Molecular Structure of Bis(hydrogen *o*-phthalato)diaquocopper(II)

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Bis(hydrogen *o*-phthalato)diaquocopper(II), $Cu(C_8H_5O_4)_2(H_2O)_2$, is monoclinic, $P2_1/c$: $a=8\cdot31$ (2), $b=14\cdot62$ (2), $c=7\cdot20$ (2) Å, $\beta=112\cdot2$ (0·2)°, $Z=2$. The crystal structure has been determined at room temperature from three-dimensional X-ray photographic data and refined by differential methods with anisotropic thermal parameters to a final $R$ value of 7·9%. Two oxygen atoms from two carboxyl groups of two different phthalate ions and two $H_2O$ molecules coordinate with copper in a centrosymmetrical planar arrangement [Cu–O(1)=1·930 (8), Cu–O(5)=1·967 (8) Å]. Two further oxygen atoms, from the same Cu-coordinated carboxyl groups, are involved in two weaker interactions with the metal atom [Cu–O(2)=2·677 (5) Å], so the coordination polyhedron can be considered also as an elongated and distorted octahedron. The two carboxyl groups are slightly rotated with respect to the benzene ring, in opposite directions from each other and their relative position is determined by a strong intramolecular hydrogen bond, O(2)H···O(3)=2·42 Å. Packing is mainly determined by two hydrogen bonds formed by the water molecule with the oxygen atoms from the carboxyl groups of two adjacent molecules: O(5)H···O(3ᶦ)=2·81, O(5)H···O(4ᶦᶦ)=2·67 Å.

## Introduction

Bis(hydrogen *o*-phthalato)diaquocopper(II), $[Cu(C_8H_5O_4)_2(H_2O)_2]$, crystallizes from acid aqueous solutions in beautiful monoclinic crystals (Cingi & Magnano, 1959), suitable for single-crystal X-ray analysis. The study of their structure was considered to be interesting because it