

Table 3. *Densities and crystal structure data for the M_2Y_2X compounds.*

	a (Å)	c (Å)	Density, g.cm ⁻³		u_1	u_2
			Calc	Pycn		
$Th_2(N,O)_2As$	4.041 ± 0.001	6.979 ± 0.002	9.58	9.3	0.293 ± 0.005	0.635
Th_2N_2Se	4.0287 ± 0.0002	7.156 ± 0.001	9.43	7.9	0.293	0.628
$Th_2(N,O)_2P$	4.0285 ± 0.0003	6.835 ± 0.001	9.08	8.5	0.278	0.630
Th_2N_2S	4.008 ± 0.001	6.920 ± 0.002	9.04	8.1	0.278	0.626
U_2N_2As	3.833 ± 0.001	6.737 ± 0.001	11.22	—	0.293	0.630
Se	3.8622 ± 0.0005	6.856 ± 0.001	10.94	9.0	0.293	0.628
P	3.802 ± 0.001	6.552 ± 0.002	10.84	8.7	0.278	0.626
S	3.828 ± 0.001	6.587 ± 0.002	10.65	9.83	0.278	0.627

	M-4Y	M-3X
$Th_2(N,O)_2As$	2.39 ± 0.02 Å	3.10 ± 0.03 Å
Th_2N_2Se	2.39	3.13
$Th_2(N,O)_2P$	2.41	3.00
Th_2N_2S	2.41	3.01
U_2N_2As	2.27	2.97
Se	2.29	3.00
P	2.29	2.85
S	2.28	2.87

able to adjust the u_2 value such that the Y atom is placed equidistantly from the four nearest M atoms.

Table 3 gives the parameter values and the bond lengths M-4Y and M-3X for the various compounds. As reported in the paper describing the Ce_2O_2S structure (Zachariasen, 1949), the M-4Y distances are shorter, and the M-3X distances longer, than would be anticipated from the atomic radii. This apparent anomaly can be attributed to the fact that the M-Y and M-X bonds do not have the same strength (Pauling, 1929; Zachariasen, 1963). Thus, in Ce_2O_2S

the bond strengths are 0.50 for the Ce-O and 0.33 for the Ce-S bonds.

Chemical analyses were done by R. D. Gardner in the Analytical Group of the Los Alamos Scientific Laboratory.

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Crystal Structure of DL-Valine*

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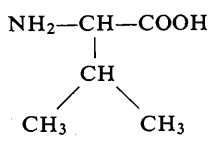
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The crystal structure of DL-valine has been determined by the use of the symbolic addition phase determination method of Karle & Karle. DL-valine crystallizes in the space group $P2_1/c$ with cell dimensions $a = 5.21 \pm 0.02$; $b = 22.10 \pm 0.04$; $c = 5.41 \pm 0.02$ Å and $\beta = 109.2^\circ$ with $Z = 4$. The molecules are held together by a series of hydrogen bonds in a three-dimensional network. The conformation of the valine molecule is found to be similar to that found in the hydrohalide derivatives of valine. A comparative account of the molecular features of the valine molecule as found here and in the other structures is briefly given at the end.

Introduction

Valine is an essential amino acid whose chemical formula is



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The crystal structures of L-valine hydrochloride monohydrate (Rao, 1967) and L-valine hydrochloride (Parthasarathy, 1966; Ando, Ashida, Sasada & Kakudo, 1967) have been recently determined. In these two structures the conformation of the valine molecule is similar except for the orientation of the methyl pair at the terminal end of the valine residue. Three different orientations are possible for the methyl pair and two of these have been found to occur, one in each of the above two structures. Recent conformational studies on poly-L-valine have indicated (C. M. Venkatachalam,

unpublished) that the polymer can exist in the α -helical form only when the methyl pair occupies the third possible orientation, which has not so far been observed in crystal structure determinations.

Interest was naturally aroused for finding out whether this third possible orientation of the methyl pair occurs in other crystal modifications of valine. For this purpose, this investigation of the crystal structure of DL-valine was undertaken. Preliminary crystal data on two crystal modifications of DL-valine are already available (Albrecht, Schnakenberg, Dunn & McCullough, 1943; Dawson & Mathieson, 1951) but no crystal structure determination has been reported as yet.

Experimental

Suitable crystals of DL-valine could be picked from commercially available samples of the compound. A suitable single crystal, approximately cubical with edge length equal to 0.15 mm, was used for the entire data collection. The cell dimensions were determined from rotation, Weissenberg and precession photographs taken with Cu $K\alpha$ radiation. The cell dimensions are given in Table 1 along with the data on DL-valine available in the literature.

The density measured by flotation in mixed solvents is 1.22 g.cm⁻³ while the density calculated on the basis of four molecules in the unit cell is 1.24 g.cm⁻³.

The intensity data were collected with Cu $K\alpha$ radiation using the Weissenberg equi-inclination method about the c and a axes (Layers: $L=0, 1, 2, 3$; and $H=0, 1, 2$). 861 independent non-zero reflexions were used in the investigation. The intensities were estimated visually with the use of calibrated film strip. They were corrected for Lorentz and polarization factors but no absorption correction was applied as it was not considered necessary because of the small size of the crystal. A correction for the elongation of spots on the higher layers was made according to Phillips (1962). The two sets of data (about the c and a axes) were correlated by the method of Rollett & Sparks (1960).

Determination of signs of structure factors

The intensity data were processed for the determination of the signs of structure factors according to the

symbolic addition method (Karle & Karle, 1963). The observed distribution of $|E|$ values and the expected theoretical values are shown in Table 2.

Table 2. Distribution of observed E -values

	Observed %	Theoretical % Centro- symmetric
$ E \geq 3$	nil	0.3
$ E \geq 2$	3.8	5.0
$ E \geq 1$	26.2	32.0

From the data about the c axis, a total of 146 reflexions with $|E| \geq 1.4$ were sorted out in decreasing order of $|E|$ values, and were divided into two groups, (a) those with $|E| \geq 1.5$ (number of reflexions = 113) and (b) those with $1.4 \leq |E| < 1.5$ (number of reflexions = 33). A computer search for the Σ_2 relations, among themselves, of the reflexions contained in the first group was made. In addition the computer program searched for Σ_2 relations between reflexions in the second group with those in the first group. This was to facilitate the extension of signs to reflexions comprising the second group. A total of 670 Σ_2 relations were found. Three origin specifying and two symbolic phases were assigned as follows:

h	k	l	$ E $	Sign	No. of Σ_2 relations for the reflexion
5	17	0	2.65	+	18
0	16	3	2.43	+	16
4	3	0	1.96	+	29
5	2	1	2.33	A	13
5	13	3	2.82	B	11

It was found possible to determine the phases of 95 out of the 113 reflexions belonging to the first group as \pm , $\pm A$, $\pm B$, or $\pm AB$. The process of sign determination was then carried over to reflexions of the second group and an additional five reflexions were allotted signs. The signs of 100 reflexions out of a total of 120 reflexions (lowest $|E|=1.48$) were thus determined.

Structure

There were very strong indications that B is positive and that A is also positive. This could be seen from

Table 1. Crystal data on DL-valine

	Present investigation	Albrecht <i>et al.</i>	Dawson & Mathieson
Crystal System	Monoclinic	Monoclinic	Triclinic
Cell dimensions: a	$5.21 \pm 0.02 \text{ \AA}$	5.20 \AA	5.25 \AA
b	22.10 ± 0.04	22.12	11.05
c	5.41 ± 0.02	5.41	5.43
α	90°	90°	91°
β	109.2	$70^\circ 58'$	109.4
γ	90	90	92.4
Space group	$P2_1/c$	$P2_1$	$P1$ or $P\bar{1}$
Number of molecules in the unit cell Z	4	4	2

the table listing the total number of Σ_2 failures considering all the reflexions to which signs had been allotted.

<i>A</i>	<i>B</i>	No. of Σ_2 failures
+	+	12
+	-	54
-	+	30
-	-	60

However, three-dimensional *E* maps were computed for all the four combinations. On examining the four *E* maps, it was found that the one corresponding to the least number of Σ_2 failures, viz. (*A* = +, *B* = +) did indeed contain the structure. The *E* map from which the structure was obtained is shown in Fig. 1. The coordinates of all the eight non-hydrogen atoms were obtained from this map and are listed in Table 3. Seven of the eight peaks corresponding to the atomic sites were well above the average level of spurious peaks. The peak corresponding to atom C(1) was just at this level. The other three *E* maps did not have any meaningful distribution of peaks.

Table 3. Atomic coordinates from three-dimensional *E*-map

	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.300	0.450	0.725
O(2)	-0.150	0.433	0.400
N	0.300	0.450	0.236
C(1)	-0.250	0.333	0.075
C(2)	0.100	0.350	0.250
C(3)	0.250	0.317	0.350
C(4)	0.050	0.425	0.250
C(5)	0.050	0.434	0.575

At this stage a structure factor calculation for the *hk0* reflexions employing an overall $B=2 \text{ \AA}^2$ gave $R=0.430$. It may be said here, that in terms of the final refined structure, it was found that only one reflexion (441; $|E|=1.76$) had been allotted a wrong sign.

Four cycles of full-matrix least-squares refinement of the positional and isotropic vibration parameters of the eight non-hydrogen atoms employing the program of Gantzel, Sparks & Trueblood (1961) reduced the *R* value from 0.405 to 0.148. A three-dimensional difference electron density distribution was then computed, with a view to locating the hydrogen atoms.

Hydrogen atom positions were calculated from geometrical considerations with (i) bond length C-H = 1.0 Å and N-H = 1.0 Å (ii) tetrahedral disposition at atomic sites and (iii) staggering of hydrogen atoms about the single bonds in the case of NH_3^+ and the two methyl groups. The difference-Fourier was then scanned for these eleven hydrogens, at corresponding locations. All the hydrogen atoms were found at peak heights ranging from 0.6 to 0.4 $e.\text{\AA}^{-3}$ (Fig. 2). Apart from these eleven peaks, there were no other peaks of appreciable strength. The positional coordinates of the hydrogens, as derived from the difference synthesis,

were essentially the same as those obtained from geometrical considerations.

Employing correlated data about the *c* and *a* axes, the positional and isotropic thermal parameters of the

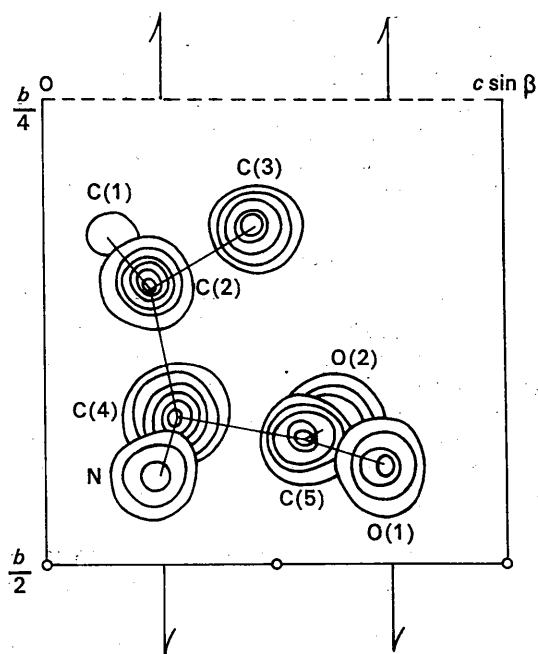


Fig. 1. Perspective diagram of the three-dimensional *E* map viewed along (100) contours at equal but arbitrary intervals.

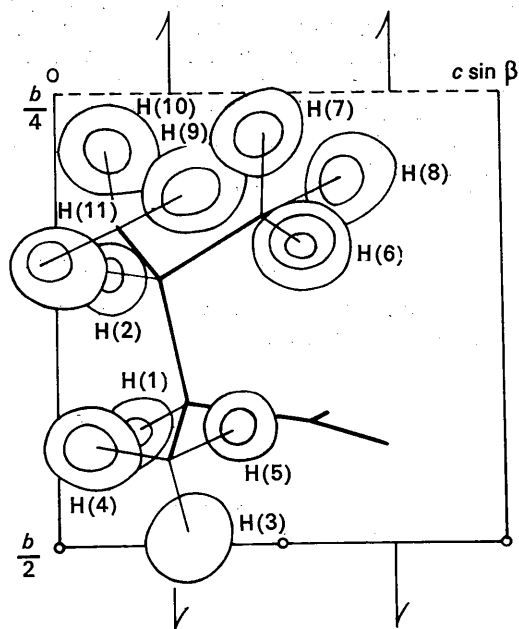


Fig. 2. Perspective diagram of the three-dimensional difference electron density map viewed along (100). Contours from 0.2 $e.\text{\AA}^{-3}$ at intervals of 0.2 $e.\text{\AA}^{-3}$.

eight non-hydrogen atoms, along with the overall scale factor, were refined by minimizing the function

$$\sum W(|F_o| - |F_c|)^2,$$

where $W = 1/6.5^2$ for $|F_o| \leq 6.5$ and $W = 1/|F_o|^2$ for $|F_o| > 6.5$.

The above weighting scheme was based on the analysis of $\langle (\Delta F)^2 \rangle$ as a function of $\langle |F_o| \rangle$ from measure-

ments of the intensities of common reflexions in the two sets of data about the c and a axes. The R value at the end of two cycles of refinement was 0.122. A further round of three cycles of refinement employing anisotropic thermal parameters for the non-hydrogen atoms reduced the R value to 0.101 for all the 861 reflexions. The shifts in the positional parameters in the final cycle were less than one tenth of the estimated standard deviations. The refinement was terminated at this stage. Throughout the refinement, the hydrogen atom parameters were kept fixed. The form factors for H, C, N and O atoms were taken from the *International Tables for X-ray Crystallography* (1962). The positional and thermal parameters are given in Table 4(a, b). The average estimated standard deviations are given in Table 5. The calculated and observed structure factors are listed in Table 6. The signs of the 100 reflexions used in computing the correct three-dimensional E map are shown along side $|F_o|$ in this table. The final electron density distribution is shown in Fig. 3.

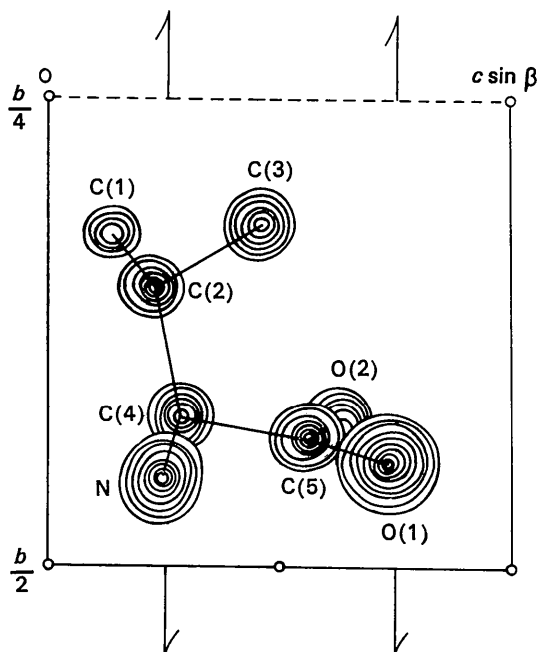


Fig. 3. Perspective diagram of the three-dimensional electron density viewed along (100). Contours from 2 e. \AA^{-3} at intervals of 1 e. \AA^{-3} .

Table 5. Average standard deviations (\AA) in the positional coordinates of non-hydrogen atoms

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
O	0.003	0.003	0.003
N	0.004	0.003	0.004
C	0.005	0.004	0.005

Discussion of the structure

The bond lengths and bond angles calculated from the atomic coordinates are shown in Fig. 4 and listed in Table 7. The estimated standard deviations in C-C,

Table 4(a). Atomic coordinates and thermal parameters of non-hydrogen atoms

The thermal parameters are of the form: $\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

	x	y	z	B_{11} $\times 10^4$	B_{22} $\times 10^4$	B_{33} $\times 10^4$	B_{12} $\times 10^4$	B_{13} $\times 10^4$	B_{23} $\times 10^4$
O(1)	0.2893	0.4471	0.7336	235	15	153	21	168	21
O(2)	-0.1534	0.4277	0.5993	215	14	230	-6	245	-5
N	0.3059	0.4530	0.2460	193	10	201	16	185	1
C(1)	-0.1950	0.3255	0.1360	317	18	551	60	259	65
C(2)	0.0873	0.3529	0.2268	242	9	216	7	170	22
C(3)	0.2762	0.3186	0.4589	408	10	391	-35	279	-14
C(4)	0.0724	0.4208	0.2852	165	8	199	-2	129	-5
C(5)	0.0703	0.4330	0.5629	174	7	181	-5	126	1

Table 4(b). Positional and (assumed) thermal parameters of the hydrogen atoms

	Bonded to	x	y	z	B
H(1)	C(4)	-0.0953	0.4385	0.1581	1.1 \AA^2
H(2)	C(2)	0.1642	0.3486	0.0784	1.6
H(3)	N	0.2904	0.4977	0.2657	1.2
H(4)	N	0.3094	0.4449	0.0610	1.2
H(5)	N	0.4819	0.4385	0.3727	1.2
H(6)	C(3)	0.4663	0.3368	0.5176	2.2
H(7)	C(3)	0.2878	0.2752	0.4250	2.2
H(8)	C(3)	0.2077	0.3233	0.6170	2.2
H(9)	C(1)	-0.2821	0.3301	0.2732	2.8
H(10)	C(1)	-0.1898	0.2818	0.0893	2.8
H(11)	C(1)	-0.3158	0.3474	-0.0299	2.8

Intramolecular non-bonded distances between third neighbours in the molecule are listed in Table 10. It will be noticed that there is a rather short non-bonded distance between C(3) and C(5) of 2.87 Å. The deviation of the angle C(4)–C(2)–C(3) from the tetrahedral value may be attributed to this. Although the distance between C(5) and C(3) is short, the distances between C(5) and the hydrogens attached to C(3) are larger than the sum of the van der Waals radii.

The nitrogen atom of the molecule has four near neighbours, O(2) (I), O(1) (III), O(2) (VI) and O(1) (V), at distances of 2.89, 2.74, 2.95 and 3.03 Å respectively. The possibility of the existence of a bifurcated hydrogen bond between N(donor) and O(2) (VI) and O(1) (V) (acceptors) was investigated. The H(3)···O(2) (VI) and H(3)···O(1) (V) distances are 2.03 and 2.51 Å respec-

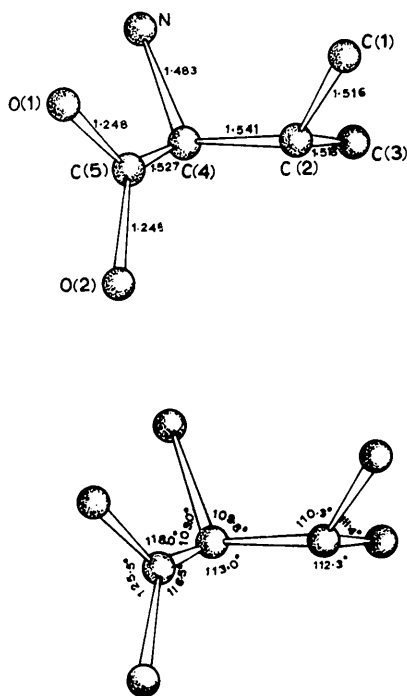


Fig. 4. Bond lengths and bond angles in the molecule.

Table 9. Intermolecular non-bonded contacts less than 3.6 Å

Atom <i>i</i>	Atom <i>j</i>	Distance d_{ij}
O(1)	O(2) (I)	3.24 Å
O(1)	C(4) (II)	3.56
O(2)	C(4) (II)	3.50
O(2)	N (III)	3.57
C(5)	N (III)	3.51
O(2)	O(1) (VI)	3.25
C(5)	O(1) (VI)	3.34
C(4)	O(1) (VI)	3.46
C(5)	O(2) (VI)	3.27
C(4)	O(2) (VI)	3.41
N	O(1) (V)	3.03
C(5)	C(5) (VI)	3.07
C(4)	C(5) (VI)	3.47
N	C(5) (VI)	3.55
N	N (V)	3.51

Table 10. Intramolecular non-bonded distances between third neighbours in the molecule

Atom <i>i</i>	Atom <i>j</i>	Distance d_{ij}
O(1)	N	2.67 Å
O(1)	C(2)	3.32
O(2)	N	3.56
O(2)	C(2)	3.16
C(5)	C(3)	2.87
C(5)	C(1)	3.28
N	C(3)	3.21

tively. In addition H(3) is too far from the line of N···O(1) (V) [$\text{N-H(3)}\cdots\text{O(1) (V)} = 112^\circ$] while the other angle $\text{N-H(3)}\cdots\text{O(2) (VI)}$ is equal to 153° (Fig. 6). Thus only the $\text{N-H(3)}\cdots\text{O(2) (VI)}$ seems to be a hydrogen bond, while $\text{N}\cdots\text{O(1) (V)}$ seems to be a normal ionic contact because the $\text{H(3)}\cdots\text{O(1) (V)}$ distance of 2.51 Å is on the border line of normal van der Waals contact, though the distance $\text{N}\cdots\text{O(1) (V)}$ ($= 3.03$ Å) corresponds to that of a very weak hydrogen bond.

Three hydrogen positions have been located around N and this, coupled with the observation that the two C–O bond lengths are very nearly equal, establishes

Table 8. Hydrogen bond distances and angles

Crystal chemical unit	Symmetrycode				
	<i>x</i>	<i>y</i>	<i>z</i>		
I	1 + <i>x</i>	<i>y</i>	<i>z</i>		
II	<i>x</i>	<i>y</i>	1 + <i>z</i>		
III	<i>x</i>	<i>y</i>	<i>z</i> – 1		
IV	1 + <i>x</i>	<i>y</i>	1 + <i>z</i>		
V	1 – <i>x</i>	1 – <i>y</i>	1 – <i>z</i>		
VI	– <i>x</i>	1 – <i>y</i>	1 – <i>z</i>		
N–H(5)···O(2) (I)	2.89 Å			N–H(5)···O(2) (I)	167°
H(5)···O(2) (I)	1.91			N–H(4)···O(1) (III)	168
N–H(4)···O(1) (III)	2.74			N–H(3)···O(2) (VI)	153
H(4)···O(1) (III)	1.74			C(4)–N···O(2) (I)	119
N–H(3)···O(2) (VI)	2.95			C(4)–N···O(1) (III)	111
H(3)···O(2) (VI)	2.03			C(4)–N···O(2) (VI)	95

that in the crystalline state, valine occurs in the zwitterionic form. The value of 1.483 Å for the C(4)-N(C^z-N) bond length is in very good agreement with the average value, C-N⁺ = 1.487 Å, for accurately determined structures of α-amino acids (Marsh & Donohue, 1967).

Although all the α-amino acids studied up to now have been found to occur in the zwitterionic form, differences between the two C-O distances and between the two C-C-O angles in the carboxyl group have often been reported. These differences have so far been attributed to hydrogen bonding. It has been observed that the C-O distance to that oxygen atom which takes part in a larger number of hydrogen bonds (or in the stronger hydrogen bonds) is longer than the other C-O distance. However, in the structure of L-glutamine (Cochran & Penfold, 1952) the reverse has been observed. In the case of DL-valine, on the other hand, though the atom O(2) takes part in two hydrogen bonds and O(1) in only one, the two C-O distances are not significantly different. As pointed out by Marsh & Donohue (1967) there seems to be no definitive evidence that the C-O distance is significantly influenced by the intermolecular environment - or, in particular, by the hydrogen bonding.

The least-squares plane through the carboxyl group is $-0.125X + 0.966Y - 0.227Z = 8.668$, where X , Y and Z are the atomic coordinates in Å referred to orthogonal axes a , b , c^* . The deviations of the atoms from this plane are not significant and are:

O(1)	-0.0004 Å
O(2)	-0.0004
C(5)	+0.0012
C(4)	-0.0003

The deviation of nitrogen from the above plane is 0.572 Å compared to 0.19 Å in L-valine hydrochloride monohydrate (Rao, 1967) and 0.13 Å in L-valine hydrochloride (Ando *et al.* 1967).

The C(2)-C(1) and C(2)-C(3) distances of 1.516 and 1.518 Å are essentially equal. The shorter value for these bond distances may be explained on the basis that the terminal atoms C(3) and C(1) have a large thermal vibration [Table 4(a)] which introduces an apparent shortening of the distances.

Conformation of the valine molecule

A method of describing the conformation of polypeptides and amino acids has been worked out in this laboratory (Ramachandran, 1962; Sasisekharan, 1962; Ramachandran, Ramakrishnan & Sasisekharan, 1963; Ramakrishnan & Ramachandran, 1965; and Ramachandran & Lakshminarayanan, 1966). The notation followed here is that of Edsall, Flory, Kendrew, Liquri, Nemethy, Ramachandran & Scheraga (1966). A brief account of the method of description for an amino acid is given below.

As far as amino acids are concerned there are two angles ψ_1 and ψ_2 which describe the two C-O bonds of the carboxyl group. The side chain conformations are described by other angles χ^{ij} .

Starting from C^z and looking along C^z-C' the clockwise rotations of the C-O bonds from the position *cis* to C^z-N measure ψ_1 and ψ_2 . Since the carboxyl group is essentially planar, $|\psi_1 - \psi_2| \simeq 180^\circ$. Looking along C^z-C^β, the clockwise rotation of C^β-C^γ from the position *cis* to C^z-N measures the angle χ^1 . If there is branching at C^β, then the angles are χ^{11} and χ^{12} , atom

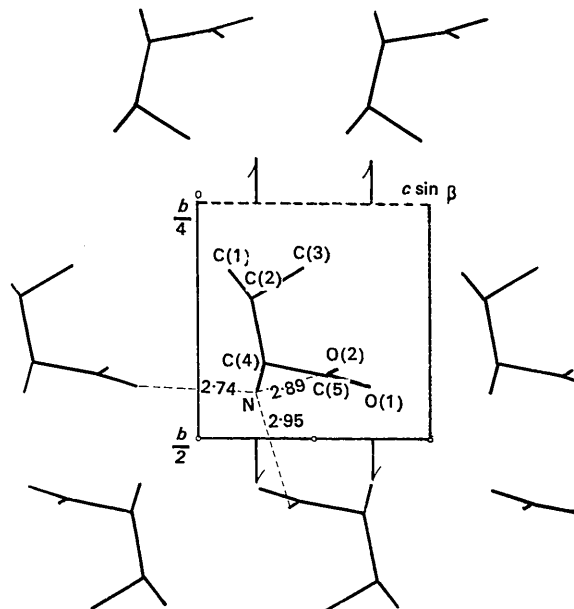


Fig. 5. The view of the structure projected on (100).

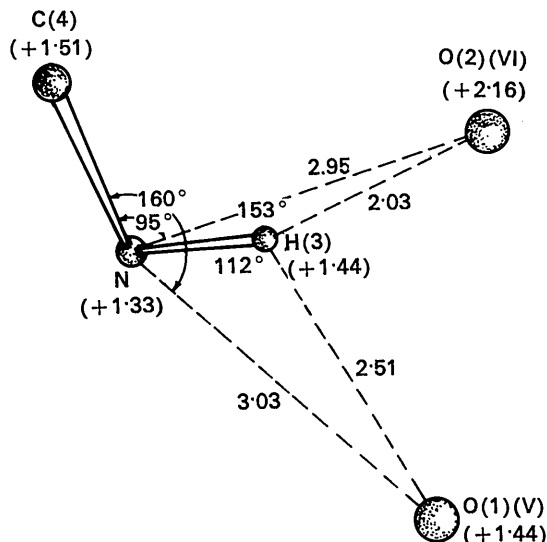


Fig. 6. Environment of H(3) viewed along the c axis.

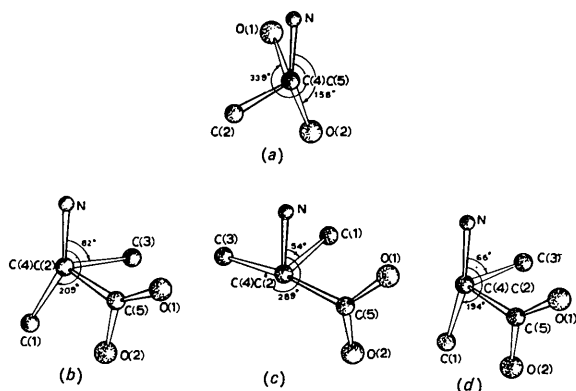


Fig. 7. Conformational diagrams: (a) Torsion around the bond C(4)-C(5) ($C\alpha-N$). (b) View of the valine molecule along the bond C(4)-C(2) ($C\alpha-C\beta$). (c) and (d) same as (b) in L-valine hydrochloride monohydrate and in L-valine hydrochloride.

2 being obtained from 1 by an anticlockwise rotation looking along the same bond. Normally the values of ψ_1 and ψ_2 are around 0° and 180° (usually less) and the χ values are around 60° , 180° and 300° . ($\pm 10^\circ$ generally) corresponding to the three staggered positions around a single bond. These are called positions I, II and III respectively in the case of an L-amino acid.

In the present investigation, the conformation of the valine molecule is as follows. The angles ψ_1 and ψ_2 are 158° and 339° respectively. The deviation of ψ_1 and ψ_2 from the values of 180° and 0° respectively by more than 20° is reflected in the structural feature in that the amino nitrogen is out of the plane of the carboxyl group. The C^γ atoms [C(3) and C(1)] go into positions I and II with $\chi^{11} = 82^\circ$ and $\chi^{12} = 209^\circ$. The conformational diagrams are shown in Fig. 7 wherein the conformation of the valine molecule as found in the other two structures is also given. In L-valine hydrochloride (Ando *et al.* 1967) the C^γ atoms go into positions I and II while in L-valine hydrochloride monohydrate (Rao, 1967), they go into positions III and I.

Thus, the positions II and III, which are favourable for the conformation of poly-L-valine in the α -helical form, have not yet been observed in any of these structures.

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