

## Structure of L-Asparagine Monohydrate by Neutron Diffraction

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A single-crystal neutron diffraction refinement of the structure of L-asparagine monohydrate,  $\text{NH}_2\text{CO}(\text{CH}_2)\text{CHNH}_2\text{COOH}\cdot\text{H}_2\text{O}$  [space group  $P2_12_12_1$ ,  $Z=4$ ,  $a=5.593$  (5),  $b=9.827$  (10),  $c=11.808$  (11) Å] has been carried out. Neutron intensities of 890 reflexions (749 non-zero) were measured at a wavelength of  $1.041$  Å, up to  $\sin \theta/\lambda=0.65$  Å<sup>-1</sup>. The ten hydrogen atoms in the asymmetric unit were located from a neutron scattering density Fourier map, computed with observed  $F_o$ 's as amplitudes and phases derived from the known X-ray positions of the non-hydrogen atoms. The structural parameters were refined by the full-matrix anisotropic least-squares method. Extinction corrections to the observed data were applied by a method due to Zachariasen (*Acta Cryst.* (1967). **23**, 558). The final  $R$  value is 0.096. The hydrogen bonding scheme and the conformation of the molecule are discussed.

### Introduction

The neutron diffraction refinement of the crystal structure of L-asparagine monohydrate,  $\text{NH}_2\text{CO}(\text{CH}_2)\text{CH}(\text{NH}_2)\text{COOH}\cdot\text{H}_2\text{O}$ , was undertaken as part of our current program of studies on the structure of amino acids and their derivatives. The X-ray structure analysis of L-asparagine monohydrate was carried out by Kartha & De Vries (1961). Their analysis did not include the location of the hydrogen atoms.

### Experimental

Single crystals of L-asparagine monohydrate were grown from an aqueous solution of the compound. The crystals obtained were prisms, elongated along the  $a$  axis and bounded by  $\{011\}$  planes. From these, one crystal weighting 37 mg was selected for data collection.

The crystal was first coated with an adhesive (brand name 'Stickfast') and dipped in liquid nitrogen to reduce extinction effects. It was then mounted on a full-circle Siemens crystal orienter so that its long edge ( $a$  axis) was along the  $\varphi$  axis. The orienter was mounted on the  $\varphi$  plate of the diffractometer 'SAND' (Chidambaram, Sequeira & Momin, 1968), located at the CIRUS reactor in Trombay, after removing the automatic crystal positioning device used for collecting zero-layer data. The orienter was aligned so that its  $\chi$  circle was in the symmetrical position with respect to the incident and diffracted neutron beams. For each reflexion, the angles  $2\theta$ ,  $\chi$  and  $\varphi$  had to be set by hand but the scanning was done automatically. The integrated intensities of 890 independent reflexions up to  $\sin \theta/\lambda=0.65$  Å<sup>-1</sup> were measured at a wavelength of  $1.041$  Å in the  $\theta$ - $2\theta$  step-scan mode ( $0.1^\circ$  step in  $2\theta$ ). The background was scanned for a minimum of  $1^\circ$  on either side of the peak. Of the measured reflexions, 749 had  $I \geq \sigma(I)$  and were treated as observables. The observed  $2\theta$  angles agreed quite well with the values

calculated from cell constants\* reported by Kartha & De Vries (1961):  $a=5.582$ ,  $b=9.812$ ,  $c=11.796$  Å. The observed extinctions,  $h=2n+1$  for  $h00$ ,  $k=2n+1$  for  $0k0$  and  $l=2n+1$  for  $00l$ , confirmed the X-ray space group  $P2_12_12_1$ . The integrated intensities were reduced to  $F_o^2$ , using the program *DATARED* (Srikanta & Sequeira, 1967). The absorption corrections were applied for  $\mu=2.74$  cm<sup>-1</sup>. The range of absorption factors was 0.515 to 0.624.

### Refinement of the structure

A three-dimensional neutron scattering density Fourier synthesis map, computed using the program *FORDAP* (Zalkin, 1962), with the observed  $F_o$ 's as amplitudes and the phases calculated from the contributions of heavy atoms alone, revealed the positions of all the ten hydrogen atoms in the asymmetric unit. The structural parameters were then subjected to a series of isotropic and anisotropic full-matrix least-squares refinements with the use of the program *XFLS* (Busing, Martin & Levy, 1962). The function minimized was  $\sum \omega(F_o^2 - |F_c|^2)^2$  where  $\omega=1/\sigma^2(F_o^2)$  and  $\sigma(F_o^2)$ 's were based solely on counting statistics. As all the 182 parameters in the anisotropic refinements could not be refined on the CDC 3600 computer (32K memory) in the same cycle, the parameters of the heavy atoms and hydrogen atoms were refined separately in alternate cycles.

It was noticed during the refinement that the data were affected by extinction (worst  $F_o^2/|F_c|^2=0.66$ ). They were corrected by the method due to Zachariasen (1967), using the equation

\* These values for the cell constants were used in the least-squares refinement. However, a refined set of cell constants,  $a=5.593$  (5),  $b=9.827$  (10) and  $c=11.808$  (11) Å, became available from an independent neutron diffraction study by Verbist, Lehmann, Koetzle & Hamilton (1972), (following paper). The latter values were used in computing interatomic distances and angles.

Table 1. Final positional and thermal parameters for L-asparagine monohydrate

Least-squares standard deviations are shown in parentheses. All parameters are  $\times 10^4$  and the expression for the thermal parameters is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	-1245 (10)	-580 (5)	360 (4)	192 (18)	51 (5)	37 (3)	-22 (10)	4 (8)	-2 (4)
C(2)	-3053 (9)	-291 (5)	1296 (4)	149 (17)	48 (5)	36 (3)	29 (8)	12 (8)	4 (3)
C(3)	-2104 (9)	562 (5)	2275 (4)	161 (17)	42 (4)	40 (4)	15 (9)	-34 (8)	2 (4)
C(4)	165 (10)	-19 (5)	2777 (4)	163 (17)	34 (4)	40 (4)	-10 (8)	10 (9)	4 (4)
N(1)	-4160 (7)	-1560 (3)	1718 (3)	159 (12)	49 (3)	39 (2)	-3 (7)	8 (6)	-1 (2)
N(2)	1069 (8)	640 (4)	3686 (3)	269 (16)	63 (4)	48 (3)	25 (8)	-32 (7)	-15 (3)
O(1)	-77 (12)	435 (6)	18 (6)	240 (23)	46 (6)	75 (5)	-27 (12)	31 (11)	-17 (5)
O(2)	-1192 (13)	-1738 (6)	-67 (5)	237 (22)	57 (6)	51 (4)	-9 (13)	31 (11)	-15 (4)
O(3)	1145 (13)	-1061 (6)	2383 (5)	185 (21)	66 (6)	55 (5)	4 (12)	29 (10)	-15 (5)
O(4)	3082 (14)	2301 (7)	1133 (5)	328 (28)	80 (7)	57 (5)	-69 (14)	-14 (12)	3 (5)
H(1)	1820 (24)	1739 (11)	704 (10)	377 (51)	84 (13)	104 (11)	-102 (25)	-27 (23)	-30 (10)
H(2)	3474 (24)	3040 (11)	599 (9)	346 (47)	79 (11)	88 (10)	-43 (25)	-52 (22)	-3 (9)
H(3)	-3107 (22)	-2020 (10)	2338 (8)	333 (47)	51 (9)	62 (8)	2 (19)	-20 (20)	17 (8)
H(4)	-4435 (23)	-2279 (9)	1067 (8)	360 (46)	38 (9)	63 (7)	-72 (19)	36 (20)	-11 (7)
H(5)	-5851 (22)	-1370 (9)	2053 (10)	289 (43)	46 (9)	92 (10)	-61 (19)	21 (21)	-1 (9)
H(6)	2506 (19)	276 (11)	4073 (9)	198 (31)	102 (14)	62 (8)	-16 (20)	6 (16)	-9 (9)
H(7)	285 (23)	1502 (12)	3948 (9)	400 (53)	84 (12)	70 (9)	-7 (25)	57 (21)	-18 (9)
H(8)	-4494 (20)	347 (10)	922 (9)	223 (35)	70 (11)	91 (9)	71 (19)	-6 (18)	23 (9)
H(9)	-1675 (22)	1596 (9)	1941 (10)	289 (42)	38 (8)	104 (10)	12 (19)	3 (20)	-15 (8)
H(10)	-3385 (22)	750 (13)	2933 (10)	221 (38)	144 (16)	89 (10)	52 (24)	33 (19)	-33 (12)

Table 2. Observed and calculated squared structure factors

The four columns in each set contain respectively the indices  $h, l, 100F_o^2$  and  $100|F_c|^2$ . The nuclear scattering lengths used are (in units of  $10^{-12}$  cm): carbon 0.661, nitrogen 0.940, oxygen 0.577 and hydrogen -0.374.

$h$	$l$	$100F_o^2$	$100 F_c ^2$
0	0	10000	10000
0	1	10000	10000
0	2	10000	10000
0	3	10000	10000
0	4	10000	10000
0	5	10000	10000
0	6	10000	10000
0	7	10000	10000
0	8	10000	10000
0	9	10000	10000
0	10	10000	10000
0	11	10000	10000
0	12	10000	10000
0	13	10000	10000
0	14	10000	10000
0	15	10000	10000
0	16	10000	10000
0	17	10000	10000
0	18	10000	10000
0	19	10000	10000
0	20	10000	10000
0	21	10000	10000
0	22	10000	10000
0	23	10000	10000
0	24	10000	10000
0	25	10000	10000
0	26	10000	10000
0	27	10000	10000
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0	30	10000	10000
0	31	10000	10000
0	32	10000	10000
0	33	10000	10000
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0	71	10000	10000
0	72	10000	10000
0	73	10000	10000
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0	87	10000	10000
0	88	10000	10000
0	89	10000	10000
0	90	10000	10000
0	91	10000	10000
0	92	10000	10000
0	93	10000	10000
0	94	10000	10000
0	95	10000	10000
0	96	10000	10000
0	97	10000	10000
0	98	10000	10000
0	99	10000	10000
0	100	10000	10000

parameter  $G=(r^*\lambda^{-1})$  in the refinement.  $\bar{T}$  for each reflexion was computed by a modification of the program *ORABS* (Wehe, Busing & Levy, 1962). The value of  $G$  after convergence of the refinement (maximum parameter shift in the last cycle less than one-tenth the corresponding standard deviation) was  $0.23 \times 10^4$ . The final  $R$  values obtained were

	$R( F )$	$R( F^2 )$	$\omega R( F^2 )^\dagger$
For 749 reflexions [with $F_o^2 > \sigma(F_o^2)$ ]	0.096	0.122	0.122
For 734 reflexions [with $F_o^2 > \sigma(F_o^2)$ and $F_o^2 < 9 F_c ^2$ ]	0.088	0.118	0.104

The final nuclear parameters, together with their least-squares estimated standard deviations, are given in Table 1. A listing of the observed and calculated  $|F^2|$  is given in Table 2.

Discussion of the structure

The structure of L-asparagine monohydrate as determined by Kartha & De Vries (1961) is essentially correct. The agreement between the neutron and X-ray coordinates of non-hydrogen atoms is satisfactory.† A stereo view of a molecule of L-asparagine monohydrate drawn with the aid of the program *ORTEP* (Johnson, 1965) is shown in Fig. 1. The bond distances and bond angles for the molecule were computed by the program *ORFFE* (Busing, Martin & Levy, 1964)

$$F_{corr} = F_o/y$$

$$\text{where } y = (1 + 2x)^{-1/2},$$

$$x = r^*\lambda^{-1}Q_o\bar{T},$$

$$\bar{T} = -A^{-1}dA/d\mu.$$

Here,  $A$  is the absorption factor and  $r^*$  is an adjustable parameter which takes extinction into account. The program *XFLS* was suitably altered to include the

†  $\omega R(|F^2|) = \left( \frac{\sum \omega(F_o^2 - |F_c|^2)^2}{\sum \omega F_o^4} \right)^{1/2}$   
‡ The labels in the coordinates table given by Kartha & De Vries, namely  $y, z$  and  $x$  are in error; these should be read as  $x, y$  and  $z$ .

and are given in Table 3. These values are compared in Fig. 2 with the weighted average values for other amino acids reported by Marsh & Donohue (1967). The agreement between the two sets is good. No value differs by more than two standard deviations except the value for angle C(1)–C(2)–C(3) ( $115^\circ$  compared with the weighted value  $111.5^\circ$ ). But, as Marsh & Donohue (1967) have noted, there is considerable scatter in the values of this angle in different amino acids. As found by Kartha & De Vries (1961), the

Table 3. *Interatomic distances and angles in L-asparagine monohydrate\**

The errors given here are the standard deviations calculated by using the standard deviations of the coordinates from the least-squares refinement and the standard deviations of the cell constants reported by Verbist, Lehmann, Koetzle & Hamilton (1972).

C(1)–O(1)	1.259 (8) Å	O(1)–C(1)–O(2)	125.6 (0.6)°
C(1)–O(2)	1.245 (7)	O(1)–C(1)–C(2)	115.4 (0.5)
C(1)–C(2)	1.525 (7)	O(2)–C(1)–C(2)	118.7 (0.5)
C(2)–C(3)	1.523 (7)	H(8)–C(2)–C(1)	107.3 (0.7)
C(2)–N(1)	1.479 (6)	H(8)–C(2)–N(1)	107.8 (0.7)
C(3)–C(4)	1.513 (7)	H(8)–C(2)–C(3)	104.2 (0.7)
C(4)–N(2)	1.352 (6)	N(1)–C(2)–C(3)	110.8 (0.4)
C(4)–O(3)	1.251 (8)	N(1)–C(2)–C(1)	111.4 (0.4)
C(2)–H(8)	1.113 (12)	C(3)–C(2)–C(1)	115.0 (0.4)
C(3)–H(9)	1.116 (11)	H(10)–C(3)–H(9)	104.1 (1.0)
C(3)–H(10)	1.072 (13)	H(10)–C(3)–C(4)	110.0 (0.8)
N(1)–H(3)	1.043 (11)	H(10)–C(3)–C(2)	114.3 (0.8)
N(1)–H(4)	1.055 (10)	H(9)–C(3)–C(4)	107.6 (0.7)
N(1)–H(5)	1.042 (13)	H(9)–C(3)–C(2)	107.9 (0.7)
N(2)–H(6)	0.992 (11)	C(4)–C(3)–C(2)	112.4 (0.4)
N(2)–H(7)	1.002 (12)	O(3)–C(4)–N(2)	121.6 (0.5)
O(4)–H(1)	1.029 (14)	O(3)–C(4)–C(3)	122.1 (0.5)
O(4)–H(2)	0.986 (13)	C(3)–C(4)–N(2)	116.3 (0.4)
H(1)–H(2)	1.583 (17)	H(5)–N(1)–H(3)	108.9 (0.9)
		H(5)–N(1)–H(4)	105.3 (1.0)
		H(5)–N(1)–C(2)	110.9 (0.6)
		H(3)–N(1)–H(4)	107.7 (0.8)
		H(3)–N(1)–C(2)	111.4 (0.7)
		H(4)–N(1)–C(2)	112.4 (0.6)
		H(6)–N(2)–H(7)	121.2 (1.0)
		H(6)–N(2)–C(4)	119.7 (0.7)
		H(7)–N(2)–C(4)	119.1 (0.8)
		H(1)–O(4)–H(2)	103.5 (1.1)

\* Uncorrected for thermal motion.

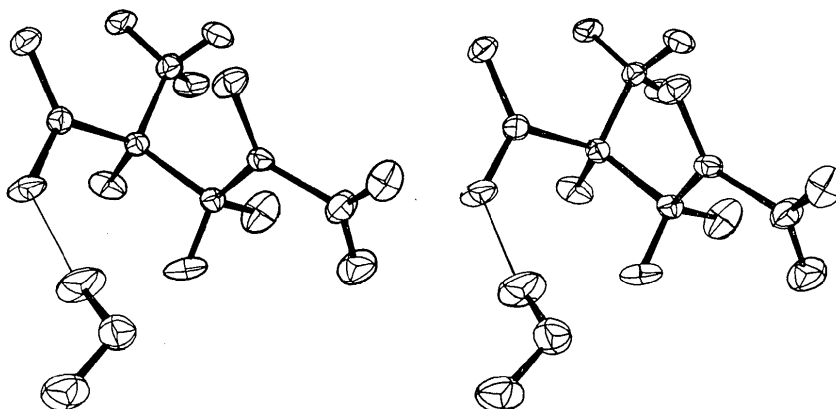


Fig. 1. Stereoscopic picture of the asparagine molecule viewed down the *a* axis.

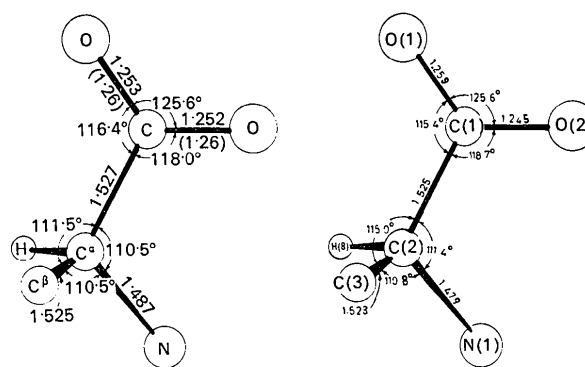


Fig. 2. The bond distances and angles in the amino acid residue. (a) The average values given by Marsh & Donohue (1967). (b) Values obtained for the asparagine molecule.

asparagine molecule exists as a zwitterion in the structure, with the C(2)–N(1)<sup>+</sup>H(3)H(4)H(5) group having a tetrahedral configuration. The two C–O bonds for the ionized carboxylic group are equal within experimental error, the average value being 1.252 Å. The values of the bond distances and angles for the side chain are also normal.

#### Hydrogen bonding

Projections of the structure viewed along [100] and [010] are shown in Figs. 3 and 4. As can be seen from Fig. 3, the molecular chains are parallel to the *c* direction. The adjacent chains are linked together by hydrogen bonds from the water molecule. In all, there are seven hydrogen bonds involving all the protons attached to N(1), N(2), O(4) (water oxygen) atoms, originating from each molecule. Six of these are shown in Fig. 3. The seventh hydrogen bond N(1)–H(5)···O(3)<sup>IV</sup> links two asparagine molecules lying exactly on top of each other along the *a* axis and is shown in Fig. 4. The H(5) hydrogen atom is too far away to form a hydrogen bond with O(3) of the same molecule. This confirms that the structure of the asparagine molecule in the crystalline state is an open chain.

All the hydrogen bond distances and angles are summarized in Table 4. It can be seen that the  $N^+-H\cdots O$  bonds are shorter and straighter than the

$N-H\cdots O$  bonds. This is in agreement with the conclusions of Chidambaram, Balasubramanian & Ramachandran (1970) that  $N^+-H\cdots O$  bonds (mean 2.81

Table 4. *Hydrogen bonds in L-asparagine monohydrate*

$X-H\cdots Y$	$d_{X-H}$	$d_{H\cdots Y}$	$d_{X\cdots Y}$	$\angle H-X\cdots Y$
$O(4)-H(1)\cdots O(1)$	1.029 (14)	1.851 (14)	2.866 (10)	7.4 (0.7)
$O(4)-H(2)\cdots O(1^i)$	0.986 (13)	1.854 (13)	2.803 (9)	12.6 (0.8)
$N(1)-H(3)\cdots O(4^{ii})$	1.043 (11)	1.925 (12)	2.839 (7)	23.2 (0.7)
$N(1)-H(4)\cdots O(2^{iii})$	1.055 (10)	1.815 (12)	2.809 (7)	15.6 (0.7)
$N(1)-H(5)\cdots O(3^{iv})$	1.042 (13)	1.751 (14)	2.784 (8)	6.0 (0.7)
$N(2)-H(6)\cdots O(1^v)$	0.992 (11)	1.949 (13)	2.935 (8)	5.1 (0.6)
$N(2)-H(7)\cdots O(2^i)$	1.002 (12)	2.235 (13)	3.050 (7)	29.7 (0.7)

Superscripts for symmetry-related atoms

None	$x$	$y$	$z$		$x-1$	$y$	$z$
i	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	iv	$\frac{1}{2}-x$	$y$	$\frac{1}{2}-z$
ii	$-x$	$y-\frac{1}{2}$	$\frac{1}{2}-z$	v	$\frac{1}{2}-x$	$y$	$\frac{1}{2}-z$
iii	$x-\frac{1}{2}$	$-\frac{1}{2}-y$	$-z$				

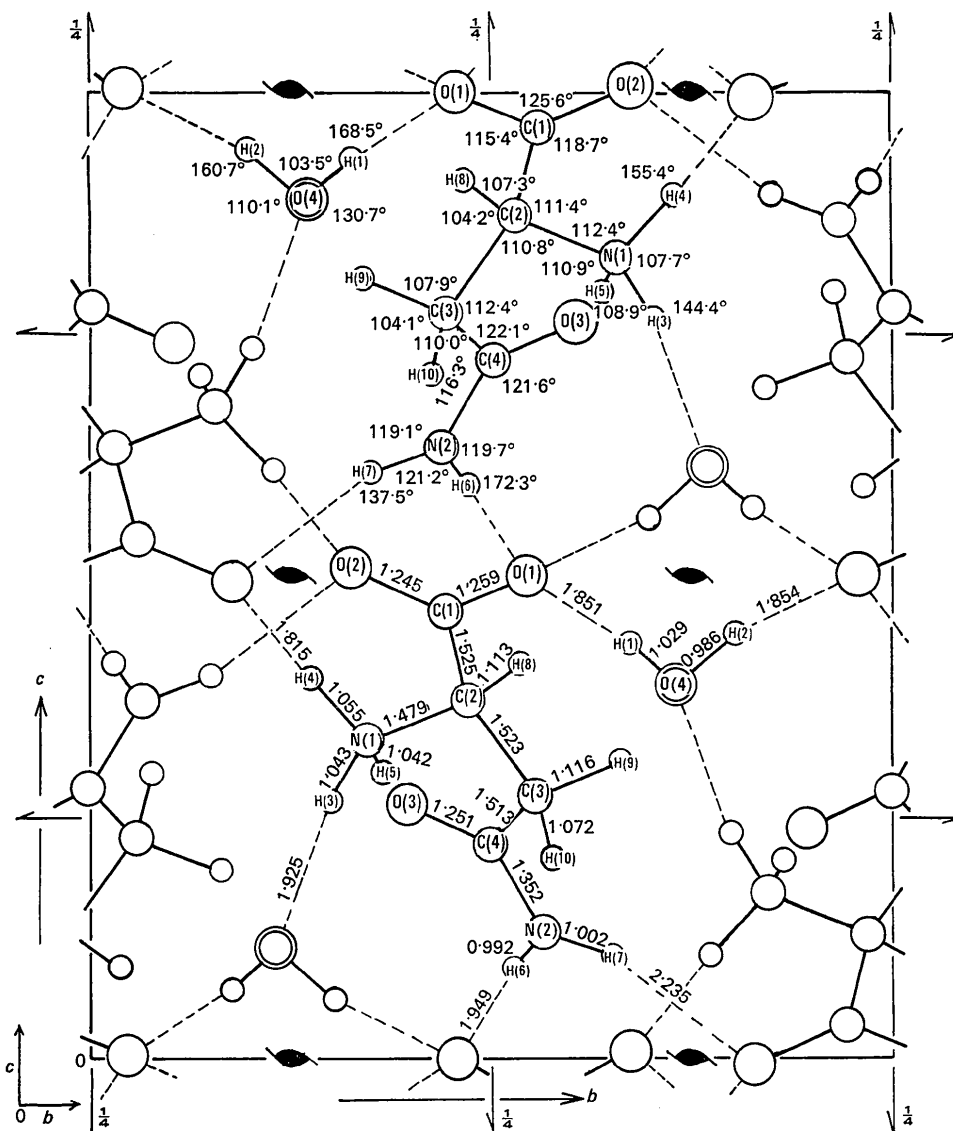


Fig. 3. Projection of the unit cell structure on the (100) plane.  $\angle C(1)-C(2)-C(3) = 115.0^\circ$ ,  $\angle N(1)-C(2)-H(8) = 107.8^\circ$ ,  $\angle C(2)-C(3)-H(10) = 114.3^\circ$ ,  $\angle C(4)-C(3)-H(9) = 107.6^\circ$ ,  $\angle H(4)-N(1)-H(5) = 105.3^\circ$ ,  $\angle C(2)-N(1)-H(3) = 111.4^\circ$ .

Å) are shorter than N-H...O bonds (mean 2.99 Å). The corresponding N<sup>+</sup>-H distances are longer than the N-H distances (see Table 3). The water oxygen acts as the donor of two hydrogen bonds and acceptor for the hydrogen bond from the N(1) atom. The coordination of the water molecule is approximately tetrahedral and is of type *K* (Chidambaram, Sequeira & Sikka, 1964) in which one of the lone pairs of the water oxygen is pointing towards a H-bond donor group (NH<sub>3</sub><sup>+</sup> group) and the other lone pair is not specifically directed. The value of 103.5° for the H-O-H angle is normal for this type of coordination (Coppens & Sabine, 1969; Sikka & Chidambaram, 1969).

#### Molecular conformation

Torsion angles about various bonds in the molecule are listed in Table 5, and views along these bonds are shown in Fig. 5. Names and signs of these angles are in accordance with the recommendations made by the IUPAC-IUB Commission on Biochemical Nomenclature (1970).

Table 5. Torsion angles in L-asparagine monohydrate

(Standard deviations are given in parentheses).

$\psi(1)$	N(1)-C(2)-C(1)-O(2)	11.9 (0.7)°
$\psi(2)$	N(1)-C(2)-C(1)-O(1)	-174.4 (0.5)
$\varphi(1)$	C(1)-C(2)-N(1)-H(4)	-36.2 (0.9)
$\varphi(2)$	C(1)-C(2)-N(1)-H(3)	84.8 (0.8)
$\varphi(3)$	C(1)-C(2)-N(1)-H(5)	-153.8 (0.8)
$\chi(1,1)$	N(1)-C(2)-C(3)-C(4)	74.3 (0.5)
$\chi(1,2)$	N(1)-C(2)-C(3)-H(9)	-167.3 (0.7)
$\chi(1,3)$	N(1)-C(2)-C(3)-H(10)	-52.1 (0.9)
$\chi(2,1)$	C(2)-C(3)-C(4)-O(3)	2.3 (0.7)
$\chi(2,2)$	C(2)-C(3)-C(4)-N(2)	-177.0 (0.4)
$\chi(3,2,1)$	O(3)-C(4)-N(2)-H(6)	-2.4 (1.0)
$\chi(3,2,2)$	O(3)-C(4)-N(2)-H(7)	176.4 (0.9)

The carboxyl group is only approximately coplanar with the carbon atom C(2). The equation of the least-squares plane passing through the atoms C(1), C(2), O(1) and O(2) is

$$-3.9240x + 2.3575y - 7.9232z - 0.0943 = 0$$

where *x*, *y* and *z* are fractional coordinates. Deviations of the atoms from this plane are:

$$C(1) - 0.027, C(2) 0.008, O(1) 0.024 \text{ and } O(2) 0.017 \text{ \AA.}$$

The values of torsion angles for non-hydrogen atoms are in good agreement with those calculated by Lakshminarayanan, Sasisekharan & Ramachandran (1967). The torsion angle  $\psi(1)^*$  corresponding to the oxygen atom O(2) is +11.9 [see Fig. 5(a)]. Most of the amino acids have a negative  $\psi(1)$  angle. A few exceptions are DL-serine (+3.8°), L-histidine-HCl.2H<sub>2</sub>O (+0.4°) and the present molecule. As noted by Sundaralingam & Putkey (1970), the positive angle  $\psi(1)$  leads to a decrease in the intramolecular C(3)...O(1) distance. This distance in the present case is 2.90 Å.

Another special feature of this molecule is that the torsion angle for the  $\gamma$ -carbon atom C(4) is 74.3° [see Fig. 5(c)]. This means that the C(3)-C(4) bond is *cis* to C(2)-C(1) bond. Hence atom C(4) occupies the gap between N(1) and C(1), even though the other two gaps, namely those between N(1) and H(8), and C(1) and H(8) are wider; the latter is owing to the fact that the hydrogen atom is smaller than both nitrogen and carbon atoms. According to Lakshminarayanan *et al.* (1967), the conformation, in which C(3)-C(4) is

\* This angle was called  $\psi(2)$  by Lakshminarayanan, Sasisekharan & Ramachandran (1967), and Sundaralingam & Putkey (1970).

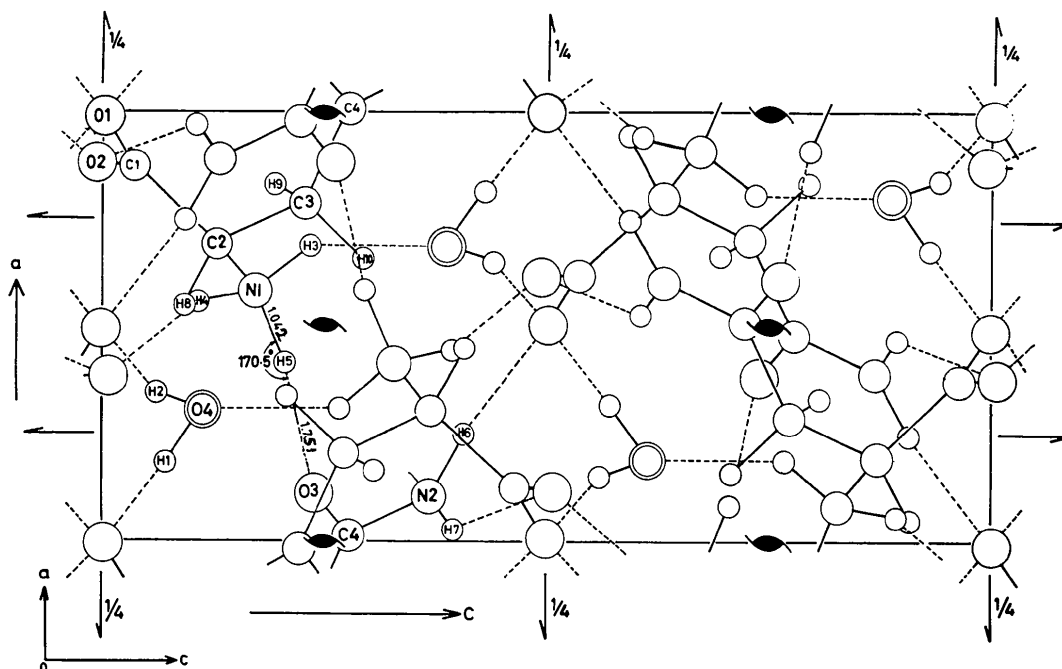


Fig. 4. Projection of the unit cell structure on the 010 plane.

*trans* to C(2)–C(1) is the most favourable and the conformation found in the case of the present molecule is the least favourable. As a result it is seen that C(2)–H(8) is *trans* to C(3)–C(4) and C(3)–H(10) is *trans* to C(2)–C(1).

The atoms C(2), C(3), C(4), N(2), O(3), H(6) and H(7) are approximately coplanar [see Figs. 5(d) and (e)]. The equation of the least-squares plane passing through the atoms C(3), C(4), O(3) and N(2) is

$$-3.0571x - 5.6525y + 7.1863z - 1.9595 = 0.$$

Deviations of the above-mentioned seven atoms from this plane are:

C(2)	0.070 Å	O(3)	0.003 Å	H(6)	0.045 Å
C(3)	0.001	N(2)	0.001	H(7)	-0.058
C(4)	-0.004				

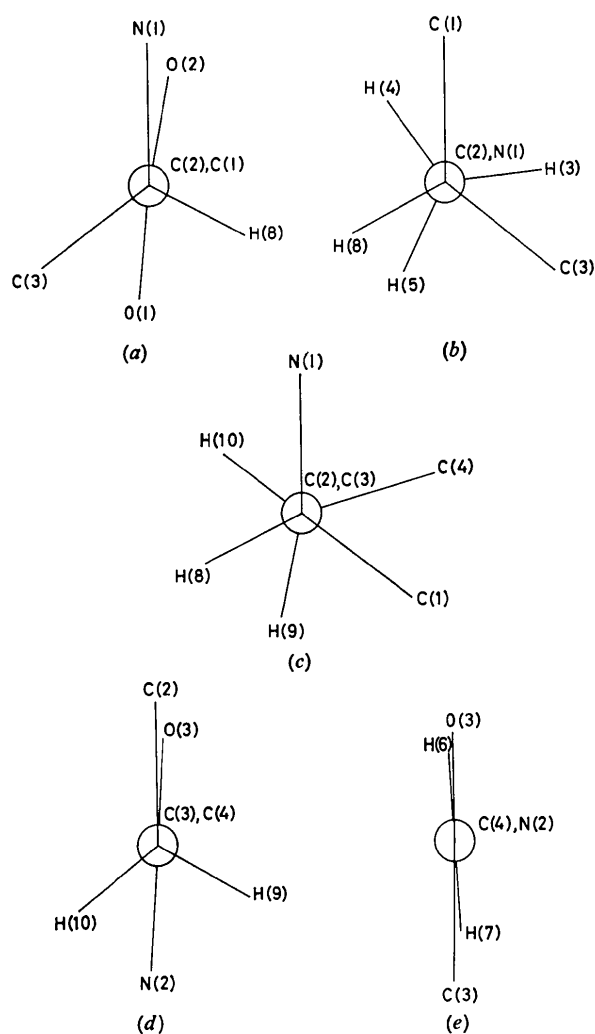


Fig. 5. Configuration of atoms looking down the bonds (a) C(2)–C(1); (b) C(2)–N(1); (c) C(2)–C(3); (d) C(3)–C(4); (e) C(4)–N(2).

The torsion angles for the hydrogen atoms of the (NH<sub>3</sub>)<sup>+</sup> group [see Fig. 5(b)] are normal. This configuration is similar to the one present in the molecule of perdeutero- $\alpha$ -glycylglycine studied by Freeman & Paul (1970).

Dihedral angles involving hydrogen atoms which are bonded to the tetrahedrally bonded carbon atoms C(2) and C(3) were calculated. As expected, these angles are close to 90° (range: 87.4 to 91.3°).

In the following paper, Hamilton and coworkers have compared our results with those of their independent neutron study of this structure.

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### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee. The CDC 3600 version incorporates modifications by W. C. HAMILTON, J. A. IBERS, C. K. JOHNSON, S. SRIKANTA and S. K. SIKKA.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Oak Ridge, Tennessee. The CDC 3600 version incorporates modifications by C. K. JOHNSON & S. SRIKANTA.
- CHIDAMBARAM, R., BALASUBRAMANIAN, R. & RAMACHANDRAN, G. N. (1970). *Biochem. Biophys. Acta*, **221**, 182.
- CHIDAMBARAM, R., SEQUEIRA, A. & MOMIN, S. N. (1968). *Indian J. Pure Appl. Phys.* **6**, 550.
- CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616.
- COPPENS, P. & SABINE, T. M. (1969). *Acta Cryst.* **B25**, 2442.
- FREEMAN, H. C. & PAUL, G. L. (1970). *Acta Cryst.* **B26**, 925.
- IUPAC-IUB Commission on Biochemical Nomenclature, (1970). *Biochem. Wash.* **9**, 3471.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee. The CDC 3600 version is due to H. RAJAGOPAL & A. S. SEQUEIRA.
- KARTHA, G. & DE VRIES, A. (1961). *Nature, Lond.* **192**, 862.
- LAKSHMINARAYANAN, A. V., SASISEKHARAN, V. & RAMACHANDRAN, G. N. (1967). In *Conformation of Biopolymers*. Edited by G. N. RAMACHANDRAN. Vol. 1, p. 61. New York: Academic Press.
- MARSH, R. E. & DONOHUE, J. (1967). *Advanc. Protein Chem.* **22**, 235.
- SIKKA, S. K. & CHIDAMBARAM, R. (1969). *Acta Cryst.* **B25**, 310.
- SRIKANTA, S. & SEQUEIRA, A. (1967). Unpublished.
- SUNDARALINGAM, M. & PUTKEY, E. F. (1970). *Acta Cryst.* **B26**, 790.
- VERBIST, J. J., LEHMANN, M. S., KOETZLE, T. F. & HAMILTON, W. C. (1972). *Acta Cryst.* **B28**, 3006.
- WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Oak Ridge, Tennessee. The CDC 3600 version is due to S. SRIKANTA.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.
- ZALKIN, A. (1962). Private communication.