

Table 3. Final thermal parameters  $U_{ij}$ 

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{31}$	$U_{23}$
Br	0.7296	0.7191	0.8846	0.0000	0.0000	0.0000
N(1)	0.9197	0.2481	1.7962	0.0000	0.0000	0.0000
N(2)	1.0066	0.4402	1.0032	0.0000	0.0000	0.0000
C(1)	0.4819	0.5160	1.0606	0.0000	0.0000	0.0000
C(2)	0.4089	0.8045	1.1151	-0.0312	0.0000	0.0000
C(3)	0.4428	0.7014	1.4909	0.0786	0.0000	0.0000
C(4)	0.6311	1.0532	0.4299	0.0000	0.0000	0.0000
C(7)	0.8676	0.5670	1.8886	-0.3743	0.0000	0.0000

HANSON, A. W. (1965). *Acta Cryst.* **19**, 610.

LISTER, D. G. & TYLER, J. K. (1966). *Chem. Commun.* p. 152.

LONGUET-HIGGINS, H. C. & SALEM, L. (1959). *Proc. Roy. Soc. (London)*, **A251**, 172.

MATSUDA, H., OSAKI, K. & NITTA, I. (1958). *Bull. Chem. Soc. Japan*, **31**, 611.

OOSHIKA, Y. (1957). *J. Phys. Soc. Japan*, **12**, 1246.

SAKURAI, T. (1965). *Acta Cryst.* **19**, 320.

THOMAS, D. D., KELLER, H. & MCCONNELL, H. M. (1963). *J. Chem. Phys.* **39**, 2321.

TURNER, J. D. & ALBRECHT, A. C. (1955). Unpublished result. See *J. Amer. Chem. Soc.* (1955), **77**, 4454 and *J. Chem. Phys.* (1963), **39**, 2321.

WALLWORK, S. C. (1961). *J. Chem. Soc.* p. 494.

*Acta Cryst.* (1968). **B24**, 1349

## The Crystal and Molecular Structure of L-Aspartic Acid

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(Received 6 May 1968)

Crystals of L-aspartic acid are monoclinic ( $P2_1$ ) with  $a=7.617$ ,  $b=6.982$ ,  $c=5.142$  Å,  $\beta=99.84^\circ$ ,  $Z=2$ . The crystals are often more or less twinned. The structure was solved in the  $h0l$  projection by the Patterson vector shift method. The structure was refined with 602 diffractometer  $hkl$  data to a final  $R$  value of 0.04. The molecules are in the zwitterionic form. A rigid three-dimensional network of intermolecular 'hydrogen bonds' is found.

### Introduction

As one of the group of naturally occurring  $\alpha$ -amino acids, L-aspartic acid is a very important compound. However, the molecular structure had not previously been determined.

A few questions arise with respect to this structure:

- (1) Is there a planar carbon skeleton or is the skeleton non-planar as in L-asparagine?
- (2) Is the structure zwitterionic as in other  $\alpha$ -amino acids?
- (3) Is there evidence for an intramolecular hydrogen bond or are all the hydrogen bonds of the common intermolecular type? (In so far as we may speak of hydrogen bonds between charged groups.) The purpose of this study is to answer these questions and to present an accurate set of molecular parameters for the crystalline state.

### Experimental

The sample used was from Fluka A.G. Buchs S.G. (puriss.). Crystals were obtained by slow evaporation of an aqueous solution at room temperature.

The cell constants have been reported as (Bernal, 1931):  $a=15.1$ ,  $b=6.9$ ,  $c=5.1$  Å,  $\beta=96^\circ$ , space group  $P2_1$ ,  $Z=4$ . These data were roughly confirmed by oscillation photographs. Weissenberg photographs, however, showed very strange extinctions: for  $h$ =odd and  $l$ =even all reflexions were absent. Also, different crystals showed very big relative intensity differences; it appears that twinning occurs in different degrees. The geometric twinning condition fulfilled in this case is that the diagonal of the  $a$ - $c$  plane is equal to the  $a$  unit-cell dimension (both according to Bernal's cell dimensions). The twinning situation is shown in Fig. 1.

The common reciprocal axis of the two lattices is  $a^*$ , the double cell according to Bernal is shown as the reciprocal 'cell'  $ABCD$ . The extinctions are easily seen in this Figure. The conclusion is that the cell dimension  $a$  should be halved, consequently  $Z=2$  with only one molecule in the asymmetric unit. We tried to find an untwinned crystal, and a crystal that was nearly untwinned was found and was used throughout this structure determination.

As for  $l$  odd, the reflexions from the two lattices are seen separately and the degree of twinning can be measured from these reflexions. This was done on an  $h0l$  Weissenberg diagram with the only two of these reflexions which were strong enough to be seen in both

lattices (*i.e.*  $\bar{3}01$  and  $101$ ). The ratio of the  $F$ -values appeared to be 0.025.

From Fig. 1 it is seen that reflexions  $hkl$  from one lattice coincide with reflexions  $h+1/2, \bar{k}, \bar{l}$  for  $l$  even. For  $l$  even, the correction applied to the observed structure factors was:

$$F_{hkl} = F_{hkl} \text{ (observed)} - 0.025F_{h+1/2, \bar{k}, \bar{l}}.$$

The unit-cell dimensions were refined by least squares (van den Berg & Rutten-Keulemans, 1963) from 20 reflexions measured on a General Electric single-crystal orienter ( $2\theta$  ranging from  $83^\circ$  to  $149^\circ$ ) with the use of the Cu  $K\alpha_1$  maxima ( $\lambda = 1.5405 \text{ \AA}$ ).

The values found and their standard deviations were:

$$a = 7.617 \pm 0.001, b = 6.982 \pm 0.001, c = 5.142 \pm 0.001 \text{ \AA}, \\ \beta = 99.84 \pm 0.02^\circ.$$

From the systematic absence of  $0k0$  reflexions for  $k$  odd, the space group was determined to be  $P2_1$ . With two molecules in the unit cell the calculated density was  $1.650 \text{ g.cm}^{-3}$ ; the density found by flotation is  $1.645 \text{ g.cm}^{-3}$ .

With a General Electric single-crystal orienter equipped with a scintillation counter and discriminator, the integrated intensities of 638 independent reflexions with  $2\theta \leq 165^\circ$  were measured by means of Ni-filtered Cu radiation. The  $2\theta$ -scanning technique was used. The background (taken as the mean background of the left and right sides) was subtracted and the scanning range adapted to the width of the peaks, each reflexion being optimized with respect to the angular settings.

The data were corrected for Lorentz and polarization factors but absorption correction was not applied. The crystal was a block of  $0.1 \times 0.2 \times 0.3 \text{ mm}^3$ .

### Structure determination

With Wilson's (1942) method an overall temperature factor ( $B = 1.81 \text{ \AA}^2$ ) and the scaling factor were determined.

A three-dimensional sharpened Patterson synthesis was calculated, using the 602 non-zero coefficients, according to Jacobsen, Wunderlich & Lipscomb (1961):

$$|F|_{\text{obs}}^2 = \frac{1}{f_2} \left( \frac{1}{6} + \sin^2\theta/\lambda^2 \right) \exp(-4 \sin^2\theta/\lambda^2)$$

with

$$f_2 = \frac{1}{9} \left( \frac{4f_C^2}{Z_C^2} + \frac{4f_O^2}{Z_O^2} + \frac{f_N^2}{Z_N^2} \right).$$

The molecule could easily be recognized in this Patterson map; the ambiguities that remained were the position of the amino-group and the position of the molecule with respect to the screw axis. The Harker section left too many possible positions; some trial structures based on them did not refine.

It was decided to solve the structure in the centrosymmetric  $h0l$  projection, because it is apparent from the Patterson map that the molecule is arranged nearly parallel to the (010) plane. The symbolic sign procedure (Beurskens, 1963) was applied. It yielded 16 possible sets of 24 signs. The corresponding Fourier synthesis, however, could not be interpreted. We then applied the Minimum Residual method of molecular location (Bhuiya & Stanley, 1964). The 'known' molecule was translated through the cell and  $R$  was calculated at small intervals in two dimensions. The minimum  $R$  position, however, did not refine either.

A two-dimensional sharpened Patterson function was calculated with the use of 98  $h0l$  reflexions (see Fig. 2). A Patterson shift over an isolated intramolecular vector yielded the usual double solution which could be interpreted (see Fig. 3).

It is seen that an oxygen atom of one carboxyl group is located nearly on the origin of the projection, while the other carboxyl group is situated quite near another centre of symmetry. The + signs yielded by both the Minimum Residual method and the Patterson vector shift method are compatible only with the trivial solution (all + signs) of the symbolic sign procedure, and

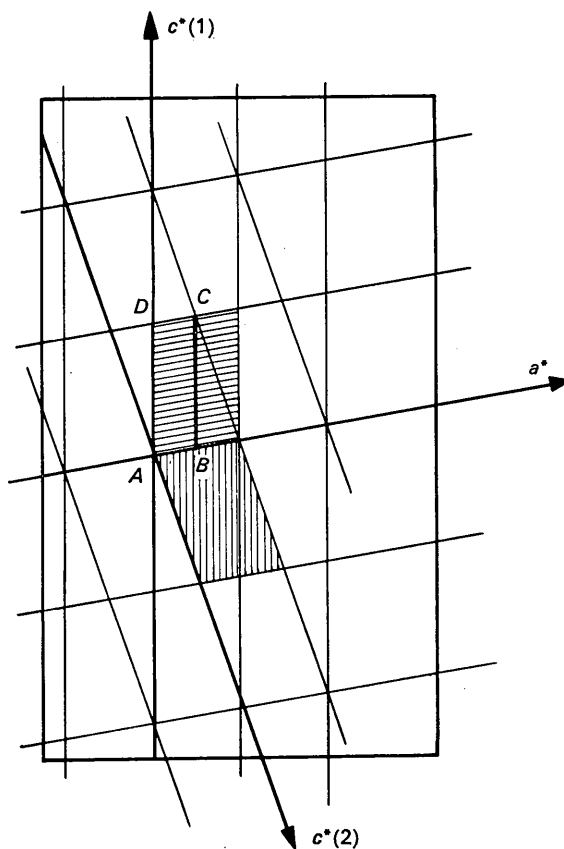


Fig. 1. Twinning situation in the reciprocal lattice of L-aspartic acid. Horizontal lines: primitive cell of one lattice, vertical lines: primitive cell of the second lattice. The 'double' reciprocal cell according to Bernal is seen as  $ABCD$ .

indeed, the true structure can be found from a Fourier synthesis with all 24 signs used in the symbolic sign procedure taken as positive.

Because of overlap and the too inaccurate model, direct refinement by least squares is not possible in the projection. After three cycles of structure factor calculations, Fourier synthesis and parameter improvement, the  $R$  value for the 50 strongest  $h0l$  reflexions was 0.23 and subsequent least-squares refinement lowered  $R$  to 0.18.

Approximate  $y$  parameters were calculated by taking into account expected bond lengths and bond angles.

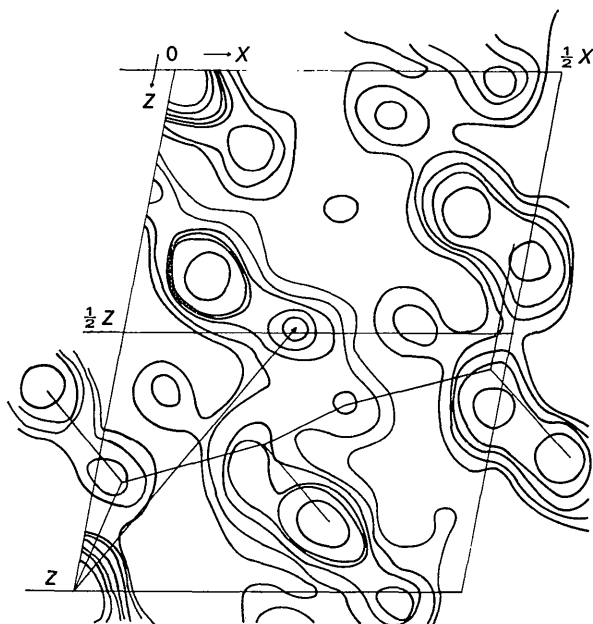


Fig. 2.  $h0l$ -sharpened Patterson function. Contours are on an arbitrary scale. The shift vector is drawn and the final molecular location is given.

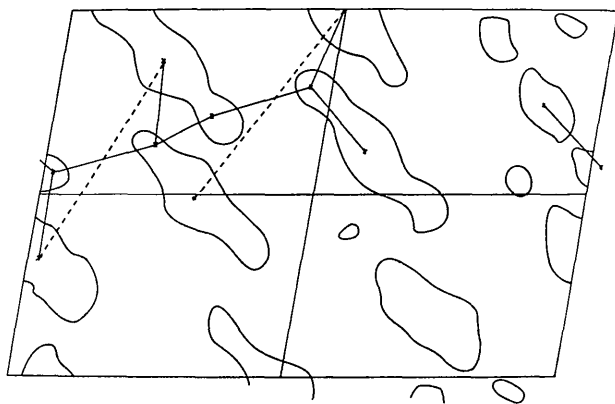


Fig. 3. Patterson vector shift in  $h0l$  projection. Contours are on an arbitrary scale. The shift vector is dashed. The final coordinates are given by crosses.

### Refinement of the structure

The structure was refined by least squares, using the block diagonal matrix program of Palm & Peterse (1964). The atomic form factors were taken from Moore's tables (1963).

Only the 602 non-zero observed reflexions were used; 36 very weak reflexions were only compared with the calculated structure factors but omitted in the refinement.

The heavy atom model was refined, with anisotropic thermal parameters, to  $R=0.068$ .

A difference Fourier synthesis revealed the positions of all the hydrogen atoms. With weight factors of 1.0 for all reflexions, refinement of all atomic positions and anisotropic thermal motion for the C and O atoms, lowered  $R$  to 0.0426. Isotropic temperature factors of H were kept constant with  $B=2.5 \text{ \AA}^2$ .

After this the weight scheme was changed. Following Killian (1967) the standard deviations of the observed structure factors were calculated, taking into account the  $L_p$  factor and the number of counts for intensity and background. However, the influence of the uncertainties in filter factors and the  $2\theta$ -angle (the latter arises from uncertainties in the cell dimensions and the angular settings) is of the same order of magnitude for many reflexions. The error in filter factors was estimated to be 1% (by repeated measurement) and the error in  $\theta$  as  $0.1^\circ$ . The standard deviations in  $|F|_{\text{obs}}$  were then calculated as:

$$\sigma|F|_{\text{obs}} = \left[ \left( \frac{|F|}{2P} \sqrt{T+B} \right)^2 + \left( \frac{|F|}{2} \cdot \frac{1}{100} \right)^2 + \left( 0.0017|F| \left\{ \frac{\cos 2\theta}{L_p} + \frac{\cos 2\theta}{\sin 2\theta} \right\} \right)^2 \right]^{1/2}$$

$T$ ,  $B$ ,  $P$  are the number of counts for (peak+background), background, and peak respectively, and  $L_p$  is the Lorentz-polarization factor. The weights are then  $W=1/\sigma^2|F|_o$ . The new weight scheme lowered  $R$  to 0.040 and the standard deviations decreased by 20%; but most important, the hydrogen positions of the amino group changed rather drastically (see Table 1), while the parameters of the heavier atoms changed less than  $0.001 \text{ \AA}$ . No extinction correction was applied, only three reflexions clearly show some extinction ( $\bar{1}20$ ,  $\bar{3}01$ ,  $011$ ) (see Table 2) but in the refinement they have very low weight factors. (Omission would lower  $R$  to 3.85%.)

Table 1. N-H distances with two weight schemes: in column 2 with all weights 1.0, column 3 with the scheme described in the text

Bond	$R=0.0426$	$R=0.0401$
N(9)-H(13)	0.587 Å	0.879 Å
N(9)-H(14)	1.109	1.013
N(9)-H(15)	1.048	1.088

Table 2. Observed and calculated structure factors

h	k	l	FO	FC	h	k	l	FO	FC	h	k	l	FO	FC	h	k	l	FO	FC
-7	0	0	1.3	1.3	3	4	1	7.4	7.7	-2	0	2	3.3	3.0	2	1	4	17.0	17.5
-8	0	0	5.0	4.9	0	0	0	0.0	0.0	-1	0	2	2.9	2.6	3	1	4	2.5	2.7
-9	0	0	9.2	9.2	0	0	0	3.6	3.6	0	0	0	0.0	0.0	0	0	0	5.1	5.2
-9	0	0	2.9	3.1	0	0	0	2.0	2.2	1	0	0	0.0	0.5	0	0	0	3.5	3.2
-4	0	0	16.3	16.4	-8	0	1	1.2	1.2	3	0	0	3.9	4.0	0	0	0	3.9	4.2
-3	0	0	14.9	14.8	-3	0	1	3.4	4.4	4	0	0	4.9	5.2	0	2	4	2.9	2.6
-2	0	0	22.0	23.6	-9	0	0	1.9	2.2	5	0	0	4.9	5.1	-7	0	0	4.4	4.0
-1	0	0	6.1	6.3	-4	0	0	2.0	2.9	-5	0	2	3.2	2.9	-8	0	0	3.7	3.7
0	0	0	1.6	1.6	-4	0	0	3.4	4.1	-5	0	0	3.5	3.7	-5	0	0	7.4	7.4
0	1	0	6.1	6.3	-2	0	0	3.6	3.9	-3	0	0	4.3	4.2	-4	0	0	11.7	12.0
0	1	0	7.3	7.3	-1	0	0	6.9	7.2	-2	0	0	2.7	2.8	-3	0	0	6.3	6.4
0	1	0	13.2	13.0	0	0	0	6.1	6.3	-1	0	0	1.4	1.9	-1	0	0	4.7	4.7
0	1	0	15.2	15.0	0	0	0	6.8	6.3	0	0	0	1.4	1.9	-1	0	0	7.9	7.8
0	1	0	15.2	15.0	1	0	0	4.0	3.8	1	0	0	4.4	4.4	0	0	0	6.0	6.0
0	1	0	9.7	10.0	2	0	0	4.0	3.8	1	0	0	2.9	2.9	0	0	0	6.1	6.1
0	1	0	7.7	7.7	3	0	0	6.0	5.9	2	0	0	2.9	2.9	1	0	0	1.2	1.2
0	1	0	15.2	15.0	4	0	0	12.7	12.7	3	0	0	1.4	1.1	3	0	0	2.6	2.6
0	1	0	13.1	13.7	5	0	0	2.1	2.2	4	0	0	1.1	1.3	4	0	0	1.5	1.6
0	1	0	19.0	12.2	6	0	0	2.3	2.3	-3	0	2	1.1	1.3	0	0	0	1.3	1.3
0	1	0	4.4	8.3	7	0	0	12.7	12.7	-2	0	0	1.3	1.3	0	0	0	1.9	2.4
0	2	0	3.3	3.2	-7	0	1	5.7	5.7	-1	0	2	1.2	1.4	0	0	0	2.2	2.3
0	2	0	7.8	7.8	-6	0	1	2.4	2.1	0	0	2	1.9	3.4	-7	0	4	7.1	6.9
0	2	0	6.0	6.0	-5	0	1	4.0	4.0	1	0	2	2.7	2.6	-8	0	4	5.6	5.6
0	2	0	14.0	14.4	-4	0	1	6.7	6.0	-6	0	3	1.9	1.8	-9	0	4	3.4	3.8
0	2	0	9.1	8.9	-3	0	1	8.0	8.6	-6	0	4	4.9	5.7	-4	0	4	1.7	1.9
0	2	0	15.5	16.1	-2	0	1	6.0	5.8	-5	0	4	2.7	3.0	-3	0	4	8.1	8.0
0	2	0	23.7	24.4	-1	0	1	6.7	6.0	-4	0	4	1.6	1.2	-2	0	4	2.1	2.4
0	2	0	39.5	34.7	0	0	1	1.5	1.8	-3	0	3	3.9	3.9	-1	0	4	3.9	4.1
0	2	0	34.5	34.9	0	0	1	6.7	6.8	-2	0	3	28.2	28.2	0	0	0	6.1	6.2
0	2	0	5.3	5.4	2	0	2	2.7	2.7	-1	0	3	1.2	1.4	0	0	0	7.9	7.2
0	2	0	1.8	1.9	3	0	3	1.8	1.7	0	0	3	13.9	12.7	2	0	0	7.0	7.8
0	2	0	12.0	12.0	4	0	4	1.3	1.8	1	0	3	5.3	5.2	3	0	0	7.0	6.9
0	2	0	8.9	8.9	5	0	5	2.0	2.0	2	0	3	2.0	2.0	4	0	0	6.0	6.7
0	2	0	6.5	6.4	-6	0	7	1.4	1.5	3	0	3	2.9	2.5	-5	0	4	9.0	2.9
0	2	0	16.5	16.9	-7	0	1	3.9	3.9	4	0	4	1.2	1.6	-7	0	4	4.3	4.2
0	2	0	2.2	2.2	-8	0	2	2.9	2.9	-5	0	4	4.2	4.0	-6	0	4	3.1	3.2
0	2	0	18.5	18.9	-9	0	2	2.9	2.9	-6	0	4	4.3	4.3	-5	0	4	2.9	2.9
0	2	0	4.3	4.2	-2	0	2	1.6	2.4	-9	1	3	1.4	1.5	-4	0	4	7.9	8.1
0	2	0	8.0	8.9	-1	0	2	9.5	9.3	-7	0	3	3.1	3.1	-3	0	4	3.0	3.3
0	2	0	6.4	6.8	0	0	2	2.4	2.3	-6	0	3	1.2	1.9	-1	0	4	4.4	4.9
0	2	0	5.4	5.3	1	0	2	3.1	2.9	-5	0	3	15.1	14.2	0	0	0	4.9	4.7
0	2	0	12.2	11.9	2	0	2	4.1	4.1	-4	0	3	11.3	11.3	1	0	0	6.7	6.7
0	2	0	15.2	15.2	3	0	1	9.1	9.0	-3	0	3	11.3	11.3	2	0	0	1.4	1.6
0	2	0	15.4	15.7	-4	0	1	1.9	1.7	-2	0	3	1.3	1.3	4	0	0	1.1	1.5
0	2	0	5.1	5.1	-5	0	1	9.8	9.7	0	0	3	7.1	7.7	0	0	0	7.9	7.2
0	2	0	8.4	8.4	-1	0	1	3.7	3.8	1	0	3	9.7	9.2	-6	0	4	3.7	3.7
0	2	0	4.3	4.3	0	0	1	8.2	7.8	2	0	3	2.3	2.0	-5	0	4	5.7	5.8
0	2	0	4.3	4.4	1	0	1	7.2	2.3	3	0	3	1.4	1.0	-3	0	4	4.6	4.6
0	2	0	4.4	4.3	2	0	2	2.4	2.3	4	0	3	6.0	6.3	-2	0	4	4.6	5.2
0	2	0	6.2	6.2	3	0	2	10.2	10.4	5	0	3	10.1	10.9	-1	0	0	3.2	3.4
0	2	0	7.5	7.7	-9	0	2	5.1	5.2	6	0	3	4.3	4.3	0	0	0	3.9	4.0
0	2	0	3.8	3.7	-8	0	3	3.8	3.9	7	0	3	1.3	1.5	1	0	0	7.8	7.7
0	2	0	3.3	3.4	-7	0	3	3.4	3.4	-6	0	3	6.8	6.5	2	0	0	4.9	4.7
0	2	0	3.8	3.8	-6	0	3	3.6	3.6	-5	0	3	3.9	3.9	3	0	0	3.1	4.2
0	2	0	4.0	4.2	-5	0	3	3.1	4.0	-4	0	3	2.0	2.1	4	0	0	2.2	2.4
0	2	0	6.5	6.4	-4	0	3	2.6	2.8	-3	0	3	3.9	4.0	-5	0	4	3.9	3.6
0	2	0	11.9	12.1	-3	0	3	11.6	12.1	-5	0	3	10.0	10.6	-4	0	4	2.2	2.3
0	2	0	4.4	4.3	-2	0	3	2.2	2.4	-4	0	3	3.2	3.3	-3	0	4	2.0	2.1
0	2	0	6.5	6.3	-1	0	3	8.6	8.2	-3	0	3	3.2	3.5	-2	0	4	3.0	3.2
0	2	0	8.5	8.8	0	0	3	14.8	14.0	-2	0	3	9.0	8.4	-1	0	4	1.8	1.9
0	2	0	5.3	5.4	1	0	3	11.2	10.9	-1	0	3	11.8	10.9	0	0	0	1.1	1.4
0	2	0	2.8	2.9	2	0	3	8.5	8.6	0	0	3	12.0	12.0	1	0	0	1.0	1.0
0	2	0	14.1	14.6	3	0	3	11.6	11.7	1	0	3	7.4	7.5	2	0	0	1.9	2.1
0	2	0	4.9	4.9	4	0	3	11.5	11.3	2	0	3	10.1	11.1	3	0	0	3.1	3.9
0	2	0	1.6	1.6	5	0	3	2.4	2.4	3	0	3	2.1	1.4	-2	0	4	3.7	4.0
0	2	0	3.3	3.3	6	0	3	9.0	9.3	4	0	3	5.4	5.6	-1	0	4	3.8	4.1
0	2	0	5.0	5.0	7	0	3	1.6	1.5	5	0	3	4.2	4.3	0	0	0	1.6	1.9
0	2	0	8.3	8.5	-9	1	2	4.0	4.0	-6	0	3	3.7	3.5	-5	0	4	5.0	5.5
0	2	0	12.7	13.0	-8	0	2	9.7	9.6	-7	0	3	3.6	3.9	-4	0	4	3.4	3.5
0	2	0	9.4	9.6	-7	0	2	4.2	4.2	-6	0	3	4.0	4.1	-3	0	4	3.1	4.7
0	2	0	45.3	49.2	-6	0	2	8.8	8.9	-5	0	3	6.9	7.3	-2	0	4	3.3	3.0
0	2	0	3.4	3.7	-5	0	2	1.7	1.9	-4	0	3	15.7	16.7	-1	0	4	11.0	11.3
0	2	0	4.0	4.0	-4	0	2	9.0	9.0	-3	0	3	4.9	4.9	0	0	0	3.0	3.0
0	2	0	13.6	11.5	-3	0	2	3.4	4.0	-1	0	3	7.9	7.9	1	0	0	2.3	2.3
0	2	0	29.9	30.3	-2	0	2	9.1	8.9	0	0	3	9.9	9.6	2	0	0	7.7	7.7
0	2	0	1.6	1.6	-1	0	2	7.9	7.9	1	0	3	3.1	3.3	3	0	0	4.8	4.8
0	2	0	8.2	8.2	0	0	2	11.9	11.6	2	0	3	8.5	8.5	4	0	0	3.1	3.0
0	2	0	13.0	13.5	1	0	2	12.9	12.0	3	0	3	3.9	3.8	-7	1	3	4.3	4.0
0	2	0	4.1	4.4	2	0	2	16.4	17.5	4	0	3	3.4	3.6	-6	0	4	3.4	3.3
0	2	0	14.5	14.9	3	0	2	8.1	7.7	5	0	3	4.0	4.0	-5	0	4	1.9	1.9
0	2	0	1.7	1.8	4	0	2	6.9	6.6	6	0	3	4.0	3.9	-4	0	4	3.8	3.8
0	2	0	3.9	3.9	5	0	2	6.0	6.3	7	0	3	9.1	9.3	-3	0	4	7.3	7.3
0	2	0	3.8	3.8	6	0	2	4.0	4.5	8	0	3	1.4	1.4	-2	0	4	4.3	4.5
0	2	0	5.1	5.0	7	0	2	4.7	4.9	-7	0	3	5.1	5.0	-1	0	4	6.0	6.0
0	2	0	9.1	9.0	8	0	2	1.2	1.4	-6	0	3	5.4	5.4	0	0	0	5.9	5.7

Table 3. Final fractional atomic coordinates, their standard deviations and thermal parameters

The  $U_{ij}$  coefficients are given by the expression for the temperature factor:

$$\exp [-(h^2U_{11}+k^2U_{22}+l^2U_{33}+2hkU_{12}+2klU_{23}+2lhU_{31})]$$

	<i>x</i>	<i>y</i>	<i>z</i>	Average standard deviation	$U_{11}$	$U_{22}$	$U_{33}$	$2U_{12}$	$2U_{23}$	$2U_{31}$
O(1)	+0.3905	+0.0334	+0.2559	0.0024 Å	0.0046	0.0206	0.0203	-0.0058	-0.0019	0.0053
O(2)	+0.5166	+0.0194	+0.6790	0.0024	0.0091	0.0164	0.0167	-0.0074	0.0015	0.0101
O(3)	+0.9983	-0.1622	+0.0168	0.0037	0.0082	0.0350	0.0466	-0.0079	-0.0482	0.0175
O(4)	+1.0802	+0.0007	+0.3875	0.0026	0.0063	0.0145	0.0278	-0.0043	-0.0072	0.0099
C(5)	+0.5203	+0.0450	+0.4410	0.0029	0.0043	0.0078	0.0197	-0.0016	-0.0039	0.0073
C(6)	+0.7035	+0.0866	+0.3636	0.0028	0.0042	0.0081	0.0164	-0.0021	0.0032	0.0052
C(7)	+0.7805	-0.1018	+0.2878	0.0034	0.0055	0.0090	0.0334	-0.0001	-0.0005	0.0102
C(8)	+0.9639	-0.0890	+0.2136	0.0032	0.0046	0.0095	0.0283	+0.0015	-0.0009	0.0069
N(9)	+0.6805	+0.2250	+0.1384	0.0026	0.0054	0.0093	0.0200	0.0005	0.0069	0.0081
H(10)	+1.203	+0.009	+0.326	0.052	<i>B</i> isotropic = 2.5 Å <sup>2</sup>					
H(11)	+0.782	-0.181	+0.446	0.051						
H(12)	+0.711	-0.164	+0.154	0.051						
H(13)	+0.635	+0.165	-0.008	0.050						
H(14)	+0.608	+0.331	+0.202	0.051						
H(15)	+0.809	+0.269	+0.095	0.050						
H(16)	+0.784	+0.150	+0.521	0.052						

Table 4. Intermolecular 'hydrogen bonds' in the structure of L-aspartic acid

Donor	Acceptor	Distance	Angle <i>d</i> -H... <i>a</i>
N(9)-H(13)	O(2) on <i>x</i> , <i>y</i> , <i>z</i> - 1	2.862 Å	174.7°
N(9)-H(14)	O(2) on 1 - <i>x</i> , <i>y</i> + ½, 1 - <i>z</i>	2.800	178.8
N(9)-H(15)	O(3) on 2 - <i>x</i> , <i>y</i> + ½, - <i>z</i>	2.813	172.6
O(4)-H(10)	O(1) on <i>x</i> + 1, <i>y</i> , <i>z</i>	2.577	175.3

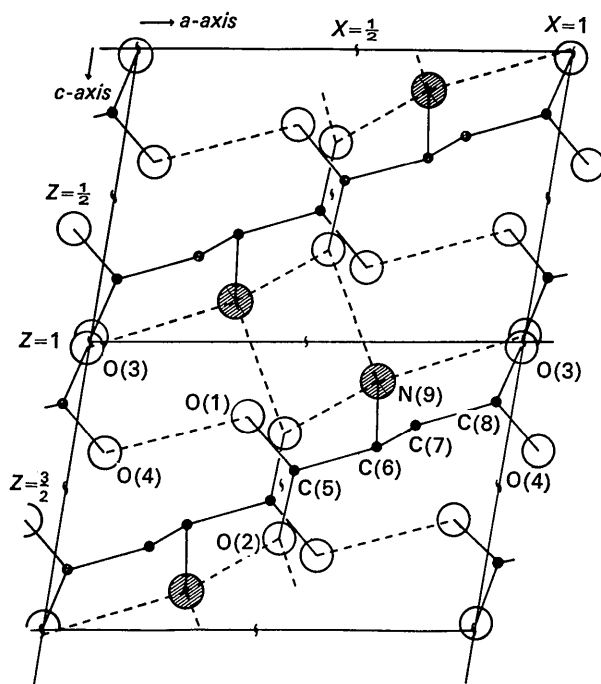


Fig. 4. L-Aspartic acid crystal structure seen along the screw axis. Hydrogen atoms are omitted. Dotted lines represent hydrogen bonds.

The final fractional atomic coordinates, their averaged standard deviations and thermal parameters are given in Table 3; the observed and calculated structure factors are given in Table 2. A final difference Fourier synthesis did not show peaks above the level of 0.15 e. Å<sup>-3</sup>. Uncertainties in the twinning correction are not important as the heavy atom parameters change only by some 0.0005 Å when the correction is wholly omitted.

### The molecular structure

Bond lengths and bond angles were calculated without correction for anisotropic motion; the average standard deviations are 0.004 Å and 0.25° respectively, except for bonds involving hydrogen atoms, in which case these values are 0.05 Å and 2° for angles of the type HXX and 4° for angles HXH. See Fig. 5.

In L-aspartic acid the ionized and the non-ionized carboxyl group can clearly be distinguished. In the ionized carboxyl group the C-O distances are 1.242 and 1.252 Å, whereas in the non-ionized group distances of 1.202 and 1.306 Å are found. These values are very similar to those found in aminomalonic acid (Kanters, Kroon, Beurskens & Vliegthart, 1966).

The angle between COO<sup>-</sup> and COOH planes is 34.8°. The intramolecular distance N(9)-O(1) of 2.737 Å is very short, even shorter than the inter-

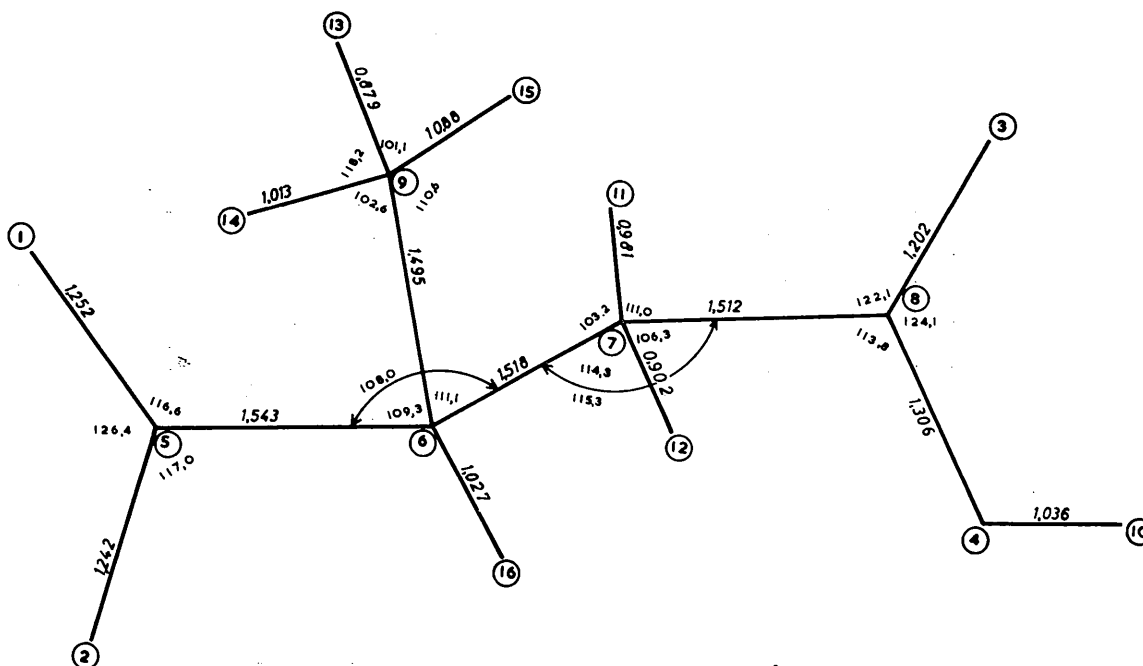


Fig. 5. The L-aspartic molecule in the crystal. Distances in Å, angles in degrees.

molecular hydrogen bonds (Table 4) from N to O. In L-asparagine (de Vries, 1963) the corresponding distance is still shorter (2.66 Å), but in that molecule the N atom is situated nearly in the C(6)–C(5)–O(1)–O(2) plane, while in our case the C–N bond makes an angle of 33.9° with this plane. In aminomalonic acid this angle is only 9.1°.

The carbon chain is nearly planar, the average deviation from planarity being less than 0.01 Å. The same situation is found in glycyl-L-asparagine (Pasternak, Katz & Corey, 1954), but in L-asparagine (de Vries, 1963) the other possible 'ethane' conformation around the bond C(7)–C(8) is found for the carbon skeleton, with a non-planar carbon chain. The differences in the carbon–carbon bond lengths are significant, as in aminomalonic acid the C–C bond, in which the carbon atom of the non-ionized carboxyl group participates, is the shorter one.

As in other amino acids in the crystalline state we find an 'ethane' conformation around the carbon–nitrogen bond.

### The crystal structure

For a description of the crystal structure we shall consider the (010) projection (Fig. 4). We can formally distinguish two 'layers' of L-aspartic acid molecules; one molecular 'layer' is transformed into the second by a screw axis. The two 'layers' are connected by hydrogen bonds (between charged atoms) in which the N atom is involved. In one 'layer' the molecules are linked together in zigzag chains, and the chains are also connected *via* the N-hydrogen bonds. For the hydrogen bonds see Table 4.

O(2) is involved twice in hydrogen bonding, while O(1) and O(4) are used for the O–H–O bond in the zigzag chain and O(3) for another O–H–N hydrogen bond, a total of four hydrogen bonds per molecule. There is no intramolecular hydrogen bond. The rigid system of hydrogen bonding fits in with the low thermal parameters (Table 3).

We are greatly indebted to Mr J. B. Hulscher for taking the Weissenberg photographs.

### References

- BERG, J. M. VAN DEN, & RUTTEN-KEULEMANS, E. W. M. (1963). *Algol Program for the Calculation of Cell Dimensions from Theta Angles*.
- BERNAL, J. D. (1931). *Z. Kristallogr.* **A78**, 363.
- BHUTYA, A. K. & STANLEY, E. (1964). *Acta Cryst.* **17**, 746. (Algol Program written by T. C. van Soest, this Laboratory).
- BEURSKENS, P. T. (1963). *Technical Report on Sign Correlation by the Sayre Equation*. The Crystallography Lab., Univ. of Pittsburgh, Pittsburgh, Pa.
- JACOBSEN, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). *Acta Cryst.* **14**, 598.
- KANTERS, J. A., KROON, J., BEURSKENS, P. T. & VLIENGENTHART, J. A. (1966). *Acta Cryst.* **21**, 990.
- KILLEAN, R. C. G. (1967). *Acta Cryst.* **23**, 54.
- MOORE, F. H. (1963). *Acta Cryst.* **16**, 1169.
- PALM, J. H. & PETERSE, W. J. A. M. (1964). *General Structure Factors and Least-Squares program in Algol for the TR-4 Computer (Version for EL X-8 computer)*.
- PASTERNAK, R. A., KATZ, L. & COREY, R. B. (1954). *Acta Cryst.* **7**, 225.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151.
- VRIES, A. DE (1963). Thesis, Rijksuniversiteit Utrecht, The Netherlands (in English).