

## The Crystal Structure of DL-Glutamic Acid Hydrochloride

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DL-Glutamic acid hydrochloride crystallizes in the orthorhombic space group  $P2_12_12_1$  with  $a=5.16$ ,  $b=11.80$ ,  $c=13.30$  Å. There are four molecules in the unit cell. The bond lengths along the carbon chain of the molecule show a systematic variation which is thought to be significant. An extensive system of hydrogen bonding produces a very compact molecular arrangement with several rather short van der Waals contact distances.

### Introduction

For some years past the problem of protein structure has been approached by means of detailed X-ray analyses of the individual amino acids which constitute the polypeptide chains of the proteins. Much information has already appeared concerning not only the dimensions and configurations of the amino-acid molecules, but also the nature and strength of the forces which bind them together. This has been used first to derive dimensions for the backbone of the polypeptide chain (Corey, 1940; Corey & Donohue, 1950) and more recently to support proposed model structures of the proteins themselves (Pauling & Corey, 1951). The importance of future work on amino acids now lies in the elucidation of the detailed configuration of the *R* groups associated with the polypeptide chains. The present paper describes the crystal structure of the hydrochloride of glutamic acid, a dicarboxylic amino acid which is a significant constituent of such proteins as insulin, edestin,  $\beta$ -lactoglobulin, ovalbumin, myosin and tropomyosin (Tristram, 1949).

### Experimental

Crystals of DL-glutamic acid hydrochloride were obtained by dissolving the pure DL-acid in excess 20% hydrochloric acid and allowing the solution to evaporate slowly at 40° C. The crystals were large and well-formed, but deliquesced on exposure to air: they were therefore coated with a thin film of cellulose acetate before X-ray examination.

The cell dimensions were determined from zero-level photographs taken on a Weissenberg X-ray camera whose radius was known accurately, and have the values\*

$$a = 5.16, \quad b = 11.80, \quad c = 13.30 \text{ Å}, \quad \pm 0.2\%$$

\* These dimensions differ slightly from those reported earlier (Dawson & Mathieson, 1951) which were obtained from oscillation photographs about the three axes.

Systematic absences in the  $h00$ ,  $0k0$  and  $00l$  reflexions indicated that the space group was  $P2_12_12_1$ . The density, measured by flotation in a chloroform-bromoform mixture, was 1.52 g.cm.<sup>-3</sup>, giving four molecules (calculated 4.04) of  $C_5H_9O_4N.HCl$  in the unit cell. Cu  $K\alpha$  radiation ( $\lambda = 1.542$  Å) was used throughout the investigation.

Intensity data for the  $h0l$  and  $0kl$  reflexions were recorded on zero-level moving films about the  $a$  and  $b$  axes by the multiple-film technique and were measured by the eye-estimation method. Absorption was minimized, but not corrected for, by the use of small crystals of almost uniform cross-section. The intensity data were made as complete as possible by exposure times of 100 hr. to record the weak reflexions. Corrections for Lorentz and polarization factors were applied in the usual way and the resultant structure amplitudes were eventually placed on an absolute basis by scaling against the calculated values. For structure amplitude calculations the scattering curves for  $Cl^-$ ,  $O^-$ ,  $N$  and  $C$  given in *Internationale Tabellen* were corrected by a temperature factor which was obtained by plotting the ratio  $\Sigma|F_o| \div \Sigma|F_c|$  against  $\sin \theta$  in the ranges of  $\sin \theta = 0-0.2$ ,  $0.2-0.4$ , etc. to 1. It was found that the Debye-Waller factors  $B = 2.6 \times 10^{-16}$  and  $2.45 \times 10^{-16}$  cm.<sup>2</sup> gave the best agreement with the  $0kl$  and  $h0l$  structure amplitudes respectively.

All Fourier summations were made with three-figure Beevers-Lipson strips at 6° intervals along the  $b$  and  $c$  axes and at 12° intervals along the  $a$  axis. The electron-density maps were drawn from contour values obtained from interpolated sections.

### Structure determination

#### *The a-axis projection*

The Patterson projection along the  $a$  axis (Fig. 1) was computed in the normal manner from the  $0kl$  intensity data. For the space group  $P2_12_12_1$ , following the convention used in *Internationale Tabellen*, an atom situated at any point  $(y, z)$  produces double vector peaks at the positions  $(2y, \frac{1}{2})$  and  $(\frac{1}{2}, \frac{1}{2}-2z)$

and single peaks at the positions  $(\frac{1}{2}-2y, \pm 2z)$ . The peaks *A*, *B* and *C*, *D* on the lines  $y = \frac{1}{2}b$  and  $z = \frac{1}{2}c$  respectively (Fig. 1) were therefore possible doubled Cl-Cl vectors.

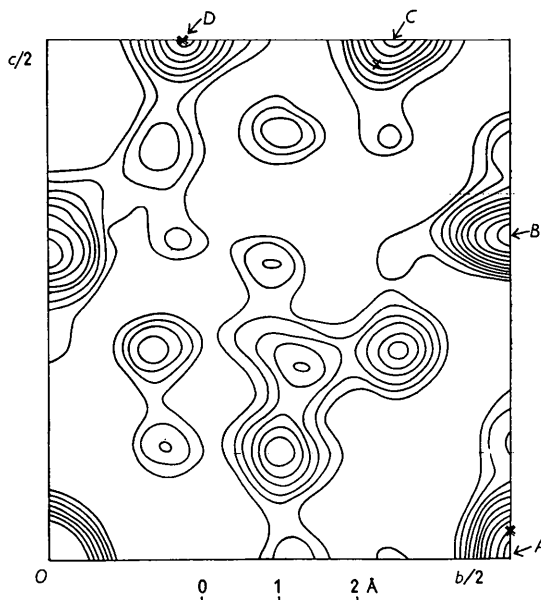


Fig. 1. Patterson projection on (100). Contours at equal arbitrary intervals.

Computation of the *a*-axis Patterson projection of glutamic acid hydrobromide, which is isomorphous with the hydrochloride (Dawson & Mathieson, 1951), showed that peaks *A*, *C* and *D* were Cl-Cl vectors. The positions of these peaks indicated that the *z*-parameter of the chlorine atom was approximately  $\frac{1}{2}c$ . The single vectors  $(\frac{1}{2}-2y, 2z)$  and  $(\frac{1}{2}-2y, -2z)$  therefore overlapped to produce a peak of the same height as the doubled vector peak  $(2y, \frac{1}{2})$ . To determine the *y* parameter it was necessary to decide which of *C* and *D* represented the single vectors. If the *z* parameter were not exactly  $\frac{1}{2}c$  then the single vectors would not coincide exactly, and their composite peak would be elongated in the *z* direction. The doubled peak, on the other hand, would show no such extension because it was centred on  $z = \frac{1}{2}$  by symmetry conditions. Peak *D* was therefore the true double peak  $(2y, \frac{1}{2})$  and peak *C* the composite peak. The vectors produced by the proposed chlorine arrangement are marked in Fig. 1.

It was not possible to fix the phases of the majority of reflexions from the phases of the contributions of the chlorine atom owing to its proximity to a symmetry axis: for reflexions with  $(k+l)$  odd, chlorine contributed strongly; but for reflexions with  $(k+l)$  even, the contribution was weak although increasing with increasing *l*. The first Fourier synthesis was therefore restricted mainly to terms of the type  $(k+l)$  odd. The omission of many terms of the type  $(k+l)$  even pro-

duced several spurious peaks but the layout of the glutamic acid molecule was shown quite clearly.

The approximate co-ordinates were refined in the normal manner by successive Fourier syntheses, and

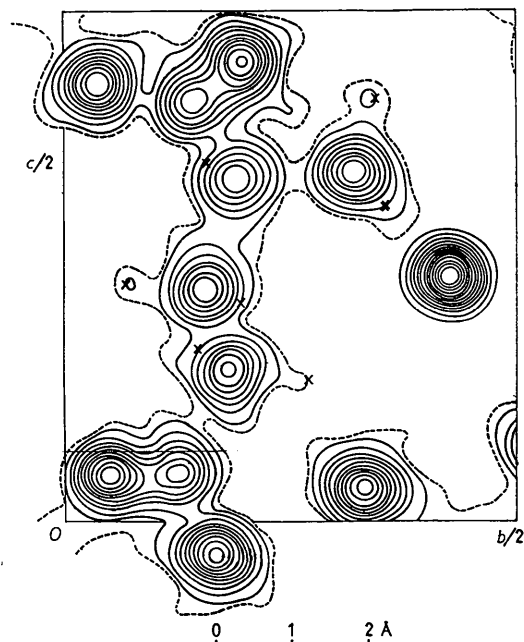


Fig. 2. Electron density projected on (100). Broken line represents  $1\frac{1}{2} e.\text{\AA}^{-2}$ . Full lines represent 2, 3, 4 etc.  $e.\text{\AA}^{-2}$  except for chlorine atom where interval is  $2 e.\text{\AA}^{-2}$ .

the parameters obtained from the final refinement were corrected for series-termination errors by the 'back-correction' method (Booth, 1946). The contributions of all hydrogen atoms except those associated with the two carboxyl groups of the molecule were included for the planes of  $\sin \theta < 0.5$ , and the final value of the discrepancy factor  $R = \frac{\sum |F_o - F_c|}{\sum |F_o|} \times 100$  was 10.6%. The co-ordinates of the hydrogen atoms were obtained by assuming carbon-hydrogen distances of 1.09 Å, nitrogen-hydrogen distances of 1.01 Å and a tetrahedral distribution of the valency bonds.

The final projection of the electron density along the *a* axis (Fig. 2) was computed from a Fourier series which included the calculated values of the non-observed reflexions. The postulated hydrogen positions are shown in Fig. 2 and are in good agreement with the electron-density map. The arrangement of the atoms in the *a*-axis projection is shown in Fig. 4.

#### The *b*-axis projection

The Patterson projection along the *b* axis gave two possible *x* parameters for the chlorine atom for both of which the vector distribution was the same. The two possibilities were tested by structure-factor calculations which included not only the chlorine atom but also the glutamic acid molecule. The approximate *x* para-

meters of the atoms in the latter were obtained as follows: first the layout of the molecule was calculated from the known  $y$  and  $z$  parameters by assuming standard bond lengths and then the unit was oriented so that its nitrogen atom was separated from its related chlorine atom by a distance of  $\frac{1}{2}a$  in the  $x$  direction. The correct positions of the chlorine atom and its associated molecular arrangement were then refined by successive Fourier syntheses. The final electron-density projection (Fig. 3) included the cal-

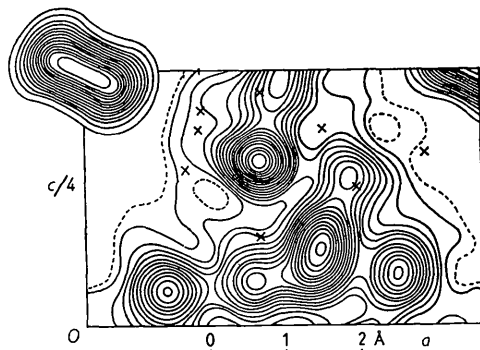


Fig. 3. Electron density projected on (010). Contours as in Fig. 2.

culated values of the non-observed reflexions, as in the  $a$ -axis projection. The structure along the  $b$  axis is illustrated in Fig. 5.

Despite the overlap of different molecules in this projection it was possible to use the Fourier method to locate all atoms except  $C_1$ ,  $O_1$  and  $C_5$  (Figs. 3 and 5) and to correct their positions for series-termination errors. The three unresolved atoms were first located by considering the shape of their composite peak in terms of their accurately known  $z$  parameters. The  $x$  parameters so obtained were tested in structure-amplitude calculations and varied so as to reduce the discrepancy factor as far as possible. The final parameters showed that the groups  $C_2C_1O_1O_2$  and  $C_4C_5O_3O_4$  were very nearly planar. Since the accurate investigations of N-acetylglycine (Carpenter & Donohue, 1950), L<sub>s</sub>-threonine (Shoemaker *et al.*, 1950) and DL-alanine (Donohue, 1950) have demonstrated the planarity of such groups in amino acids it was assumed that the slight departure from planarity observed here resulted from inaccuracies in the  $x$  parameters of  $C_1$ ,  $C_5$  and  $O_1$  determined by the trial-and-error method described above. The parameter of  $C_5$  was therefore refined by calculating the position required for it to lie in the plane defined by  $C_4$ ,  $O_3$  and  $O_4$ . For the group  $C_2C_1O_1O_2$  this procedure could not be used directly since, with the  $x$  parameters of two atoms in doubt, it was not possible to calculate the plane defining the group. However, the  $x$  parameters obtained earlier had shown that the asymmetry of bond lengths and bond angles in the two carboxyl groups was almost the same. It

was therefore a simple matter to find, by structure-factor calculations, the best positions for  $C_1$  and  $O_1$  such that the group  $C_2C_1O_1O_2$  was planar. It is obvious that the two assumptions made in this refinement, first that parameters determined by Fourier methods are free from error, and secondly that the degree of asymmetry in the two carboxyl groups is the same, are not completely justified. However, the reduction in the discrepancy factor obtained with the new parameters for  $C_1$ ,  $C_5$  and  $O_1$  indicated that a further improvement in the location of these atoms had been achieved. Inclusion of the hydrogen contributions for all planes of  $\sin \theta < 0.5$  gave a further reduction, and the final  $R$  value was 13.3%. The postulated hydrogen positions are shown in Fig. 3.

The final atomic co-ordinates, relative to the origin given in *Internationale Tabellen*, are listed in Table 1.

Table 1. Final atomic co-ordinates

	$x/a$	$y/b$	$z/c$
$C_1$	0.379	0.144	0.410
$C_2$	0.562	0.195	0.334
$C_3$	0.477	0.157	0.227
$C_4$	0.669	0.183	0.145
$C_5$	0.580	0.126	0.047
$O_1$	0.422	0.036	0.428
$O_2$	0.209	0.198	0.451
$O_3$	0.425	0.051	0.044
$O_4$	0.701	0.168	-0.032
N	0.560	0.323	0.341
Cl	0.060	0.427	0.238

The observed and calculated structure amplitudes of the  $F0kl$ 's and  $Fh0l$ 's are given in Table 2. It is important to note that the phases have been calculated relative to the centrosymmetrical origins  $P$  and  $Q$  of Figs. 4 and 5 respectively.

### Discussion

The interatomic bond lengths and bond angles found in the glutamic acid molecule are given in Table 3.

In view of the good agreement obtained in structure-factor calculations it is considered unlikely that any bond length is in error by more than  $\pm 0.03$  Å or any bond angle by more than  $\pm 3^\circ$ .

The planarity of the groups  $C_2C_1O_1O_2$  and  $C_4C_5O_3O_4$  has already been mentioned in describing the method used for determining the  $x$  parameters of  $C_1$ ,  $C_5$  and  $O_2$ . The asymmetry of the carboxyl groups about the  $C_1-C_2$  and  $C_4-C_5$  bonds is similar to that found in DL-alanine,  $\beta$ -glycylglycine (Hughes & Moore, 1949) and N-acetylglycine. The shorter bond lengths  $C_1-O_2 = 1.21$  Å and  $C_5-O_3 = 1.20$  Å are close to the value of 1.19 Å proposed by Goldschmidt & Llewellyn (1950) for a pure double bond, which suggests that these bonds possess considerable double-bond character. However the longer bond lengths  $C_1-O_1 = 1.31$  Å and  $C_5-O_4 = 1.32$  Å are much shorter than the sum of the single-bond radii, 1.43 Å (Pauling, 1940),

Table 2. Comparison of observed and calculated structure amplitudes

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
000		96	406	< 1	-0.5	028	2	-2
200	9.5	12	407	6.5	6.5	029	5	-5
400	< 1	-0.4	408	1.5	1	0,2,10	< 0.5	0.2
600	2.5	-3.5	409	2.5	3	0,2,11	< 0.5	0.3
002	1.5	-1.5	4,0,10	1.5	0.5	0,2,12	1.5	-1.5
004	12.5	12.5	4,0,11	1.5	1.5	0,2,13	4	-3.5
006	10	9.5	4,0,12	< 1	-0.7	0,2,14	1	0.5
008	2	-2.5	4,0,13	1.5	1.5	0,2,15	< 0.5	0.5
0,0,10	13.5	14	501	< 1	0.2	0,2,16	2.5	-2
0,0,12	2	2	502	2.5	3	0,2,17	1.5	-1.5
0,0,14	3	2.5	503	5.5	-6	031	7	-7
0,0,16	2	-1.5	504	4	3.5	032	2.5	2.5
101	9.5	-8.5	505	2	2.5	033	1.5	-2
102	5	-5	506	< 1	0.7	034	11	-11
103	18.5	21	507	2.5	-4	035	8	-8
104	7	7.5	508	< 1	0.4	036	5	-4.5
105	6	5	509	< 0.5	-0.4	037	3.5	4
106	4.5	3.5	5,0,10	1.5	1.5	038	4	-4.5
107	10	10	5,0,11	< 0.5	-0.1	039	< 0.5	-0.2
108	2	-1.5	601	1	-1	0,3,10	1	-0.5
109	4	5	602	< 1	-0.1	0,3,11	6.5	6.5
1,0,10	3.5	4	603	< 1	-0.9	0,3,12	4.5	-4.5
1,0,11	< 1	-1.3	604	1	-1.5	0,3,13	1	-1
1,0,12	1.5	-1	605	1	1	0,3,14	1.5	1
1,0,13	2.5	2	606	1	-1.5	0,3,15	4.5	3.5
1,0,14	2.5	2.5	607	1	0.5	0,3,16	< 0.5	0.6
1,0,15	2.5	2	020	4	3	041	13	12.5
1,0,16	2	1.5	040	10.5	-9.5	042	4.5	4
1,0,17	3.5	2.5	060	8.5	-6.5	043	15	-15.5
201	4.5	4	080	12.5	-14	044	4.5	-3.5
202	13	12.5	0,10,0	3	3	045	2.5	2.5
203	2	-1.5	0,12,0	1	1	046	2	1.5
204	5.5	4.5	0,14,0	1	-1	047	10	-9.5
205	4	-3	002	1.5	1.5	048	2	-2.5
206	6.5	6.5	004	12.5	12.5	049	3.5	3.5
207	3.5	4.5	006	10	-9	0,4,10	1	1
208	3	2.5	008	2	-2.5	0,4,11	4	-3.5
209	4	4	0,0,10	13.5	-13.5	0,4,12	< 0.5	-0.1
2,0,10	3	3	0,0,12	2	2	0,4,13	1.5	1.5
2,0,11	1.5	1	0,0,14	3	-2	0,4,14	1.5	1
2,0,12	4.5	4	0,0,16	2	-1.5	0,4,15	1	-1
2,0,13	2	2.5	011	1	-1.5	0,4,16	1.5	1
2,0,14	< 1	0.5	012	3.5	-3	051	1	-1
2,0,15	< 1	0.5	013	7	6.5	052	2.5	-2.5
2,0,16	< 0.5	0.2	014	4	-3.5	053	5	-5
301	1.5	1	015	6	6.5	054	9.5	-10
302	2	2	016	2	-2	055	1	1
303	4.5	4	017	1	-1	056	6	-5
304	6.5	6.5	018	7.5	7	057	0.5	-0.5
305	2.5	-2.5	019	6	5.5	058	4	-4.5
306	3	2.5	0,1,10	< 0.5	-0.2	059	1.5	1.5
307	6	6	0,1,11	6.5	-6	0,5,10	2.5	2.5
308	1.5	-1	0,1,12	1.5	2	0,5,11	< 0.5	-0.2
309	< 1	-0.1	0,1,13	< 0.5	-0.1	0,5,12	2.5	-2.5
3,0,10	2.5	3	0,1,14	4.5	-3.5	0,5,13	2	1.5
3,0,11	1.5	1.5	0,1,15	1	-1	0,5,14	3.5	3
3,0,12	4	3.5	0,1,16	< 0.5	0.6	0,5,15	2.5	-2
3,0,13	1	0.5	0,1,17	< 0.5	0.3	061	0.5	0.5
3,0,14	2.5	2.5	021	1.5	0.5	062	7	-8
3,0,15	< 0.5	-0.4	022	2	2.5	063	7.5	8.5
401	< 1	-1	023	17	18.5	064	7.5	7.5
402	2.5	2	024	9.5	-9	065	< 0.5	1.1
403	2.5	-2.5	025	1.5	1	066	6	-7
404	4	3	026	11.5	12.5	067	5.5	6
405	1.5	-1.5	027	5	5.5	068	4.5	4.5
						069	1	-1
						0,6,10	1	-0.5

Table 2 (cont.)

<i>hkl</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>hkl</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>	<i>hkl</i>	<i>F</i> <sub>o</sub>	<i>F</i> <sub>c</sub>
0,6,11	1	-1	091	1	0.5	0,11,9	1.5	1
0,6,12	1	1	092	1	-1	0,11,10	2	2
0,6,13	1.5	-2	093	1	1.5	0,11,11	2.5	-2.5
0,6,14	1.5	-1.5	094	2	2	0,11,12	< 0.5	0.2
0,6,15	< 0.5	-0.2	095	2	2			
			096	2	2	0,12,1	2	-2.5
071	2.5	1.5	097	2	2	0,12,2	4.5	-5
072	1.5	-2	098	1.5	-2	0,12,3	2	2
073	3	-3	099	4	-4	0,12,4	2.5	2.5
074	4	4	0,9,10	1	1	0,12,5	1	-1
075	2.5	-2	0,9,11	< 0.5	-0.1	0,12,6	< 0.5	-0.4
075	4.5	-4	0,9,12	< 0.5	0.4	0,12,7	1	1
077	1.5	-2	0,9,13	2.5	-2.5	0,12,8	4	3.5
078	2	2				0,12,9	1.5	-1.5
079	3	-3	0,10,1	4.5	5.5	0,12,10	< 0.5	-0.3
0,7,10	2.5	-3	0,10,2	1	1			
0,7,11	2	2	0,10,3	1	-1	0,13,1	< 0.5	0.2
0,7,12	4.5	4	0,10,4	2	2	0,13,2	< 0.5	-0.3
0,7,13	2	1.5	0,10,5	5.5	6.5	0,13,3	< 0.5	0.2
0,7,14	2	-1.5	0,10,6	3.5	-3.5	0,13,4	< 0.5	0.3
0,7,15	< 0.5	0.3	0,10,7	1.5	-1.5	0,13,5	0.5	-0.5
			0,10,8	< 0.5	0.2	0,13,6	< 0.5	-0.2
081	5	-5	0,10,9	2.5	2.5	0,13,7	< 0.5	0.4
082	4	4	0,10,10	0.5	0.5	0,13,8	< 0.5	0.4
083	2	2	0,10,11	2.5	-2.5	0,13,9	< 0.5	0.5
084	3.5	-4.5	0,10,12	< 0.5	-0.1			
085	4.5	-4.5				0,14,1	1	-1
086	1	0.5	0,11,1	2	3	0,14,2	3	2.5
087	4.5	5	0,11,2	1	-1	0,14,3	2	-2
088	1.5	-2	0,11,3	< 0.5	0	0,14,4	3	-2.5
089	< 0.5	0.5	0,11,4	1	1.5	0,14,5	1	-1
0,8,10	6.5	6	0,11,5	2.5	2.5	0,14,6	3	3
0,8,11	2	2	0,11,6	3.5	3.5			
0,8,12	1.5	-1.5	0,11,7	2.5	-2.5	0,15,1	< 0.5	0.9
0,8,13	< 0.5	0	0,11,8	1	1	0,15,2	< 0.5	0.7
0,8,14	1	1						

which indicates that carboxyl ion resonance is present to some extent.

The C-N length of 1.52 Å is in good agreement with the values found for similar bonds in L<sub>3</sub>-threonine, 1.49 Å, and in DL-alanine, 1.50 Å. The N atom lies 0.44 Å out of the plane C<sub>2</sub>C<sub>1</sub>O<sub>1</sub>O<sub>2</sub>, a distance similar to that found in DL-alanine (0.39 Å) but somewhat smaller than that observed in L<sub>3</sub>-threonine (0.59 Å).

Table 3. Interatomic bond lengths and bond angles

C <sub>1</sub> -C <sub>2</sub>	1.51 Å	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	109°
C <sub>2</sub> -C <sub>3</sub>	1.55	C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	115
C <sub>3</sub> -C <sub>4</sub>	1.51	C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub>	109
C <sub>4</sub> -C <sub>5</sub>	1.54	C <sub>2</sub> -C <sub>1</sub> -O <sub>2</sub>	123
C <sub>1</sub> -O <sub>1</sub>	1.31	C <sub>2</sub> -C <sub>1</sub> -O <sub>1</sub>	114
C <sub>1</sub> -O <sub>2</sub>	1.21	O <sub>1</sub> -C <sub>1</sub> -O <sub>1</sub>	124
C <sub>5</sub> -O <sub>3</sub>	1.20	C <sub>4</sub> -C <sub>5</sub> -O <sub>3</sub>	124
C <sub>5</sub> -O <sub>4</sub>	1.32	C <sub>4</sub> -C <sub>5</sub> -O <sub>4</sub>	112
C <sub>2</sub> -N	1.52	O <sub>3</sub> -C <sub>5</sub> -O <sub>4</sub>	125
		C <sub>1</sub> -C <sub>2</sub> -N	111
		C <sub>3</sub> -C <sub>2</sub> -N	110

The systematic variation of bond lengths along the carbon chain may be real, although within the limits of experimental error. Support for its reality is the fact that the shortness of the C<sub>1</sub>-C<sub>2</sub> bond with respect to the C<sub>2</sub>-C<sub>3</sub> bond is also found in L<sub>3</sub>-threonine and L-hydroxyproline (Donohue, private communication).

A similar short-long-short sequence has also been observed in α- and β-DL-methionine (Mathieson, 1952) and DL-norleucine (Mathieson, to be published). The variations here are again within the limits of experimental error, but their existence in all three compounds is evidence in favour of their reality. Further, if one considers the variations in glutamic acid from the other end of the carbon chain, i.e. the C<sub>5</sub>O<sub>3</sub>O<sub>4</sub>H group, then the sequence, which is long-short-long, is in accord with the sequence proposed in the 'even' dicarboxylic acids, adipic and sebacic acid (Morrison & Robertson, 1949). It might be argued, therefore, that short-long-short and long-short-long sequences along a chain are produced by the presence of -CH(NH<sub>2</sub>)COOH and -COOH end-groups respectively. The variations along the glutamic acid chain would then result from the reinforcement of the opposite sequences arising at the two ends of the molecule. Such an argument is speculative, however, and proof of the reality of the variations must await a more accurate determination by three-dimensional methods. Nevertheless it will be interesting to determine whether an investigation, comparable in accuracy to the present one, on the other dicarboxylic amino acid, aspartic acid, reveals any variations along the chain. This chain contains one fewer carbon atoms than glutamic acid

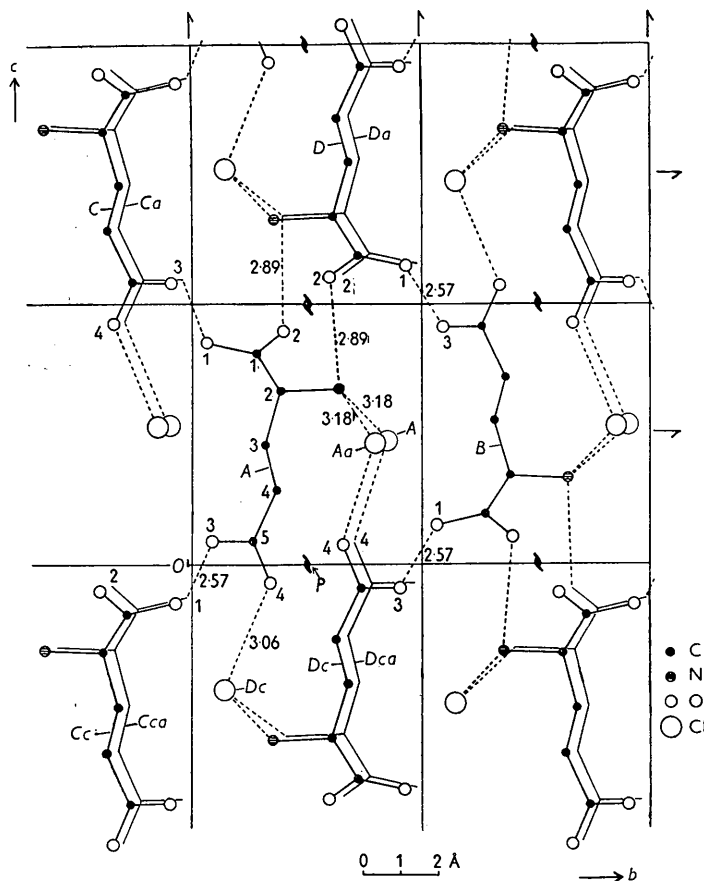


Fig. 4. Structure of DL-glutamic acid hydrochloride projected on (100). Broken lines represent hydrogen bonds.

so that the opposite sequences from the two ends of the molecule should interfere and reduce, if not entirely cancel, variations along the chain. The situation would then be similar to that observed in the 'odd' dicarboxylic acid  $\beta$ -glutaric acid (Morrison & Robertson, 1949). The results of this examination will be reported later.

The molecular arrangement viewed along the  $a$  and  $b$  axes is shown in Figs. 4 and 5. To show the bonding more clearly certain equivalent molecules have been displaced slightly in Fig. 4. The molecules are designated  $A$ ,  $B$ ,  $C$ ,  $Ca$ ,  $Cc$ ,  $Cca$ ,  $D$ ,  $Da$ ,  $Dc$  and  $Dca$ .  $C$  and  $Ca$  are equivalent molecules separated by the repeat distance,  $a$ , in the  $x$  direction.  $D$  and  $Da$  are related similarly.  $Cc$  and  $Cca$  are related to  $C$  and  $Ca$  by translation along the  $z$  axis.  $Dc$  and  $Dca$  are similarly related to  $D$  and  $Da$ . Any atom is then described as follows: e.g.  $O_3(Ca)$  where  $(Ca)$  indicates the molecule and  $O_3$  corresponds to the numbering used in Table 1.

The nitrogen atom forms three hydrogen bonds, two to chlorine atoms,  $N(A) \cdots Cl(A)$  and  $N(A) \cdots Cl(Aa)$  and the third to an oxygen atom,  $N(A) \cdots O_2(D)$ . This is in accord with the fact that we are investigating the hydrochloride which can be regarded as (glutamic

acid) $^+Cl^-$ , so that the amino group is of the form  $-NH_3^+$ . The lengths of the  $NH \cdots Cl$  bonds, 3.18 Å, and of the  $NH \cdots O$  bond, 2.89 Å, are normal, similar values being found elsewhere (Brown, 1949, 1951). The angles  $C_2(A)-N(A)-Cl(A)$ ,  $C_2(A)-N(A)-Cl(Aa)$  and  $Cl(A)-N(A)-Cl(Aa)$  are all very close to the tetrahedral angle,  $109.5^\circ$ , so that the hydrogen atoms in the  $N \cdots Cl$  bonds must lie in the lines of these bonds. This is supported by the  $a$ -axis electron-density projection (Fig. 2) in which the two atoms are superposed and show up quite clearly. A small peak also appears at the position which the third hydrogen atom should occupy if disposed tetrahedrally to the other two atoms and to the  $C_2(A)-N(A)$  bond. However, such a position is not in the line of the  $N(A) \cdots O_2(D)$  bond as the angle  $C_2(A)-N(A)-O_2(D)$  is only  $88^\circ$ . Whether the hydrogen occupies its tetrahedral position, as was assumed in structure-factor calculations, or is shifted into the line of  $N(A)$  and  $O_2(D)$ , must await a more precise investigation.

The oxygen atoms of adjacent carboxyl groups are linked by strong hydrogen bonds of length 2.57 Å, e.g.  $O_3(A) \cdots O_1(Cca)$  and  $O_1(A) \cdots O_3(Ca)$ . Similar  $O \cdots O$  bonds are found in N-acetyl glycine. Zigzag chains of molecules along the  $z$  direction are thus

