

Table 12. *Torsion angles for average pyranose rings* (°)

	Allose	Altrose	Glucose	Mannose	Gulose	Idose	Galactose	Talose
O(5)–C(1)–C(2)–C(3)	48.12	47.90	56.63	53.01	52.10	51.21	56.30	57.18
C(1)–C(2)–C(3)–C(4)	–50.05	–45.07	–53.61	–52.69	–51.03	–46.61	–53.78	–55.81
C(2)–C(3)–C(4)–C(5)	55.21	50.29	53.66	54.68	52.74	48.72	53.83	56.63
C(3)–C(4)–C(5)–O(5)	–57.85	–57.68	–56.43	–56.11	–55.14	–54.24	–56.99	–57.75
C(4)–C(5)–O(5)–C(1)	58.96	62.20	62.05	58.25	58.51	60.96	62.42	61.81
C(5)–O(5)–C(1)–C(2)	–53.76	–57.27	–62.21	–56.84	–56.70	–59.81	–61.66	–61.86

a comparison of the standard deviations of the coordinates, from which it appears that the σ 's of the z coordinates (the z axis is only a few degrees away from being perpendicular to the least-squares best plane of the ring) are, on average, 1.7 times the σ 's of the x and y coordinates, which have σ 's similar to each other.

Examination of the variations due to axial or equatorial O atoms has not given any clear indication of a systematic effect on the coordinates due to the different directions of these atoms.

Conclusion

The average coordinates have been presented for the pyranose-sugar ring atoms, for each pyranose sugar and for an overall average ring, based on crystal structures listed in the Cambridge Crystallographic Data File dated May 1979 by a least-squares iterative refinement of the fixed groups. The results show variations between pyranose rings, though qualified by the meagre number of samples of five of the pyranoses

and, within each ring, a difference between the standard deviation of the z coordinates and the standard deviations of the x and y coordinates in the specified orientation.

We acknowledge the helpful advice of the staff of the Cambridge Crystallographic Data Centre and the Leeds University Computer Centre for facilities.

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A Short Hydrogen Bond between Near Identical Carboxyl Groups in the α Modification of L-Glutamic Acid

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Abstract

The structure of the α modification of L-glutamic acid, $C_5H_9NO_4$, has been determined from neutron diffraction data using direct methods. The space group is $P2_12_12_1$ with $a = 10.282$ (10), $b = 8.779$ (8), $c = 7.068$ (7) Å and $Z = 8$ and the final R value is 0.026

for 1160 observations. As in the β modification of the compound a short hydrogen bond with an O...O length of 2.58 Å was found between the two carboxyl groups. The location of the H atom in the bond is explained from acid–base considerations, and the shortness of the bond is accounted for using bond-length–bond-strength considerations. The conformation of the side chain containing the δ -carboxyl group differs considerably in the two modifications, showing this part of the molecule to be highly flexible.

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Introduction

L-Glutamic acid is found in two modifications: α (Bernal, 1931) and β (Hiokawa, 1955; Lehmann, Koetzle & Hamilton, 1972; see also Sakata & Takenouchi, 1963, and references therein). The β modification, for which detailed X-ray and neutron diffraction studies have been performed, shows a short intermolecular hydrogen bond with an O...O length of 2.519 Å between the two carboxyl groups in the molecule. The bond is very asymmetric with the H atom bound to the δ -carboxyl, and this was explained from the acidity of the two groups with the δ -carboxyl group being the weaker acid of the two and therefore more likely to accept the H atom. The shortness of the bond was related to the relatively small difference in acid strength of the two groups. We would expect a similar behaviour in the α form, and in order to verify this we decided to undertake a neutron diffraction study.

The structure of the α form has not been determined by X-rays, but, as the structures of two similar compounds have been solved easily by applying direct methods to neutron diffraction data, it is reasonable to bypass the X-ray work.

Data collection and treatment

Crystals of the α modification of L-glutamic acid (C₅H₉NO₄) were prepared as described by Sakata, Suzuki & Takenouchi (1962). Aqueous solutions left to evaporate produced, after several weeks, colourless transparent crystals of millimetre dimensions. The sample used for the study was 5.1 mm³ in volume, with transverse dimensions between 1.5 and 3.0 mm, and was bounded by the clearly defined faces {010}, {111}, and {110}.

The crystal was mounted with its a axis near the principal axis of the goniometer head. Bragg intensities were measured at room temperature at the High Flux Beam Reactor of the Institut Laue-Langevin. The four-circle diffractometer D9 located at the 'hot source' was used, employing neutrons of wavelength 0.8176 (6) Å. Reflections were recorded with the ω -step scan technique for scattering angles (2θ) less than 60°, and with ω - 2θ -step scans for 2θ between 60 and 80°. Each scan was divided into 45 steps, while the scan range was varied as a function of 2θ in order to keep a constant number of steps in the peak. In all, 2416 reflections were observed.

The space group determined from X-ray films is $P2_12_12_1$. Unit-cell dimensions were determined by least-squares techniques applied to 15 reflections centred on the neutron diffractometer. The values compare well with those of Bernal (1931). The calculated crystal density of 1.53 Mg m⁻³ agrees with

the value of 1.54 Mg m⁻³ measured in a mixture of carbon tetrachloride and acetone.

Background corrections were made by use of a method which divides peak and background in such a way that $\sigma(I)/I$ is minimized, where I is the integrated intensity and $\sigma(I)$ its standard deviation based on counting statistics (Lehmann & Larsen, 1974). Squared observed structure factors, obtained as $F_o^2 = I \sin 2\theta$, were corrected for absorption using Gaussian numerical integration. The linear absorption coefficient was calculated to be 0.167 mm⁻¹, using an incoherent scattering cross section for H of 33×10^2 fm², which was obtained from measurements on similar compounds at the same wavelength and neglecting all other types of absorption. Calculated transmission coefficients were in the range 0.76 to 0.84.

Symmetry-related reflections were averaged, yielding 1389 independent observations. The agreement factor between symmetry-related reflections was found to be 0.025. Data were then corrected for the second-order wavelength contamination of the incident beam. The magnitude of this contamination was determined from measurements of a number of symmetry-forbidden reflections. The corrected squared structure factor was determined as $F_{\text{corr}}^2(h, k, l) = F_{\text{obs}}^2(h, k, l) - 0.0155F_{\text{obs}}^2(2h, 2k, 2l)$.

Structure solution and refinement

The data were phased using the computer program *MULTAN* (Germain, Main & Woolfson, 1971). As in previous cases (Verbist, Lehmann, Koetzle & Hamilton, 1972; Frey, Lehmann, Koetzle & Hamilton, 1973) where direct methods have been applied to amino acid neutron data, the negative scattering lengths of the H atom did not create any problem.

Heavy-atom positions were determined by *MULTAN*. H atoms were then inserted in chemically reasonable locations, and the resulting coordinates used as the starting set for the refinement. The coherent scattering lengths used were $b_N = 9.4$, $b_O = 5.75$, $b_C = 6.626$, and $b_H = -3.72$ fm.

In addition to the scale factor, K , positional parameters and anisotropic temperature factors, an isotropic extinction parameter in the type I Lorentzian approximation (Becker & Coppens, 1974, 1975) was introduced in the refinement. The quantity minimized was $\sum W|F_o^2 - K^2F_c^2|^2$, where $1/W = [\sigma_{\text{count}}^2(F_o^2) + (0.02F_o^2)^2]$ and only reflections for which $F_o^2 > 3\sigma_{\text{count}}(F_o^2)$ were included in the refinement. This resulted in 1160 observations for the 173 parameters. The extinction factor was larger than 0.9 for most reflections, though a few had lower values, the smallest being 0.57 for the 080 reflection. The agreement between observed and calculated squared structure amplitudes is $R = (\sum |F_o - F_c|^2 / \sum F_o^2)^{1/2} = 0.026$, $R_w =$

Table 1. Fractional atomic coordinates and thermal parameters

The Debye-Waller factor is $\exp(-B \sin^2 \theta / \lambda^2)$. Errors here and throughout this paper are given in parentheses in units of the last digit.

	x	y	z	B (Å ²)
N	0.59792 (6)	0.33146 (7)	0.20969 (10)	1.61 (1)
O(1)	0.76382 (10)	0.48704 (13)	0.45663 (19)	2.14 (1)
O(2)	0.62845 (10)	0.68407 (11)	0.42296 (18)	1.98 (1)
O ^ε (1)	0.21971 (11)	0.43912 (14)	0.63722 (24)	2.83 (1)
O(2)	0.33460 (11)	0.65263 (13)	0.62428 (20)	2.31 (1)
C	0.65626 (8)	0.54346 (9)	0.41785 (13)	1.33 (1)
C ^α	0.54672 (8)	0.43405 (9)	0.36040 (12)	1.27 (1)
C ^β	0.50098 (8)	0.33529 (10)	0.52589 (14)	1.71 (1)
C ^γ	0.44929 (9)	0.42570 (11)	0.69558 (14)	1.88 (1)
C ^δ	0.32320 (9)	0.50525 (9)	0.65085 (13)	1.60 (1)
H(1)	0.6450 (2)	0.3939 (2)	0.1029 (3)	2.79 (2)
H(2)	0.6640 (2)	0.2554 (2)	0.2661 (3)	2.92 (2)
H(3)	0.5220 (2)	0.2689 (2)	0.1505 (3)	2.69 (2)
H ^ε (2)	0.2475 (2)	0.7062 (2)	0.6019 (3)	2.96 (2)
H ^α	0.4658 (2)	0.4981 (2)	0.2979 (3)	2.44 (2)
H ^β (1)	0.4253 (2)	0.2564 (3)	0.4758 (4)	3.45 (3)
H ^β (2)	0.5842 (2)	0.2669 (2)	0.5742 (3)	3.47 (3)
H ^γ (1)	0.4301 (3)	0.3454 (3)	0.8108 (3)	3.88 (3)
H ^γ (2)	0.5218 (2)	0.5088 (3)	0.7448 (3)	3.49 (3)

$(\sum W|F_o - F_c|^2 / \sum WF_o^2)^{1/2} = 0.021$, $R(F^2) = (\sum |F_o^2 - F_c^2| / \sum F_o^2)^{1/2} = 0.037$, $R_w(F^2) = (\sum W|F_o^2 - F_c^2| / \sum WF_o^2)^{1/2} = 0.042$. Table 1* gives the final atomic positions and isotropic temperature parameters.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35167 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Summary of algorithms used

The set of 'observed structure factors', $F_o(h, k, l)$, was obtained by application of the following group of programs: initial values of F_i^2 were obtained from the step scan data by the program *COLLS* (Lehmann & Wilson, 1974); absorption corrections and averaging were performed by *DAPATH* and *DSORTH* (Coppens, 1975); the correction for $\lambda/2$ was carried out by *LA2* (Nunes, 1975).

The data were phased and heavy atoms (C, O, N) located with the *MULTAN* set of programs (Germain, Main & Woolfson, 1971). Structure refinement was carried out by *LINEX* (Coppens, 1975).

Discussion

Table 2 gives the interatomic distances and angles in both the α and β forms. These distances are quite similar in the two forms, as is found in other studies comparing different conformations of the same molecule [for example, L-serine and DL-serine (Frey, Lehmann, Koetzle & Hamilton, 1973)]. There are larger differences among the angles, and the reason for this can be seen in Table 3, which summarizes the torsion angles. Whereas the α -amino part of the molecule is nearly identical in the two cases, the side chains are different, and obviously the energy difference between the various configurations is small as crystals of α and β can coexist in aqueous solution (Sakata, 1962). This is also shown in Fig. 1, which shows the molecule in the

Table 2. Interatomic distances (Å) and angles (°)

The β form is included for comparison. The atom designations follow the recommendations of IUPAC-IUB Commission on Biochemical Nomenclature (1970).

	α	β		α	β		α	β
C-O(1)	1.242 (1)	1.263 (2)	O(1)-C-O(2)	125.6 (1)	126.02 (2)	C ^γ -C ^β -H ^β (1)	109.4 (2)	107.0 (2)
C-O(2)	1.268 (1)	1.243 (2)	O(1)-C-C ^α	117.5 (1)	115.6 (1)	C ^γ -C ^β -H ^β (2)	108.0 (1)	109.9 (2)
C-C ^α	1.535 (1)	1.533 (2)	O(2)-C-C ^α	116.8 (1)	118.3 (1)	H ^β (1)-C ^β -H ^β (2)	107.8 (2)	106.5 (3)
C ^α -N	1.491 (1)	1.490 (2)	C-C ^α -N	107.9 (1)	109.3 (1)	C ^β -C ^γ -C ^δ	112.0 (1)	116.1 (1)
C ^α -C ^β	1.530 (1)	1.530 (2)	C-C ^α -C ^β	112.2 (1)	107.3 (1)	C ^β -C ^γ -H ^γ (1)	108.1 (2)	112.8 (2)
C ^α -H ^α	1.097 (2)	1.091 (3)	C-C ^α -H ^α	110.0 (1)	110.5 (2)	C ^β -C ^γ -H ^γ (2)	110.9 (1)	108.0 (2)
N-H(1)	1.051 (2)	1.038 (3)	N-C ^α -C ^β	108.2 (1)	111.5 (1)	C ^δ -C ^γ -H ^γ (1)	107.4 (1)	106.8 (2)
N-H(2)	1.033 (2)	1.038 (4)	N-C ^α -H ^α	106.8 (1)	107.5 (2)	C ^δ -C ^γ -H ^γ (2)	110.0 (1)	106.6 (2)
N-H(3)	1.042 (2)	1.027 (3)	C ^β -C ^α -H ^α	111.4 (1)	110.9 (2)	H ^γ (1)-C ^γ -H ^γ (1)	108.3 (2)	105.9 (4)
C ^β -H ^β (1)	1.100 (2)	1.102 (4)	C ^α -N-H(1)	111.1 (1)	110.8 (2)	C ^γ -C ^δ -O ^ε (1)	123.3 (1)	124.1 (1)
C ^β -H ^β (2)	1.099 (2)	1.079 (4)	C ^α -N-H(2)	110.3 (1)	110.1 (2)	C ^γ -C ^δ -O ^ε (2)	114.2 (1)	112.2 (2)
C ^β -C ^γ	1.533 (1)	1.523 (2)	C ^α -N-H(3)	109.9 (1)	112.3 (2)	O ^ε (1)-C ^δ -O ^ε (2)	122.5 (1)	123.7 (2)
C ^γ -H ^γ (1)	1.095 (2)	1.080 (4)	H(1)-N-H(2)	108.1 (2)	108.6 (3)	C ^δ -O ^ε (2)-H ^ε (2)	113.4 (2)	115.1 (2)
C ^γ -H ^γ (2)	1.100 (3)	1.086 (4)	H(1)-N-H(3)	109.4 (2)	107.1 (2)			
C ^γ -C ^δ	1.506 (1)	1.501 (2)	H(2)-N-H(3)	107.9 (2)	107.8 (3)			
C ^δ -O ^ε (1)	1.216 (2)	1.219 (2)	C ^α -C ^β -C ^γ	114.3 (1)	117.8 (1)			
C ^δ -O ^ε (2)	1.313 (1)	1.312 (2)	C ^α -C ^β -H ^β (1)	109.2 (2)	107.9 (2)			
O ^ε (2)-H ^ε (2)	1.024 (2)	1.050 (4)	C ^α -C ^β -H ^β (2)	107.9 (1)	107.1 (3)			

various forms and includes the protonated molecule from L-glutamic acid hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972). The side chain in the protonated form is extended whereas it is strongly twisted in the β form, leading to very strained C—C—C angles in the latter case.

Of main interest and probably of major influence on the molecular conformation is the hydrogen bond between the two carboxyl groups. As in the β form we find the bond to be short. A summary of the hydrogen bonding is given in Table 4.

The acidic pK values for the α -amino, the α -carboxyl and the δ -carboxyl groups are 9.47, 2.10 and 4.07 respectively (Simms, 1928), so in aqueous solution the amino and the δ -carboxyl groups will be protonated, and the probability of finding a protonated α -carboxyl group is approximately two orders of magnitude smaller than for the δ -carboxyl group. It is therefore unlikely that protons will be found covalently bound to the α -carboxyl group, and indeed we do not observe this. If we now look further at the interatomic distances, we can see, using bond-strength—bond-length arguments (Pauling, 1960; Brown & Shannon, 1973), that this type of hydrogen bond should be strong. Each of the carboxyl groups has a valence of one, and as the

carboxyl groups are only bound to H atoms the sum of the strengths of the bonds should be about one valence unit. For long hydrogen bonds one bond contributes with well below 0.2 valence units (Brown, 1976), so in order to obtain the sum of one either the O must accept many hydrogen bonds, which is generally excluded for steric reasons, or it must participate in at least one strong bond. In the present case only one H atom with a total valence of one is available for the two groups, so the O...O distance must be short, in order that each H...O bond has a strength of near half a valence unit. If the two carboxyl groups are identical we would expect a symmetric bond, as, for example, in many acid salts of carboxylic acids (Speakman, 1972), but it is not a requirement as local environment can destroy this symmetry (McGregor, Speakman & Lehmann, 1977). As soon as more H atoms are bound to the groups, as in glutamic acid hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972) where two H atoms are available, the O—H...O hydrogen bond is as long as 2.64 (1) Å.

The short O—H...O bond, however, does not have the same length in the two cases, mainly because in the β form the acceptor atom O(1) only participates in one bond whereas in the α form O(2) accepts two bonds. In agreement with this, we find the bond in the β form to be the shortest. We can estimate the total bond strength for the hydrogen bonding around the α -carboxyl group using the expression $S = [r(\text{H}\cdots\text{O})/0.87]^{-2.2}$ (Brown & Wu, 1976), where S is the bond strength and $r(\text{H}\cdots\text{O})$ is the bond length. The expression is, in general, only valid in the range $1.7 \text{ \AA} < r(\text{H}\cdots\text{O}) < 1.9 \text{ \AA}$, but we extend its use in order to carry out a comparison looking at relative rather than absolute values. For both forms we find a bond-strength sum of 0.69 valence units, in good agreement with the expectation that these should be identical. Extending the range of use of the expression even further we find for the δ -carboxyl group bond-strength sums of 0.87 and 0.84, again with a good agreement between the two. In addition, we note further that the values are higher in this case showing the group to have a higher affinity for H atoms in accordance with the higher pK value.

Table 3. *Torsion angles* ($^\circ$)

IUPAC—IUB Commission on Biochemical Nomenclature (1970)		α	β
ϕ^1	C—C $^\alpha$ —N—H(1)	−48.7 (1)	−48.9 (2)
ϕ^2	C—C $^\alpha$ —N—H(2)	71.2 (1)	71.3 (2)
ϕ^3	C—C $^\alpha$ —N—H(3)	−169.9 (1)	−168.6 (2)
ψ^1	N—C $^\alpha$ —C—O(1)	−50.2 (1)	−42.3 (2)
ψ^2	N—C $^\alpha$ —C—O(2)	130.3 (1)	141.2 (2)
χ^1	N—C $^\alpha$ —C $^\beta$ —C $^\gamma$	178.2 (1)	−51.8 (1)
χ^2	C $^\alpha$ —C $^\beta$ —C $^\gamma$ —C $^\delta$	68.3 (1)	−73.1 (2)
$\chi^{3,4,1}$	C $^\beta$ —C $^\gamma$ —C $^\delta$ —O $^\epsilon$ (1)	74.2 (1)	18.8 (2)
$\chi^{3,4,2}$	C $^\beta$ —C $^\gamma$ —C $^\delta$ —O $^\epsilon$ (2)	−104.6 (1)	−160.7 (1)
$\chi^{4,2}$	O $^\epsilon$ (1)—C $^\delta$ —O $^\epsilon$ (2)—H $^\epsilon$ (2)	4.6 (1)	−11.4 (2)
θ_C^2	C $^\gamma$ —C $^\delta$ —O $^\epsilon$ (2)—H $^\epsilon$ (2)	−176.5 (1)	168.2 (2)

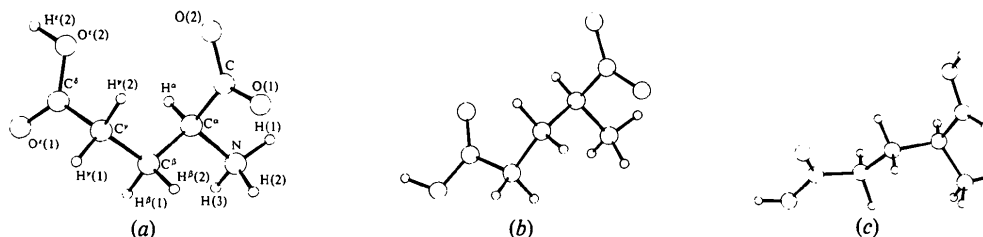


Fig. 1. Molecules of L-glutamic acid in (a) the α form, (b) the β form and (c) the protonated form. The α group is oriented in approximately the same manner in the three cases.

Table 4. Distances (Å) and angles (°) in the hydrogen bonds

$A-H \cdots B-C$	$A-H$	$H \cdots B$	$A \cdots B$	$\angle A-H \cdots B$	$\angle H \cdots B-C$
α Modification					
$N-H(1) \cdots O(1)-C$	1.051 (2)	1.744 (2)	2.786 (1)	170.5 (1)	111.7 (2)
$N-H(2) \cdots O^{\epsilon}(1)-C^{\delta}$	1.033 (2)	1.926 (2)	2.895 (1)	154.9 (2)	130.9 (2)
$N-H(3) \cdots O(2)-C$	1.042 (2)	1.794 (2)	2.823 (1)	168.8 (2)	126.2 (2)
$O^{\epsilon}(2)-H^{\epsilon}(2) \cdots O(2)-C$	1.024 (2)	1.568 (2)	2.581 (1)	169.3 (2)	114.8 (2)
β Modification					
$N-H(1) \cdots O(2)-C$	1.038 (3)	1.845 (4)	2.868 (2)	167.8 (3)	125.4 (2)
$N-H(2) \cdots O(2)-C$	1.038 (4)	1.868 (4)	2.888 (2)	166.9 (3)	130.4 (2)
$N-H(3) \cdots O^{\epsilon}(1)-C^{\delta}$	1.027 (3)	1.896 (4)	2.919 (3)	174.1 (3)	126.7 (3)
$O^{\epsilon}(2)-H^{\epsilon}(2) \cdots O(1)-C$	1.050 (4)	1.475 (5)	2.519 (2)	172.3 (3)	116.6 (2)

The hydrogen bonds involving the ammonium group are as normally found in amino acids with $H \cdots O$ lengths in the range 1.74 to 1.93 Å, and as usual the $N-H$ and the $H \cdots O$ bond lengths show an inverse relationship (Koetzle & Lehmann, 1976). Finally, it should be noted that the $C-(OH)$ bond length in the protonated α -carboxyl group in glutamic acid hydrochloride is shorter [1.296 (8) Å] than the three values observed for the δ -carboxyl groups [1.313 (1), 1.312 (2), 1.315 (8) Å, mean 1.313 Å]. Andersen (1971) has shown that there is a near linear relationship between this bond length and the pK value, reflecting the fact that a strong acid has a loosely bound H atom and therefore one would expect $C-(OH)$ to be short. From his observations we can predict a pK value for the α -carboxyl group of 1 and a pK for the δ group of 3, in quite good agreement with the solution values quoted above. We are thus able not only to rationalize the distributions of hydrogen-bond lengths but also to carry out reasonable predictions concerning most of the interatomic distances involving the hydrogen bond.

We are indebted to Dr G. Zaccari for his continued interest in this work and for fruitful discussions in this and related areas.

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