Acta Cryst. (1973). B**29**, 2571

Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. XIII. Molecular and Crystal Structure of the Amino Acid L-Glutamine*

BY THOMAS F. KOETZLE,† MICHEL N. FREY,‡ MOGENS S. LEHMANN§ AND WALTER C. HAMILTON‖

Chemistry Department, Brookhaven National Laboraotry, Upton, New York 11973, *U.S.A.*

(*Received* 14 *May* 1973; *accepted* 15 *June* 1973)

A neutron diffraction study of L-glutamine, $C_5H_{10}N_2O_3$, has been carried out. Space group $P2_12_12_1$; $Z=4$; $a=16{\cdot}020$ (10), $b=7{\cdot}762$ (6), $c=5{\cdot}119$ (4) Å. Full-matrix least-squares refinements, including anisotropic temperature factors for all atoms and an extinction correction, have led to a conventional R value of 0·032. The neutron-diffraction results confirm the structure found by X-ray diffraction [Cochran, W. & Penfold, B. R. (1952). *Acta Cryst.* **5**, 644–653] to be essentially correct; the main new feature here is the location of all hydrogen atoms with a precision of 0·005 Å. The glutamine zwitterions are in the keto form, as expected, and the crystal structure is stabilized by a three-dimensional network of N–H···O hydrogen bonds. One such hydrogen bond is formed by each of the five hydrogens attached to nitrogen.

Introduction

A neutron diffraction study of L-glutamine has been carried out as part of a series of investigations of amino acids, small peptides, nucleosides and nucleotides, the aim of which is to provide precise information about hydrogen-atom stereochemistry and hydrogen bonding in these systems.

The structure of L-glutamine has previously been studied with X-ray diffraction techniques by Cochran & Penfold (1952).

Crystal data

L-Glutamine

$C_5H_{10}N_2O_3$; F.W. 146·15

Orthorhombic; $a=16{\cdot}020$ (10), $b=7{\cdot}762$ (6), $c=5{\cdot}119$ (4) Å

Space group $P2_12_12_1$; $Z=4$

Density $\varrho_{calc}=1{\cdot}525$ g cm^{-3}, $\varrho_{obs}=1{\cdot}54$ g cm^{-3} (Cochran & Penfold, 1952)

Absorption coefficient $\mu=2{\cdot}37$ cm^{-1}

Experimental

Large crystals of L-glutamine were grown by introducing seed crystals into a saturated aqueous solution at 65 °C and cooling to room temperature over a period of three days in a thermostatted bath. The seeds were allowed to continue to grow for approximately one week. The crystals are colorless needles elongated in the **c** direction with major bounding faces {110}. A well-formed sample, having maximum and minimum linear dimensions of 4 and 0·4 mm and a volume of 1·46 mm^3, was mounted on a four-circle diffractometer at the Brookhaven High-Flux Beam Reactor. The cell constants were refined by least-squares techniques from the diffractometer setting angles observed for 24 reflections well distributed in reciprocal space, and these cell parameters agree to within 0·4 % with the less precise values found by Cochran & Penfold (1952). Intensity data were collected automatically under the Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & Van Norton, 1966) with a θ–2θ step-scan technique and a crystal-monochromated neutron beam of wavelength $\lambda=1{\cdot}014$ Å. Intensities were measured for 1983 hkl and $h\bar{k}l$ reflections with $d^*<1{\cdot}35$ Å^{-1}; these were corrected for background by a method described by Lehmann, Hamilton & Larsen (1972). An absorption correction computed by numerical integration over a Gaussian grid was applied to the observed intensities. The absorption coefficient $\mu=2{\cdot}37$ cm^{-1} was calculated with the incoherent scattering cross-section for hydrogen assumed to be 40 barns, and transmission coefficients ranged from 0·80 to 0·92.

Squared observed structure factors were obtained as $F_o^2=I\sin 2\theta$, and were averaged for symmetry-related reflections. The agreement factor is $R_c=\sum|F_o^2-\bar{F}_o^2|/\sum F_o^2=0{\cdot}044$, where $\bar{F}_o^2$ is the mean value for the symmetry-related reflections. Of 941 unique reflections measured, 136 reflections with $\bar{F}_o^2<3\sigma_{count}(\bar{F}_o^2)$ were omitted from subsequent refinements.

Structure refinement

The structure was refined by full-matrix least-squares techniques, starting from the atomic positions found by

* Research performed under the auspices of the U.S. Atomic Energy Commission. Part XII: 'A Study of Hydrogen Bonding in the Purine–Pyrimidine Base Pair 9-Methyladenine–1-Methylthymine' by Frey, Koetzle, Lehmann & Hamilton, *J. Chem. Phys.* (1973). **59**, 915–924.

† U.S. National Institutes of Health Postdoctoral Fellow, 1970–72.

‡ Chargé de Recherches au C.N.R.S. On leave from Laboratoire de Cristallographie Minéralogie, Université 14, Caen, France. Holdei of a grant from NATO.

§ On leave from Kemisk Institut, Århus Universitet, Denmark, and supported in part by a grant from Statens Naturvidenskabelige Forskningsråd, Copenhagen, Denmark. Present address: Institut v. Laue–Langevin, Avenue des Martyrs, 38 Grenoble-Gare, France.

‖ Deceased.

Cochran & Penfold and applying the transformation $x+\frac{1}{4},y,z-\frac{1}{4}$ to these coordinates. Neutron scattering lengths used were $b_C=0{\cdot}6625$, $b_H=-0{\cdot}3723$, $b_N=0{\cdot}940$, and $b_O=0{\cdot}575$ (10^{-12} cm). The quantity minimized in the refinements was $\sum w|F_o^2-|F_c|^2|^2$, and weights were chosen as $w=1/\sigma^2(F_o^2)$, with $\sigma^2(F_o^2)=\sigma^2_{\text{count}}(F_o^2)+(0{\cdot}02\ F_o^2)^2$, and with $\sigma_{\text{count}}(F_o^2)$ based on counting statistics. In all, 182 parameters were refined, including anisotropic temperature factors for all atoms and an extinction correction parameter (Zachariasen, 1967). No parameter shifted by more than 0·1 σ in the last cycle and the final unweighted and weighted R values based on F^2 are

$$R_{F^2}=[\sum|F_o^2-|F_c|^2|]/\sum F_o^2=0{\cdot}041$$

$$R_{wF^2}=\{[\sum w|F_o^2-|F_c|^2|^2]/\sum wF_o^4\}^{1/2}=0{\cdot}049\ .$$

Table 1. *Fractional coordinates* ($\times10^4$) *and thermal parameters* ($\times10^4$)

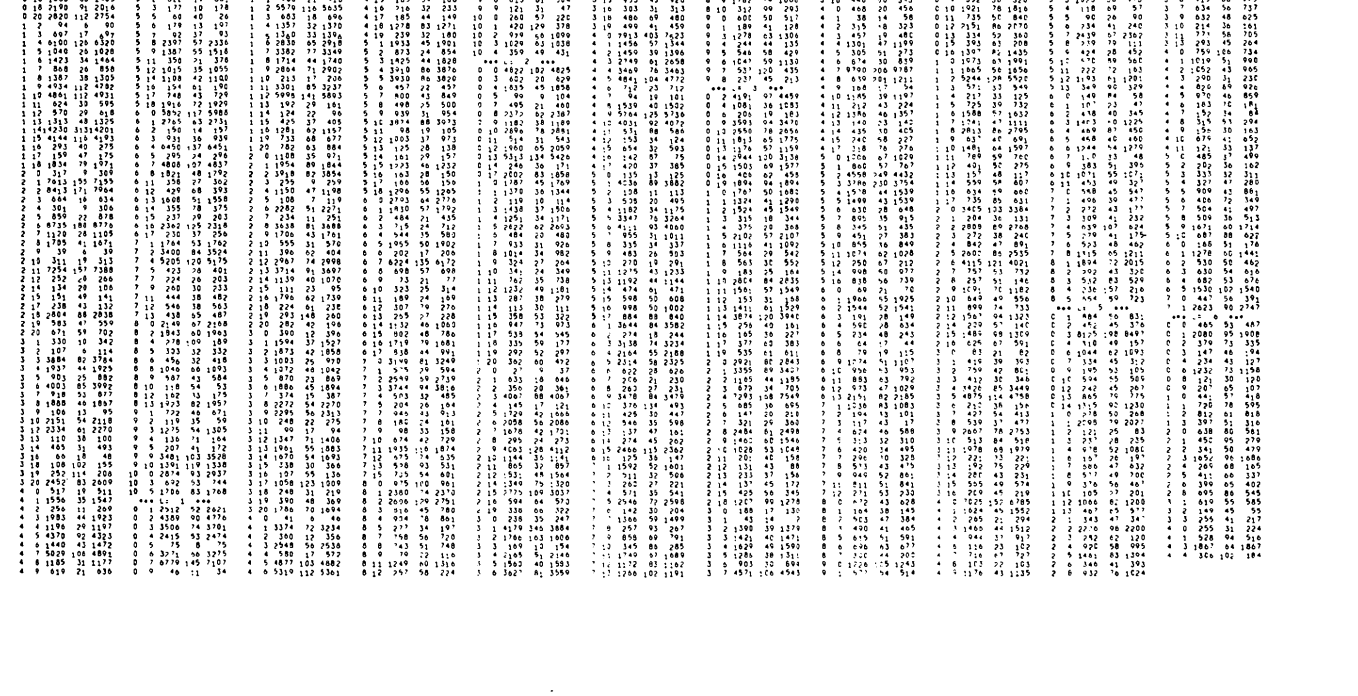
The form of the anisotropic Debye–Waller factor is

$$\exp[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}ha^*kb^*+2u_{13}ha^*lc^*+2u_{23}kb^*lc^*)].$$

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
C	4924 (1)	5851 (2)	7520 (4)	172 (8)	159 (7)	174 (10)	12 (6)	−13 (7)	− 2 (7)
C^α	4104 (1)	6659 (2)	6290 (4)	168 (8)	138 (7)	173 (9)	− 3 (6)	−14 (7)	−12 (8)
C^β	3418 (1)	5298 (2)	6154 (4)	160 (8)	167 (8)	215 (10)	−23 (6)	43 (8)	−23 (8)
C^γ	3635 (1)	3762 (2)	4451 (4)	181 (9)	164 (8)	235 (11)	−32 (6)	68 (8)	−43 (8)
C^δ	2978 (1)	2369 (2)	4512 (4)	189 (7)	128 (7)	216 (10)	−28 (7)	27 (8)	12 (7)
N	4231 (1)	7500 (2)	3691 (3)	220 (6)	161 (6)	190 (7)	− 9 (5)	−12 (6)	22 (5)
$N^{\varepsilon2}$	3054 (1)	1162 (2)	2680 (3)	341 (8)	207 (6)	330 (9)	−52 (6)	56 (8)	−102 (7)
O^1	5499 (1)	5640 (3)	5665 (5)	208 (10)	501 (14)	273 (13)	98 (10)	49 (10)	108 (12)
O^2	4921 (1)	5407 (3)	9618 (4)	297 (11)	244 (10)	161 (12)	71 (9)	−35 (9)	41 (9)
$O^{\varepsilon1}$	2419 (1)	2352 (2)	6153 (5)	281 (10)	215 (9)	352 (14)	−84 (9)	150 (11)	−37 (10)
H^1	4576 (2)	6716 (4)	2447 (9)	359 (19)	325 (18)	327 (21)	46 (15)	72 (19)	− 4 (20)
H^2	3673 (2)	7740 (5)	2795 (9)	367 (21)	397 (19)	322 (23)	29 (17)	−74 (19)	68 (19)
H^3	4541 (2)	8667 (4)	3995 (9)	419 (21)	255 (17)	362 (25)	−63 (15)	−21 (21)	53 (18)
H^α	3921 (2)	7678 (4)	7648 (9)	360 (19)	247 (16)	341 (21)	48 (15)	11 (17)	−101 (19)
$H^{\beta1}$	3299 (3)	4860 (5)	8165 (9)	534 (25)	470 (23)	288 (24)	−162 (19)	123 (20)	17 (19)
$H^{\beta2}$	2843 (2)	5904 (5)	5444 (11)	229 (17)	345 (19)	658 (31)	52 (14)	−63 (20)	−34 (21)
$H^{\gamma1}$	3744 (3)	4138 (5)	2425 (10)	762 (33)	458 (24)	324 (26)	−287 (23)	242 (26)	−65 (22)
$H^{\gamma2}$	4208 (2)	3169 (5)	5133 (13)	266 (19)	389 (21)	977 (45)	62 (16)	−96 (26)	−154 (26)
$H^{\varepsilon22}$	3543 (3)	1160 (5)	1438 (10)	479 (24)	360 (19)	471 (28)	−44 (19)	123 (25)	−118 (21)
$H^{\varepsilon21}$	2669 (3)	147 (5)	2639 (10)	513 (26)	276 (16)	559 (29)	−122 (18)	9 (24)	−90 (22)

Table 2. *Observed and calculated squared structure factors*

The quantities given are $100F_o^2$, $100\sigma(F_o^2)$, $100|F_c|^2$. Values of F_o^2 are corrected for extinction.



The conventional R value is $R_F = 0.032$. The extinction parameter converged to a value $g = 1.7\ (4) \times 10^3$, corresponding to a maximum correction of 7% on F^2 for the 120 reflection. The refined atomic coordinates are given in Table 1 and observed and calculated squared structure factors are listed in Table 2. Calculations were performed on CDC 6600 computers with programs which have been described briefly by Schlemper, Hamilton & La Placa (1971).

Table 3. *Covalent bond distances* (Å) *and angles* (°)

Distance	Neutron: Uncorrected	Neutron: Corrected for thermal motion	X-ray* (Cochran & Penfold, 1952)
C —C^α	1·537 (2)	1·540	1·52
C^α—C^β	1·525 (2)	1·528	1·50
C^β—C^γ	1·517 (3)	1·520	1·47
C^γ—C^δ	1·509 (2)	1·511	1·54
C^α—N	1·496 (2)	1·498	1·51
C^δ—$N^{\varepsilon 2}$	1·332 (2)	1·334	1·28
C —O^1	1·238 (3)	1·240	1·27
C —O^2	1·260 (3)	1·262	1·22
C^δ—$O^{\varepsilon 1}$	1·228 (3)	1·231	1·27
C^α—H^α	1·093 (4)	1·097	
C^β—$H^{\beta 1}$	1·101 (5)	1·110	
C^β—$H^{\beta 2}$	1·096 (4)	1·105	
C^γ—$H^{\gamma 1}$	1·091 (5)	1·104	
C^γ—$H^{\gamma 2}$	1·085 (5)	1·100	
N—H^1	1·040 (4)	1·044	
N—H^2	1·023 (4)	1·027	
N—H^3	1·045 (4)	1·048	
$N^{\varepsilon 2}$–$H^{\varepsilon 21}$	1·001 (4)	1·004	
$N^{\varepsilon 2}$–$H^{\varepsilon 22}$	1·008 (5)	1·010	

Angle	Neutron	X-ray† (Cochran & Penfold, 1952)
C^α—C —O^1	118·7 (2)	116
C^α—C —O^2	114·6 (2)	116
O^1 —C —O^2	126·7 (2)	128
C —C^α—C^β	110·3 (1)	114
C —C^α—N	110·2 (1)	111
C^β—C^α—N	111·1 (1)	110
C —C^α—H^α	108·7 (2)	
C^β—C^α—H^α	109·7 (2)	
N—C^α—H^α	106·6 (2)	
C^α—C^β—C^γ	114·0 (1)	113
C^α—C^β—$H^{\beta 1}$	107·2 (3)	
C^α—C^β—$H^{\beta 2}$	108·8 (2)	
C^γ—C^β—$H^{\beta 1}$	109·5 (3)	
C^γ—C^β—$H^{\beta 2}$	109·8 (3)	
$H^{\beta 1}$—C^β—$H^{\beta 2}$	107·3 (4)	
C^β—C^γ—C^δ	113·1 (1)	115
C^β—C^γ—$H^{\gamma 1}$	111·8 (2)	
C^β—C^γ—$H^{\gamma 2}$	110·0 (3)	
C^δ—C^γ—$H^{\gamma 1}$	108·9 (3)	
C^δ—C^γ—$H^{\gamma 2}$	106·2 (2)	
$H^{\gamma 1}$—C^γ—$H^{\gamma 2}$	106·5 (5)	
C^γ—C^δ—$N^{\varepsilon 2}$	115·2 (1)	118
C^γ—C^δ—$O^{\varepsilon 1}$	122·1 (2)	118
$N^{\varepsilon 2}$—C^δ—$O^{\varepsilon 1}$	122·7 (2)	123
C^α—N—H^1	111·2 (2)	
C^α—N—H^2	111·0 (3)	
C^α—N—H^3	108·1 (3)	
H^1—N—H^2	107·3 (4)	
H^1—N—H^3	110·2 (3)	
H^2—N—H^3	109·0 (3)	
C^δ—$N^{\varepsilon 2}$–$H^{\varepsilon 21}$	120·8 (3)	
C^δ—$N^{\varepsilon 2}$–$H^{\varepsilon 22}$	121·1 (3)	
$H^{\varepsilon 21}$–$N^{\varepsilon 2}$–$H^{\varepsilon 22}$	117·7 (4)	

* $\sigma = 0.02$ Å.
† $\sigma = 1°$.

The molecular structure

The glutamine molecule (Fig. 1) is a zwitterion in the keto form, as was found to be the case for L-asparagine in neutron-diffraction studies of L-asparagine H_2O (Ramanadham, Sikka & Chidambaram, 1972; Verbist, Lehmann, Koetzle & Hamilton, 1972). The atomic positions found earlier by X-ray diffraction have been confirmed by this study. The main new feature is the precise determination of the hydrogen-atom positions. Covalent bond distances and angles are given in Table 3; the maximum discrepancy between the neutron and X-ray values is 0·05 Å for distances and 4° for angles. Torsion angles calculated according to the IUPAC conventions (IUPAC-IUB Commission on Biochemical Nomenclature, 1970) are given in Table 4.

Table 4. *Torsion angles* (°)

IUPAC designation		
φ^1	C —C^α–N—H^1	44·6 (3)
φ^2	C —C^α–N—H^2	164·0 (3)
φ^3	C —C^α–N—H^3	− 76·5 (3)
ψ^1	N—C^α–C—O^1	− 15·6 (2)
ψ^2	N—C^α–C—O^2	167·0 (2)
χ^1	N—C^α–C^β –C^γ	66·1 (2)
χ^2	C^α—C^β–C^γ –C^δ	175·5 (2)
$\chi^{3,1}$	C^β –C^γ–C^δ –$O^{\varepsilon 1}$	− 13·3 (3)
$\chi^{3,2}$	C^β—C^γ–C^δ –$N^{\varepsilon 2}$	167·2 (2)
$\chi^{4,2,1}$	$O^{\varepsilon 1}$–C^δ–$N^{\varepsilon 2}$–$H^{\varepsilon 21}$	−3·4 (4)
$\chi^{4,2,2}$	$O^{\varepsilon 1}$–C^δ–$N^{\varepsilon 2}$–$H^{\varepsilon 22}$	−175·6 (4)

The molecule includes two planar groups: C^α, C, O^1, O^2 and C^γ, C^δ, $O^{\varepsilon 1}$, $N^{\varepsilon 2}$, $H^{\varepsilon 21}$, $H^{\varepsilon 22}$; these are oriented approximately perpendicular to one another. In the latter group $H^{\varepsilon 21}$ and $H^{\varepsilon 22}$ are displaced 0·043 (5) and 0·049 (5) Å, respectively in the same direction from the least-squares plane through the remaining 4 atoms. The geometry of the glutamine amide group is very similar to that observed in L-asparagine.H_2O (Ramanadham *et al.*, 1972; Verbist *et al.*, 1972). Bond lengths in this group agree to 0·01 Å and bond angles to 1·5°, excluding values involving hydrogen which are expected to show significant variation due to hydrogen bonding.

Hydrogen bonding and packing

The structure is stabilized by a three-dimensional network of N–H···O hydrogen bonds as shown in Fig. 2, which illustrates the packing in one unit cell. There are five unique hydrogen bonds, one for each hydrogen attached to nitrogen; distances and angles in the hydrogen bonds are given in Table 5. The five N–H···O bonds are all significantly bent and are distributed over

five neighboring molecules, resulting in a complicated hydrogen-bonding pattern. An interesting feature here is the approximate coplanarity of the hydrogen bonds C^{δ}–$O^{\varepsilon 1}\cdots H^{2}$, $N^{\varepsilon 2}$–$H^{\varepsilon 21}\cdots O^{\varepsilon 1}$, and $N^{\varepsilon 2}$–$H^{\varepsilon 22}\cdots O^{1}$ around the amide group. H^{2}, O^{1} and $O^{\varepsilon 1}$ all lie within 0·5 Å of the amide group plane. The slight non-planarity of the amide group mentioned above is such as to make the hydrogen bonds involving $H^{\varepsilon 21}$ and $H^{\varepsilon 22}$ more nearly linear.

There is a systematic inverse correlation of N–H and H···O distances for the ammonium group; this type of correlation has been observed to be quite general for N–H···O hydrogen bonds in amino acids. The N–H bonds in the amide group are approximately 0·02 Å shorter than would be predicted from a curve of N–H *vs.* H···O distances for 16 amino acids we have studied by neutron diffraction. This result is expected, for an sp^{2} hybridized nitrogen should form slightly shorter N–H bonds than an sp^{3} nitrogen. A similar difference in N–H bond lengths was found for the amino and guanidinium groups in L-arginine.$2H_2O$ (Lehmann, Verbist, Hamilton & Koetzle, 1973).

The C–O distances in the carboxyl group are unequal: C–O^{2} is 0·022 (4) Å longer than C–O^{1}, reflecting the fact that O^{2} accepts two hydrogen bonds while O^{1} accepts only one. We also observe that the angle C^{α}–C–O^{1} is approximately 4° larger than C^{α}–C–O^{2}, implying that C–O^{1} possesses more double-bond

Table 5. *Distances* (Å) *and angles* (°) *in the hydrogen bonds*

N–H···O–C	N–H	H···O	N···O	∠N–H···O	∠H···O–C
N—H^{1} ···O^{2} –C	1·040 (4)	1·854 (5)	2·866 (3)	163·3 (4)	127·1 (2)
N—H^{2} ···$O^{\varepsilon 1}$–C^{δ}	1·023 (4)	1·941 (5)	2·948 (3)	167·3 (3)	162·5 (3)
N—H^{3} ···O^{2} –C	1·045 (4)	1·752 (4)	2·772 (3)	164·2 (4)	126·8 (2)
$N^{\varepsilon 2}$–$H^{\varepsilon 22}\cdots O^{1}$ –C	1·008 (5)	1·919 (5)	2·911 (3)	167·3 (4)	159·3 (2)
$N^{\varepsilon 2}$–$H^{\varepsilon 21}\cdots O^{\varepsilon 1}$–$C^{\delta}$	1·001 (4)	2·088 (4)	2·937 (3)	141·3 (4)	108·0 (2)

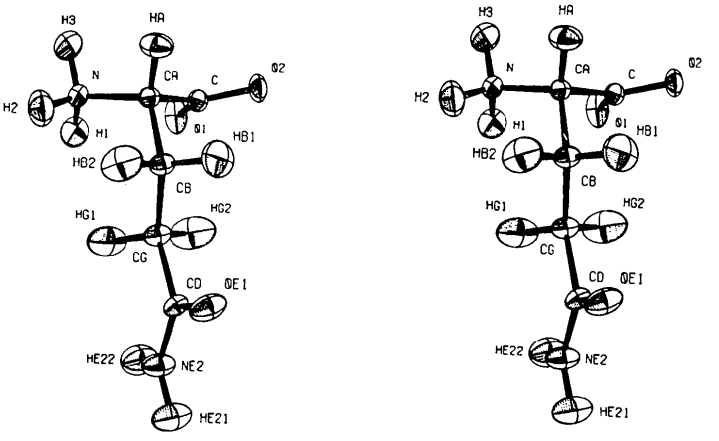


Fig. 1. Stereoview of the glutamine molecule with thermal ellipsoids drawn to enclose 50% probability.

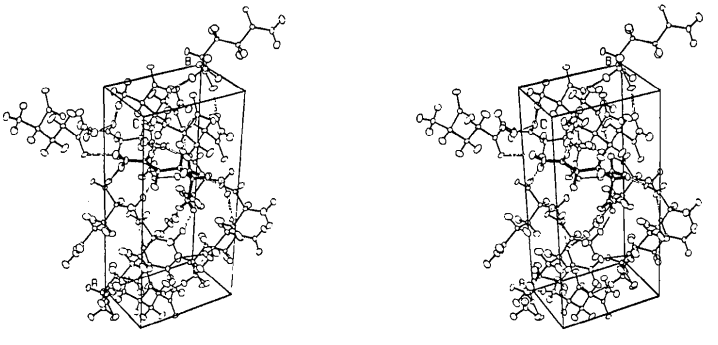


Fig. 2. Stereoview of the packing in one unit cell, with hydrogen bonds drawn open and covalent bonds solid. Thermal ellipsoids drawn to enclose 30% probability.

character than does C–O². Our results here disagree with those of Cochran & Penfold (1952) who concluded that C–O¹ was apparently shorter than C–O².

There is no evidence for formation of an intramolecular hydrogen bond between the ammonium and carboxyl groups. The α-nitrogen lies 0·34 Å from the plane of the carboxyl group, while the ammonium group is rotated approximately 30° from the orientation which would place H^1 and O^1 in an eclipsed conformation, and the contact $H^1\cdots O^1$ is 2·365 (5) Å. This value is only slightly less than 2·4 Å, the sum of van der Waals radii for hydrogen and oxygen, assuming a radius of 1·0 Å for hydrogen as suggested by Baur (1972).

Thermal motion

In order to obtain the best geometrical parameters, the nonhydrogen atoms in the molecule were assumed to behave as a rigid body whose motion was described in terms of **T**, **L** and **S** tensors (Schomaker & Trueblood, 1968). The largest principal axis of **L** corresponds to an r.m.s. librational amplitude of 2·9°, while the r.m.s. difference between observed and calculated thermal parameters u_{ij} is 0·004 Å². This latter value may be compared to the average $\sigma(u_{ij})=0{\cdot}0008$ Å² from the least-squares refinement to give an estimate of the magnitude of non-rigid body motions present. The calculated rigid-body librations were used to derive corrections to bond lengths for the non-hydrogen atom backbone and the corrected distances are included in Table 3. Bond lengths involving hydrogen were corrected for thermal motion with the minimum correction of Busing & Levy (1964), which has been shown to give good results in the case of L-lysine.HCl.$2H_2O$ (Koetzle, Lehmann, Verbist & Hamilton, 1972), and in other amino acids.

An additional rigid-body calculation was carried out for the NH_3^+ group in order to estimate the magnitude of torsional motion for this group. C^α, N, H^1, H^2 and H^3 were included in the rigid body, and no constraints were applied to the motion based on symmetry. The fit is quite good, with $\overline{\Delta u_{ij}^2}^{1/2}=0{\cdot}002$ Å², and the maximum principal axis of **L** lies along C^α–N with an r.m.s. amplitude of 7·6 (7)°. With a harmonic oscillator approximation to a threefold cosine-hindered rotor (Schlemper *et al.*, 1971), this librational amplitude can be shown to correspond to a librational frequency of 420 cm^{-1} and to a rotational barrier of 9·8 kcal/mole. These values are typical of frequencies and barriers derived for hydrogen-bonded NH_3^+ groups in other amino acids.

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