Conclusion

The present structure indicates the strong tenacity of highly polarizing cations for residual water molecules, as has been noticed for other zeolites. Further progress in understanding cation assignments requires analysis of mono- or dicationic varieties, and appropriate studies are planned. Detailed analysis of Ω is needed to test whether it has the same framework as mazzite.

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Studies in Molecular Structure, Symmetry and Conformation.
XI. The Crystal and Molecular Structure of Glycyl-DL-threonine Monohydrate*

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The title compound is orthorhombic, space group $Pca2_1$, with $a = 16.26$ (1), $b = 4.87$ (1), $c = 23.24$ (1) Å, $Z = 8$. The structure was solved by direct methods with visual X-ray intensities. The asymmetric unit contains two molecules which are related by an approximate centre of inversion. The dimensions of the peptide group are in agreement with the weighted mean values of Marsh & Donohue [Advanc. Protein Chem. (1967). 22, 235–256]. The peptide chain is in the extended conformation. The conformation of the threonine side group is different from that in free threonine.

Introduction

In earlier parts of this series (parts VIII, IX and X: Swaminathan & Srinivasan, 1975a,b,c) we discussed the structural and conformational aspects of allo-threonine and its derivatives. This paper deals with the structure determination of glycyl-DL-threonine monohydrate.

Experimental

Single crystals of glycyl-DL-threonine monohydrate were grown by evaporation of an aqueous solution. Preliminary photographs showed the crystals to be orthorhombic, space group $Pca2_1$ (or $Pcam$). The density was determined by flotation in a mixture of benzene and bromoform.

Crystal data

$C_6H_{12}N_2O_4 \cdot H_2O$. Orthorhombic, $a = 16.26$ (1), $b = 4.87$ (1), $c = 23.24$ (1) Å; systematic absences $0kl$, $l =$

$2n+1$; $h0l$, $h=2n+1$, space group $Pca2_1$; $Z=8$, $m=$ 194·2, $D_o=1·418$, $D_c=1·403$ g cm^{-3}; $\mu=10·7$ cm^{-1}, λ (for Cu $K\alpha$ radiation)$=1·5418$ Å.

A crystal ($0·2 \times 0·4 \times 0·2$ mm) was used to collect intensities by the multiple-film equi-inclination Weissenberg technique with Ni-filtered Cu $K\alpha$ radiation. The intensities of 1517 independent reflexions ($k=$ 0–4, $h=0$–2) were estimated visually and corrected for Lorentz and polarization factors, and spot shape (Phillips, 1962). No absorption corrections were made ($\mu t=0·27$). The data about the two axes were brought to a single scale (Rollett & Sparks, 1960).

Statistical test

To resolve the ambiguity in space group ($Pca2_1$ or $Pcam$) the statistical methods of Ramachandran & Srinivasan (1959) were used with the normalized structure factors $|E|$. For calculating $|E|$ the molecular scattering factors (spherically averaged) computed from the Debye (1915) formula:

$$g^2 = \sum_i^m \sum_j^m \frac{\sin k\gamma_{ij}}{k\gamma_{ij}} \times f_i f_j$$

(where $k=4\pi \sin \theta/\lambda$, $\gamma_{ij}=$distance between the atoms i and j, m is the number of atoms in the molecule) were used.* This method was adopted because the molecular structure significantly affects the $|E|$ values, which should be accurately determined for a satisfactory start in the direct method of solving the structure. Fig. 1 gives the experimental distribution (crosses) of $|E|$ values with the theoretical curves (Swaminathan & Srinivasan, 1975d). The distribution suggested that the structure should have a degree of centrosymmetry of nearly 90%. However, the structure solution was attempted in both the space groups.

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* This was suggested by Dr Peter Main, University of York, during his visit to the author's laboratory.
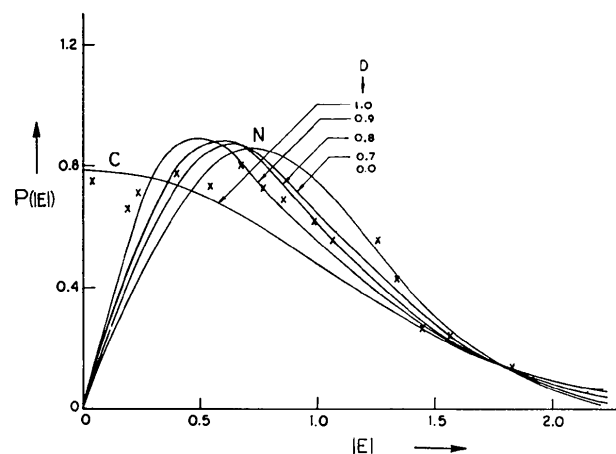

Fig. 1. $P(|E|)$ distribution for various values of the degree of of centrosymmetry. Theoretical curves are shown by solid lines and experimental points by crosses.

Structure determination and refinement

The solution was first attempted in the space group $Pcam$ using the symbolic addition procedure of Karle & Karle (1963); this did not give an acceptable model. Refinement was therefore attempted in the non-centrosymmetric space group $Pca2_1$ with the multisolution methods of Germain & Woolfson (1968). The phase determination was carried out with the program MULTAN (Main, Woolfson & Germain, 1971). Table 1, gives the starting set of phases. The phases of the first three reflexions were determined from the Σ_2 formula of Hauptman & Karle (1953). The tangent formula results gave three sets of phases for the reflexions 743, 14,0,3 and 12,3,13 with the figures of merit given below.

	Phase			Figure of merit
I	$3\pi/4$,	$\pi/4$,	$\pi/4$	2·542
II	$3\pi/4$,	$\pi/4$,	$-\pi/4$	2·506
III	$3\pi/4$,	$\pi/4$,	$3\pi/4$	2·458

Table 1. *Starting set of phases*

h	k	l	$|E|$	Phase
20	0	0	1·74	2π
12	0	0	1·63	π
14	0	0	1·54	2π
15	3	0	2·83	2π ⎫
6	1	1	2·46	2π ⎬ Origin
7	4	0	2·32	2π ⎭
7	4	3	4·83	$\pm\pi/4$, $\pm3\pi/4$ (enantiomorph)
14	0	3	4·02	$\pm\pi/4$, $\pm3\pi/4$
12	3	13	3·20	$\pm\pi/4$, $\pm3\pi/4$

An E map computed with the third set of phases revealed all the non-hydrogen atoms except those of the water molecules whose positions were determined from a difference map. Three cycles of full-matrix least-squares refinement on an IBM 370 computer at I.I.T. Madras with the program LALS (Gantzel, Sparks & Trueblood, 1961) reduced R to 0·15. At this stage the H atoms were located from a difference map. Hughes's (1941) weighting scheme was employed with

$$w=(\tfrac{1}{15})^2 \quad \text{for} \quad |F_o| < 15$$

and

$$w=\left(\frac{1}{|F_o|}\right)^2 \quad \text{for} \quad |F_o| \geq 15.$$

Since the origin is defined anywhere along z, the z coordinate of one atom was clamped during refinement. In the case of larger equal-atom structures, fixing just one C or N is not found to be sufficient. Hence the z coordinates of different sets of five adjacent atoms were kept fixed during different cycles of refinement. A similar procedure has been adopted for reserpine (Karle & Karle, 1968).

For anisotropic refinement only one molecule was refined at a time. This procedure was adopted because of core limitations in the computer. After four cycles of refinement the final R was 10·8%. The shifts in the parameters during the last cycle of refinement were

⅓th of the estimated standard deviations. The final positional and thermal parameters of all non-hydrogen atoms are listed in Table 2. The observed and calculated structure factors are given in Table 3.*

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30934 (18 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Discussion of the structure

Intramolecular features, bond lengths and angles

The bond lengths and angles are given in Fig. 2. There are two molecules in the asymmetric unit (labelled *A* and *B*). The average standard deviations

Table 2. *Fractional positional and thermal parameters with their standard deviations in parentheses*

The thermal parameter is defined by the expression $T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

All values are multiplied by 10^4.

|	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	1432 (4)	10602 (15)	7600 (4)	19 (2)	125 (32)	20 (1)	−5 (15)	−11 (3)	20 (11)
N(2)	2026 (4)	6423 (16)	7781 (3)	10 (2)	141 (36)	10 (1)	−13 (14)	−5 (3)	−8 (10)
C(3)	2780 (4)	7563 (18)	8031 (3)	7 (2)	128 (35)	8 (1)	−34 (15)	−0 (3)	−1 (11)
N(1)	−11 (4)	8362 (16)	7237 (4)	9 (2)	172 (35)	11 (1)	7 (16)	1 (3)	22 (12)
C(1)	636 (5)	6451 (23)	7466 (5)	9 (2)	118 (46)	12 (2)	−0 (18)	−5 (4)	10 (17)
C(2)	1397 (6)	8081 (24)	7616 (5)	11 (3)	60 (51)	11 (2)	7 (21)	−1 (4)	5 (16)
C(4)	3557 (4)	6385 (20)	7729 (4)	7 (2)	199 (41)	7 (1)	14 (16)	2 (3)	15 (13)
O(2)	4226 (3)	7428 (15)	7901 (3)	10 (1)	226 (36)	13 (1)	−31 (13)	2 (2)	−6 (11)
O(3)	3481 (3)	4451 (16)	7380 (3)	12 (1)	336 (38)	9 (1)	52 (15)	−1 (2)	−19 (10)
C(5)	2838 (5)	7115 (20)	8690 (4)	14 (2)	116 (40)	11 (1)	6 (16)	0 (3)	−0 (13)
O(4)	2973 (5)	4160 (15)	8780 (3)	34 (3)	239 (32)	11 (1)	78 (18)	2 (3)	35 (11)
C(6)	2054 (7)	7919 (25)	9018 (5)	21 (3)	369 (53)	15 (2)	47 (24)	11 (5)	−15 (17)
N(3)	2564 (3)	3090 (14)	1433 (3)	7 (1)	181 (30)	13 (1)	−6 (13)	−5 (2)	−15 (9)
C(7)	1914 (5)	1270 (19)	1168 (4)	14 (2)	157 (38)	17 (1)	−26 (18)	−10 (4)	−22 (13)
C(8)	1181 (4)	3023 (18)	986 (3)	15 (2)	139 (37)	10 (1)	−24 (17)	4 (3)	−9 (12)
O(5)	1223 (3)	5606 (12)	984 (3)	16 (1)	193 (29)	23 (1)	−18 (13)	−10 (2)	1 (11)
N(4)	519 (3)	1520 (15)	837 (3)	7 (1)	164 (31)	14 (1)	−3 (12)	−3 (2)	−16 (9)
C(9)	−208 (4)	2787 (18)	580 (3)	4 (2)	175 (36)	15 (1)	−25 (14)	1 (2)	5 (12)
C(10)	−999 (4)	1764 (18)	891 (3)	10 (2)	196 (37)	11 (1)	−26 (15)	4 (3)	−34 (11)
O(6)	−928 (3)	−25 (15)	1306 (3)	17 (2)	325 (33)	12 (1)	−41 (14)	−8 (2)	35 (10)
O(7)	−1657 (3)	2830 (15)	721 (3)	13 (2)	365 (36)	21 (1)	2 (13)	4 (2)	33 (12)
C(11)	−253 (5)	2248 (19)	−57 (4)	15 (2)	223 (38)	11 (1)	−30 (17)	0 (3)	9 (12)
O(8)	−418 (4)	−629 (13)	−151 (3)	29 (2)	196 (29)	138 (1)	−1 (14)	5 (3)	0 (9)
C(12)	528 (6)	3149 (22)	−377 (4)	23 (3)	331 (47)	15 (1)	−20 (21)	15 (4)	26 (16)
O$_w$(1)	9568 (5)	8227 (20)	8666 (4)	38 (3)	300 (49)	15 (1)	−8 (21)	−2 (4)	−25 (14)
O$_w$(2)	7956 (4)	7060 (17)	9957 (3)	37 (2)	340 (35)	13 (1)	20 (17)	−3 (3)	−2 (11)
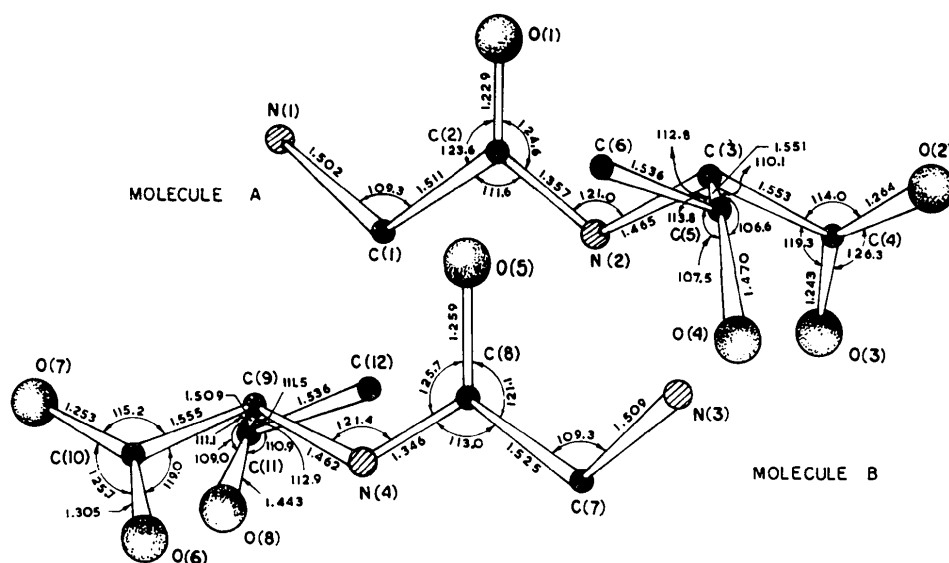
Fig. 2. Bond lengths (Å) and angles (°) observed in the molecule. N(2)–C(3)–C(4) = 111·2°; C(10)–C(9)–N(4) = 110·1°.

in the bond lengths and angles are 0·01 Å and 0·6°. The bond lengths and angles agree with standard values within experimental error. Both molecules exist as zwitterions. In B, C(10)–O(6) and C(10)–O(7) are 1·305 (11) and 1·254 (10) Å. C(10)–O(6) is larger (nearly 5σ) than the weighted mean value of 1·252 Å (Marsh & Donohue, 1967). It has been suggested (Levy & Corey, 1941; Donohue & Trueblood, 1952) that the hydrogen bonding might have an indirect influence on the C–O distances. In the present case O(6) accepts two protons from N(1) and N(3) forming N–H···O hydrogen bonds and O(7) accepts one proton from N(3) and one from O$_w$(2) forming N–H···O and O–H···O hydrogen bonds. The equations of the least-squares planes passing through the carboxyl groups of A and B are given in Table 4.

Peptide group

C(1), C(2), O(1), N(2) and C(3) form the peptide group in A and C(7), C(8), O(5), N(4) and C(9) in B. The dimensions of the peptide group are not significantly different from the weighted mean values proposed by Marsh & Donohue (1967). N(2)–C(2) and N(4)–C(8) are slightly larger (about 2σ) than the weighted mean value of Marsh & Donohue (1967). The least-squares planes fitted to the peptide group

and the amide group and the deviations from these planes are listed in Table 4.

Molecular packing and hydrogen bonding

The projection of the structure down **b** is shown in Fig. 3. The molecules run approximately parallel to **a**. There are eight molecules in the cell of which four are D- and four L-isomers. The two isomers in the cell are related by an approximate centre of inversion and the mean deviation $\langle|\Delta y|\rangle$ of the atoms from the centroid of the two isomers is 0·13 Å, which corresponds to a value of 0·87 for D, the degree of centrosymmetry (Luzzati, 1952), in reasonable agreement with the value of 0·90 obtained from the $P(|E|)$ distribution (Fig. 1).

There are 14 protons available for hydrogen bonding and all are involved in fairly strong hydrogen bonds. The various hydrogen-bond distances and angles are listed in Table 5. There are two C···O distances, 3·14 and 3·00 Å, which are less than the sum of the van der Waals radii for C and O. Such short C···O distances are observed in a number of other structures, *e.g.* oxysuran (Karle, 1974); L-threonyl-L-phenylalanine *p*-nitrobenzyl ester hydrobromide (Mallikarjunan, Rao, Venkatesan & Sarma, 1969). The shortest C···O distance observed in those cases is 3·14 Å.

Table 4. *Least-squares planes*

Equation of the plane: $AX + BY + CZ = D$ with respect to the crystallographic axes a, b and c, where x, y, z and D are in Å.

Plane	Atom	Deviation (Å)	Equation of the plane
Molecule A			
Peptide group	C(1)	0·044	$-0·3560X + 0·0590Y + 0·9325Z = 15·9380$
	C(2)	−0·023	
	O(1)	−0·006	
	N(2)	−0·075	
	C(3)	0·06	
Amide group	C(1)	0·0020	$-0·3082X + 0·0514Y + 0·9499Z = 16·3228$
	C(2)	0·0073	
	O(1)	0·0029	
	N(2)	0·0023	
	C(3)*	0·2027	
Carboxyl group	O(2)	0·009	$+0·0767X − 0·6732Y + 0·7354Z = 11·5861$
	O(3)	0·009	
	C(4)	−0·025	
	C(3)	0·007	
	N(2)*	−0·138	
Molecule B			
Peptide group	C(7)	0·039	$-0·3600X + 0·2149Y + 0·9326Z = 1·4635$
	C(8)	0·014	
	O(5)	0·011	
	N(4)	0·062	
	C(9)	−0·055	
Amide group	C(7)	0·0001	$-0·3200X + 0·0215Y + 0·9471Z = 1·5880$
	C(8)	−0·0005	
	O(5)	0·0002	
	N(4)	0·0001	
	C(9)*	−0·1738	
Carboxyl group	O(6)	0·003	$+0·0997X + 0·7377Y + 0·6677Z = 1·8650$
	O(7)	0·003	
	C(10)	−0·009	
	C(9)	0·002	
	N(4)*	0·063	

* Omitted from least-squares plane calculations.

Molecular conformation

The notation followed for describing the conformation is that suggested by the IUPAC-IUB Commission on Biochemical Nomenclature (1971). The rotations about $N–C^\alpha$ are denoted by ϕ, about $C^\alpha–C'$ by ψ, about $C'–N$ by ω, and about $C^\alpha–C^\beta$ by χ. The pertinent torsion angles are given in Table 6. The backbone conformation around the α-carbon atom is given by the torsion angles $\phi_{21} = -130\cdot4°$; $\psi_T^1 = 175\cdot6°$ (for A), $\phi_{21} = -132\cdot0°$; $\psi_T^1 = 176\cdot6°$ (for B); These values lie within the allowed region of the (ϕ, ψ) conformational map of Ramachandran & Sasisekharan (1968) trans-

Table 5. *Hydrogen-bond lengths* (Å) *and angles* (°)

Donor	Acceptor	$D\cdots A$	$H\cdots A$	$\angle D-H\cdots A$	$\angle C-D\cdots A$	$\angle H-D\cdots A$
C(1)—N(1)–H(1)	O(6^i)	2·77	2·06	152·8	94·0	19·8
C(1)—N(1)–H(2)	O(3^{ii})	2·82	2·17	147·3	105·3	24·4
C(1)—N(1)–H(3)	O(2^{ii})	2·84	2·35	136·8	123·9	34·3
C(3)—N(2)–H(6)	O(1^v)	3·02	2·11	157·8	132·6	15·2
C(7)—N(3)–H(13)	O(6^{iii})	2·88	1·92	165·9	104·4	9·3
C(7)—N(3)–H(14)	O(3^x)	2·86	1·96	147·3	92·0	21·7
C(7)—N(3)–H(15)	O(7^{vi})	2·87	2·21	147·7	118·5	24·2
C(9)—N(4)–H(18)	O(5^v)	3·11	2·21	155·8	137·0	16·9
C(5)—O(4)–H(12)	O$_w$(2^{viii})	2·79	1·97	163·6	110·1	11·4
C(11)–O(8)–H(24)	O$_w$(1^x)	2·80	2·02	168·5	109·8	8·2
O$_w$(1)–H(25)	O(4^{iv})	2·85	1·41	144·4		16·7
O$_w$(1)–H(26)	O(2^{vii})	2·81	1·53	157·3		12·0
O$_w$(2)–H(27)	O(7^{ix})	2·79	2·00	149·5		21·1
O$_w$(2)–H(28)	O(8^{xi})	2·88	1·57	161·2		10·1

Symmetry code

i	$-x$	$1-y$	$\frac{1}{2}+z$
ii	$x-\frac{1}{2}$	$1-y$	z
iii	$\frac{1}{2}+x$	$-y$	z
iv	$1-x$	$1-y$	$\frac{1}{2}+z-1$
v	x	$y-1$	z
vi	$\frac{1}{2}+x$	$1-y$	z
vii	$1-x$	$2-y$	$\frac{1}{2}+z$
viii	$-x$	$1-y$	$\frac{1}{2}+z-1$
ix	$\frac{1}{2}-x$	$y-1$	$\frac{1}{2}+z-1$
x	$-x-\frac{1}{2}$	y	$\frac{1}{2}+z$
xi	$-x-\frac{1}{2}$	$y+1$	$\frac{1}{2}+z$
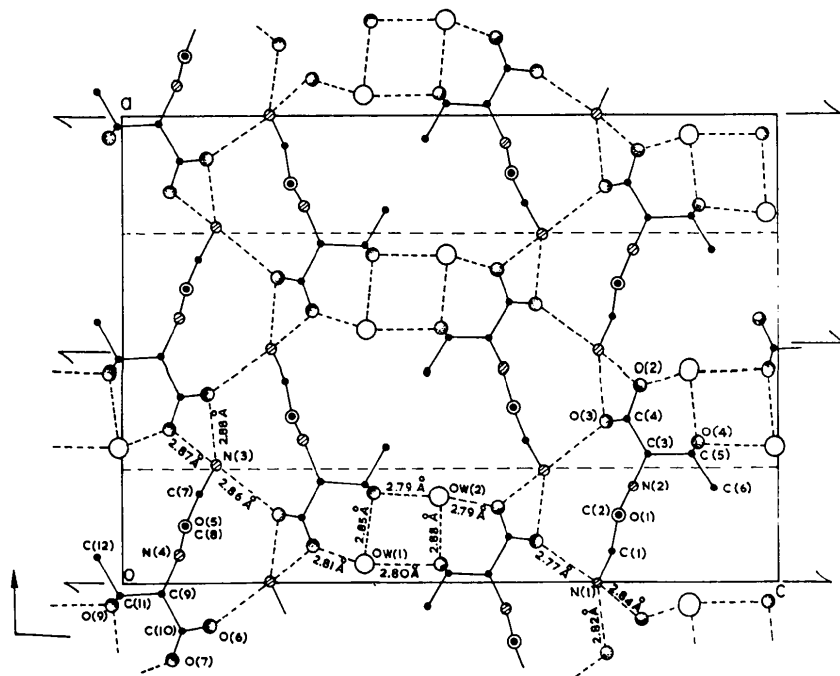
Fig. 3. Packing of the molecules viewed down b.

posed into the standard convention. The torsion angle ω is $-170 \cdot 6°$ (for A) and $-172 \cdot 1°$ (for B). These conformational angles can be compared with the corresponding angles $(\phi = \psi = \omega = 180°)$ for a fully extended conformation of the polypeptide chain.

Table 6. *Torsional angles* (°) *in glycyl-*DL-*threonine*

Molecule	Bond	Atoms	Designation	Angle
A	C^α–C'	N(1)–C(1)–C(2)—N(2)	ψ_{11}	$-175 \cdot 0$
		–O(1)	ψ_{12}	$6 \cdot 1$
	C'–N	C(1)–C(2)–N(2)—C(3)	ω	$-170 \cdot 6$
	N–C^α	C(2)–N(2)–C(3)—C(4)	φ_{21}	$-130 \cdot 4$
		–C(5)	φ_{22}	$105 \cdot 2$
	C^α–C'	N(2)–C(3)–C(6)—O(2)	ψ_T^1	$175 \cdot 6$
		–O(3)	ψ_T^2	$-9 \cdot 2$
	C^α–C^β	N(2)–C(3)–C(4)—O(4)	χ_{21}	$70 \cdot 0$
		–C(6)	χ_{22}	$-48 \cdot 5$
B	C^α–C'	N(7)–C(7)–C(8)—N(4)	ψ_{11}	$-169 \cdot 2$
		–O(5)	ψ_{12}	$+10 \cdot 6$
	C'–N	C(7)–C(8)–N(4)—C(9)	ω	$-172 \cdot 1$
	N–C^α	C(8)–N(4)–C(9)—C(10)	φ_{21}	$-132 \cdot 0$
		–C(11)	φ_{22}	$104 \cdot 1$
	C^α–C'	N(4)–C(9)–C(10)—O(6)	ψ_T^1	$176 \cdot 6$
		–O(7)	ψ_T^2	$-1 \cdot 5$
	C^α–C^β	N(4)–C(9)–C(11)—O(8)	χ_{21}	$68 \cdot 7$
		–C(12)	χ_{22}	$-54 \cdot 9$

The torsion angles ψ_T^1 and ψ_T^2 at the carboxyl terminus are in general found to be close to 180 and 0° (360°) with $\psi_T^1 = \psi_T^2 + 180°$. In the presence of a β-carbon atom ψ_T^2 is usually about $-15°$ (Sundaralingam & Putkey, 1970). The torsion angles at the C-terminus are

$$\psi_T^1 = 175 \cdot 6° \qquad \psi_T^2 = -9 \cdot 2° \text{ (for } A)$$

$$\psi_T^1 = 176 \cdot 6° \qquad \psi_T^2 = -1 \cdot 5° \text{ (for } B)$$

close to the expected value.

The side-chain conformation is described by the torsion angles around C^α–C^β. These angles are close to 60, 180 and 300° respectively, corresponding to the three staggered positions around the bond marked as I, II and III (Lakshminarayanan, Sasisekharan & Ramachandran, 1967) and the γ-atom is said to go into these positions. In A the C^γ atom [C(6)] goes to position III ($\chi_{22} = 311 \cdot 5°$) and O^γ [O(4)] to position I ($\chi_{21} = 70 \cdot 0°$). Similarly in B the C^γ [C(12)] and O^γ [O(8)] atoms go to positions III ($\chi_{22} = 305 \cdot 1°$) and I ($\chi_{21} = 68 \cdot 7°$) respectively.

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