

The Crystal Structure of Acetyl-L-proline-N-methylamide

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The crystal structure of acetyl-L-proline-N-methylamide has been determined by the symbolic addition method. The crystal is orthorhombic, space group $P2_12_12_1$ with four molecules in a cell of dimensions $a = 9.74 \pm 0.01$, $b = 13.20 \pm 0.01$, $c = 7.17 \pm 0.01$ Å. Refinement was carried out by the full-matrix least-squares method including anisotropic thermal parameters. The final R value for 1213 reflexions was 0.098. The main chain of the molecule containing two *trans* planar peptide groups takes a folded conformation, the dihedral angle between the two peptide planes being 69.4° . The two imino nitrogen atoms are arranged nearly in *cis* position and the torsion angles, φ and ψ are 103.7 and 164.2° respectively, indicating that the conformation is fairly close to that of the right-handed α -helix. The molecules are bound together through N-H...O hydrogen bonds to form a chain about the twofold screw axis parallel to c .

Introduction

In the course of a study on near-infrared spectra containing two peptide groups, Mizushima, Shimanouchi, Tsuboi, Sugita, Kurosaki, Mataga & Souda (1952) suggested that the molecule of acetylproline-N-methylamide in carbon tetrachloride solution takes a folded form which is stabilized by the intramolecular hydrogen bond as shown in Fig. 1. According to the representation of Edsall, Flory, Kendrew, Liquori, Némethy, Ramachandran & Scheraga (1966), this conformation may be described as $\varphi \simeq 120$, $\psi \simeq 240^\circ$. These values correspond in the φ - ψ chart (Fig. 6) to a point lying just outside the outer limit of the allowed conformation for di- and tri-peptides, suggesting that the structure might be a ribbon structure (see Ramachandran, Ramakrishnan & Sasisekharan, 1963) which has not yet been found. We have, therefore, undertaken the crystal structure analysis in order to determine the conformation of the molecule in the crystalline state.

Experimental

The crystals recrystallized from carbon tetrachloride solution are colourless transparent plates with well developed (010) faces elongated along the c axis. The density was measured by the flotation method in a carbon tetrachloride-toluene mixture. Because the crystals are deliquescent, the sample for analysis was sealed in glass capillary. The unit-cell dimensions were determined from $0kl$ and $h0l$ precession photographs using Cu $K\alpha$ radiation.

Crystal data

Acetyl-L-proline-N-methylamide (APNMA)
 $C_8H_{14}N_2O_2$
 Orthorhombic
 $P2_12_12_1$
 $Z = 4$

$$\begin{aligned} a &= 9.74 \pm 0.01 \text{ \AA} \\ b &= 13.20 \pm 0.01 \\ c &= 7.17 \pm 0.01 \\ U &= 921.4 \text{ \AA}^3 \\ D_m &= 1.219 \text{ g.cm}^{-3} \\ D_x &= 1.227 \text{ g.cm}^{-3} \\ \mu(\text{Cu } K\alpha) &= 8.7 \text{ cm}^{-1} \\ F(000) &= 368 \end{aligned}$$

The intensity data were collected from equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation by use of the multiple-film method. The layers from $0kl$ to $8kl$ for the a axis and from $hk0$ to $hk6$ for the c axis were recorded. Intensities were measured with a Joyce-Loebl flying-spot integrating microdensitometer. The weaker spots were measured by visual comparison with a calibrated intensity scale. After correction for Lorentz and polarization factors, the structure factors on various layers were correlated and scaled to a common base. Since the size of the crystal was about $0.3 \times 0.5 \times 0.5$ mm, no absorption correction was applied. A Wilson plot was then made to estimate the scale factor and an overall temperature factor. The value of B was found to be 3.18 \AA^2 . The normalized structure factors, E , are given below, with the statistical values:

	Observed	Theoretical (for non- centrosym- metric struc- tures)
$\langle E ^2 \rangle$	0.959	1.000
$\langle E \rangle$	0.847	0.886
$\langle E^2 - 1 \rangle$	0.777	0.736

Determination of the structure

The structure was solved by the symbolic addition method (Karle & Karle, 1966). The program, which

facilitates the symbolic addition procedure and the application of the tangent formula for all space groups, was written by one of us (T.M.). The specification of the origin and the assignment of unknown symbols was as follows:

h	k	l	$ E $	Phase angle
9	2	0	2.76	$\pi/2$
0	9	4	2.70	$\pi/2$
5	0	7	2.49	$\pi/2$
3	10	2	2.54	a
2	9	0	2.58	b
4	0	5	2.26	c
3	1	6	2.25	d

The phase angle of the reflexion 606 was found to be zero from the \sum_1 formula with probability 0.93. On the basis of the phases of these eight reflexions, the phase angles of the reflexions having E values greater than 1.8 were assigned by use of the formula, $\varphi_h = \langle \varphi_k + \varphi_{h-k} \rangle_k$. During the application of the \sum_2 relationship it became apparent that $a=0$, $d=\pi/2$ or $a=\pi$, $d=-\pi/2$. The former set was chosen to specify the enantiomorph. No information was obtained for b and c , but the phases of these reflexions should naturally be chosen to be 0 or π for b , and $\pi/2$ or $-\pi/2$ for c , to satisfy the space group requirements. Therefore, four possible combinations were examined. In each case the tangent formula was applied in a progressive way, dividing the whole process into four steps. In the first step, the eight phases of the starting set were extended to obtain the phases of reflexions with $|E| \geq 1.8$ and the resulting phases were refined. In the second step, the phases of reflexions having $|E|$ values between 1.8 and 1.4 were determined in terms of those of reflexions having $|E| \geq 1.8$. In the third step, the phases of reflexions with $|E| \geq 1.4$ were refined by the use of the tangent formula.

In the final step, the phases of reflexions with $|E|$ between 1.4 and 1.0 were determined in terms of those of reflexions having $|E| \geq 1.4$. At the end of each step, the R index for the normalized structure factors was calculated. Table 1 shows the variation of the R index during application of the tangent formula, indicating that sets 2 and 4 may be correct. The E maps calculated for the two cases showed that they are actually equivalent to each other and the maps could well be interpreted in terms of the known chemical structure. A careful examination of the final phase angles revealed that in case 4, the phase angle of the reflexion 920 which had been assigned as an origin-specifying phase was inverted during the re-cycling process in the third step and the final result became equivalent to that of case 2. The E map for case 2 is shown in Fig. 2. It was found that the minimum height of a peak corresponding to an atomic site was 202, on an arbitrary scale, whereas the maximum height of spurious peaks was only 104. No difficulty was experienced in recognizing the correct structure.

Table 1. Variations of the R index during application of the tangent formula

Incorporated reflexions	Cycle	Variation of the R index* for each phase assignment			
		Set 1 $b=0,$ $c=\pi/2$	Set 2 $b=0,$ $c=-\pi/2$	Set 3 $b=\pi,$ $c=\pi/2$	Set 4 $b=\pi,$ $c=-\pi/2$
1st step					
60 planes with $ E \geq 1.8$	1	0.200	0.200	0.200	0.200
	2	0.191	0.199	0.198	0.192
	3	0.196	0.216	0.187	0.221
	4	0.217	0.234	0.185	0.196
	5	0.198	0.207	0.183	0.184
3rd step					
164 planes with $ E \geq 1.4$	1	0.320	0.284	0.295	0.227
	2	0.319	0.216	0.290	0.192
Total number of phases determined		339	385	348	388
Result		incorrect	correct	incorrect	correct†

$$* R = \sum_h \frac{||E_h|_{\text{obs}} - |E_h|_{\text{calc}}|}{\sum_h |E_h|_{\text{obs}}}$$

† The phase angle of reflexion 920 was inverted from $\pi/2$ to $-\pi/2$ in the 3rd step.

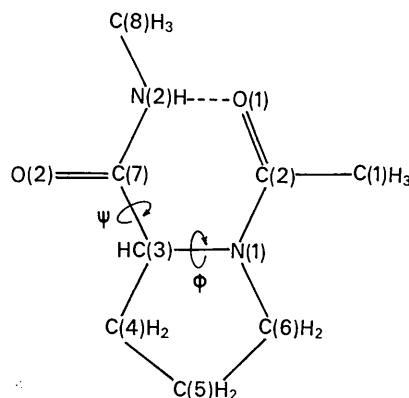


Fig. 1. Proposed structure of acetylproline- N -methylamide.

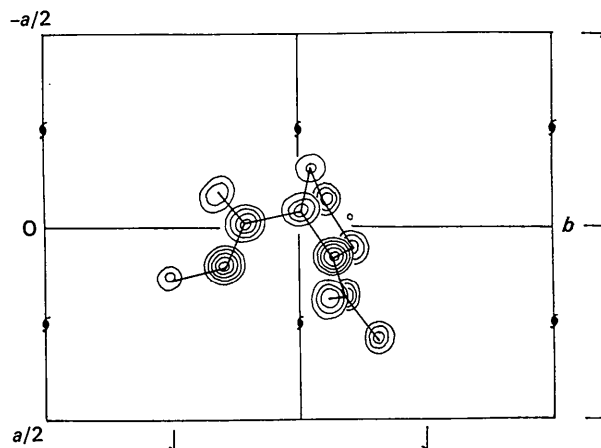


Fig. 2. E map calculated using 385 reflexions with $|E| \geq 1.0$. Contours are on an arbitrary scale.

Table 3. Final atomic parameters and their standard deviations

Temperature factors are of the form: $T = \exp [- (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
Standard deviations are listed in parentheses denoting the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.2915 (3)	0.6577 (2)	0.1196 (5)	0.0082 (3)	0.0041 (2)	0.0199 (7)	-0.0007 (2)	0.0002 (4)	0.0001 (3)
C(2)	0.1821 (3)	0.5920 (2)	0.2000 (4)	0.0074 (3)	0.0026 (1)	0.0158 (6)	0.0004 (2)	-0.0007 (4)	0.0002 (2)
O(1)	0.1858 (2)	0.5596 (2)	0.3629 (3)	0.0108 (3)	0.0047 (1)	0.0170 (5)	-0.0014 (2)	-0.0033 (3)	0.0019 (2)
N(1)	0.0782 (2)	0.5665 (2)	0.0874 (3)	0.0063 (2)	0.0032 (1)	0.0135 (5)	-0.0003 (1)	-0.0007 (3)	0.0014 (2)
C(3)	-0.0385 (3)	0.5061 (2)	0.1553 (4)	0.0066 (3)	0.0033 (1)	0.0184 (7)	-0.0006 (2)	0.0005 (4)	-0.0002 (3)
C(4)	-0.1493 (3)	0.5242 (3)	0.0077 (6)	0.0071 (3)	0.0061 (2)	0.0262 (9)	-0.0003 (2)	-0.0041 (5)	0.0015 (4)
C(5)	-0.0710 (4)	0.5476 (3)	-0.1678 (5)	0.0105 (4)	0.0076 (2)	0.0204 (8)	0.0002 (3)	-0.0049 (5)	0.0026 (4)
C(6)	0.0534 (3)	0.6082 (2)	-0.1006 (5)	0.0095 (3)	0.0051 (2)	0.0163 (7)	0.0006 (2)	-0.0016 (4)	0.0029 (3)
C(7)	-0.0076 (3)	0.3932 (2)	0.1786 (4)	0.0083 (3)	0.0035 (2)	0.0164 (6)	-0.0013 (2)	0.0019 (4)	0.0010 (3)
O(2)	-0.0892 (3)	0.3422 (2)	0.2700 (4)	0.0135 (3)	0.0054 (1)	0.0371 (8)	-0.0018 (2)	0.0112 (5)	0.0033 (3)
N(2)	0.1031 (3)	0.3568 (2)	0.0972 (4)	0.0102 (3)	0.0026 (1)	0.0170 (5)	-0.0003 (2)	0.0021 (4)	0.0006 (2)
C(8)	0.1358 (4)	0.2496 (2)	0.1064 (6)	0.0170 (5)	0.0032 (2)	0.0243 (8)	0.0008 (2)	0.0030 (7)	-0.0000 (3)
H(1)	0.3365 (34)	0.6159 (26)	0.0198 (49)	1.90 (0.68)					
H(2)	0.2595 (52)	0.7255 (37)	0.0691 (75)	5.14 (1.20)					
H(3)	0.3771 (64)	0.6661 (58)	0.2048 (87)	7.19 (1.62)					
H(4)	-0.0528 (49)	0.5292 (39)	0.2795 (70)	5.16 (1.21)					
H(5)	-0.2107 (30)	0.4647 (23)	0.0093 (45)	1.08 (0.63)					
H(6)	-0.2239 (45)	0.5879 (33)	0.0708 (68)	3.92 (1.01)					
H(7)	-0.1383 (39)	0.5771 (30)	0.2554 (53)	2.54 (0.80)					
H(8)	-0.0256 (48)	0.4847 (38)	-0.2060 (66)	4.58 (1.13)					
H(9)	0.1294 (28)	0.6007 (22)	-0.1805 (41)	0.51 (0.54)					
H(10)	0.0281 (36)	0.6798 (27)	-0.0858 (51)	2.09 (0.73)					
H(11)	0.1511 (46)	0.3959 (35)	0.0241 (66)	3.79 (1.06)					
H(12)	0.2143 (42)	0.2344 (32)	0.0478 (63)	2.57 (0.97)					
H(13)	0.0581 (69)	0.2036 (57)	0.0153 (114)	11.35 (2.10)					
H(14)	0.0924 (74)	0.2235 (55)	0.2336 (100)	6.48 (1.87)					

Table 4. Comparison of the lengths and angles found in proline residues

Compound	Acetyl-L-proline-N-methylamide	L-Leucyl-L-prolyl-glycine	Tosyl-L-prolyl-L-hydroxyproline · H ₂ O	p-Bromocarbo-benzoxyglycyl-L-prolyl-L-leucyl-glycine	Peptide model
Bond lengths					
C(1)–C(2)	1.490 Å	1.499 Å		1.51 Å	1.53 Å
C(2)–O(1)	1.245	1.272		1.26	1.24
C(2)–N(1)	1.337	1.339		1.37	1.32
N(1)–C(3)	1.472	1.452	1.49 Å	1.46	1.47
N(1)–C(6)	1.476	1.458	1.50	1.46	
C(3)–C(4)	1.530	1.497	1.56	1.55	
C(4)–C(5)	1.503	1.512	1.56	1.41	
C(5)–C(6)	1.530	1.504	1.56	1.49	
C(3)–C(7)	1.530	1.519	1.51	1.49	1.53
C(7)–O(2)	1.231	1.236	1.24	1.22	1.24
C(7)–N(2)	1.316	1.314	1.32	1.36	1.32
N(2)–C(8)	1.453	1.454	1.45	1.42	1.47
e.s.d.	(0.004)	(0.015)	(0.06)*	(0.023)	
Bond angles					
O(1)–C(2)–C(1)	122.9°	118.9°		122°	121°
O(1)–C(2)–N(1)	120.2	122.4		120	125
C(1)–C(2)–N(1)	117.0	118.6		119	114
C(3)–N(1)–C(2)	121.4	120.6		122	123
C(3)–N(1)–C(6)	112.2	113.3	111.6°	114	
C(2)–N(1)–C(6)	125.6	126.1		124	
C(4)–C(3)–N(1)	103.4	103.7	98.8	102	
C(4)–C(3)–C(7)	111.5	113.3	100.7	115	
N(1)–C(3)–C(7)	114.3	111.2	109.3	117	110
C(5)–C(4)–C(3)	104.7	106.9	115.2	108	
C(6)–C(5)–C(4)	104.2	105.7	95.1	109	
N(1)–C(6)–C(5)	102.8	103.4	107.8	104	
O(2)–C(7)–C(3)	117.6	121.4	132.7	122	121
O(2)–C(7)–N(2)	124.4	123.2	114.0	122	125
C(3)–C(7)–N(2)	117.9	115.3	110.9	116	114
C(8)–N(2)–C(7)	121.0	122.2	114.8	122	123
e.s.d.	(0.3)	(1.0)		(1.4)	
φ	103.7°	111.8°	77.9°	122.3°	
ψ	164.2	–18.1	–23.0	146.6	
Deviation of C ^γ from the plane of pyrrolidine	0.53	0.44† 0.29†		0.26	
Reference	(1)	(2)	(3)	(4)	(5)

* Limit of error.

† C^γ atom is distributed in two sites.

(1) Present study.

(2) Leung & Marsh (1958).

(3) Fridrichsons & Mathieson (1962).

(4) Ueki *et al.* (1969).

(5) Pauling & Corey (1953)

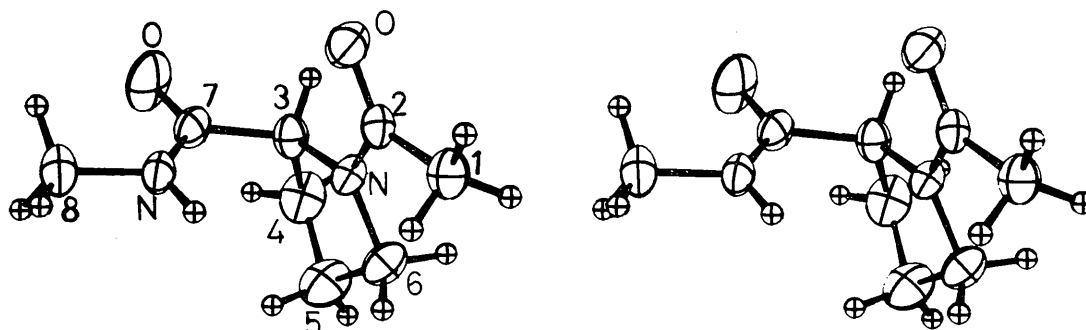


Fig. 3. Stereoscopic drawing of the molecule. The ellipsoid encloses the region in which the centre of the atom is found with probability 50%.

Fig. 4. In Table 4, the distances and angles are compared with standard values for peptide groups (Pauling & Corey, 1953) and the values found in other peptides and amino acids containing proline. Bond lengths and angles involving the hydrogen atoms are given in Table 5 and short intramolecular contacts between non-bonded atoms are shown in Fig. 5.

Table 5. Bond lengths and angles involving hydrogen atoms

Bond lengths			
H(1)—C(1)	1.00 Å	C(4)—C(3)—H(4)	120°
H(2)—C(1)	1.01	N(1)—C(3)—H(4)	104
H(3)—C(1)	1.04	C(7)—C(3)—H(4)	104
H(4)—C(3)	0.95	C(5)—C(4)—H(5)	119
H(5)—C(4)	0.99	C(5)—C(4)—H(6)	119
H(6)—C(4)	1.20	C(3)—C(4)—H(5)	107
H(7)—C(5)	0.99	C(3)—C(4)—H(6)	106
H(8)—C(5)	0.98	H(5)—C(4)—H(6)	101
H(9)—C(6)	0.94	C(6)—C(5)—H(7)	121
H(10)—C(6)	0.98	C(6)—C(5)—H(8)	100
		C(4)—C(5)—H(7)	106
		C(4)—C(5)—H(8)	107
		H(7)—C(5)—H(8)	117

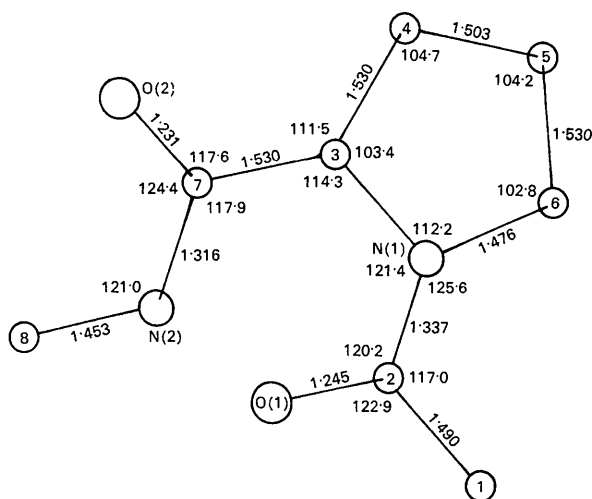


Fig. 4. Bond lengths (Å) and angles (°). E.s.d.'s are 0.004 Å and 0.3°.

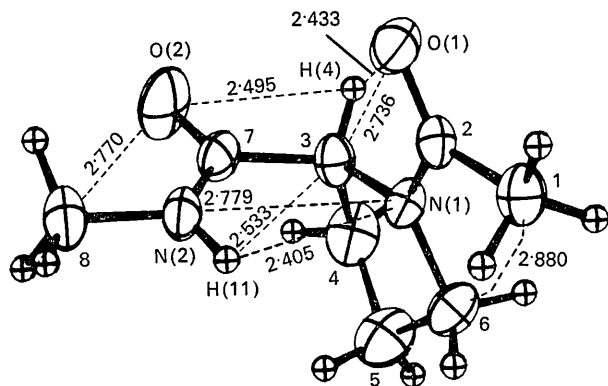


Fig. 5. Short intramolecular distances (Å) between non-bonded atoms.

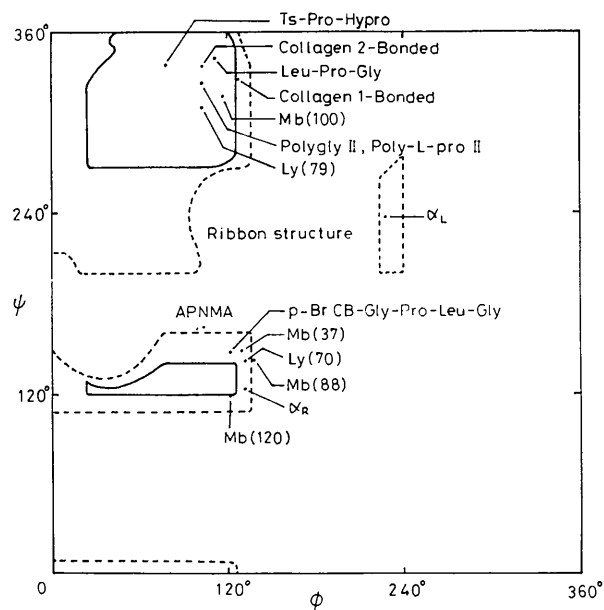


Fig. 6. ϕ - ψ chart showing the conformation of proline residues in various oligo- and polypeptides.

Abbreviations are: Mb(100), 100th residue in myoglobin; Ly(79), 79th residue in lysozyme; Ts-Pro-Hydro, tosyl-L-prolyl-L-hydroxyproline; *p*-BrCB-Gly-Pro-Leu-Gly, *p*-bromocarbobenzoxy-glycyl-L-prolyl-L-leucyl-glycine; APNMA, acetyl-L-proline-*N*-methylamide; α_R , α_L , right and left-handed α -helix.

Table 5 (cont.)

H(11)—N(2)	0.87	N(1)—C(6)—H(9)	113
H(12)—C(8)	0.90	N(1)—C(6)—H(10)	108
H(13)—C(8)	1.17	C(5)—C(6)—H(9)	112
H(14)—C(8)	1.06	C(5)—C(6)—H(10)	110
		H(9)—C(6)—H(10)	111
e.s.d.	0.05	C(7)—N(2)—H(11)	119
		C(8)—N(2)—H(11)	119
Bond angles			
C(2)—C(1)—H(1)	106°	N(2)—C(8)—H(12)	113
C(2)—C(1)—H(2)	116	N(2)—C(8)—H(13)	110
C(2)—C(1)—H(3)	114	N(2)—C(8)—H(14)	105
H(1)—C(1)—H(2)	111	H(12)—C(8)—H(13)	100
H(1)—C(1)—H(3)	97	H(12)—C(8)—H(14)	132
H(2)—C(1)—H(3)	111	H(13)—C(8)—H(14)	93
		e.s.d.	3

The molecule of APNMA is composed of three planes: peptide group I [formed by the atoms C(1), C(2), O(1), N(1), C(3) and C(6) involving the *N*-acetyl group], peptide group II [C(3), C(7), O(2), N(2), H(11) and C(8) involving the *N*-methylamide group] and the pyrrolidine group [N(1), C(3), C(4) and C(6)]. The equations of the least-squares planes and the distances of individual atoms from the planes are given in Table 6. As is commonly observed in proline molecules and proline residues, the pyrrolidine ring takes a puckered form and the γ -carbon atom, C(5), is displaced from the plane of the four remaining atoms by 0.53 Å in the direction *cis* to the carbonyl carbon atom C(7) of the proline residue. The direction of the displacement with

respect to the carbonyl group is exactly opposite to that found in *p*-bromocarbobenzoxy-Gly-Pro-Leu-Gly (Ueki, Ashida, Kakudo, Sasada & Katsube, 1969). This may be the result of intermolecular interactions which will be discussed later. The peptide group I and the pyrrolidine group are nearly coplanar and the carbonyl oxygen atom and the δ -carbon atom are situated at the *trans* position to each other as is usually found in peptides containing proline residues, the dihedral angle between the planes of these two groups being 11.4° . The planes of the peptide groups I and II intersect at the large angle of 69.4° and the two imino nitrogen atoms of the neighbouring amide groups are arranged nearly in *cis* positions rather than taking *trans* positions. As a result of this particular arrangement, the molecule takes a folded conformation as was supposed from infrared spectroscopy. This point will be discussed in detail in terms of the torsion angles.

Table 6. *Least-squares planes through peptide groups and the pyrrolidine ring*

The equations of the planes are of the form

$$AX + BY + CZ = D,$$

where X , Y and Z are coordinates (in Å) referred to the orthogonal axes, $X \parallel a$, $Y \parallel b$ and $Z \parallel c$ respectively, and D is the origin-to-plane distance.

Table 6 (cont.)

Peptide group I

$$-0.480 X + 0.809 Y + 0.339 Z = 5.959$$

Deviations of atoms from the plane

C(1)	-0.009 Å	N(1)	-0.063 Å
C(2)	-0.003	C(3)	0.004
O(1)	0.030	C(6)	0.041

Peptide group II

$$0.549 X + 0.192 Y + 0.813 Z = 1.985$$

Deviations of atoms from the plane

C(3)	0.000 Å	N(2)	0.039 Å
C(7)	0.014	C(8)	-0.004
O(2)	-0.018	H(11)	-0.032

Pyrrolidine ring

$$-0.318 X + 0.835 Y + 0.450 Z = 6.237$$

Deviations of atoms from the plane

N(1)	0.043 Å	C(4)	0.025 Å
C(3)	-0.041	C(6)	-0.027
C(5)*	-0.527		

* Not included in the least-squares calculation.

The torsion angles, φ and ψ , defined by Edsall *et al.* (1966), are listed in Table 4 and compared with those found in related oligopeptides. The φ and ψ values are also plotted on the φ - ψ chart shown in Fig. 6. It is seen

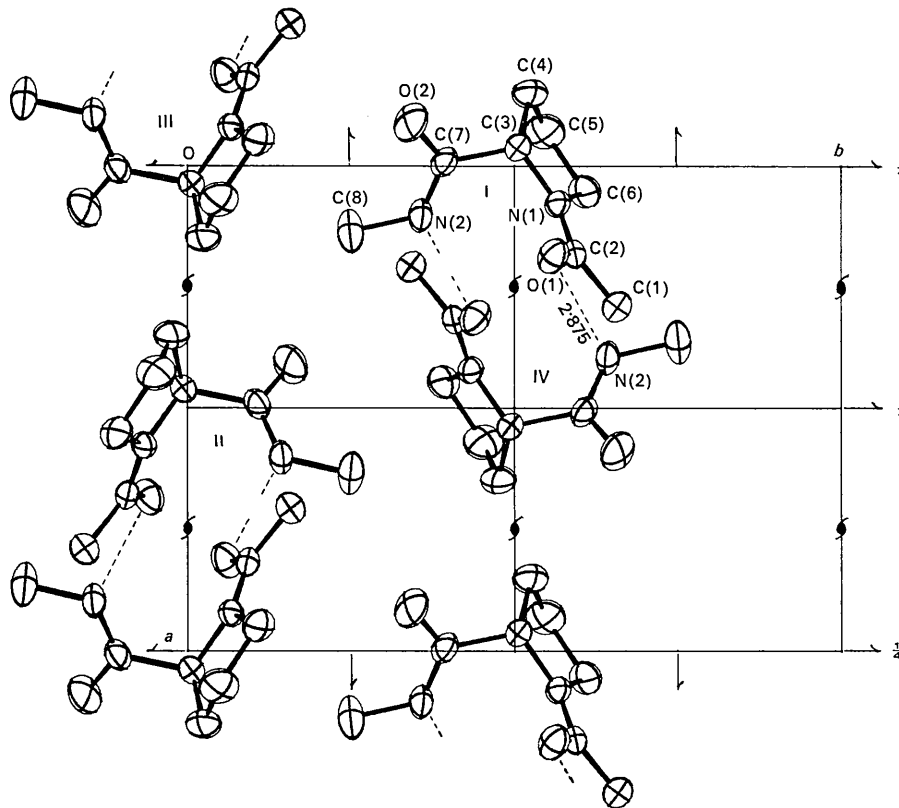


Fig. 7. Projection of the crystal structure along the c axis. The coordinates of the molecules I, II, III and IV are shown in Table 7.

that the values found in APNMA are not so different from those of the proline residue in *p*-bromocarboxy-Gly-Pro-Leu-Gly (Ueki *et al.*, 1969) and they are nearly at the outer limit of the right-handed α -helix region of the φ - ψ chart. The existence of such a folded conformation of the proline residue in these simple peptides may be of great interest since it indicates that this is a stable conformation for peptides containing a proline residue even if the conformations of proline residues in poly-L-proline II (Sasisekharan, 1959) and one-bonded (Rich & Crick, 1961; Traub, Yonath & Segal, 1969) and two-bonded (Ramachandran & Sasisekharan, 1965) model structures of collagen are, as shown in Fig. 6, all assumed to be extended-chain in which the φ and ψ values are in the range 100–130 and 320–340° respectively. This collagen type conformation is also found in simple peptides such as Leu-Pro-Gly (Leung & Marsh, 1958) and tosyl-Pro-Hydro (Fridrichsons & Mathieson, 1962). In proteins, it is generally observed that the proline residues occur at corners or in non-helical regions. However, in lysozyme (Blake, Mair, North, Phillips & Sarma, 1967) and in myoglobin (we are indebted to Dr J. C. Kendrew for the myoglobin coordinates), the φ - ψ values of the proline residues fall within either of the above two regions, *i.e.* the regions corresponding to the α -helix and collagen type conformations. In myoglobin, proline 120 which lies in a non-helical region takes a collagen type conformation, whereas prolines 37, 88 and 100 which lie at the corners or nearly at the terminal portion of a helical region take an α -helical conformation. It may, therefore, be said that the stable conformations of the

proline residues can be accommodated in either of the two helical structures, one being the collagen type and the other the α -helix type, as far as the torsion angles of the N-C α and C α -C' bonds are concerned. In the latter structure, however, the hydrogen bonding between the imide and carbonyl groups of the successive turns of the helix cannot be formed, because the δ -carbon atom of the pyrrolidine ring occupies the position of the imide hydrogen atom, which renders it impossible for an α -helix to be formed. In the present molecule and in *p*-bromocarboxy-Gly-Pro-Leu-Gly, the α -helical conformation is stabilized by either intermolecular or intramolecular hydrogen bonds.

Crystal structure

The arrangement of the molecules in the crystal is shown in Figs. 7 and 8, which were drawn by the plotter program of Johnson (1965). The surface of each ellipsoid encloses the region in which the centre of the atom is found with probability 50%. In these figures the molecules are designated by the Roman numbers denoting the symmetry operations, followed by the components of translation vectors in parentheses. It will be seen in Fig. 7 that the molecules are bound together through N(2)-H(11)···O(1) hydrogen bonds to form a hydrogen-bonded chain about the twofold screw axis parallel to *c*. The interatomic distances and angles associated with the hydrogen bond are shown in Fig. 9. The two chains *A* and *B*, each consisting of molecules I and II and III and IV, respectively, are contained in the unit cell. In each chain, as is clear from Fig. 8, the C=O and N-H bonds are directed roughly parallel to

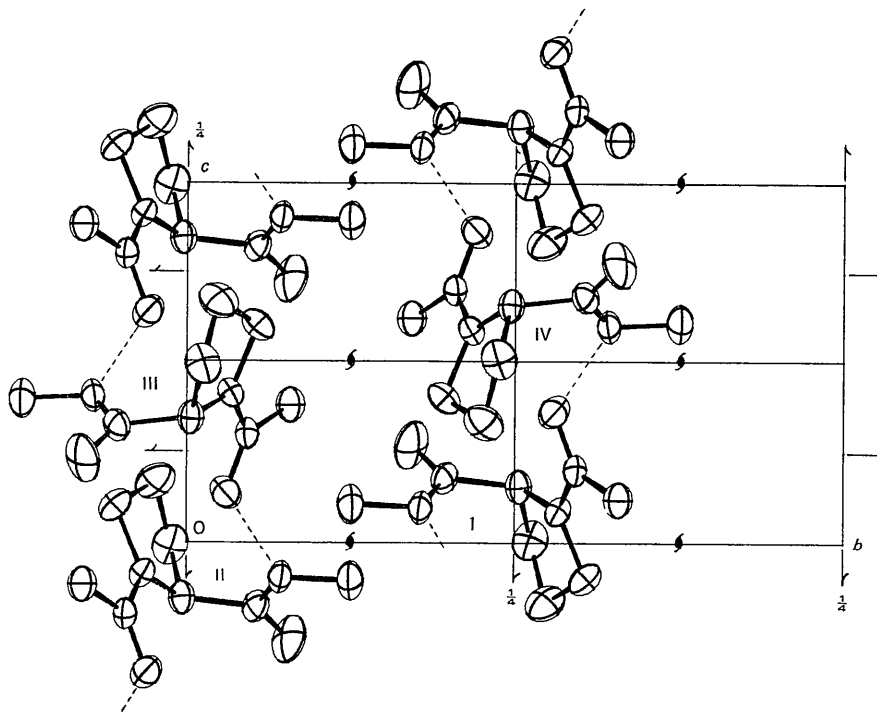


Fig. 8. Projection of the crystal structure along the *a* axis.

the *c* axis, which will make a large contribution to the dipole moment along the chain axis. The two chains *A* and *B* are arranged antiparallel to each other and the dipole-dipole interaction between the chains would greatly stabilize the packing of the chains. It is of note that in the present structure one of the carbonyl oxygen atoms O(2) does not participate in any hydrogen bonding.

The closest approaches of atoms of different molecules with distances less than 3.8 Å are listed in Table 7. Most of the shortest distances involve the atoms O(1) and O(2).

Table 7. Packing distances shorter than 3.8 Å

From molecule I(000)	To atom	Of molecule	Translation	Distance
O(1)	N(1)	IV	000	3.262 Å
O(1)	N(2)	IV	000	2.875*
O(1)	C(1)	IV	000	3.415
O(1)	C(2)	IV	000	3.391
O(1)	C(6)	IV	000	3.381
O(1)	C(8)	IV	000	3.523
C(1)	N(2)	IV	000	3.580
C(1)	C(8)	IV	000	3.766
C(2)	N(2)	IV	000	3.598
O(2)	C(1)	III	000	3.231
O(2)	C(2)	III	000	3.431
O(2)	N(1)	III	000	3.781
C(8)	C(3)	III	000	3.761
O(2)	C(4)	IV	100	3.536
O(2)	C(5)	IV	100	3.643
C(4)	C(5)	IV	100	3.706
			e.s.d.	0.004

* Hydrogen bond

The coordinates of the equivalent positions are

I	<i>x</i>	<i>y</i>	<i>z</i>
II	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
III	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
IV	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$

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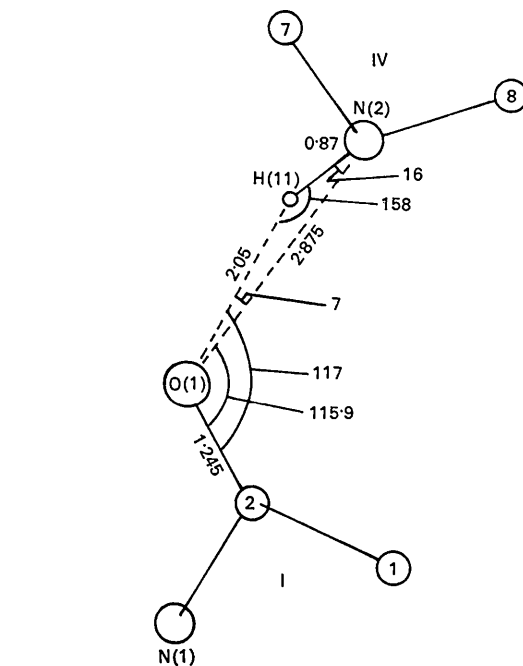


Fig. 9. Interatomic distances and angles associated with the hydrogen bond.

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