

### Discussion

The structure of  $\text{YbP}_3\text{O}_9$  is illustrated in Figs. 1 and 2. The basic structural units are helical ribbons,  $(\text{PO}_3)_n$ , formed by corner-sharing of  $\text{PO}_4$  tetrahedra. The ribbons run along the  $c$  axis and are joined to each other by Yb–O bonds. Each Yb atom is coordinated with six O atoms to form slightly distorted octahedra that are isolated from each other. The shortest Yb–Yb distance is 5.610 Å. Each O atom is bonded to two cations, either two P atoms or one P and one Yb atom; no O atom is common to two Yb atoms. In contrast, in  $\text{NdP}_3\text{O}_9$ , every Nd atom shares two O atoms with a second Nd atom. In that structure, each Nd atom is coordinated to eight O atoms. Most P–O distances are longer for O atoms bonded to two P atoms than for those bonded to one P and one Yb atom, probably because of the repulsion between  $\text{P}^{5+}$  ions. Longer bond distances in P–O–P bonding were also observed in  $\text{NdP}_3\text{O}_9$ ,  $\text{NdP}_5\text{O}_{14}$  (Hong, 1974) and  $\text{YbP}_5\text{O}_{14}$  (Hong & Pierce, 1974). Due to ionic repulsion,  $\text{P}^{5+}$  ions do not form edge-shared tetrahedra, although they can exhibit corner-sharing. Because of their increased charge,  $\text{Mo}^{6+}$ ,  $\text{W}^{6+}$  or  $\text{Re}^{7+}$  can form only isolated tetrahedra.

The fact that the  $\text{Nd}^{3+}$  fluorescence lifetime is considerably longer in  $\text{Y}_{0.9}\text{Nd}_{0.1}\text{P}_3\text{O}_9$  (490  $\mu\text{s}$ ) than in  $\text{La}_{0.9}\text{Nd}_{0.1}\text{P}_3\text{O}_9$  (160  $\mu\text{s}$ ) can be attributed in part to the reduction in Nd–Nd pair interactions and therefore to reduction of concentration quenching in the  $\text{YbP}_3\text{O}_9$  structure because of the isolation of the rare-earth ions from each other. The difference also results in part because the limiting lifetime for very dilute solutions of  $\text{Nd}^{3+}$  in  $\text{YP}_3\text{O}_9$  is at least 490  $\mu\text{s}$ , compared with 375 and 325  $\mu\text{s}$  for such solutions in  $\text{LaP}_3\text{O}_9$  and  $\text{LaP}_5\text{O}_{14}$ , respectively (Dwight, Hong & Pierce, 1973).

The observation of a particularly high lifetime in  $\text{Y}_{0.9}\text{Nd}_{0.1}\text{P}_3\text{O}_9$  makes the  $\text{Y}_{1-x}\text{Nd}_x\text{P}_3\text{O}_9$  solid solution a source of promising materials for efficient  $\text{Nd}^{3+}$  lasers. Another potential advantage is that the concentration of rare-earth ions in the  $\text{YbP}_3\text{O}_9$  structure is  $5.4 \times 10^{21} \text{ cm}^{-3}$ , compared with only  $3.9 \times 10^{21} \text{ cm}^{-3}$  in  $\text{La}_{1-x}\text{Nd}_x\text{P}_5\text{O}_{14}$  solid solutions, which have already been used for the fabrication of lasers. However, since  $\text{YP}_3\text{O}_9$  and  $\text{NdP}_3\text{O}_9$  have different structures, the solubility of  $\text{Nd}^{3+}$  in  $\text{YP}_3\text{O}_9$  must be limited. The maximum value of the solubility was observed about  $x=0.20$  in the series of  $\text{Y}_{1-x}\text{Nd}_x\text{P}_3\text{O}_9$ .

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## The Crystal Structure of t-Amyloxy-carbonyl-L-prolyl-L-prolyl-L-proline

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The crystal is orthorhombic, space group  $P2_12_12_1$ , with  $a=14.315$ ,  $b=9.924$ ,  $c=15.916$  Å,  $Z=4$ . 1897 non-zero reflexions collected on a diffractometer ( $\sin \theta/\lambda=0.575$ ) were used in the structure determination. The structure was solved by the symbolic addition method and refined by the least-squares method to an  $R$  of 0.06. The steric hindrance between pyrrolidine rings of nearest neighbours significantly affects the bond angles of the peptide linkages in order to suppress the effect of overcrowding. One of the  $\text{C}^\gamma$  atoms of a pyrrolidine ring shows remarkable anomalous behaviour. The peptide bonds are *trans*, and the conformation of the peptide chains is fairly close to those of poly-L-proline II.

### Introduction

X-ray studies on a group of synthetic peptides, which are related to collagen as collagenase substrates or as

collagen model polypeptides, have been carried out as one of the main research projects in this laboratory. The present study of the crystal structure of t-amlyoxy-carbonyl-L-prolyl-L-prolyl-L-proline is part of this project. Conformational studies of proline oligomers carried out recently by spectroscopic methods revealed the following structural characteristics (Isemura,

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Okabayashi & Sakakibara, 1968; Okabayashi, Isemura & Sakakibara, 1968; Okabayashi & Isemura, 1970; Deber, Bovey, Carver & Blout, 1970; Tonelli, 1970; Rippon, Koenig & Walton, 1970). The oligomers with five or more proline residues assume a poly-L-proline II type left-handed helical structure with *trans* peptide bonds. The lower members with 2, 3 or 4 residues assume most of the conformations consistent with *cis-trans* isomerization of the peptide bonds, while it was also reported that even the trimer lyophilized from the aqueous solution possesses the all-*trans* peptide conformation. Meanwhile the crystal structure of t-butyloxycarbonyl-tetra-L-proline benzyl-ester was determined (Matsuzaki, 1972), and the molecule was found to form one turn of a poly-L-proline II-like helix.

### Experimental

The crystals of t-amyloxycarbonyl-L-prolyl-L-prolyl-L-proline,  $C_{21}H_{33}N_3O_6$ , obtained from an ethyl acetate solution are well defined rods elongated along the *b* axis. The crystal is orthorhombic with cell dimensions  $a = 14.315 \pm 0.002$ ,  $b = 9.924 \pm 0.002$ ,  $c = 15.916 \pm 0.002$  Å. The systematic absences determined the space group to be  $P2_12_12_1$ . The observed density of the crystal by the flotation method,  $1.24 \text{ g cm}^{-3}$ , suggested the number of molecules in a unit cell to be 4, the calculated density being  $1.28 \text{ g cm}^{-3}$ .

The intensity measurements were made on a Rigaku automatic four-circle diffractometer equipped with a

pulse-height analyser. Ni-filtered Cu  $K\alpha$  radiation was used. The  $\omega$ - $2\theta$  scan method with a scan range of  $\Delta\omega = 0.8 + 0.15 \tan \theta$  and scan speed of  $2^\circ \text{ min}^{-1}$  was adopted. The background intensities were measured for 15 s at both ends of the scan. A crystal of dimensions  $0.35 \times 0.1 \times 0.1$  mm was used in the experiment. In total, 2073 reflexions with  $2\theta$  less than  $125^\circ$  were collected, of which 1897 non-zero reflexions were used in the structure determination. No corrections for absorption and extinction effects were made.

### Structure determination

The structure was determined by *MULTAN* (Germain, Main & Woolfson, 1971). Though the structure could not be revealed directly, some plausible starting sets of phases were deduced after several trials including inspections of a few set of *E* maps. One of the *E* maps thus obtained showed up all the atoms unambiguously, a few incorrect peaks being readily discerned.

The refinement was carried out by the block-diagonal least-squares method (*HBLIS*: Ashida, 1967), and the final *R* index was 0.060 for non-zero reflexions. The non-hydrogen atoms were assigned anisotropic temperature factors, while the isotropic temperature factors for all the hydrogen atoms were fixed at 7. If the hydrogen atoms were not included, the *R* index increased to 0.085. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme utilizing  $\sigma(F)$  due

Table 1. The atomic parameters ( $\times 10^4$ ) and their e.s.d.'s in parentheses

Thermal parameters are in the form:  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
N(1)	939 (3)	3337 (4)	2411 (2)	60 (2)	125 (4)	39 (2)	-20 (6)	-9 (3)	37 (5)
C(1A)	1196 (3)	4716 (5)	2591 (3)	55 (2)	142 (6)	39 (2)	-6 (7)	-1 (4)	-1 (6)
C(1B)	1491 (5)	4724 (8)	3530 (3)	98 (4)	244 (11)	38 (2)	-20 (12)	-18 (5)	9 (8)
C(1C)	1783 (6)	3272 (9)	3666 (4)	135 (6)	257 (12)	44 (3)	127 (15)	-49 (7)	-7 (9)
C(1D)	1244 (4)	2373 (7)	3052 (4)	62 (3)	189 (8)	55 (2)	20 (8)	-6 (5)	89 (8)
C(1)	2005 (3)	5183 (5)	2030 (3)	43 (2)	113 (5)	38 (2)	8 (6)	-17 (3)	-10 (5)
O(1)	2576 (2)	4386 (3)	1750 (2)	52 (2)	116 (4)	54 (2)	35 (4)	0 (3)	-8 (4)
N(2)	2095 (2)	6494 (4)	1882 (3)	46 (2)	98 (4)	54 (2)	2 (5)	-2 (3)	-11 (5)
C(2A)	2928 (3)	6961 (5)	1446 (3)	52 (2)	126 (6)	49 (2)	-18 (7)	-12 (4)	17 (6)
C(2B)	2739 (5)	8470 (6)	1309 (6)	82 (4)	129 (7)	114 (5)	-23 (10)	-39 (8)	69 (10)
C(2C)	1968 (8)	8796 (8)	1903 (9)	145 (8)	129 (9)	210 (11)	71 (13)	71 (17)	72 (17)
C(2D)	1481 (5)	7599 (6)	2155 (5)	83 (4)	117 (6)	94 (4)	50 (9)	11 (7)	-42 (9)
C(2)	3783 (3)	6729 (5)	1982 (3)	49 (2)	117 (5)	44 (2)	-31 (6)	-2 (4)	-2 (6)
O(2)	3763 (3)	6966 (4)	2750 (2)	66 (2)	190 (5)	43 (1)	-11 (6)	1 (3)	-35 (5)
N(3)	4554 (3)	6280 (4)	1607 (2)	48 (2)	131 (5)	39 (1)	-25 (5)	-3 (3)	-9 (5)
C(3A)	5400 (3)	6012 (5)	2086 (3)	56 (2)	98 (5)	48 (2)	-21 (6)	-12 (4)	15 (6)
C(3B)	6021 (4)	5237 (5)	1476 (4)	69 (3)	107 (6)	68 (3)	26 (7)	-9 (5)	-8 (7)
C(3C)	5724 (4)	5763 (6)	623 (4)	73 (3)	153 (7)	65 (3)	27 (9)	31 (6)	-10 (8)
C(3D)	4672 (4)	5947 (6)	706 (3)	72 (3)	162 (7)	41 (2)	-6 (9)	9 (4)	-14 (7)
C(3)	5857 (3)	7342 (5)	2349 (3)	45 (2)	104 (5)	38 (2)	-18 (6)	-1 (3)	9 (5)
O(31)	5695 (3)	8403 (3)	2045 (3)	75 (2)	102 (4)	77 (2)	-19 (5)	-52 (4)	28 (5)
O(32)	6505 (3)	7131 (4)	2938 (2)	67 (2)	125 (4)	58 (2)	-27 (5)	-35 (3)	12 (5)
C(41)	656 (3)	2916 (5)	1655 (3)	51 (2)	117 (5)	52 (2)	-19 (6)	-9 (4)	35 (6)
C(42)	449 (7)	3878 (6)	249 (3)	162 (7)	143 (7)	40 (2)	-72 (13)	-39 (7)	16 (7)
C(431)	-373 (11)	3110 (11)	-22 (7)	252 (14)	299 (18)	109 (6)	-209 (28)	-203 (16)	86 (18)
C(432)	461 (10)	5366 (9)	-25 (5)	244 (13)	200 (10)	55 (3)	-74 (20)	-80 (11)	79 (10)
C(433)	1369 (10)	3198 (11)	-83 (5)	241 (12)	295 (16)	56 (3)	81 (27)	41 (12)	-41 (13)
C(44)	-1236 (8)	3675 (15)	346 (8)	120 (7)	513 (30)	135 (8)	-177 (25)	-81 (13)	217 (26)
O(41)	521 (3)	1743 (4)	1463 (3)	104 (3)	103 (4)	66 (2)	-49 (6)	-26 (4)	18 (5)
O(42)	497 (3)	3998 (3)	1149 (2)	77 (2)	112 (4)	39 (1)	-17 (5)	-20 (3)	14 (4)

to the counting statistics of the intensity measurements was first applied, but at the final stage of the refinement the following scheme seemed to be more appropriate:

$$\begin{aligned} |F_o| \leq 8 & \quad \omega = 1 \\ |F_o| > 8 & \quad \omega = [1 + 0.23(|F_o| - 8)]^{-1}. \end{aligned}$$

All calculations were carried out on a NEAC 2200-700 of this University.

The final parameters are listed in Tables 1 and 2.\* The accuracy of the positional parameters of the

\* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as supplementary Publication No. SUP 30428 (17 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *The positional parameters of hydrogen atoms* ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	bonded to		<i>x</i>	<i>y</i>	<i>z</i>	bonded to
H(1)	72	527	255	C(1A)	H(18)	580	490	15	C(3C)
H(2)	104	491	400	C(1B)	H(19)	609	673	47	C(3C)
H(3)	195	570	359	C(1B)	H(20)	447	494	64	C(3D)
H(4)	176	315	426	C(1C)	H(21)	444	696	24	C(3D)
H(5)	261	313	371	C(1C)	H(22)	673	793	300	O(32)
H(6)	61	179	330	C(1D)	H(23)	-33	207	18	C(A31)
H(7)	171	152	310	C(1D)	H(24)	-36	317	-80	C(A31)
H(8)	298	645	91	C(2A)	H(25)	38	543	-60	C(A32)
H(9)	266	879	53	C(2B)	H(26)	-23	558	-4	C(A32)
H(10)	326	903	135	C(2B)	H(27)	108	583	-4	C(A32)
H(11)	165	965	170	C(2C)	H(28)	186	409	22	C(A33)
H(12)	240	895	247	C(2C)	H(29)	152	302	-65	C(A33)
H(13)	86	735	177	C(2D)	H(30)	149	256	11	C(A33)
H(14)	121	756	264	C(2D)	H(31)	-200	300	7	C(A4)
H(15)	525	533	255	C(3A)	H(32)	-147	337	81	C(A4)
H(16)	578	440	154	C(3B)	H(33)	-117	441	9	C(A4)
H(17)	662	548	151	C(3B)					

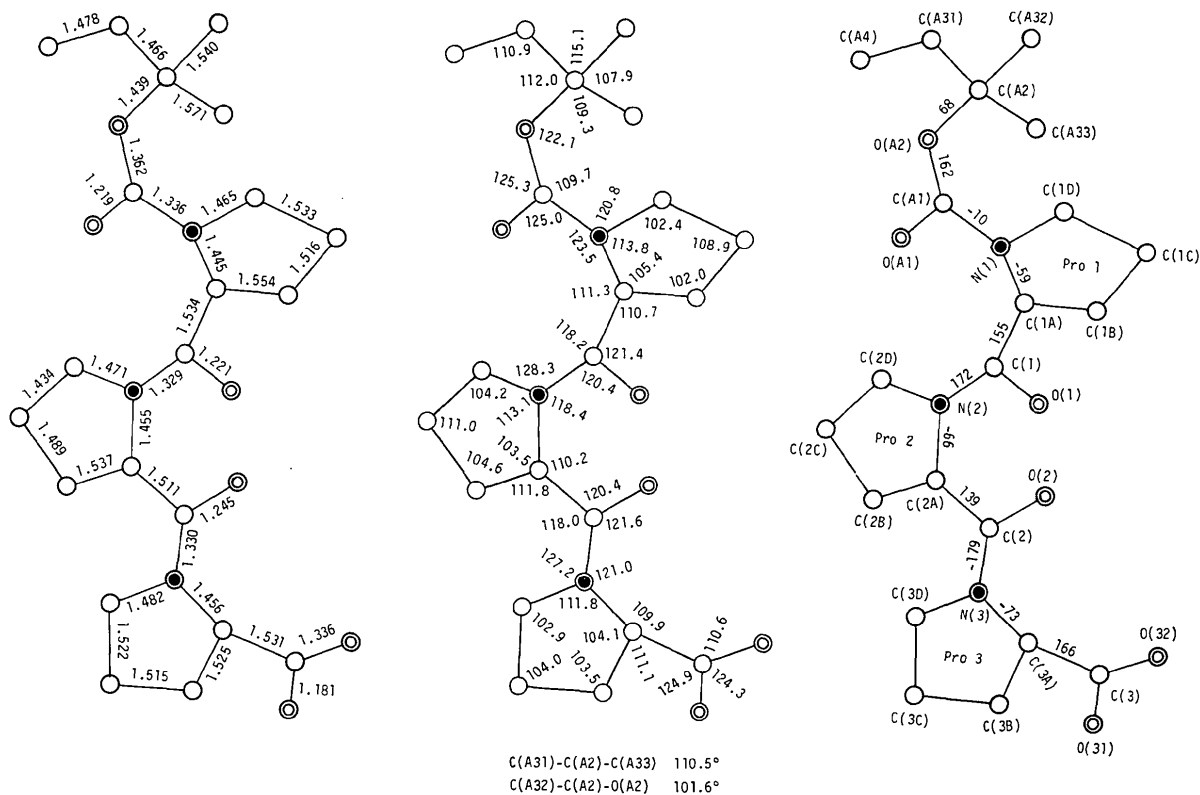


Fig. 1. Bond distances, angles, and conformational angles of the peptide main chain. The definition is that adopted by IUPAC-IUB Commission on Biochemical Nomenclature (1970).

terminal amyl group is rather low due to the large thermal vibration. Excluding the five C atoms of the amyl group and C(2C) which shows an abnormality mentioned below, the e.s.d.'s of C, N and O atoms range from 0.0036 to 0.0087 Å. These values correspond to the e.s.d.'s of the bond distances, 0.006 to 0.012 Å with an average of 0.008 Å, and the average e.s.d. of the bond angles, 0.4°.

### Discussion

The bond distances, angles and the torsion angles of the peptide main chain are shown in Fig. 1; the definition of the torsion angles and the notation of the atoms of the amino acid residues, which will be seen elsewhere in this report, are those adopted by the IUPAC-IUB Commission on Biochemical Nomenclature (1970). An ORTEP (Johnson, 1965) drawing of the molecule with thermal ellipsoids enclosing 30% probability is shown in Fig. 2. The structure viewed along the *b* axis is shown in Fig. 3, where some shorter intermolecular contacts and the only hydrogen bond in the crystal are shown.

The shapes and sizes of the three prolyl residues are, on the whole, consistent with each other, and are also close to those reported so far for various crystals. There is, however, one interesting point about the bond angles of the peptide bonds. The angle of C(41)–N(1)–C(1D), 121°, is significantly smaller than C(1)–N(2)–

C(2D), 128°, and C(2)–N(3)–C(3D), 127°, while C(41)–N(1)–C(1A), 124°, is larger than C(1)–N(2)–C(2A), 118°, and C(2)–N(3)–C(3A), 121°. The C(1A)–C(1)–N(2) and C(2A)–C(2)–N(3) angles, both 118°, are larger than usual (*e.g.* 114°: Corey & Pauling, 1953). The structure of tosyl-L-prolyl-L-hydroxyproline (Sabesan & Venkatesan, 1971) also shows the same tendency. These facts are certainly due to the steric hindrance between the C<sup>α</sup>–C<sup>β</sup> part and the C<sup>δ</sup> methylene group of the immediately following residue. On the other hand no atoms are in close contact with C(1D),

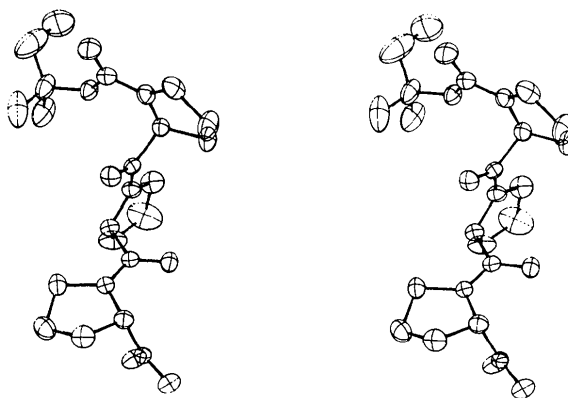


Fig. 2. Stereo drawing of the molecule with thermal ellipsoids drawn to enclose 30% probability.

Table 3. Best planes

(a) Equations – *X*, *Y* and *Z* in Å

I	0.9247 <i>X</i> – 0.0890 <i>Y</i> – 0.3701 <i>Z</i> = –0.3788	peptide oxycarbonyl-Pro(1)
II	–0.5346 <i>X</i> – 0.0964 <i>Y</i> – 0.8396 <i>Z</i> = –4.7700	peptide Pro(1)–Pro(2)
III	–0.2984 <i>X</i> – 0.9389 <i>Y</i> + 0.1716 <i>Z</i> = –7.3455	peptide Pro(2)–Pro(3)
IV	–0.7003 <i>X</i> + 0.1425 <i>Y</i> + 0.6994 <i>Z</i> = –2.2366	carboxyl Pro(3)
V	0.9288 <i>X</i> – 0.0755 <i>Y</i> – 0.3628 <i>Z</i> = –0.3395	Pro(1)
VI	–0.5159 <i>X</i> – 0.1648 <i>Y</i> – 0.8407 <i>Z</i> = –5.1857	Pro(2)
VII	–0.4244 <i>X</i> – 0.8792 <i>Y</i> + 0.2165 <i>Z</i> = –7.7507	Pro(3)

(b) Displacements (Å) of atoms from the planes – Atoms with asterisks are not included in the best-plane calculations.

I		II		III		IV	
O(41)	0.054	C(1A)	–0.059	C(2A)	0.004	C(3A)	–0.004
O(42)	0.008	C(1)	0.027	C(2)	0.001	C(3)	0.018
C(41)	0.016	O(1)	0.041	O(2)	–0.002	O(31)	–0.008
N(1)	–0.092	N(2)	0.031	N(3)	–0.012	O(32)	–0.006
C(1A)	0.020	C(2A)	–0.068	C(3A)	0.007		
C(1D)	0.019	C(2D)	0.030	C(3D)	0.002		
C(1B)*	–0.143	C(2B)*	0.115	C(3B)*	0.297		
C(1C)*	0.291	C(2C)*	–0.119	C(3C)*	–0.299		
V		VI		VII			
N(1)	–0.054	N(2)	0.059	N(3)	0.059		
C(1A)	0.081	C(2A)	–0.049	C(3A)	–0.057		
C(1B)	–0.070	C(2B)	0.026	C(3B)	0.032		
C(1D)	0.054	C(2D)	–0.034	C(3D)	–0.033		
C(1C)*	0.349	C(2C)*	–0.252	C(3C)*	–0.540		
C(1)*	1.445	C(2)*	–1.360	C(3)*	–1.404		

(c) Dihedral angles between the planes

between	I and II	100.1°	I and V	0.9°
	II and III	83.9	II and VI	4.1
	III and IV	78.8	III and VII	8.4

as is clearly shown in Fig. 2. The  $C^\delta$  methylene group is much larger than the hydrogen atom which links to the amide nitrogen atom in other amino acid residues.

The equations of the best planes of several planar groups and the displacements of atoms from the planes are listed in Table 3. Of three peptide groups, only the one between Pro(2) and Pro(3) is strictly planar. The other two are significantly twisted, and the torsion angles  $\omega$  differ by about  $10^\circ$  from the ideal one. In the peptide at the N-terminus N(1) deviates from the plane by about  $0.1 \text{ \AA}$  in the reverse direction from O(1), the  $N(1)\cdots O(1)$  distance being  $2.77 \text{ \AA}$ . These  $N\cdots O$  contacts are  $2.80$  and  $2.76 \text{ \AA}$  in the other two groups. The average value of  $2.78 \text{ \AA}$  for the three may be a normal separation for such a structure. In view of this, the displacement of N(1) is significant, and lengthens the  $N(1)\cdots O(1)$  distance to the normal one; otherwise the distance is too short.

Table 4. Torsion angles of pyrrolidine rings

	Pro(1)	Pro(2)	Pro(3)	Mean
$\theta_1(C^\delta-N-C^\alpha-C^\beta)$	$-14^\circ$	$-10^\circ$	$-10^\circ$	$-11^\circ$
$\chi_1(N-C^\alpha-C^\beta-C^\gamma)$	25	17	29	23
$\chi_2(C^\alpha-C^\beta-C^\gamma-C^\delta)$	-27	-20	-38	-28
$\chi_3(C^\beta-C^\gamma-C^\delta-N)$	19	14	31	21
$\chi_4(C^\gamma-C^\delta-N-C^\alpha)$	-3	-2	-13	-9

The torsion angles in the pyrrolidine rings are listed in Table 4. Each of the rings of Pro(1) and Pro(2) has approximate  $C_s$  symmetry, the  $C^\beta$  atom being on the mirror plane, while that of Pro(3) has approximate  $C_2$  symmetry with the twofold axis passing through N(3). Thus in Pro(1) and Pro(2) the planarity of  $NC^\alpha C^\gamma C^\delta$  is much better than that of  $NC^\alpha C^\beta C^\delta$ , but the equations for the latter groups are listed in Table 3 in order to make an easy comparison with other structures reported so far. A detailed study of the conformations of the pyrrolidine rings in peptides will be published elsewhere.

As is shown in Fig. 2, the vibrational amplitude of  $C^\gamma$  of Pro(1) is not so large, and that of  $C^\gamma$  of Pro(3) is as normal as those of the other atoms. The  $C^\gamma$  atom of Pro(2) has, however, an unusually large vibrational amplitude perpendicular to the plane of the pyrrolidine ring. As a result, the bond distances  $C^\gamma-C^\beta$  and  $C^\gamma-C^\delta$  appear to be significantly shorter than the normal C-C single bond, and the  $C^\beta-C^\gamma-C^\delta$  angle is larger than usual by as much as  $5^\circ$ , the angle usually being not larger than  $105^\circ$ . Such an effect has also been found in *p*-bromocarbobenzoxy-gly-L-pro-L-leu-gly (Ueki, Ashida, Kakudo, Sasada & Katsube, 1969) and in carbobenzoxy-gly-L-pro-L-leu-gly-L-pro (Bando, Tana-

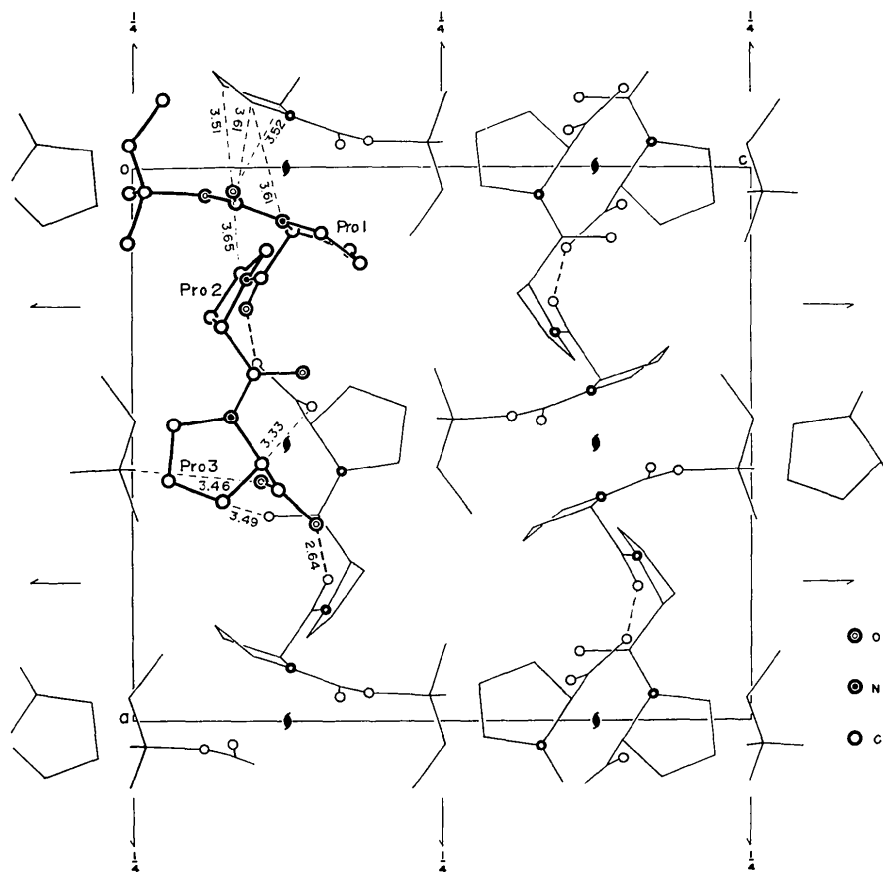


Fig. 3. The structure viewed along the  $b$  axis, the  $b$  axis downwards. A hydrogen bond and some intermolecular contacts are shown.

ka, Ashida & Kakudo, 1974), in which the  $C^\beta-C^\gamma$  and  $C^\gamma-C^\delta$  distances and the  $C^\beta-C^\gamma-C^\delta$  angles are 1.41, 1.49 Å and 109°, and 1.44, 1.45 Å and 111°, respectively. DL-Proline hydrochloride (Mitsui, Tsuboi & Iitaka, 1969) shows a similar tendency. For the  $C^\gamma$  atom of the pyrrolidine ring there are usually two geometrically possible sites above and below the pyrrolidine plane, the distance between the two being about 0.8 Å. The actual site of  $C^\gamma$  of Pro(2) is found on the line joining the two possible sites, 0.2 Å from the nearer one and 0.6 Å from the site on the other side of the plane. The vicinity of these sites was carefully scrutinized on both the regular and the difference electron-density maps at various stages of the refinement. No anomalies such as were found in leu-pro-gly (Leung & Marsh, 1958) were found, but the refinement employing the usual anisotropic temperature factor seemed to be reasonably terminated. It should be noted, however, that this fact does not necessarily rule out the possibility of a disordered structure as postulated for leu-pro-gly, in which two half-atoms were located with equal probability on either side of the pyrrolidine plane. The anomalies in the bond distances and angles involving  $C^\gamma$  can be explained not only by the disordered structure but by a simple but large thermal vibration of the atom. The X-ray method cannot distinguish between the two models. In the present crystal, however, if the disordered model exists, the probability that the  $C^\gamma$  atom is located at the site closer to the actually determined site is much larger than the probability of its being located at the other side of the pyrrolidine plane. The ratio should be about 4/1 or more, judging from the electron density map.

The torsion angles of the main chain of the poly-L-proline II helix are:  $\varphi = -80^\circ$  (rotation about N-C $^\alpha$ ),  $\psi = 155^\circ$  (rotation about C $^\alpha$ -C $^\gamma$ ), and  $\omega = 180^\circ$  (rotation about C $^\gamma$ -N;  $\omega = 180^\circ$  means the *trans* peptide bond). In the present molecule both of the peptide bonds between the prolyl residues are *trans*, and the mean torsion angles are  $\varphi = -63$  and  $\psi = 153^\circ$ . The conformation of this peptide is, as a whole, not so far from that of poly-L-proline II. Thus in the solid state,

the structure like poly-L-proline II is confirmed to be appropriate even for extremely small oligopeptides such as tri- and tetraproline (Matsuzaki, 1972).

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