Acta Cryst. (1974). B30, 1029

The Crystal Structure of t-Butyloxycarbonyltetra-L-proline Benzyl Ester*

BY TAKAO MATSUZAKI†

Central Research Laboratory, Mitsubishi Chemical Industries Limited, 290 Hisamoto, Takatsuku, Kawasaki 213, Japan

(*Received* 4 *September* 1973; *accepted* 10 *December* 1973)

Crystals of t-butyloxycarbonyltetra-L-proline benzyl ester monohydrate, $C_{32}H_{44}N_4O_7.H_2O$, are monoclinic with cell dimensions $a=21{\cdot}426\pm0{\cdot}003$, $b=8{\cdot}738\pm0{\cdot}002$, $c=17{\cdot}469\pm0{\cdot}003$ Å, $\beta=91{\cdot}11\pm0{\cdot}02°$. The space group is $C2$, $Z=4$. The structure was refined by a block-matrix least-squares method including anisotropic thermal parameters. The final R value for 2530 reflexions, which were measured on a diffractometer, is 0·080. The four proline residues in the molecule form one turn of poly-L-proline II-like helix. The torsion angles of the main chain are $\omega_0=-1{\cdot}1$, $\varphi_1=-67{\cdot}7$, $\psi_1=151{\cdot}8$, $\omega_1=168{\cdot}8$, $\varphi_2=-69{\cdot}9$, $\psi_2=164{\cdot}9$, $\omega_2=176{\cdot}4$, $\varphi_3=-61{\cdot}1$, $\psi_3=152{\cdot}3$, $\omega_3=179{\cdot}8$, $\varphi_4=-57{\cdot}8$, $\psi_4=-38{\cdot}5°$. The pyrrolidine rings in Pro(2) and Pro(4) residues take the puckered form in which the β-carbon atom deviates from the plane of the remaining four atoms in the ring. Several short intramolecular distances were found, the shortest C–C and C–O distances of which were 2·921 and 2·618 Å, respectively.

Introduction

The conformations of a series of L-proline oligomer derivatives [t-butyloxycarbonyl-(L-proline)$_n$ benzyl ester; $n=2,3,4,5,6$ and t-amyloxycarbonyl-(L-proline)$_n$; $n=2,3,4,5,6,8$] were investigated, with regard to the degree of polymerization, by infrared spectroscopy (Isemura, Okabayashi & Sakakibara, 1968), ultraviolet absorption spectroscopy (Okabayashi & Isemura, 1968, 1970*a*), Raman spectroscopy (Rippon, Koenig & Walton, 1970), nuclear magnetic resonance (Deber, Bovey, Carvar & Blout, 1970; Okabayashi & Isemura, 1970*b*) and calculation of the intramolecular energies (Tonelli, 1970). The results of these investigations agree well in the case of the oligomers containing five or more residues, which were assumed to have a left-handed helical structure identical with poly-L-proline II except for the terminal residues. For the conformation of the tetramer, however, Deber *et al.* (1970) indicated from their 220-MHz n.m.r. study that out of 16 possible peptide bond conformational isomers of the tetramer, eight are apparently present, while the other investigators reported that the tetramer assumes a helical structure similar to that of poly-L-proline II, though not conclusively as in the case of the pentamer. Thus, the tetramer seems to be on a boundary where the poly-L-proline II-like helical conformation begins to appear. The present paper describes the crystal structure of t-butyloxycarbonyltetra-L-proline benzyl ester (BOC–Pro$_4$–Bz), which crystallizes with a water molecule. The serial numbering of the proline residues and the atoms in the molecule is shown in Fig. 1.

Experimental

The material was synthesized according to the method described by Miyoshi, Kimura & Sakakibara (1970). The crystals recrystallized from ethyl acetate solution were colourless transparent plates with well developed (001) faces. The density was measured by flotation in a carbon tetrachloride–ether mixture. The unit-cell dimensions were measured on a single-crystal diffractometer using Cu $K\alpha$ ($\lambda=1{\cdot}5405$ Å) radiation monochromated by a graphite crystal and refined by a least-squares method.

Crystal data

t-Butyloxycarbonyl-tetra-L-proline benzyl ester monohydrate, $C_{32}H_{44}N_4O_7.H_2O$
Monoclinic
$C2$
$Z=4$
$a=21{\cdot}426\pm0{\cdot}003$ Å
$b=8{\cdot}738\pm0{\cdot}002$
$c=17{\cdot}469\pm0{\cdot}003$
$\beta=91{\cdot}11\pm0{\cdot}02°$
$U=3269{\cdot}9$ Å^3
$D_m=1{\cdot}23_8$ g cm^{-3}
$D_x=1{\cdot}24_8$
μ(Cu $K\alpha$) = 8·6 cm^{-1}
$F(000)=1320$

The intensity data were collected on the diffractometer by an ω–2θ continuous scan. 3165 independent reflexions with $\sin\theta/\lambda$ less than 0·61 were measured, of which 5230 reflexions had $|F|$ greater than $2\sigma(|F|)$ and were used in the structure determination. Since the size of the crystal was $0{\cdot}2\times0{\cdot}2\times0{\cdot}2$ mm, no absorption

* Presented at the Ninth International Congress of Crystallography (1972).

† Present address: Biophysics Department, Roswell Park Memorial Institute, 666 Elm Street, Buffalo, N.Y. 14203, U.S.A.

correction was applied. After the Lorentz and polarization corrections, the value of an overall temperature factor B was determined to be 5·75 Å^2 by a Wilson plot.

Determination of the structure

The structure was solved by the symbolic addition method and the application of the tangent formula (Karle & Karle, 1966). The procedure was similar to that described before (Matsuzaki & Iitaka, 1971). Fifteen atoms of the BOC–Pro$_4$–Bz molecule were recognized in an E map calculated with 833 phases having $|E| \geq 1{\cdot}1$. The phases were refined and extended by applying the tangent formula to the structure factors which were calculated with the parameters of the 15 atoms. The second E map based on 874 phases revealed 40 atoms of the molecule and three remaining atoms were found in a subsequent difference Fourier map. The parameters of the 43 atoms were then refined by a block-matrix least-squares method to yield an R index of 0·146, where the function minimized was $\sum(||F_o|-|F_c||)^2$. At this stage a new difference Fourier map was calculated. The map showed two additional peaks (A and B) 1·127 Å apart and near the diad axis at $x=0$ and $z=\frac{1}{2}$. The interatomic distances between these two peaks and carbonyl oxygen atoms of the tetramers, O(1) and O(2), are shown in Fig. 2, where the values are based on the final parameters. It seems reasonable to assume that the two peaks should be assigned to two independent water molecules and that one molecule occupies the A peak and the other the B' peak, which is related to B by the diad axis. In this case the water molecule at A is hydrogen-bonded to O(1)′ and O(2) atoms while another water molecule at B' is hydrogen-bonded to O(2)′ and the oxygen atom of the water molecule at A. The values of the angles, 108·1° for O(1)′–A–O(2) and 96·4° for O(2)′–B'–A, together with the distances, support this interpretation. Should this be the case, the true space group would be $P2_1$. But there were no extra reflexions of $h+k=2n+1$ type even in the heavily exposed Weissenberg photographs. A disordered structure was therefore assumed for the water molecules and a halved occupancy factor was assigned to the A and B oxygen atoms.

Refinement of the structure

The parameters of 45 non-hydrogen atoms were refined by eight cycles of block-matrix least-squares calculations with anisotropic temperature factors. In the last cycle of the refinement every parameter shift was within one half of its standard deviation. The final R value was 0·080 for 2530 reflexions. The final difference Fourier map did not show any peaks or troughs with magnitudes of electron density greater than 0·2 e Å^{-3} and no attempt was made to locate the hydrogen atoms.

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

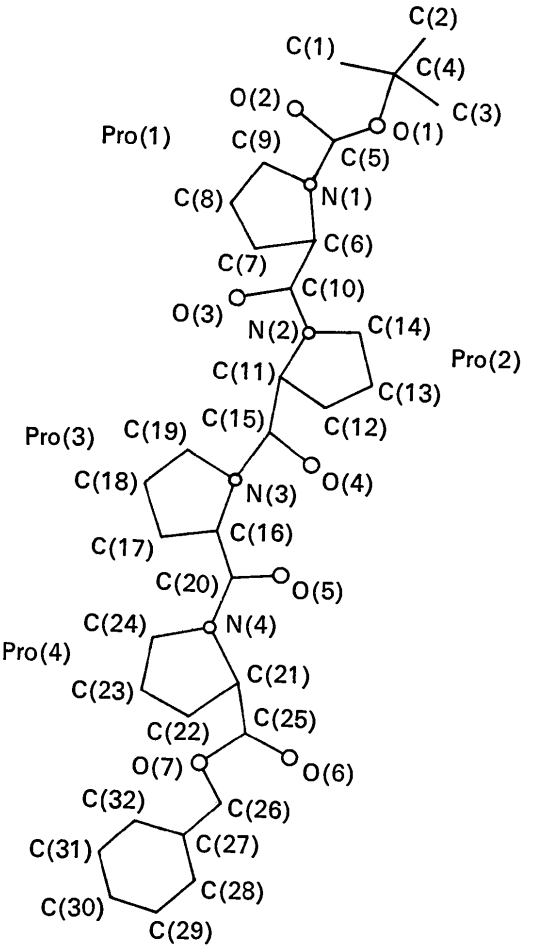


Fig. 1. Serial numbering of the proline residues and atoms in a BOC–Pro$_4$–Bz molecule.

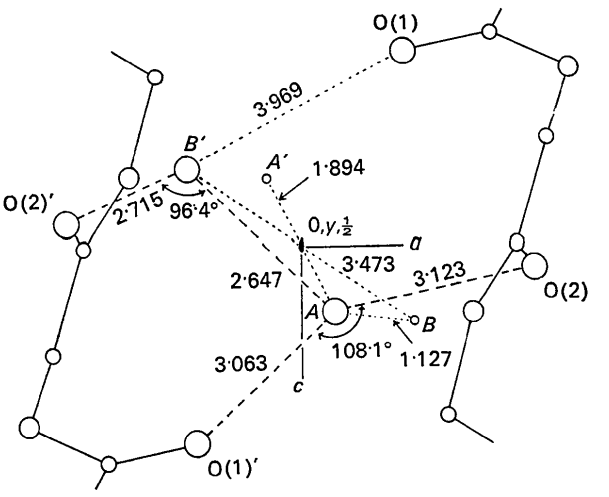


Fig. 2. The arrangement of atoms around the diad axis at $x=0$, $z=\frac{1}{2}$. A', B', O(1′) and O(2′) are symmetry-equivalent atoms to A, B, O(1) and O(2).

Table 1. *Observed and calculated structure factors* ($\times 10$)

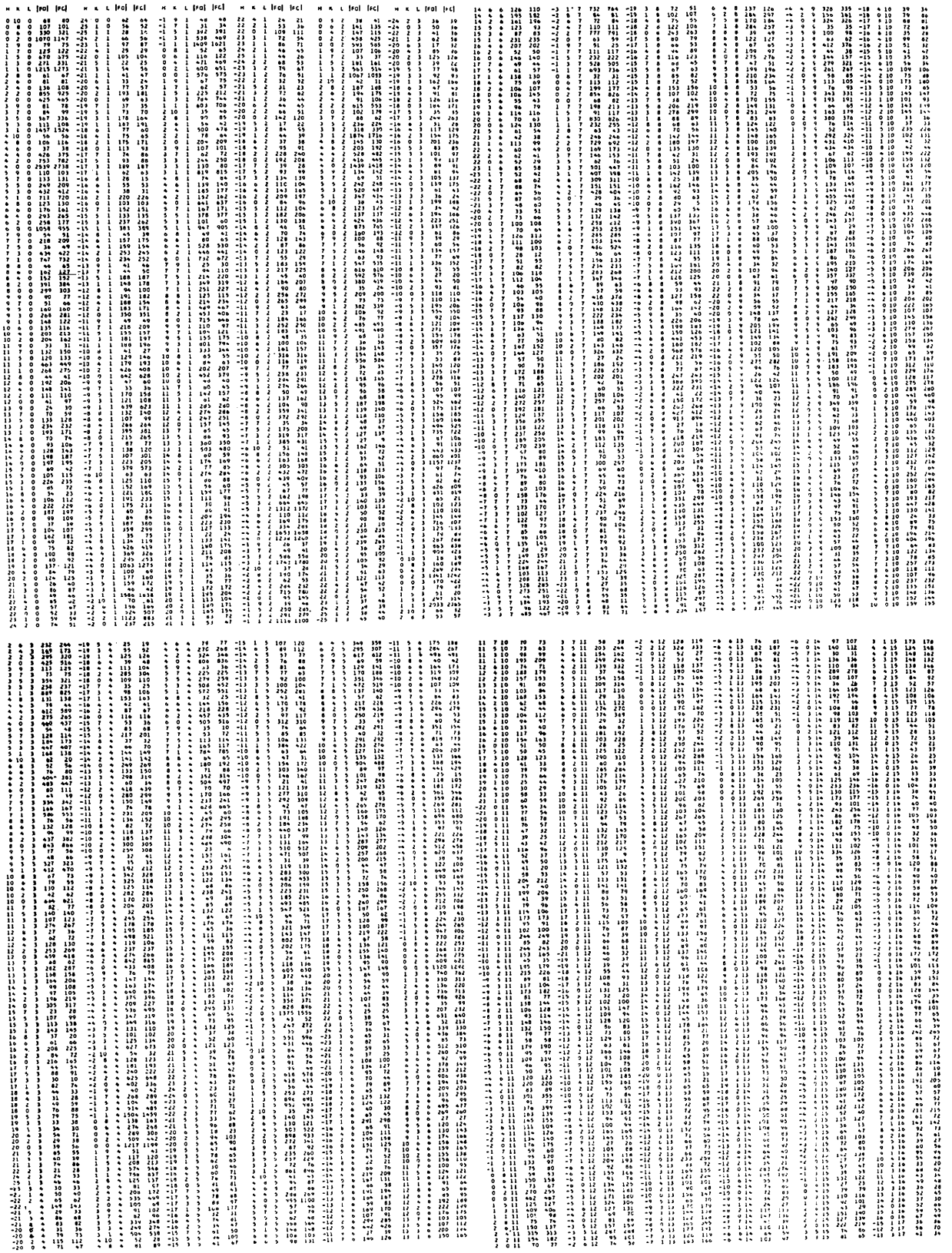
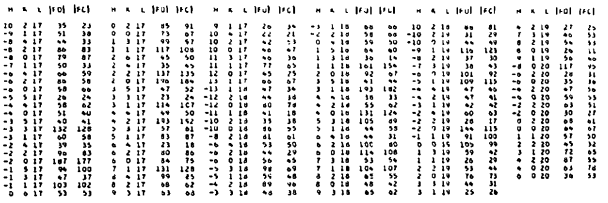


Table 1 (*cont.*)



In the last three cycles of the least-squares refinement, the following weighting system was adopted:

$$\sqrt{w} = 59/|F_o| \text{ when } |F_o| > 59$$
$$\sqrt{w} = 1{\cdot}0 \text{ when } 59 \geq |F_o| \geq 5{\cdot}9$$
$$\sqrt{w} = 0{\cdot}7 \text{ when } 5{\cdot}9 > |F_o| .$$

A comparison of the observed and calculated structure factors is given in Table 1. The final atomic parameters and their estimated standard deviations are listed in Table 2. In the next section the atoms are designated as listed in the last column of Table 2, in accordance with the IUPAC–IUB Commission (1970) rules.

Discussion of the structure

Molecular structure

A stereoscopic drawing of the molecule is shown in Fig. 3. The bond lengths and angles are shown in Fig. 4. The standard deviations are 0·012 Å for lengths and 0·7° for angles. The values are reasonable except for two lengths; 1·581 Å for Pro(2)Cα–Pro(2)Cβ and 1·402 Å for Pro(4)Cβ–Pro(4)Cγ, which are probably result from the large temperature factors. The four

Table 2. *Final atomic parameters and their standard deviations* ($\times 10^4$)

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)	396 (5)	2498 (15)	1339 (7)	51 (4)	242 (22)	119 (7)	−43 (8)	24 (4)	−48 (12)	BOC–C(1)
C(2)	1150 (5)	3796 (14)	413 (5)	68 (4)	270 (22)	41 (4)	−4 (9)	15 (3)	−20 (8)	BOC–C(2)
C(3)	1582 (6)	2044 (13)	1460 (7)	59 (4)	186 (20)	96 (6)	45 (8)	−2 (4)	−43 (10)	BOC–C(3)
C(4)	1055 (4)	3169 (10)	1234 (5)	41 (3)	167 (14)	50 (3)	−4 (5)	3 (2)	−24 (6)	BOC–C(4)
C(5)	782 (3)	5629 (9)	1822 (4)	32 (2)	132 (12)	31 (2)	0 (4)	0 (2)	8 (5)	BOC–C(5)
C(6)	1386 (4)	6024 (10)	3024 (4)	36 (2)	165 (14)	32 (3)	−5 (5)	−9 (2)	−4 (5)	pro(1)Cα
C(7)	1384 (4)	7391 (12)	3590 (5)	48 (3)	188 (16)	60 (4)	−14 (7)	−8 (3)	−31 (8)	pro(1)Cβ
C(8)	998 (6)	8603 (16)	3237 (9)	69 (5)	316 (30)	145 (9)	62 (10)	−37 (6)	−143 (14)	pro(1)Cγ
C(9)	611 (4)	7936 (11)	2570 (5)	37 (3)	201 (18)	69 (5)	18 (6)	−5 (3)	−48 (8)	pro(1)Cδ
C(10)	1199 (3)	4561 (10)	3449 (4)	27 (2)	186 (14)	30 (2)	−11 (4)	0 (2)	−8 (5)	pro(1)C′
C(11)	1529 (3)	2463 (10)	4242 (4)	31 (2)	147 (12)	29 (2)	−1 (4)	1 (2)	1 (5)	pro(2)Cα
C(12)	2169 (4)	1573 (12)	4323 (5)	35 (2)	205 (17)	64 (4)	10 (6)	6 (3)	11 (8)	pro(2)Cβ
C(13)	2646 (4)	2842 (13)	4175 (7)	32 (3)	251 (22)	95 (6)	−2 (6)	−4 (3)	35 (10)	pro(2)Cγ
C(14)	2344 (3)	3946 (12)	3624 (5)	25 (2)	231 (18)	56 (4)	−3 (5)	−2 (2)	22 (7)	pro(2)Cδ
C(15)	1329 (3)	3101 (10)	5007 (4)	28 (2)	174 (14)	35 (3)	0 (4)	−3 (2)	−8 (5)	pro(2)C′
C(16)	876 (3)	2688 (12)	6243 (4)	26 (2)	260 (18)	36 (3)	3 (5)	2 (2)	−14 (6)	pro(3)Cα
C(17)	553 (4)	1368 (15)	6597 (6)	41 (3)	320 (24)	66 (5)	−27 (8)	19 (3)	−19 (10)	pro(3)Cβ
C(18)	760 (7)	19 (17)	6178 (7)	87 (6)	293 (28)	83 (6)	−21 (11)	38 (5)	32 (11)	pro(3)Cγ
C(19)	919 (4)	519 (12)	5366 (5)	44 (3)	188 (17)	54 (4)	−29 (6)	9 (3)	7 (7)	pro(3)Cδ
C(20)	1478 (3)	3155 (10)	6704 (4)	28 (2)	198 (15)	33 (3)	10 (5)	4 (2)	−2 (6)	pro(3)C′
C(21)	1955 (4)	4665 (11)	7693 (4)	33 (2)	197 (16)	44 (3)	−4 (5)	−4 (2)	−3 (6)	pro(4)Cα
C(22)	1670 (5)	5789 (12)	8287 (6)	46 (3)	200 (18)	64 (4)	8 (6)	0 (3)	−48 (8)	pro(4)Cβ
C(23)	1062 (6)	6114 (31)	8023 (13)	36 (4)	1101 (85)	251 (17)	29 (15)	−5 (6)	−424 (34)	pro(4)Cγ
C(24)	824 (4)	5042 (14)	7446 (6)	35 (3)	308 (24)	73 (5)	13 (7)	7 (3)	−79 (9)	pro(4)Cδ
C(25)	2276 (3)	3343 (11)	8102 (4)	28 (2)	203 (16)	39 (3)	−7 (5)	2 (2)	−9 (6)	pro(4)C′
C(26)	2195 (4)	1054 (13)	8779 (6)	32 (3)	271 (21)	80 (5)	−2 (6)	3 (3)	69 (9)	Bz–C(7)
C(27)	1690 (3)	99 (9)	9135 (4)	28 (2)	154 (13)	42 (3)	5 (4)	3 (2)	2 (5)	Bz–C(1)
C(28)	1860 (4)	−751 (12)	9781 (5)	34 (2)	236 (18)	50 (3)	13 (6)	−8 (2)	−2 (7)	Bz–C(2)
C(29)	1428 (4)	−1689 (12)	10137 (5)	39 (3)	217 (17)	43 (3)	3 (6)	3 (2)	18 (7)	Bz–C(3)
C(30)	822 (4)	−1775 (11)	9857 (5)	37 (2)	205 (17)	50 (4)	18 (6)	2 (2)	14 (7)	Bz–C(4)
C(31)	654 (4)	−890 (13)	9223 (5)	34 (2)	237 (19)	69 (4)	1 (6)	−9 (3)	22 (9)	Bz–C(5)
C(32)	1082 (4)	24 (11)	8863 (5)	30 (2)	208 (17)	55 (4)	−12 (5)	−2 (2)	24 (7)	Bz–C(6)
N(1)	907 (3)	6448 (7)	2451 (3)	32 (2)	133 (10)	38 (2)	9 (4)	−3 (2)	−7 (4)	pro(1)N
N(2)	1673 (2)	3679 (7)	3726 (3)	25 (1)	158 (10)	32 (2)	−2 (3)	−2 (1)	4 (4)	pro(2)N
N(3)	1048 (3)	2192 (8)	5488 (3)	29 (2)	190 (11)	31 (2)	−1 (4)	2 (1)	6 (5)	pro(3)N
N(4)	1408 (3)	4189 (8)	7242 (3)	30 (2)	203 (13)	33 (2)	16 (4)	4 (1)	−6 (5)	pro(4)N
O(1)	1162 (2)	4400 (7)	1790 (3)	34 (1)	148 (9)	44 (2)	18 (3)	−3 (1)	−14 (4)	BOC–O(1)
O(2)	400 (3)	5992 (7)	1330 (3)	36 (2)	207 (11)	45 (2)	14 (4)	−10 (1)	−4 (4)	BOC–O(2)
O(3)	659 (2)	4260 (9)	3579 (3)	24 (1)	285 (13)	55 (2)	−3 (4)	2 (1)	17 (5)	pro(1)O
O(4)	1425 (3)	4448 (7)	5175 (3)	54 (2)	173 (10)	44 (2)	−3 (4)	2 (2)	−16 (4)	pro(2)O
O(5)	1983 (2)	2536 (8)	6586 (3)	27 (1)	276 (13)	52 (2)	26 (4)	−1 (1)	−31 (5)	pro(3)O
O(6)	2839 (2)	3305 (9)	8186 (4)	27 (1)	287 (14)	69 (3)	−19 (4)	−6 (2)	11 (6)	pro(4)O
O(7)	1892 (2)	2325 (7)	8377 (3)	25 (1)	205 (10)	58 (2)	−1 (3)	−1 (1)	24 (5)	Bz–O
O(8)	206 (7)	6291 (21)	5484 (13)	47 (6)	237 (30)	201 (19)	2 (11)	12 (7)	−33 (19)	water A
O(9)	−681 (10)	6835 (25)	4444 (12)	95 (9)	321 (46)	128 (12)	−48 (17)	3 (8)	49 (20)	water B′

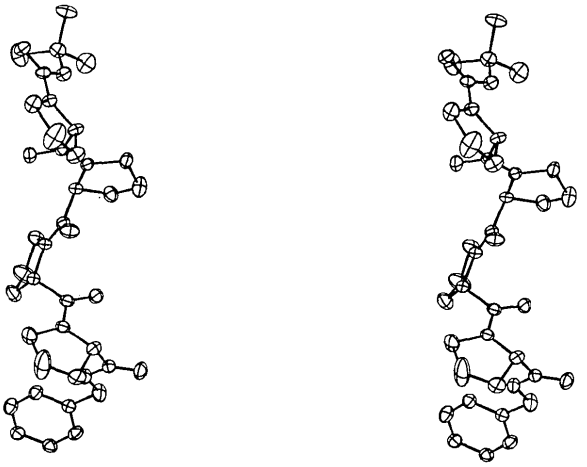


Fig. 3. Stereoscopic drawing of BOC–Pro_4–Bz molecule. Each ellipsoid encloses the region in which the atom is found with probability 20%.

proline residues in the BOC–Pro_4–Bz molecule form one turn of poly-L-proline II-like helix as shown in Fig. 3.

The internal rotation angles [designated on the basis of the IUPAC-IUB (1970) rules] are shown in Fig. 5. The values of φ, ψ, ω and the average translation per residue along the helix axis, h, are listed in Table 3 together with those of poly-L-proline II and collagen 1-bonded and 2-bonded models. In Fig. 6 these structures are plotted on a φ–ψ chart. The values of Pro(1) and Pro(3) residues lie between those of collagen 1-bonded and 2-bonded models and Pro(2) is located near the collagen 2-bonded model. The chart indicates that the three successive proline residues from the N-terminal do not assume the exact threefold screw-axis symmetry as poly-L-proline II does and that their structures are close to those of collagen models rather than that of poly-L-proline II. As can be seen in Table 3, the unit height of BOC–Pro_4–Bz is also consistent with those of collagen models. The C-terminal Pro(4)

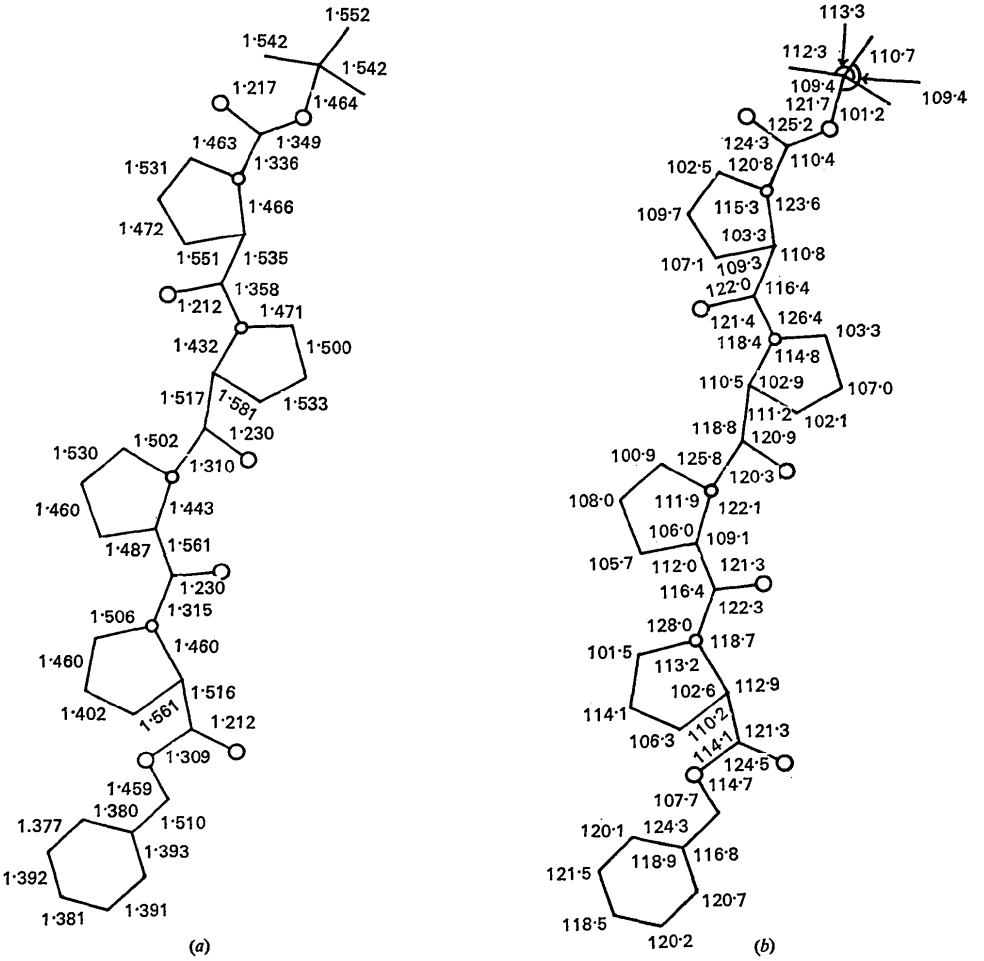


Fig. 4. (*a*) Bond lengths (Å). E.s.d. is ±0·012 Å. (*b*) Bond angles (°). E.s.d. is ±0·7°.

Table 3. *Torsion angles and unit heights*

	BOC–Pro_4–Bz						Collagen	
	Pro(0)	Pro(1)	Pro(2)	Pro(3)	Pro(4)	Poly-L-proline II	1-bonded model	2-bonded model
φ (°)		−67·7	−69·9	−61·1	−57·8	−75	−52·5	−77
ψ (°)		151·8	164·9	152·3	−38·5	145	148·5	157
ω (°)	−1·1	168·8	176·4	179·8		180	180	180
h (Å)			2·87			3·12	2·86	2·91
Reference			(1)			(2)	(3)	(4)

(1) Present study. (2) Sasisekharan (1959). (3) Rich & Crick (1961). (4) Ramachandran & Sasisekharan (1965).

residue takes the α-helix type conformation which was found in a simple peptide, acetyl-L-proline-*N*-methylamide (Matsuzaki & Iitaka, 1970) and seems to be another stable conformation of proline residues. The N-terminal peptide bond takes the *cis* conformation, the presence of which was suggested by Deber *et al.* (1970) and Tonelli (1970). As for the planarity of the peptide bonds, the bond between Pro(1) and Pro(2) deviates from a plane at an angle ω of 168·8°, while the other three are nearly planar.

The equations of the least-squares planes of the pyrrolidine rings and the distances of the individual atoms from the planes are given in Table 4. The puckered form in which the β-carbon atom deviates from the least-squares plane is observed in Pro(2) and Pro(4) residues. In Pro(1) and Pro(3) residues, γ-carbon atoms are shifted from the planes as is usually found in proline residues. The directions of the displacements of the γ-carbon atoms from the planes with respect to the carbonyl carbon atoms are *trans*, *cis*, *cis* and *trans* for Pro(1), Pro(2), Pro(3) and Pro(4), respectively. The intramolecular distances that are shorter than the allowed values proposed by Ramachandran, Rama-

Table 4. *Least-squares planes through the pyrrolidine rings and the benzene 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 axis, $X \| a^*$, $Y \| b$ and $Z \| c$ respectively, and D is the origin-to-plane distance.

Pro(1) residue

$$0{\cdot}715X+0{\cdot}447Y-0{\cdot}551Z=6{\cdot}371$$

Deviations of atoms from the plane

N	−0·008 Å	Cγ*	0·218 Å
Cα	0·008	Cδ	0·005
Cβ	−0·004		

Pro(2) residue

$$-0{\cdot}047X+0{\cdot}673Y+0{\cdot}739Z=0{\cdot}330$$

Deviations of atoms from the plane

N	0·021 Å	Cγ	0·012 Å
Cα	−0·013	Cδ	−0·020
Cβ*	−0·500		

Pro(3) residue

$$0{\cdot}875X-0{\cdot}264Y+0{\cdot}389Z=1{\cdot}828$$

Deviations of atoms from the plane

N	−0·038 Å	Cγ*	0·392 Å
Cα	0·038	Cδ	0·023
Cβ	−0·022		

Table 4 (*cont.*)

Pro(4) residue

$$0{\cdot}220X+0{\cdot}671Y-0{\cdot}713Z=0{\cdot}312$$

Deviations of atoms from the plane

N	0·015 Å	Cγ	0·009 Å
Cα	−0·010	Cδ	−0·015
Cβ*	−0·225		

Benzene ring

$$-0{\cdot}262X+0{\cdot}761Y+0{\cdot}599Z=3{\cdot}450$$

Deviations of atoms from the plane

Bz–C(1)	−0·008 Å	Bz–C(4)	−0·009 Å
Bz–C(2)	0·008	Bz–C(5)	0·010
Bz–C(3)	0·000	Bz–C(6)	−0·001

*Not included in the least-squares calculation.

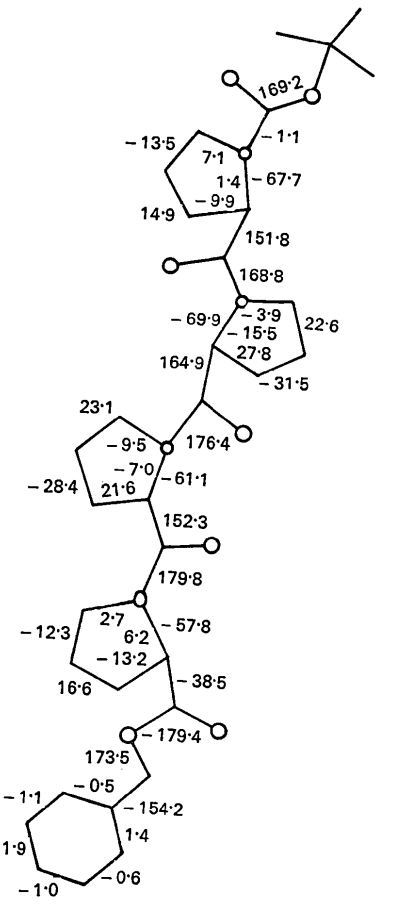


Fig. 5. Internal rotation angles (°).

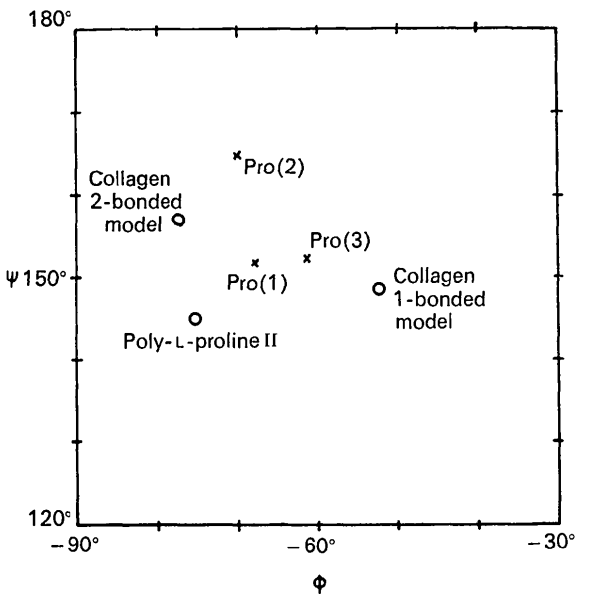


Fig. 6. φ–ψ chart. Pro(1), Pro(2) and Pro(3) are the proline residues in the BOC–Pro_4–Bz molecule.

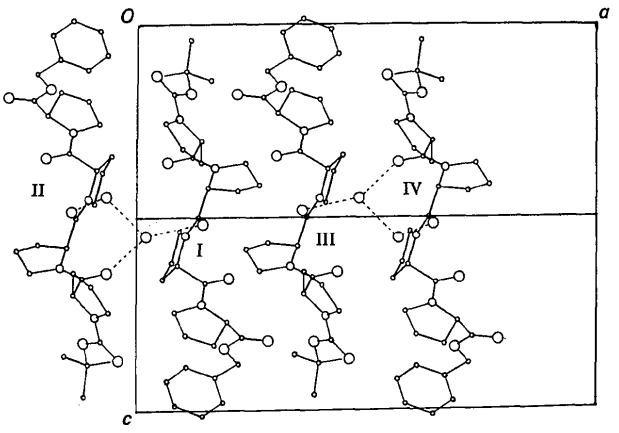


Fig. 7. Projection of the crystal structure along the *b* axis. The coordinates of the molecules I, II, III and IV are shown in Table 6.

krishnan & Sasisekharan (1963) are listed in Table 5. The distances between the α-carbon and δ-carbon atom of the next residue, between the carbonyl carbon and carbonyl carbon atom of the next residue, and between the α-carbon and carbonyl oxygen atom of the preceding residue are all included in this table. Some are shorter than the outer limit by about 0·08 Å.

Crystal structure

The projections of the crystal structure along the *b* axis and *c* axis are shown in Figs. 7 and 8, respectively [*ORTEP*, Johnson (1965)]. Two antiparallel chains of the tetramers I and II are linked together by the hydrogen bonds through the water molecules. Two of these hydrogen-bonded pairs of BOC–Pro_4–Bz molecules constitute a unit cell but there is no hydrogen bond between the pairs.

The short intermolecular contacts within 3·8 Å are listed in Table 6. The shortest, with a length of 2·991 Å, is between *B'* and pro(3)Cγ II(010). But this is not the C–H···O type hydrogen bond suggested for the structures of poly-L-proline II (Sasisekharan, 1959) and the collagen 2-bonded model (Ramachandran & Sasisekharan, 1965), since the distance between the oxygen atom of the water and the hydrogen atom attached to the Cγ atom is 2·40 Å, where the coordinates of the hydrogen atom were calculated to be $x=0{\cdot}0423$, $y=0{\cdot}0774$ and $z=0{\cdot}6151$.

Table 6. *Packing distances shorter than* 3·8 Å

From atom of I(000)	To atom		Distance
BOC–O(2)	Bz–C(3)	I(01$\bar{1}$)	3·672 Å
BOC–O(2)	Bz–C(4)	I(01$\bar{1}$)	3·366
Pro(2)Cγ	Pro(2)O	III(0$\bar{1}$0)	3·736
Pro(3)Cγ	water *A*	I(0$\bar{1}$0)	3·665
water *B'*	Pro(3)Cγ	II(010)	2·991
Pro(3)O	Pro(1)Cα	III(0$\bar{1}$0)	3·787
Pro(3)O	Pro(1)Cβ	III(0$\bar{1}$0)	3·521
Pro(3)O	Pro(2)Cδ	III(0$\bar{1}$0)	3·475
Pro(4)O	BOC–C(5)	III(0$\bar{1}$0)	3·769
Pro(4)O	Pro(1)Cα	III(0$\bar{1}$0)	3·369
Pro(4)O	Pro(1)Cβ	III(0$\bar{1}$0)	3·639
Pro(4)O	Pro(1)Cδ	III(0$\bar{1}$0)	3·613

Table 5. *Intramolecular distances between non-bonded atoms*

C–C distances	
Allowed value	3·20 Å
Outer limit	3·00
Pro(1)Cα—Pro(2)Cδ	2·921 Å
Pro(2)Cα—Pro(3)Cδ	2·923
Pro(3)Cα—Pro(4)Cδ	2·945
BOC–C(5)–Pro(1)C′	3·106
Pro(1)C′—Pro(2)C′	3·015
Pro(2)C′—Pro(3)C′	2·976
Pro(3)C′—Pro(4)C′	2·959
BOC–C(1)–BOC–C(5)	2·975
BOC–C(2)–BOC–C(5)	3·052
N–O distance	
Allowed value	2·70 Å
Outer limit	2·60
Pro(2)N—Pro(2)O	2·683 Å
C–O distances	
Allowed value	2·80 Å
Outer limit	2·70
Pro(1)Cα–BOC–O(1)	2·618 Å
Pro(2)Cα–Pro(1)O	2·683
Pro(3)Cα–Pro(2)O	2·704
Pro(4)Cα–Pro(3)O	2·685
Pro(1)Cδ–BOC–O(2)	2·783
Pro(4)C′—Pro(3)O	2·800
Bz–C(7)—Pro(4)O	2·626
Bz–C(6)—Bz–O	2·799

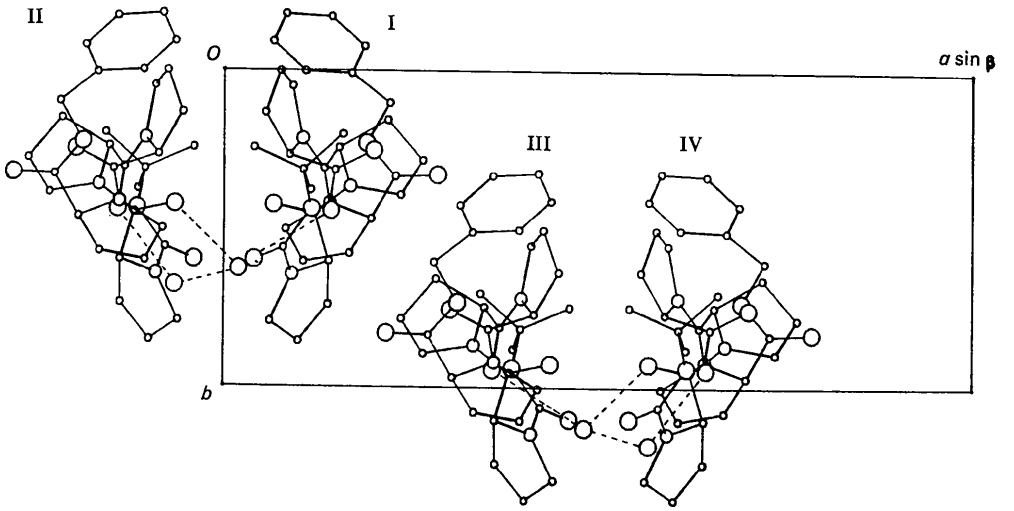


Fig. 8. Projection of the crystal structure along the *c* axis.

Table 6 (*cont.*)

Pro(4)O	Pro(1)N	III($0\bar{1}0$)	3·348
BOC–C(5)	Pro(4)Cδ	II(000)	3·729
Pro(1)Cγ	Pro(4)O	III(000)	3·564
Pro(4)Cγ	BOC–O(2)	II(000)	3·353
BOC–O(2)	Pro(4)Cδ	II(000)	3·513
Pro(1)O	Pro(3)Cα	II(000)	3·583
Pro(1)O	Pro(3)Cβ	II(000)	3·632
Pro(1)O	Pro(4)Cδ	II(000)	3·680
Pro(2)O	Pro(2)Cβ	III(000)	3·631
Pro(4)O	BOC–C(3)	III(000)	3·545
water *B'*	Pro(2)C'	II(000)	3·680
water *B'*	Pro(4)Cδ	II(000)	3·663
Pro(4)Cγ	Bz–C(4)	I(010)	3·742
Pro(4)Cγ	Bz–C(5)	I(010)	3·477
Pro(4)Cγ	Bz–C(6)	I(010)	3·718
BOC–O(2)	Bz–C(5)	II(010)	3·657
water *B'*	Pro(3)Cδ	II(010)	3·277
Bz–C(4)	Bz–C(4)	II(001)	3·566
Bz–C(4)	Bz–C(5)	II(001)	3·657
Pro(4)O	Bz–C(2)	III(001)	3·690
Pro(4)O	Bz–C(3)	III(001)	3·296
	e.s.d.		(0·014)

The coordinates of the equivalent positions are

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

followed by the components of translation vectors in parentheses.

The author wishes to thank Professor Y. Iitaka for valuable discussions and also Mr T. Hori for the reflexion-data measurement.

References

DEBER, C. M., BOVEY, F. A., CARVAR, J. P. & BLOUT, E.R. (1970). *J. Amer. Chem. Soc.* **92**, 6191–6198.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

ISEMURA, T., OKABAYASHI, H. & SAKAKIBARA, S. (1968). *Biopolymers*, **6**, 307–321.

IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

MATSUZAKI, T. & IITAKA, Y. (1971). *Acta Cryst.* B**27**, 507–516.

MIYOSHI, M., KIMURA, T. & SAKAKIBARA, S. (1970). *Bull. Chem. Soc. Japan*, **43**, 2941–2944.

OKABAYASHI, H. & ISEMURA, T. (1968). *Biopolymers*, **6**, 323–330.

OKABAYASHI, H. & ISEMURA, T. (1970*a*). *Bull. Chem. Soc. Japan*, **43**, 20–23.

OKABAYASHI, H. & ISEMURA, T. (1970*b*). *Bull. Chem. Soc. Japan*, **43**, 359–361.

RAMACHANDRAN, G. N., RAMAKRISHNAN, C. & SASISEKHARAN, V. (1963). *J. Mol. Biol.* **7**, 95–99.

RAMACHANDRAN, G. N. & SASISEKHARAN, V. (1965). *Biochim. Biophys. Acta*, **109**, 314–316.

RICH, A. & CRICK, F. H. C. (1961). *J. Mol. Biol.* **3**, 483–506.

RIPPON, W. B., KOENIG, J. L. & WALTON, A. G. (1970). *J. Amer. Chem. Soc.* **92**, 7455–7459.

SASISEKHARAN, V. (1959). *Acta Cryst.* **12**, 897–909.

TONELLI, A. E. (1970). *J. Amer. Chem. Soc.* **92**, 6187–6190.