Fig. 2. Projection of the crystal structure down the a axis. Molecules with filled bonds are centered at $x = 0.63$ and 0.87, while those with open bonds are at $x = 0.13$ and 0.37.

adopted by polyether macrocycles are determined primarily by intramolecular interactions (*e.g.* Goldberg, 1978; Dunitz & Seiler, 1974).

The bond distances and angles exhibit no extraordinary features, and are in good agreement with the average values of the corresponding parameters in previously reported crown ether structures. The geometry of the carboxyl group has been determined with a relatively low precision because of the disorder. The packing diagram (Fig. 2) shows that the mean planes of the molecular units are roughly perpendicular to the a axis; on cooling to $-160\,^\circ$C the unit cell is contracted mainly along this direction.

more, O(ring)$\cdots$C=O dipole–dipole attractive interactions involving the carboxyl substituent and two of the ether O atoms result in relatively short intramolecular contacts: O(2)$\cdots$C(24) 2.84 Å and O(16)$\cdots$C(24) 2.87 Å. In the observed conformation, the planar phenyl and pyridine rings are nearly parallel to each other; they form dihedral angles of 57 and 60° with the plane of the C–COOH fragment. All polar groups of the molecule are hidden within the macrocycle and covered by a lipophilic skin of C–H bonds.

In good correspondence with the above observations, this crystal structure, as well as that of BACR5, seems to be stabilized mainly by ordinary van der Waals forces. The remarkable similarity of the molecular conformations in both structures, differing significantly in their intermolecular arrangements, leads us to assume that crystal forces have little influence on the molecular geometry. Frequently, the conformations

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Benzyloxycarbonylglycyl-D,L-proline

BY T. KOJIMA, T. YAMANE AND T. ASHIDA

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Abstract. $C_{15}H_{18}N_2O_5$, $M_r = 306.3$, orthorhombic, $Pbc2_1$; $a = 10.227$ (3), $b = 10.490$ (1), $c = 28.590$ (1) Å; $Z = 8$, $D_x = 1.327$, $D_m = 1.324$ g cm^{-3}. $R = 0.060$ for 3014 reflections. Two independent molecules exist in the crystal, and are related to each other by a spurious center of symmetry.

Introduction. Benzyloxycarbonyl(Z)-Gly-D,L-Pro was prepared and crystallized by slow evaporation of an ethyl acetate solution. The intensity data were collected on a Hilger & Watts automatic four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation, and the $\omega-2\theta$ step scan method. A crystal of dimensions $0.20 \times 0.10 \times 0.03$ mm was selected. 3014 independent reflections with $2\theta \leq 144°$ were obtained, of which 2927 were non-zero. The intensity data were corrected for Lorentz and polarization effects.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the block-diagonal least-squares method with *HBLS* (Ashida, 1973). In the refinement, the weights $w = a$ for $|F_o| =$

Table 1. *Positional parameters* $(\times 10^4)$ *with their standard deviations in parentheses*

Molecule A	x	y	z
C(1)	1565 (5)	5455 (5)	−2142 (1)
C(2)	1923 (6)	6210 (6)	−2525 (2)
C(3)	1758 (6)	5780 (7)	−2962 (2)
C(4)	1240 (7)	4633 (8)	−3035 (2)
C(5)	854 (6)	3828 (5)	−2655 (2)
C(6)	1015 (4)	4261 (4)	−2205 (1)
C(7)	537 (4)	3458 (3)	−1808 (1)
C(8)	79 (4)	4824 (3)	−1172 (1)
C(9)	−248 (3)	6251 (3)	−525 (1)
C(10)	435 (3)	6580 (3)	−73 (1)
C(11)	378 (3)	7800 (3)	645 (1)
C(12)	−770 (4)	8449 (6)	907 (2)
C(13)	−1907 (4)	8216 (7)	664 (2)
C(14)	−1628 (3)	7671 (3)	192 (1)
C(15)	1391 (3)	8791 (3)	513 (1)
N(1)	538 (3)	5344 (3)	−786 (1)
N(2)	−262 (2)	7285 (2)	230 (1)
O(1)	899 (3)	3968 (2)	−1356 (1)
O(2)	−998 (3)	5049 (3)	−1346 (1)
O(3)	1559 (2)	6259 (3)	9 (1)
O(4)	1524 (3)	9249 (2)	134 (1)
O(5)	2100 (3)	9099 (3)	882 (1)

Molecule B			
C(1)	2872 (7)	5707 (6)	1681 (2)
C(2)	2493 (9)	4903 (8)	2033 (3)
C(3)	3411 (9)	4619 (10)	2385 (3)
C(4)	4583 (10)	5180 (11)	2373 (3)
C(5)	4967 (7)	6009 (8)	2012 (2)
C(6)	4069 (5)	6271 (4)	1665 (1)
C(7)	4431 (5)	7221 (4)	1286 (2)
C(8)	4842 (4)	5903 (3)	627 (1)
C(9)	5157 (4)	4557 (3)	−39 (1)
C(10)	4492 (3)	4250 (3)	−496 (1)
C(11)	4593 (4)	3081 (3)	−1224 (1)
C(12)	5769 (4)	2687 (8)	−1509 (2)
C(13)	6808 (4)	2462 (6)	−1187 (2)
C(14)	6556 (3)	3155 (3)	−743 (1)
C(15)	3640 (3)	2012 (3)	−1101 (1)
N(1)	4379 (3)	5452 (3)	228 (1)
N(2)	5187 (3)	3580 (2)	−803 (1)
O(1)	4027 (3)	6753 (3)	828 (1)
O(2)	5902 (3)	5643 (3)	794 (1)
O(3)	3360 (2)	4579 (3)	−574 (1)
O(4)	3514 (3)	1559 (3)	−721 (1)
O(5)	2973 (3)	1628 (3)	−1478 (1)

0, and $w = 1/[\sigma_{cs}^2(F_o) + b|F_o| + c|F_o|^2]$ for $|F_o| \neq 0$ were assigned, $\sigma_{cs}(F_o)$ being the e.s.d. of $|F_o|$ based on counting statistics. The final refinement ($a = 0.3026$, $b = -0.0203$, $c = 0.0036$) gave an R of 0.060 for all reflections (0.056 for 2927 non-zero reflections). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All the calculations were carried out on the FACOM 230-60/75 computer of Nagoya University. The final atomic parameters of the non-hydrogen atoms are listed in Table 1.*

Discussion. The bond distances, angles and torsion angles of the molecules are shown in Fig. 1. The mean e.s.d.'s of the bond distances and angles are 0.007 Å and $0.4°$, respectively. The definition of torsion angles given by the IUPAC–IUB Commission on Biochemical Nomenclature (1970) is adopted.

Two independent molecules exist in the crystal, and are related to each other by a spurious center of symmetry. The conformations of the peptide chains of the two molecules are very similar, and the chains are *trans* zig-zag except for the C(7)—O(1) bonds (*gauche*). Thus, the molecules are elongated, and the carbonyl and carboxyl groups stick out. However, the conformations of the pyrrolidine rings of the two molecules
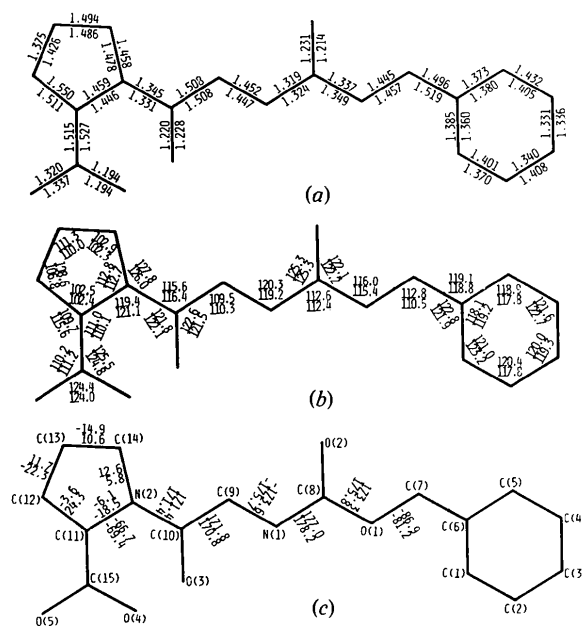
Fig. 1. (a) Bond lengths (Å), (b) bond angles (°) and (c) torsion angles (°).

Table 2. *The structure of Gly-Pro in peptides*

Peptides*	φ (G)	ψ (G)	ω (G-P)	φ (P)	Reference†
Molecule A	−173·6°	171·8°	171·4°	−66·7°	(1)
Molecule B	−175·7	170·8	171·4	−69·4	(1)
Z-GP	−107·7	176·4	179·6	−69·5	(2)
Boc-GP	172·0	177·8	177·4	−70·5	(3)
Boc-GP-OBz	−109·5	164·4	−179·9	−75·6	(3)
Z-GPL	−78·8	174·3	−3·8	−71·7	(4)
(p-Br)-Z-GPLG	90·8	170·5	−174·3	−57·6	(5)
Z-GPLGP	−86·5	−175·4	−176·5	−63·2	(6)
Z-GPLGP	116·3	174·8	−178·7	−67·2	(6)
(o-Br)-Z-GPLGP	−97·4	−165·0	−168·7	−65·4	(7)
(o-Br)-Z-GPLGP	117·0	178·0	177·8	−71·9	(7)

* (o-Br)-Z-GPLGP is o-Br-benzyloxycarbonyl-Gly-Pro-Leu-Gly-Pro, and so on. For the pentapeptides the values for the underlined part are listed.

† (1) Present study. (2) Tanaka, Kojima, Ashida, Tanaka & Kakudo (1977). (3) Marsh, Narasimha Murthy & Venkatesan (1977). (4) Yamane, Ashida, Shimonishi, Kakudo & Sasada (1976). (5) Ueki, Ashida, Kakudo, Sasada & Katsube (1969). (6) Bando, Tanaka, Ashida & Kakudo (1978). (7) Ueki, Bando, Ashida & Kakudo (1971).

Fig. 2. The hydrogen bond between two molecules around a spurious center of symmetry.

Table 3. *Hydrogen bonds*

Donor D–H	Acceptor A	Distances (Å) D···A	H···A	Angle (°) D–H···A
N(1)A	O(3)Bⁱ	3·056	2·14	169
O(5)A	O(2)Bⁱⁱ	2·620	1·66	166
N(1)B	O(3)Aⁱ	3·069	2·11	172
O(5)B	O(2)Aⁱⁱⁱ	2·639	1·64	176

Symmetry code

(i) x,y,z; (ii) $-x, -\frac{1}{2} + y, z$; (iii) $1 - x, \frac{1}{2} + y, z$

are quite different. The ring in molecule A is C_s–C^γ-*exo*, and that in the molecule B is C_s–C^β-*exo* (Ashida & Kakudo, 1974).

In Table 2 the torsion angles of the Gly-Pro groups in several peptides are listed. It is found that ψ(Gly) is distributed in the narrow range of 180 ± 15°, while in other X-Pro sequences (X is any other amino acid), $\psi(X)$ is distributed through a much wider range.

The hydrogen bonds are listed in Table 3. The molecular packing around a spurious center of symmetry is shown in Fig. 2. The molecules make a ten-
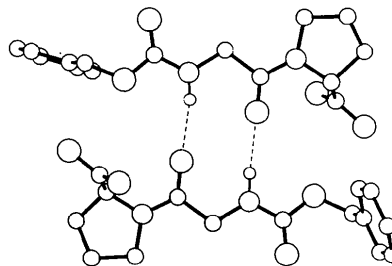
membered ring by hydrogen bonding, which is similar to that of Z-Gly-L-Pro (Tanaka, Kojima, Ashida, Tanaka & Kakudo, 1977).

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