The crystal structure projected along the *a* axis is shown in Fig. 2. The hydrogen bonds are given in Table 2, together with short intermolecular contacts less than 3·3 Å. The cyanidin molecule is hydrogen bonded to bromide ions through O(7)H and O(3′)H, and also to water molecules through O(3)H and O(4′)H. The O(5)H group forms a bifurcated hydrogen bond with O(3′) and O(4′).

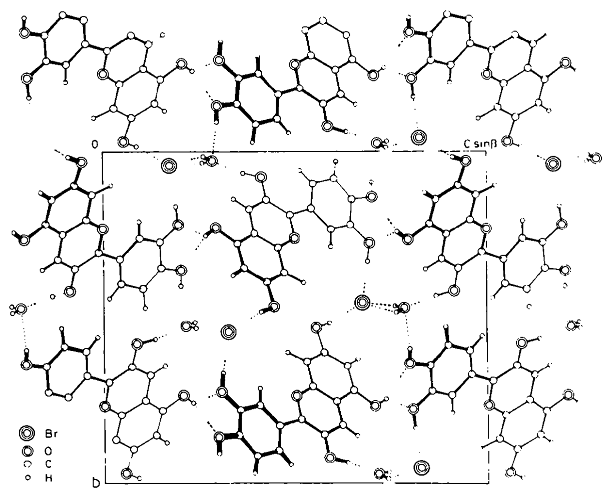

Fig. 2. Crystal structure projected along the *a* axis. The hydrogen bonds are indicated by broken lines.

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Benzyloxycarbonylglycyl-L-proline

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Abstract. $C_{15}H_{18}N_2O_5$, tetragonal, $P4_32_12$; $a = 9{\cdot}455$ (1), $c = 34{\cdot}889$ (5) Å; $Z = 8$, $D_x = 1{\cdot}305$, $D_m = 1{\cdot}288$ g cm^{-3}. The structure was solved by the direct method and refined to a final R value of 0·051. The molecules are in an antiparallel arrangement and are connected by hydrogen bonds.

Introduction. A series of oligopeptides containing Gly-Pro sequences, such as (*o*-Br)-*Z*-Gly-Pro-Leu-Gly-Pro (Ueki, Bando, Ashida & Kakudo, 1971), *Z*-Gly-Pro-Leu-Gly-Pro (Bando, Tanaka, Ashida & Kakudo, 1976), (*p*-Br)-*Z*-Gly-Pro-Leu-Gly (Ueki, Ashida, Kakudo, Sasada & Katsube, 1969) and *Z*-Gly-Pro-Leu (Yamane, Ashida, Shimonishi, Kakudo & Sasada, 1976) have been studied by X-ray diffraction. It was revealed that the tetra- and pentapeptides have essentially the same conformation, *i.e.* β-turn. On the other hand, the structure of the tripeptide was found to be different from those of the tetra- and pentapeptides, and was shown to have a *cis* conformation at the peptide bond between Gly and Pro.

The present paper describes the crystal structure of $C_{15}H_{18}N_2O_5$ (*Z*-Gly-Pro), and the conformation is compared with those of the longer peptides.

The X-ray diffraction data were collected on a Rigaku four-circle automatic diffractometer with Ni-filtered Cu $K\alpha$ radiation, the θ–2θ scan, and a scan rate of 4° (2θ) min^{-1}. 1445 independent reflexions with $\sin\theta/\lambda$ less than 0·562 were measured. The structure was solved by *MULTAN* (Germain, Main & Woolfson,

1971) and refined by the block-diagonal least-squares method to the final R index of 0·052, including all the H atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \frac{1}{2}$ for $|F_o|$, $w = 1$ for $0 \leq |F_o| \leq 15$, and $w = (15/|F_o|)^2$ for $|F_o| < 15$. The atomic scattering factors of the C, N and O atoms were taken from *International Tables for X-ray Crystallography* (1962), and that of the H atom from *International Tables for X-ray Crystallography* (1974). The final parameters are listed in Tables 1 and 2.*

Discussion. The bond distances, bond angles and torsion angles of the molecule are shown in Fig. 1. The C—H bond length varies from 0·91 to 1·14 Å (average 1·03 Å). An *ORTEP* (Johnson, 1965) drawing of the molecule with thermal ellipsoids enclosing 50% probability is shown in Fig. 2.

In the main part of the molecule, from the phenyl to the pyrrolidine group, only the N—C^{α} bond of Gly is *gauche*, while all the others are *trans*. Thus, the molecule is elongated as a rod, and the carboxyl and carbonyl groups stick out laterally. The molecule consists of four planar groups: phenyl, *N*-oxycarbonyl, peptide and carboxyl, each of which is nearly perpendicular to the nearest planar groups.

The proline ring structures are divided into classes *A* and *B* by Balasubramanian, Lakshminarayanan, Sabesan, Tegoni, Venkatesan & Ramachandran (1971). In class *A* both of the C^{γ} and carboxyl C′ atoms are on the same side of the proline ring plane (C^{γ}-*endo*), while in class *B* the two atoms are on the opposite side (C^{γ}-*exo*). In the proline rings in peptides, however, the puckerings of the pyrrolidine rings occur at any of the C^{β} or C^{γ} atoms, or simultaneously at both atoms in the opposite directions. Therefore a more precise classification of the structure is presented by Ashida & Kakudo (1974); this classification denotes the approximate symmetry of the ring, such as C_2 or C_s, and the direction of the shift of the atom from the plane with respect to the C′ atom.

Table 2. *Positional* ($\times 10^3$) *and thermal parameters for the hydrogen atoms*

Standard deviations are given in parentheses.

	Bonded to	x	y	z	B
H(1)	C(1)	762 (6)	435 (6)	362 (1)	8·7 (15)
H(2)	C(2)	1016 (10)	531 (8)	378 (3)	14·1 (23)
H(3)	C(3)	1042 (7)	683 (7)	421 (2)	11·8 (19)
H(4)	C(4)	855 (8)	793 (7)	461 (2)	12·1 (20)
H(5)	C(5)	617 (6)	722 (6)	449 (1)	9·0 (15)
H(6)	C(7)	507 (9)	487 (7)	366 (2)	11·6 (20)
H(7)	C(7)	465 (9)	630 (8)	389 (2)	14·4 (25)
H(8)	C(9)	138 (4)	160 (4)	441 (1)	4·3 (9)
H(9)	C(9)	102 (4)	290 (4)	418 (1)	3·9 (8)
H(10)	C(11)	−140 (5)	444 (5)	510 (1)	5·9 (11)
H(11)	C(12)	−347 (6)	397 (6)	481 (1)	8·3 (14)
H(12)	C(12)	−366 (4)	291 (4)	517 (1)	4·7 (9)
H(13)	C(13)	−375 (4)	175 (4)	452 (1)	4·8 (9)
H(14)	C(13)	−268 (4)	89 (5)	488 (1)	5·5 (11)
H(15)	C(14)	−155 (5)	247 (5)	422 (1)	5·6 (11)
H(16)	C(14)	−91 (5)	105 (5)	449 (1)	5·6 (10)
H(17)	N(1)	329 (6)	272 (5)	456 (1)	7·9 (14)
H(18)	O(5)	−109 (7)	296 (7)	586 (2)	10·2 (17)

Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10^5$) *parameters with their standard deviations in parentheses*

The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	7875 (5)	5252 (6)	3824 (1)	1737 (70)	2463 (83)	174 (5)	456 (117)	132 (32)	249 (35)
C(2)	9235 (6)	5610 (8)	3910 (2)	1801 (76)	3529 (22)	235 (7)	1125 (165)	169 (40)	455 (52)
C(3)	9494 (6)	6468 (7)	4200 (2)	2027 (78)	2997 (111)	259 (7)	−1550 (154)	−114 (44)	422 (51)
C(4)	8477 (8)	7030 (7)	4415 (2)	3097 (118)	2879 (110)	239 (7)	−1246 (189)	−426 (53)	−135 (53)
C(5)	7022 (6)	6658 (7)	4336 (1)	2484 (88)	2709 (97)	178 (5)	533 (158)	45 (40)	59 (40)
C(6)	6767 (4)	5744 (5)	4036 (1)	1288 (47)	2011 (62)	117 (3)	−439 (91)	65 (21)	262 (25)
C(7)	5280 (5)	5408 (7)	3926 (1)	1569 (61)	3581 (111)	160 (4)	−1824 (131)	−102 (29)	758 (38)
C(8)	3384 (4)	4042 (4)	4144 (1)	1087 (41)	2103 (60)	89 (2)	−464 (83)	−19 (18)	136 (22)
C(9)	1474 (4)	2655 (4)	4399 (1)	1270 (46)	1781 (56)	111 (3)	−683 (84)	−44 (20)	96 (23)
C(10)	693 (4)	3256 (4)	4743 (1)	1408 (47)	1174 (43)	98 (2)	−680 (74)	−94 (19)	144 (18)
C(11)	−1549 (4)	3471 (4)	5074 (1)	1548 (50)	1460 (48)	102 (3)	−103 (78)	−41 (22)	39 (21)
C(12)	−3058 (5)	3092 (6)	4949 (2)	1402 (53)	2624 (80)	142 (4)	75 (106)	44 (27)	−21 (33)
C(13)	−2873 (4)	1808 (6)	4699 (1)	1364 (52)	2526 (78)	141 (4)	−1149 (110)	24 (25)	−188 (31)
C(14)	−1477 (4)	2045 (5)	4491 (1)	1430 (50)	2017 (62)	116 (3)	−1197 (96)	−34 (23)	−76 (25)
C(15)	−1141 (4)	2690 (4)	5440 (1)	1549 (52)	1433 (49)	115 (3)	−120 (83)	155 (22)	−60 (22)
N(1)	2934 (3)	3101 (4)	4395 (1)	1130 (36)	2225 (54)	117 (2)	−678 (73)	−37 (17)	351 (21)
N(2)	−685 (3)	2962 (3)	4757 (1)	1283 (37)	1556 (40)	94 (2)	−739 (66)	7 (16)	8 (16)
O(1)	4732 (3)	4396 (3)	4204 (1)	1250 (32)	2750 (52)	105 (2)	−960 (67)	−75 (14)	395 (18)
O(2)	2682 (3)	4556 (4)	3890 (1)	1468 (36)	2745 (53)	109 (2)	−758 (72)	−207 (15)	401 (19)
O(3)	1277 (3)	3942 (3)	4992 (1)	1693 (36)	1414 (32)	118 (2)	−792 (56)	−202 (16)	23 (16)
O(4)	−732 (3)	1502 (3)	5452 (1)	2100 (43)	1436 (35)	138 (2)	188 (65)	92 (18)	85 (16)
O(5)	−1353 (4)	3470 (3)	5745 (1)	3405 (67)	1832 (43)	113 (2)	1528 (91)	95 (22)	21 (18)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31962 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

In the present prolyl residue, the displacements of the atoms from the $C^{\alpha}NC^{\delta}$ plane are: C^{β} 0·317, C^{γ} −0·231 and C′ −1·380 Å. Thus the structure is C_2—C^{γ}-*endo*, conformation *A*.

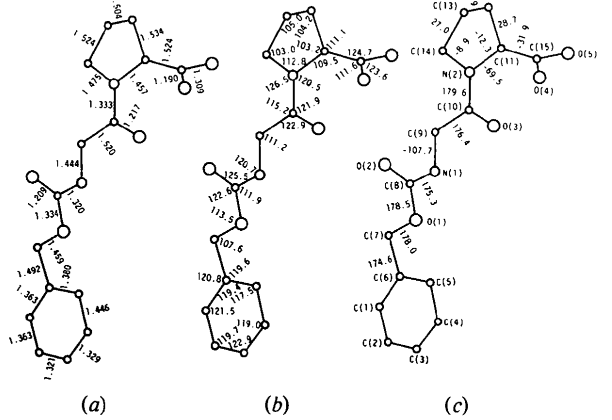

Fig. 1. (*a*) Bond lengths (Å), (*b*) bond angles (°) and (*c*) torsion angles (°). The estimated standard deviations are 0·005–0·010 Å in distances and 0·3–0·7° in angles. The IUPAC–IUB Commission on Biochemical Nomenclature (1970) convention is adopted.

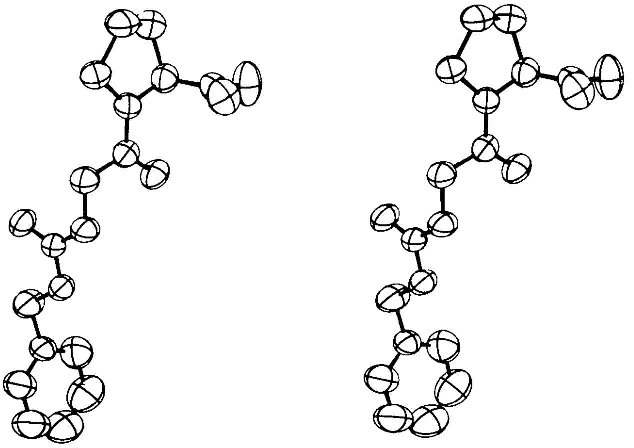

Fig. 2. A stereoscopic drawing of one molecule of *Z*-Gly-Pro.

In Table 3 the torsion angles of the Gly-Pro groups in several peptides are listed. As a whole, the Gly-Pro structure in the present peptide is more similar to those with terminal C than those with terminal N in the tetra- and pentapeptides, whose structures are constrained by the intramolecular β-turn hydrogen bonds.

The hydrogen bonds are listed in Table 4. The molecular packing around a twofold axis is shown in Fig. 3. The molecules are in an antiparallel arrangement and are hydrogen bonded to each other, although the details are not very similar to those of the β-structure.

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Table 4. *Hydrogen bonds*

Donor *D*—H	Acceptor *A*	Distances (Å) *D*···*A*	 H···*A*	Angle (°) ∠*D*—H···*A*
N(1)	O(3) (*a*)	2·906	2·16	167
O(5)	O(2) (*b*)	2·646	2·04	150

Symmetry code: (*a*) *y*, *x*, 1·0-*z*, (*b*) −0·5 + *y*, 0·5 − *x*, 0·25 + *z*.

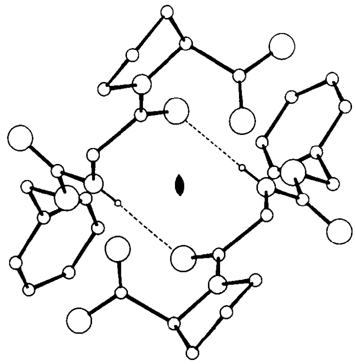

Fig. 3. The hydrogen bond between two molecules around a twofold axis.

Table 3. *The structure of Gly–Pro in peptides*

The torsion angles of Br-tetra- and Br-pentapeptides are given by Ashida & Kakudo (1974).

Peptides*	ψ (G)	ω (G-P)	φ (P)	θ	χ_1	χ_2	χ_3	χ_4	Pyrrolidine ring	Reference†
Z-GP	176·4°	179·6°	−69·5°	−12·3°	28·7°	−34·9°	27·0°	−8·9°	*B*, C_2—C^{γ}-*endo*	(1)
Z-GPL	174·3	−3·8	−71·7	−13·4	28·0	−32·9	24·0	−5·9	*B*, C_2—C^{γ}-*endo*	(2)
(*p*-Br)-*Z*-GPLG	171	−174	−58	6	−16	21	−17	6	*A*, C_2—C^{γ}-*exo*	(3)
Z-GPLGP	−175	−177	−63	−2	−7	14	−14	9	*A*, C_s—C^{γ}-*exo*	(4)
Z-GPLGP	175	−179	−67	−5	24	−33	29	−14	*B*, C_s—C^{γ}-*endo*	(4)
(*o*-Br)-*Z*-GPLGP	−165	−169	−65	13	−24	27	−19	3	*A*, C_s—C^{β}-*endo*	(5)
(*o*-Br)-*Z*-GPLGP	178	178	−72	−15	32	−38	27	−7	*B*, C_2—C^{γ}-*endo*	(5)

* (*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) Yamane *et al.* (1976). (3) Ueki *et al.* (1969). (4) Bando *et al.* (1976). (5) Ueki *et al.* (1971).

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trans-Di-1,2-(6-methyl-2-thio-3-*p*-tolyl-1,2,3,4-tetrahydro-1,3,2-benzodiazaphosphorine)

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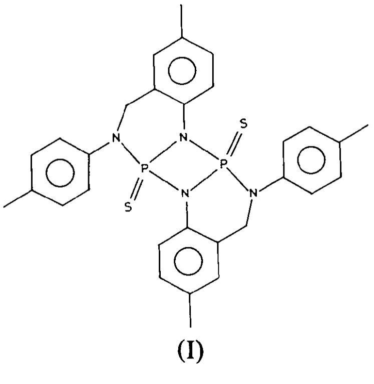
Abstract. $(C_{15}H_{15}N_2PS)_2$, monoclinic, $P2_1/b$; $a = 11{\cdot}94\,(1)$, $b = 22{\cdot}44\,(2)$, $c = 7{\cdot}00\,(1)$ Å, $\beta = 106{\cdot}9\,(1)^\circ$; $Z = 2$, $D_c = 1{\cdot}23$, $D_m = 1{\cdot}23$ g cm^{-3}; μ(Mo $K\alpha$) = $2{\cdot}7$ cm^{-1}, $\lambda = 0{\cdot}7107$ Å. The crystals are poor diffractors of X-rays and slowly decompose on irradiation. The structure was determined from 529 independent reflexions measured on a linear diffractometer, and was refined by constrained full-matrix least squares to $R = 0{\cdot}14$. The molecule contains two N atoms with pyramidal configurations and P—N bond lengths between 1·74 and 1·80 Å.

Introduction. The title compound (I) contains two N atoms in different environments, one in a phosphazane ring and the other, also bonded to P, in a six-membered heterocycle. The structure of the compound was determined in order to examine the effect of the different environments upon the N atoms.

The crystals are very thin needles and have an approximate square cross-section of side ~ 0·05 mm. Several crystals were mounted about the needle axis (001) inside capillary tubes and the dimensions of the unit cell were determined from oscillation and Weissenberg photographs. Systematic extinctions $0kl$, $k = 2n + 1$; $00l$, $l = 2n + 1$ uniquely indicated space group $P2_1/b$. Only one crystal was found that gave a reasonable number of X-ray reflexions. From this, 529 unique reflexions were measured on a Hilger & Watts linear diffractometer ($hk0$–7). This is about 13% of those available with Cu radiation.

The crystal steadily decomposed in the X-ray beam and there was a 30% reduction of the intensity of the $hk0$ reflexions between the start and end of data collection. There did not, however, appear to be any appreciable difference in the relative intensities of the reflexions. The data were corrected for Lorentz and polarization factors but not for absorption.



(I)