SHELDRICK, G. M. (1986). *SHELXS86*. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.

SPEK, A. L. (1982). *The EUCLID package*. In *Computational Crystallography*, edited by D. SAYRE, p. 528. Oxford: Clarendon Press.

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Structure of a 1:1 Complex between *N*-Boc-L-Pro-L-Val-OCH_3 (I) and *N*-Boc-L-Pro-C^β-Methylated-L-Val-OCH_3 (II)

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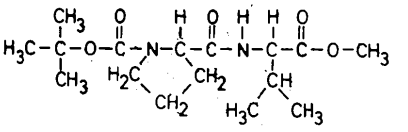
Abstract. $C_{16}H_{28}N_2O_5.C_{17}H_{30}N_2O_5$, $M_r = 670{\cdot}84$, triclinic, $P1$, $a = 9{\cdot}698$ (4), $b = 10{\cdot}173$ (3), $c = 10{\cdot}557$ (2) Å, $\alpha = 110{\cdot}19$ (2), $\beta = 97{\cdot}49$ (2), $\gamma = 90{\cdot}64$ (2)°, $V = 967{\cdot}4$ (5) Å^3, $Z = 1$, $D_m = 1{\cdot}104$ (5), $D_x = 1{\cdot}151$ (5) g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 6{\cdot}63$ cm^{-1}, $F(000) = 364$, $T = 298$ K, final $R = 0{\cdot}061$ for 2772 unique observed reflections. The peptides were synthesized by combination of *N*-Boc-L-Pro and valine methyl ester (I) and *N*-Boc-L-Pro and C^β-methylated valine methyl ester (II). The molecules of the 1:1 complex are hydrogen-bonded together *via* the carbonyl O atoms of the Pro residues of (I) and (II) and the amino N atoms of valine and C^β-methylated valine respectively. The molecular dimensions in the methyl ester moieties of (I) and (II) show significant departures from the standard values. The backbone conformations of the two peptides are similar. The Boc groups adopt *trans–cis* conformations. The pyrrolidine rings of the Pro residues exist in C^γ-*endo* conformations. The torsion angles that define the conformations of the valine residues are close to −60 and 60° respectively. The crystal structure is essentially stablilized by a network of van der Waals interactions and hydrogen bonds.

Introduction. The conformational preferences of amino acid side chains are of fundamental importance in determining the interactions that govern the preferred conformations of polypeptides and proteins (Chandrasekharan & Ramachandran, 1970; Janin, Wodak, Levitt & Maigret, 1978; Bhat, Sasisekharan & Vijayan, 1979) and of oligopeptides (Benedetti, Morelli, Nemethy & Scheraga, 1983). Conformational preferences may be determined by conformational-energy computations (Zimmerman, Pottle, Nemethy & Scheraga, 1977; Vasquez, Nemethy & Scheraga, 1983). They are basically governed to a large extent by interactions of a given side chain with atoms of the two neighbouring units. It is therefore worthwhile to examine the backbone and side-chain conformations of peptides with only marginal differences in the size of the side chains. We report here the crystal structure of a 1:1 complex between *N*-Boc-L-Pro-L-Val-OCH_3 (I) and *N*-Boc-L-Pro-C^β-methylated-L-Val-OCH_3 (II). The peptide (I) has been synthesized earlier (Crisma, Fasman, Balaram & Balaram, 1984).

(I)



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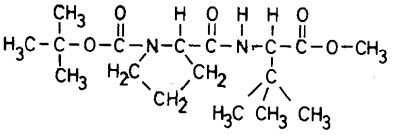
(II)



Experimental. The amino acids valine and *tert*-butylglycine (C^β-methylated valine) were obtained from Sigma Chemical Company. The valine methyl ester and C^β-methylated valine methyl ester were synthesized by reacting valine and C^β-methylated valine separately in methanol with thionyl chloride, which was added drop by drop. The mixture was stirred for 10 min at 263 K. *N*-Boc-L-Pro-L-Val-OCH_3 (I) and *N*-Boc-L-Pro-C^β-methylated-L-Val-OCH_3 (II) were synthesized by coupling *N*-Boc-L-Pro-OH with valine methyl ester and C^β-methylated valine methyl ester, respectively, using the procedure described by Poisel (1977). A 1:1 mixture of peptides (I) and (II) was crystallized from their solution in methanol at 298 K. Large, irregular and colourless crystals; one with

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dimensions 0·80 × 0·30 × 0·20 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Cu $K\alpha$ radiation in ω–2θ scan mode. Unit-cell parameters refined with 25 high-angle reflections ($\theta = 16$ to 45°). The density of the sample was measured by the flotation technique. Standard reflection $11\bar{1}$ showed changes $\leq 4{\cdot}8\%$ in intensity during the complete data collection. All reflections (h: 0 to 10; k: −11 to 11, l: −11 to 11) in the range $1 < \theta < 55°$ were measured. Of the 3075 measured reflections, 2772 unique reflections were considered observed [$I \geq 2\sigma(I)$]. Corrections were made for Lorentz and polarization effects but not for absorption ($\mu R = 0{\cdot}30$). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986) and refined by full-matrix least-squares procedure by minimizing $\sum w|(\Delta F)|^2$ with *SHELX*76 (Sheldrick, 1976), initially with isotropic and then anisotropic thermal parameters for non-H atoms. Calculated H-atom positions were included in the refinement with fixed parameters. Final values for 2772 observed reflections: $R = 0{\cdot}061$, $wR = 0{\cdot}061$ and $S = 0{\cdot}50$, weights $w = 1$ were used. Final $\Delta\rho$ was −0·14 to 0·18 e Å^{-3} and maximum shift to e.s.d. ratio, $(\Delta/\sigma)_{max}$, was 0·19. Atomic scattering factors for non-H atoms from Cromer & Mann (1968) and H-atom scattering factors from Stewart, Davidson & Simpson (1965).

Discussion. Atomic coordinates of non-H atoms with equivalent isotropic thermal parameters are listed in Table 1.* The atomic numbering scheme together with a perspective view as seen along the c axis is shown in Fig. 1. The bond lengths and angles involving non-H atoms are given in Table 2. The values of bond lengths and valence angles in the side chains of valine and C^{β}-methylated valine, and in the OCH_3 groups of the peptides show significant departures from the standard values. The temperature factors and the electron densities for these atoms did not suggest any disorder.

The convention for describing the peptide conformational angles used in this article follows the recommendations of the IUPAC–IUB Commission on Biochemical Nomenclature (1970). The backbone conformations of the two peptides are very similar. The backbone torsion angles in (I) are $\theta_0^1 = 179{\cdot}4$ (6), $\omega_0 = 2{\cdot}9$ (10), $\varphi_1 = -73{\cdot}9$ (8), $\psi_1 = 159{\cdot}5$ (5), $\omega_1 = 168{\cdot}0$ (6), $\varphi_2 = -98{\cdot}5$ (9), $\psi_2^T = 7{\cdot}4$ (15)° while those in (II) are $\theta_{01}^1 = -178{\cdot}7$ (6), $\omega_{01} = -1{\cdot}0$ (9), $\varphi_{11} = -70{\cdot}3$ (7), $\psi_{11} = 157{\cdot}8$ (5), $\omega_{11} = 166{\cdot}8$ (5), $\varphi_{12} = -82{\cdot}8$ (7), $\psi_{12}^T = 165{\cdot}4$ (6)°. The conformations of the Boc groups as characterized by θ^1 and ω_0 are *trans–cis* (Benedetti, Pedone, Toniolo, Nemethy, Pottle & Scheraga, 1980) and the urethane moiety is planar. This conformation is very similar to that observed in *N*-Boc-L-Pro-dehydro-Leu-OCH_3 (Narula, Patel, Singh, Chauhan & Sharma, 1988). The torsion angles θ^1 [C(4)—O(1)—C(5)—O(2)] and θ_1^1 [C(14)—O(11)—C(15)—O(12)] of 0·9 (12) and −0·9 (10)° in peptides (I) and (II) respectively indicate that the C(5)═O(2) bond is synperiplanar with the C(4)—O(1) bond as seen for esters in general (Bender, 1960; Dunitz & Strickler, 1968). The values of φ_1, ψ_1 and φ_2 in (I) and φ_{11}, ψ_{11} and φ_{12} in (II) indicate that the backbones of the peptides

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^3$) *of non-H atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11}a^2a^{*2} + U_{22}b^2b^{*2} + U_{33}c^2c^{*2} + U_{12}aba^*b^*\cos\gamma + U_{13}aca^*c^*\cos\beta + U_{23}bcb^*c^*\cos\alpha).$$

	x	y	z	U_{eq}(Å^2)
Peptide (I)				
C(1)	−4024 (10)	−3791 (10)	−2718 (9)	142 (7)
C(2)	−3860 (10)	−4443 (8)	−636 (11)	136 (7)
C(3)	−6119 (8)	−3761 (9)	−1497 (10)	126 (6)
C(4)	−4556 (7)	−3530 (8)	−1377 (7)	94 (5)
O(1)	−4108 (5)	−2109 (5)	−415 (4)	85 (3)
C(5)	−4610 (8)	−996 (8)	−659 (8)	98 (5)
O(2)	−5439 (6)	−999 (6)	−1607 (6)	129 (4)
N(1)	−4084 (5)	187 (6)	342 (6)	88 (3)
C^{α}(1)	−3065 (6)	252 (6)	1486 (6)	77 (4)
C^{β}(1)	−2595 (8)	1817 (7)	2089 (10)	114 (6)
C^{γ}(1)	−3640 (16)	2496 (10)	1539 (17)	273 (14)
C^{δ}(1)	−4421 (9)	1568 (8)	270 (11)	138 (7)
C′(1)	−3649 (6)	−207 (6)	2529 (7)	75 (4)
O′(1)	−4900 (4)	−154 (5)	2658 (5)	98 (3)
N(2)	−2691 (5)	−589 (5)	3349 (5)	78 (3)
C^{α}(2)	−2962 (7)	−815 (9)	4580 (7)	99 (5)
C^{β}(2)	−2392 (9)	−2150 (10)	4727 (9)	123 (6)
$C^{\gamma 1}$(2)	−3054 (13)	−3392 (11)	3559 (12)	190 (11)
$C^{\gamma 2}$(2)	−771 (9)	−2072 (10)	4851 (10)	131 (7)
C′(2)	−2501 (12)	414 (15)	5810 (12)	147 (9)
O′(2)	−2618 (11)	389 (11)	6970 (8)	229 (9)
O(3)	−2105 (10)	1476 (9)	5702 (9)	173 (7)
C(6)	−1640 (15)	2561 (12)	7274 (14)	257 (13)
Peptide (II)				
C(11)	2483 (11)	−4532 (11)	2525 (12)	198 (10)
C(12)	1979 (11)	−6091 (9)	21 (12)	166 (9)
C(13)	82 (9)	−5359 (10)	1431 (11)	139 (7)
C(14)	1512 (8)	−4956 (7)	1197 (9)	108 (5)
O(11)	1471 (4)	−3621 (4)	944 (5)	83 (3)
C(15)	649 (6)	−3511 (7)	−103 (7)	77 (4)
O(12)	−129 (5)	−4434 (5)	−963 (5)	103 (3)
N(11)	809 (5)	−2204 (5)	−143 (5)	70 (3)
C^{α}(11)	1722 (5)	−1087 (5)	825 (5)	60 (3)
C^{β}(11)	1684 (8)	46 (7)	184 (7)	94 (5)
C^{γ}(11)	446 (12)	−276 (10)	−784 (11)	178 (9)
C^{δ}(11)	−16 (8)	−1778 (7)	−1197 (7)	97 (5)
C′(11)	1221 (6)	−536 (6)	2198 (6)	64 (3)
O′(11)	−13 (4)	−620 (5)	2338 (4)	81 (3)
N(12)	2221 (4)	122 (5)	3232 (4)	63 (3)
C^{α}(12)	1871 (7)	957 (6)	4545 (6)	74 (4)
C^{β}(12)	3027 (10)	961 (11)	5675 (8)	128 (7)
$C^{\gamma 1}$(12)	3164 (11)	−574 (14)	5642 (11)	187 (10)
$C^{\gamma 2}$(12)	4213 (14)	2043 (18)	5662 (15)	268 (15)
$C^{\gamma 3}$(12)	2794 (28)	1611 (19)	7054 (17)	364 (24)
C′(12)	1528 (10)	2393 (8)	4532 (8)	107 (5)
O′(12)	1735 (12)	2809 (7)	3665 (8)	253 (12)
O(13)	906 (6)	3117 (6)	5542 (6)	127 (4)
C(16)	537 (13)	4505 (10)	5629 (11)	179 (9)

* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, torsion angles, bond lengths and angles involving H atoms and details of hydrogen bonds and van der Waals distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52149 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

adopt a collagen-like helix conformation (Rich & Crick, 1961; Ramachandran, Ramakrishnan & Sasisekharan, 1963). The values of ψ_2^T and ψ_{12}^T are very different and indicate the influence of an additional methyl group at C$^\beta$(12) in peptide (II). The torsion angles of the pyrrolidine rings are $\chi_1^1 = 17{\cdot}7$ (9), $\chi_1^2 = -23{\cdot}4$ (13), $\chi_1^3 = 18{\cdot}3$ (13), $\chi_1^4 = -5{\cdot}8$ (10), $\theta_1^0 = -7{\cdot}1$ (8)° and $\chi_{11}^1 = 19{\cdot}9$ (8), $\chi_{11}^2 = -21{\cdot}9$ (10), $\chi_{11}^3 = 14{\cdot}6$ (9), $\chi_{11}^4 = -1{\cdot}0$ (8), $\theta_{11}^0 = -11{\cdot}5$ (7)° in peptides (I) and (II) respectively. The atoms C$^\gamma$(1), C′(1) in (I) and C$^\gamma$(11), C′(11) in (II) are displaced by 0·206 (7), 2·234 (7) and 0·163 (8), 1·402 (7) Å, respectively, from the least-squares planes through the pyrrolidine rings. The torsion angles and the displacements mentioned above show that the five-membered rings are puckered and adopt the C$^\gamma$-*endo* conformation (Benedetti, 1977). The conformations of the backbone and the pyrrolidine ring are very similar to those found in *N*-Boc-L-Pro-dehydro-Leu-OCH$_3$ (Narula *et al.*, 1988). The torsion angles that define the conformations of the valyl side chains are $\chi_2^{1,1} = -60{\cdot}9$ (10), $\chi_2^{1,2} = 63{\cdot}5$ (9)° in (I) and $\chi_{12}^{1,1} = -61{\cdot}8$ (9), $\chi_{12}^{1,2} = 78{\cdot}3$ (9), $\chi_{12}^{1,3} = -173{\cdot}4$ (12)° in (II) respectively. These values correspond to a staggered position of the α-methyl group, between NH and CO groups (Bhat *et al.*, 1979). This side-chain conformation of the valyl residue is rarely observed (Benedetti, 1977).

Puckering of the pyrrolidine ring. The pyrrolidine ring of the Pro residue invariably occurs in puckered conformations, and C$^\gamma$-*endo* and C$^\gamma$-*exo* conformations are defined as those in which the C$^\gamma$ atom and the C=O group of Pro lie on the same side and opposite sides, respectively, of the mean plane of the ring (Ashida & Kakudo, 1974).

For the Pro residue in L configuration, the C$^\gamma$-*endo* conformation may be characterized by positive χ^1 and χ^3, and negative χ^2 and χ^4 values while the C$^\gamma$-*exo* conformation may be characterized by negative χ^1 and χ^3 and positive χ^2 and χ^4.

The dependence of the puckering of the Pro residue on the backbone conformation can be ration-

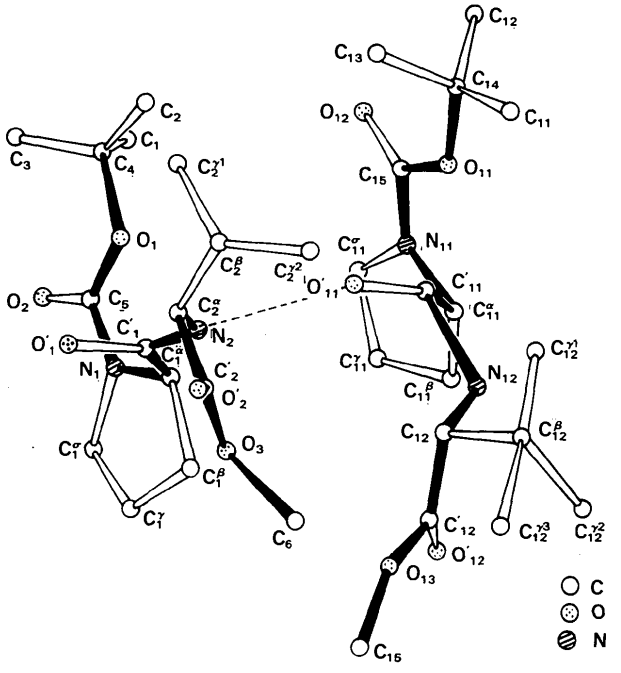

Fig. 1. The perspective view of peptides (I) and (II) as seen down the *c* axis, with atomic numbering.

Table 2. *Bond lengths* (Å) *and angles* (°) *involving non*-H *atoms*

Peptide (I)		Peptide (II)	
C(1)—C(4)	1·509 (13)	C(11)—C(14)	1·505 (14)
C(2)—C(4)	1·518 (14)	C(12)—C(14)	1·500 (12)
C(3)—C(4)	1·513 (10)	C(13)—C(14)	1·517 (13)
C(4)—O(1)	1·473 (7)	C(14)—O(11)	1·472 (10)
O(1)—C(5)	1·329 (10)	O(11)—C(15)	1·314 (8)
C(5)—O(2)	1·198 (10)	C(15)—O(12)	1·222 (7)
C(5)—N(1)	1·339 (8)	C(15)—N(11)	1·353 (9)
N(1)—C$^\alpha$(1)	1·440 (8)	N(11)—C$^\alpha$(11)	1·435 (6)
N(1)—C$^\delta$(1)	1·471 (11)	N(11)—C$^\delta$(11)	1·475 (9)
C$^\alpha$(1)—C$^\beta$(1)	1·535 (9)	C$^\alpha$(11)—C$^\beta$(11)	1·524 (10)
C$^\alpha$(1)—C′(1)	1·504 (11)	C$^\alpha$(11)—C′(11)	1·510 (8)
C$^\beta$(1)—C$^\gamma$(1)	1·407 (17)	C$^\beta$(11)—C$^\gamma$(11)	1·426 (13)
C$^\gamma$(1)—C$^\delta$(1)	1·451 (16)	C$^\gamma$(11)—C$^\delta$(11)	1·483 (12)
C′(1)—O′(1)	1·238 (7)	C′(11)—O(11)	1·230 (7)
C′(1)—N(2)	1·339 (8)	C′(11)—N(12)	1·337 (6)
N(2)—C$^\alpha$(2)	1·451 (11)	N(12)—C$^\alpha$(12)	1·440 (7)
C$^\alpha$(2)—C$^\beta$(2)	1·522 (14)	C$^\alpha$(12)—C$^\beta$(12)	1·526 (11)
C$^\alpha$(2)—C′(2)	1·472 (13)	C$^\alpha$(12)—C′(12)	1·506 (11)
C$^\beta$(2)—C$^{\gamma1}$(2)	1·493 (12)	C$^\beta$(12)—C$^{\gamma1}$(12)	1·557 (19)
C$^\beta$(2)—C$^{\gamma2}$(2)	1·560 (12)	C$^\beta$(12)—C$^{\gamma2}$(12)	1·588 (20)
C′(2)—O′(2)	1·254 (17)	C$^\beta$(12)—C$^{\gamma3}$(12)	1·426 (20)
C′(2)—O(3)	1·189 (19)	C′(12)—O′(12)	1·170 (14)
O(3)—C(6)	1·645 (14)	C′(12)—O(13)	1·296 (10)
		O(13)—C(16)	1·436 (12)
C(2)—C(4)—C(3)	108·6 (7)	C(12)—C(14)—C(13)	110·4 (8)
C(1)—C(4)—C(3)	114·3 (7)	C(11)—C(14)—C(13)	109·0 (8)
C(1)—C(4)—C(2)	110·9 (7)	C(11)—C(14)—C(12)	116·0 (8)
C(3)—C(4)—O(1)	109·6 (6)	C(13)—C(14)—O(11)	109·6 (7)
C(2)—C(4)—O(1)	101·9 (6)	C(12)—C(14)—O(11)	110·7 (7)
C(1)—C(4)—O(1)	110·9 (6)	C(11)—C(14)—O(11)	100·9 (7)
C(4)—O(1)—C(5)	120·0 (5)	C(14)—O(11)—C(15)	120·7 (6)
O(1)—C(5)—N(1)	110·4 (7)	O(11)—C(15)—N(11)	110·1 (6)
O(1)—C(5)—O(2)	126·9 (8)	O(11)—C(15)—O(12)	127·0 (7)
O(2)—C(5)—N(1)	122·7 (8)	O(12)—C(15)—N(11)	122·9 (6)
C(5)—N(1)—C$^\delta$(1)	120·8 (7)	C(15)—N(11)—C$^\delta$(11)	121·6 (5)
C(5)—N(1)—C$^\alpha$(1)	125·0 (6)	C(15)—N(11)—C$^\alpha$(11)	125·3 (5)
C$^\alpha$(1)—N(1)—C$^\delta$(1)	113·9 (6)	C$^\alpha$(11)—N(11)—C$^\delta$(11)	113·1 (5)
N(1)—C$^\alpha$(1)—C′(1)	113·5 (5)	N(11)—C$^\alpha$(11)—C′(11)	112·2 (5)
N(1)—C$^\alpha$(1)—C$^\beta$(1)	102·4 (5)	N(11)—C$^\alpha$(11)—C$^\beta$(11)	103·7 (5)
C$^\beta$(1)—C$^\alpha$(1)—C′(1)	110·6 (6)	C$^\beta$(11)—C$^\alpha$(11)—C′(11)	110·2 (5)
C$^\alpha$(1)—C$^\beta$(1)—C$^\gamma$(1)	105·3 (9)	C$^\alpha$(11)—C$^\beta$(11)—C$^\gamma$(11)	105·8 (7)
C$^\beta$(1)—C$^\gamma$(1)—C$^\delta$(1)	112·6 (10)	C$^\beta$(11)—C$^\gamma$(11)—C$^\delta$(11)	110·6 (8)
N(1)—C$^\delta$(1)—C$^\gamma$(1)	101·0 (8)	N(11)—C$^\delta$(11)—C$^\gamma$(11)	102·2 (6)
C$^\alpha$(1)—C′(1)—N(2)	114·3 (5)	C$^\alpha$(11)—C′(11)—N(12)	114·1 (5)
C$^\alpha$(1)—C′(1)—O′(1)	122·1 (6)	C$^\alpha$(11)—C′(11)—O′(11)	122·8 (5)
O′(1)—C′(1)—N(2)	123·5 (6)	O′(11)—C′(11)—N(12)	123·1 (5)
C′(1)—N(2)—C$^\alpha$(2)	124·0 (5)	C′(11)—N(12)—C$^\alpha$(12)	120·6 (5)
N(2)—C$^\alpha$(2)—C′(2)	111·9 (8)	N(12—C$^\alpha$(12)—C′(12)	109·1 (5)
N(2)—C$^\alpha$(2)—C$^\beta$(2)	114·1 (6)	N(12)—C$^\alpha$(12)—C$^\beta$(12)	110·4 (6)
C$^\beta$(2)—C$^\alpha$(2)—C′(2)	111·3 (8)	C$^\beta$(12)—C$^\alpha$(12)—C′(12)	114·4 (7)
C$^\alpha$(2)—C$^\beta$(2)—C$^{\gamma2}$(2)	110·2 (8)	C$^\alpha$(12)—C$^\beta$(12)—C$^{\gamma3}$(12)	118·2 (12)
C$^\alpha$(2)—C$^\beta$(2)—C$^{\gamma1}$(2)	109·5 (8)	C$^\alpha$(12)—C$^\beta$(12)—C$^{\gamma2}$(12)	105·1 (8)
C$^{\gamma1}$(2)—C$^\beta$(2)—C$^{\gamma2}$(2)	112·6 (8)	C$^\alpha$(12)—C$^\beta$(12)—C$^{\gamma1}$(12)	108·4 (7)
C$^\alpha$(2)—C′(2)—O(3)	119·9 (10)	C$^{\gamma3}$(12)—C$^\beta$(12)—C$^{\gamma2}$(12)	98·3 (12)
C$^\alpha$(2)—C′(2)—O′(2)	120·6 (12)	C$^{\gamma1}$(12)—C$^\beta$(12)—C$^{\gamma3}$(12)	99·1 (11)
O′(2)—C′(2)—O(3)	119·3 (11)	C$^{\gamma1}$(12)—C$^\beta$(12)—C$^{\gamma2}$(12)	128·4 (10)
C′(2)—O(3)—C(6)	105·3 (10)	C$^\alpha$(12)—C′(12)—O(13)	113·7 (7)
		C$^\alpha$(12)—C′(12)—O′(12)	124·0 (8)
		O′(12)—C′(12)—O(13)	122·2 (8)
		C′(12)—O(13)—C(16)	118·2 (7)

Table 3. *Torsion angles* (°) *of Pro residues*

Peptide	φ	ψ	χ^1	χ^2	χ^3	χ^4	θ^0		
N-Boc-L-Pro-dehydro-Phe-L-Gly-OH	−48	137	−24	34	−30	15	6	C^γ-*exo*	Patel, Singh, Chauhan & Kaur (1989)
N-Boc-L-Pro-dehydro-L-Leu-$NHCH_3$	−51	133	−25	38	−34	20	2	C^γ-*exo*	Singh, Narula, Chauhan, Sharma & Hinrichs (1988)
N-Boc-L-Pro-OH	−72	166	31	−35	24	−4	−17	C^γ-*endo*	Benedetti, Ciajolo & Maisto (1974)
N-Boc-L-Pro-L-Gly-OH	−61	147	5	1	−7	11	−10	C^γ-*exo*	Benedetti, Pavone, Toniolo, Bonora & Palumbo (1977)
N-Boc-L-Pro-Sar-OH	−67	152	22	−30	25	−11	−7	C^γ-*endo*	Benedetti, Ciajolo, Di Blasio, Pavone, Pedone, Toniolo & Bonora (1979)
Z-Pro-L-Leu-OEt	−62	171	30	−37	29	−9	−14	C^γ-*endo*	Sugino, Tanaka & Ashida (1978)
N-Boc-Aib-L-Leu-L-Pro-$NHMe.2H_2O$	−69	151	16	−16	10	0·8	−10	C^γ-*endo*	Prasad, Balaram & Balaram, (1984)
N-Boc-L-Pro-L-Val-OCH_3	−74	159	18	−23	18	−6	−7	C^γ-*endo*	Present work
N-Boc-L-Pro-C^β-methylated-L-Val-OCH_3	−70	158	20	−22	15	−1	−12	C^γ-*endo*	
N-Boc-L-Pro-dehydro-L-leu-OCH_3(I)	−72	141	11	−11	6	2	−9	C^γ-*endo*	Narula *et al.* (1988)
N-Boc-L-Pro-dehydro-L-Leu-OCH_3(II)	−64	148	−18	31	−31	21	−1	C^γ-*exo*	
p-Bromo-Z-Gly-L-Pro-L-Leu-Gly	−58	−33	−16	21	−17	6	6	C^γ-*exo*	Ueki, Ashida, Kakudo, Sasada & Katsube (1969)
o-Bromo-Z-Gly-L-Pro-L-Leu-L-Gly-L-Pro-OH	−65	−26	−24	27	−19	−3	13	C^γ-*exo*	Ueki, Bando, Ashida & Kakudo (1971)
Proteinase K Pro 175	−61	−33	−27	43	−42	26	−0	C^γ-*exo*	Betzel (1986)
N-Ac-didehydro-Pro	−58	−58	1	4	−7	8	−6	C^γ-*exo*	Ajò, Busetti, Granozzi & Liakopoulou-Kyriakides (1984)

alized in terms of steric repulsion involving the side-chain atoms such as C^β and C^δ with the neighbouring atoms of the backbone. The values of the torsion angles of the Pro residue in some representative structures are listed in Table 3. It is clear from Table 3 that the C^γ-*endo* conformation is observed more frequently than the C^γ-*exo* conformation. The conformation of the backbone of the Pro residue is commonly found to be *trans* but the *cis* conformation has also been observed in some cases (Table 3). As seen from Table 3, if the Pro residue is in the *trans* conformation, the pyrrolidine ring adopts either the C^γ-*endo* or the C^γ-*exo* conformation. However, if the Pro residue is in the *cis* conformation then the pyrrolidine ring adopts the C^γ-*exo* conformation only.

The crystal structure and the hydrogen-bonding scheme are illustrated in Fig. 2. The molecules of peptides (I) and (II) form a complex through two hydrogen bonds: N(2)—H(2)···O(11) = 2·931 (7) and N(12)—H(12)···O(1) = 2·931 (6) Å. As seen from Fig. 2, the molecules are packed along **c** in the crystal. The structure is stabilized by weak van der Waals forces and hydrogen bonds.

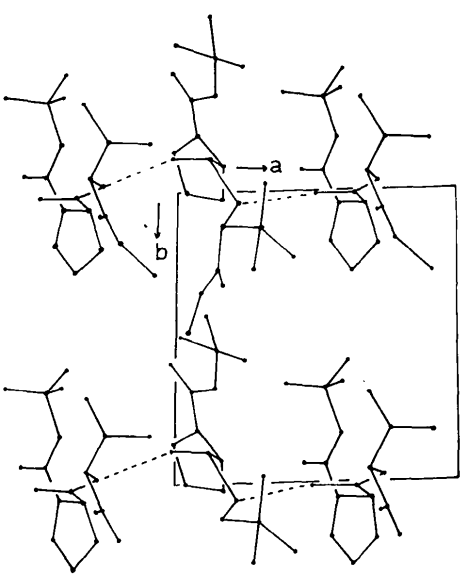

Fig. 2. The crystal structure as seen along the *c* axis.

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References

AJÒ, D., BUSETTI, V., GRANOZZI, G. & LIAKOPOULOU-KYRIAKIDES, M. (1984). *Acta Cryst.* C**40**, 327–330.

ASHIDA, T. & KAKUDO, M. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1129–1133.
BENDER, M. L. (1960). *Chem. Rev.* **60**, 53–113.
BENEDETTI, E. (1977). *Peptide Proceedings of the Fifth American Peptide Symposium*, edited by M. GOODMAN & J. MEIENHOFER, pp. 257–273.
BENEDETTI, E., CIAJOLO, A., DI BLASIO, B. PAVONE, V., PEDONE, C., TONIOLO, C. & BONORA, G. M. (1979). *Macromolecules*, **12**(3), 438–445.
BENEDETTI, E., CIAJOLO, M. R. & MAISTO, A. (1974). *Acta Cryst.* B**30**, 1783–1788.
BENEDETTI, E., MORELLI, G., NEMETHY, G. & SCHERAGA, H. A. (1983). *Int. J. Pept. Protein Res.* **22**, 1–15.
BENEDETTI, E., PAVONE, V., TONIOLO, C., BONORA, G. M. & PALUMBO, M. (1977). *Macromolecules*, **10** (6), 1350–1356.
BENEDETTI, E., PEDONE, C., TONIOLO, C., NEMETHY, G., POTTLE, M. S. & SCHERAGA, H. A. (1980). *Int. J. Pept. Protein Res.* **16**, 156–172.
BETZEL, C. (1986). PhD Thesis, Free Univ. Berlin, Federal Republic of Germany.
BHAT, T. N., SASISEKHARAN, V. & VIJAYAN, M. (1979). *Int. J. Pept. Protein Res.* **13**, 170–184.
CHANDRASEKHARAN, R. & RAMACHANDRAN, G. N. (1970). *Int. J. Pept. Protein Res.* **2**, 223–233.
CRISMA, M., FASMAN, G. D., BALARAM, H. & BALARAM, P. (1984). *Int. J. Pept. Protein Res.* **23**, 411–419.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
DUNITZ, J. D. & STRICKLER, P. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & M. DAVIDSON, pp. 595–602. San Francisco: Freeman.
IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.
JANIN, J., WODAK, S., LEVITT, M. & MAIGRET, B. (1978). *J. Mol. Biol.* **125**, 357–386.
NARULA, P., PATEL, H. C., SINGH, T. P., CHAUHAN, V. S. & SHARMA, A. K. (1988). *Biopolymers*, **27**, 1595–1606.
PATEL, H. C., SINGH, T. P., CHAUHAN, V. S. & KAUR, P. (1989). *Biopolymers*. In the press.
POISEL, H. (1977). *Chem. Ber.* **110**, 942–947.
PRASAD, B. V. V., BALARAM, H. & BALARAM, P. (1984). *Int. J. Pept. Protein Res.* **24**, 135–140.
RAMACHANDRAN, G. N., RAMAKRISHNAN, C. & SASISEKHARAN, V. (1963). *Aspects of Protein Structure*, edited by G. N. RAMACHANDRAN, p. 39. New York: Academic Press.
RICH, A. & CRICK, F. H. C. (1961). *J. Mol. Biol.* **3**, 483–489.
SHELDRICK, G. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. (1986). *SHELXS*86. *A Program for the Automatic Solution of Crystal Structures*. Univ. of Göttingen, Federal Republic of Germany.
SINGH, T. P., NARULA, P., CHAUHAN, V. S., SHARMA, A. K. & HINRICHS, W. (1988). *Int. J. Pept. Protein Res.* **33**, 167–172.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
SUGINO, H., TANAKA, I. & ASHIDA, T. (1978). *Bull. Chem. Soc. Jpn*, **51**(10), 2855–2861.
UEKI, T., ASHIDA, T., KAKUDO, M., SASADA, Y. & KATSUBE, Y. (1969). *Acta Cryst.* B**25**, 1840–1849.
UEKI, T., BANDO, S., ASHIDA, T. & KAKUDO, M. (1971). *Acta Cryst.* B**27**, 2219–2223.
VASQUEZ, M., NEMETHY, G. & SCHERAGA, H. A. (1983). *Macromolecules*, **16**, 1043–1049.
ZIMMERMAN, S. S., POTTLE, M. S., NEMETHY, G., & SCHERAGA, H. A. (1977). *Macromolecules*, **10**, 1–9.

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N-(3,4-Dichlorophenyl)cyclopropanecarboxamide and *N*-(3,4-Dichlorophenyl)acetamide

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Abstract. $C_{10}H_9Cl_2NO$ (1), $M_r = 230{\cdot}10$, monoclinic, $P2_1/c$, $a = 5{\cdot}025$ (1), $b = 22{\cdot}051$ (5), $c = 9{\cdot}615$ (2) Å, $\beta = 101{\cdot}53$ (2)°, $V = 1044{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}46$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}6$ mm^{-1}, $F(000) = 472$, $T = 293$ K. The structure was refined to $R = 0{\cdot}038$ for 1525 unique observed reflections. $C_8H_7Cl_2NO$ (2), $M_r = 204{\cdot}05$, triclinic, $P\bar{1}$, $a = 7{\cdot}254$ (2), $b = 9{\cdot}848$ (2), $c = 13{\cdot}441$ (3) Å, $\alpha = 90{\cdot}86$ (2), $\beta = 99{\cdot}78$ (2), $\gamma = 103{\cdot}61$ (2)°, $V = 917{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}48$ Mg m^{-3}, $\mu = 0{\cdot}7$ mm^{-1}, $F(000) = 416$, $T = 293$ K. The structure was refined to R 0·047 for 2930 unique observed reflections. In (1) the N—H bond is *syn* to the *meta*-Cl substituent, whereas in both independent molecules of (2) the conformation is *anti*. The C—N—C bond angles are wide (127–129°), consistent with a known correlation with the dihedral angle between phenyl and amide planes and attributable to steric interactions between the O atom and H(2), the *ortho* H atom. In both

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