five-membered ring caused by the intermolecular hydrogen bond, as discussed previously (Kanazawa, Ohashi, Sasada & Kawai, 1978*a*). The bond angles listed in Table 2 are in fairly good agreement with those of related compounds.

The crystal structure is very similar to that of L-leucine NCA. The polymerizing moieties, five-membered rings, are sandwiched by the hydrophobic side chains. Such a sandwiched structure has been proposed as favorable for polymerization in the solid state (Kanazawa, Ohashi, Sasada & Kawai, 1978*b*). The polymerization of L-valine NCA is far more reactive in the solid state than in an acetonitrile solution (Kanazawa & Kawai, 1980). The relation between the polymerizability and the structure of the present crystal will be discussed elsewhere.

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Acta Cryst. (1984). C**40**, 1096–1098

Structure of *N-tert*-Butoxycarbonyl-L-prolyl-D-valine, $C_{15}H_{26}N_2O_5$

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(*Received* 19 *October* 1983; *accepted* 1 *March* 1984)

Abstract. $M_r = 314{\cdot}38$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}426$ (1), $b = 11{\cdot}876$ (1), $c = 16{\cdot}085$ (1) Å, $V = 1800{\cdot}6$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}160$ (2) Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}639$ mm^{-1}, $F(000) = 680$, room temperature, final $R = 0{\cdot}0493$ for 3024 reflexions. Boc-L-Pro-D-Val-OH was isolated after activation of the carboxy group of its L,L-diastereoisomer for peptide coupling. The Boc-L-Pro urethane bond adopts the *cis* conformation. For the proline ring system an envelope conformation is observed with C(7) situated about 0·2 Å above the best plane through the ring atoms.

Introduction. The polypeptide antibiotics alamethicin F30 and suzukacillin A (Jung, Brückner & Schmitt, 1981; Jung, Bosch, Katz, Schmitt, Voges & Winter, 1983) have similar C-terminal heptapeptide segments except for some natural amino-acid exchanges (Katz, König & Jung, 1984): L-Pro-L-Val-Aib(Val)-Aib(Val)-L-Glu-L-Gln-L-Pheol (alamethicin F30) and L-Pro-L-Val-Aib-D-Iva(Aib)-L-Gln-L-Gln-L-Pheol (suzukacillin A).† During the finally successful synthesis of alamethicin F30 (Schmitt & Jung, 1984) an unusually high tendency for racemization of the L-valine residue was observed, when Boc-L-Pro-L-Val-OH was coupled with Aib derivatives as amino components. We suggest that the formation of the oxazolone derived from Boc-L-Pro-L-Val-OH will be faster than the formation of the amide bond. Therefore we could isolate Boc-L-Pro-D-Val-OH (1) from the reaction mixture. Suitable crystals of (1) were obtained from ethyl acetate/light petroleum (b.p. 40–60° C).

Experimental. Single crystal 0·4 × 0·4 × 0·2 mm, Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation with graphite monochromator, 25 reflexions used to measure lattice parameters, 3510 reflexions ($|F| > 0$), 3027 unique, ω/θ scan, $\theta = 3$–70°, $0 \le h \le 11$, $0 \le k \le 14$, $0 \le l \le 19$, $R_{int} = 0{\cdot}02$, 2 standard reflexions ($0\bar{6}2$ and $1\bar{1}\bar{8}$) with constant intensity; Lp

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† Aib = α-aminoisobutyric acid; Iva = isovaline; Pheol = phenylalaninol.

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correction, absorption ignored; direct methods (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refinement on F with *SHELX*76 (Sheldrick, 1976), nonhydrogen atoms anisotropic, hydrogen atoms isotropic as rigid groups with fixed distance of 0·96 Å, O–H group and hydrogen atoms contained in proline ring allowed to refine freely, common temperature factor for all hydrogen atoms ($U = 0{\cdot}08$ Å^2); final $R = 0{\cdot}0493$, $R_w = 0{\cdot}0493$ for 3024 reflexions, unit weights (3 extinction-damaged reflexions excluded),* max. Δ/σ $\pm 0{\cdot}3$, no electron density $>0{\cdot}23$ e Å^{-3} in last difference Fourier maps; scattering factors from Cromer & Mann (1968); f' and f'' from Cromer & Liberman (1970).

Discussion. Final positional parameters are given in Table 1, bond lengths and angles in Table 2. Fig. 1 shows a perspective view of the dipeptide together with the atomic numbering. There are no unusual deviations of the bond lengths and angles from ideal geometry. The recently reported disorder of C$^\beta$ in the proline ring of the free dipeptide L-prolyl-L-valine monohydrate (Narasimhan, Chacko & Swaminathan, 1982) could not be found in (1).

A comparison of the recently compiled data of Boc groups in 31 derivatives (Benedetti, Pedone, Toniolo, Némethy, Pottle & Scheraga, 1980) showed no major deviations from the averages of the reported bond lengths and angles. The *cis* conformation of the Boc-L-Pro part of (1) differs from the corresponding Boc-L-Pro part of the 3^1_{10}-helical pentapeptide Boc-L-Pro-L-Ala-Aib-L-Ala-Aib-OH (Bosch, Jung, Schmitt, Sheldrick & Winter, 1984), in which the *trans* conformation is adopted.

The diastereoisomer Boc-L-Pro-L-Val-OH has a peptide bond which is more solvent exposed from one side, whereas the lipophilic groups are assembled on the other side. The carboxy group to be activated in peptide coupling reactions is situated in a sort of hydrophobic pocket. This may be the reason for facilitated racemization, *e.g. via* oxazolone formation. Ring opening would be preferred to the direction of the L,D diastereoisomer (1).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39279 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

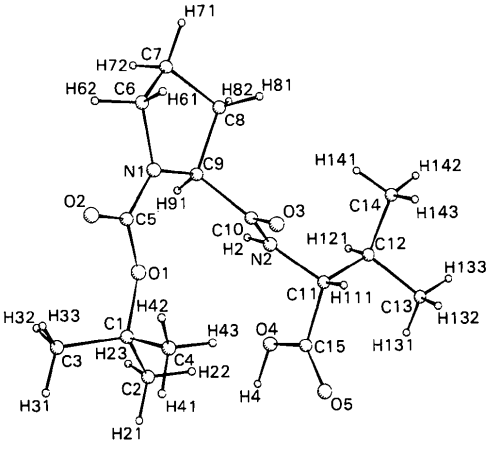

Fig. 1. Perspective view of Boc-L-Pro-D-Val-OH with the atomic numbering.

Table 1. *Atomic parameters and equivalent isotropic thermal parameters* (Å^2 $\times 10^2$) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
C(1)	0·6188 (5)	1·1069 (3)	0·5208 (2)	7·0 (2)
C(2)	0·6998 (7)	1·1026 (4)	0·4390 (2)	10·5 (4)
C(3)	0·6583 (7)	1·2103 (3)	0·5692 (3)	10·2 (3)
C(4)	0·4626 (5)	1·0980 (5)	0·5081 (3)	12·2 (4)
C(5)	0·6208 (3)	0·9737 (3)	0·6372 (2)	4·9 (2)
C(6)	0·6258 (4)	0·8178 (3)	0·7359 (2)	5·7 (2)
C(7)	0·7118 (4)	0·7108 (4)	0·7338 (2)	6·6 (2)
C(8)	0·7054 (4)	0·6750 (3)	0·6420 (2)	6·2 (2)
C(9)	0·7112 (3)	0·7872 (2)	0·5946 (2)	4·5 (2)
C(10)	0·6243 (3)	0·7800 (2)	0·5141 (2)	4·2 (1)
C(11)	0·6401 (3)	0·7339 (2)	0·3658 (2)	4·6 (2)
C(12)	0·6731 (4)	0·6140 (3)	0·3363 (2)	6·1 (2)
C(13)	0·6206 (6)	0·5960 (4)	0·2474 (2)	9·4 (3)
C(14)	0·6039 (5)	0·5283 (3)	0·3947 (2)	8·3 (3)
C(15)	0·6922 (3)	0·8224 (3)	0·3040 (2)	5·4 (2)
N(1)	0·6507 (3)	0·8680 (2)	0·6535 (1)	4·6 (1)
N(2)	0·7035 (2)	0·7551 (2)	0·4473 (1)	4·3 (1)
O(1)	0·6688 (2)	1·0037 (2)	0·5618 (1)	5·5 (1)
O(2)	0·5597 (2)	1·0372 (2)	0·6861 (1)	6·2 (1)
O(3)	0·4961 (2)	0·7905 (2)	0·5134 (1)	5·0 (1)
O(4)	0·8292 (2)	0·8369 (2)	0·3062 (1)	6·8 (1)
O(5)	0·6152 (3)	0·8707 (2)	0·2571 (2)	9·5 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·522 (5)	N(1)–C(9)	1·464 (3)
C(1)–C(3)	1·501 (5)	C(9)–C(10)	1·534 (3)
C(1)–C(4)	1·490 (6)	C(10)–O(3)	1·215 (3)
C(1)–O(1)	1·469 (4)	C(10)–N(2)	1·341 (3)
O(1)–C(5)	1·342 (3)	N(2)–C(11)	1·463 (3)
C(5)–O(2)	1·233 (3)	C(11)–C(12)	1·533 (4)
C(5)–N(1)	1·314 (4)	C(12)–C(13)	1·531 (5)
N(1)–C(6)	1·471 (3)	C(12)–C(14)	1·531 (5)
C(6)–C(7)	1·507 (5)	C(11)–C(15)	1·527 (4)
C(7)–C(8)	1·537 (4)	C(15)–O(4)	1·303 (4)
C(8)–C(9)	1·537 (4)	C(15)–O(5)	1·194 (3)

C(2)–C(1)–C(3)	110·5 (4)	C(8)–C(9)–C(10)	110·6 (2)
C(2)–C(1)–C(4)	112·0 (4)	C(9)–C(10)–O(3)	122·3 (2)
C(2)–C(1)–O(1)	101·5 (3)	C(9)–C(10)–N(2)	113·0 (2)
C(4)–C(1)–C(3)	112·0 (4)	C(10)–N(2)–C(11)	121·9 (2)
C(3)–C(1)–O(1)	111·7 (3)	N(2)–C(11)–C(12)	110·8 (2)
C(1)–O(1)–C(5)	121·3 (3)	C(11)–C(12)–C(13)	110·7 (3)
O(1)–C(5)–O(2)	124·9 (3)	C(11)–C(12)–C(14)	110·0 (3)
O(1)–C(5)–N(1)	111·2 (3)	C(13)–C(12)–C(14)	110·1 (3)
C(5)–N(1)–C(6)	122·2 (3)	N(2)–C(11)–C(15)	109·5 (2)
C(5)–N(1)–C(9)	125·4 (2)	C(12)–C(11)–C(15)	111·9 (2)
N(1)–C(6)–C(7)	103·6 (3)	C(11)–C(15)–O(4)	113·0 (3)
C(6)–C(7)–C(8)	103·5 (3)	C(11)–C(15)–O(5)	123·1 (3)
C(7)–C(8)–C(9)	103·6 (3)	O(4)–C(15)–O(5)	123·8 (3)
N(1)–C(9)–C(8)	103·4 (2)		

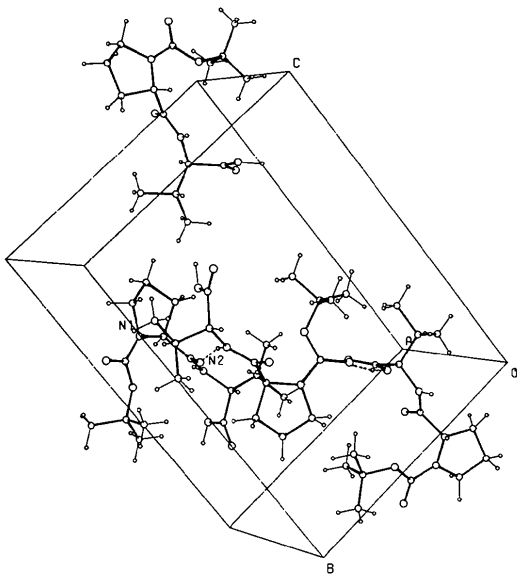

Fig. 2. Perspective view of the crystal packing of Boc-L-Pro-D-Val-OH. Hydrogen bonds are indicated by dashed lines.

The molecular arrangement in the crystal (Fig. 2) is influenced by two intermolecular hydrogen bonds: N(2)···O(3′) = 2·880 (4) Å (symmetry code: 0·5 + x, 1·5 − y, 1 − z) and O(4)···O(2′) = 2·659 (4) Å (symmetry code: 1·5 − x, 2 − y, −0·5 + z) linking the molecules along $\overline{ac}$. As observed in the crystal structure of related oligopeptides this favours an intermolecular packing of polymeric hydrogen-bonded sheets of peptide molecules which have only van der Waals contacts between each other.

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 76) and the Fonds der Chemischen Industrie for financial support of this work.

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Acta Cryst. (1984). C**40**, 1098–1101

Tris(3,5-dimethyl-1-pyrazolyl)methane, $C_{16}H_{22}N_6$

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(*Received* 9 *December* 1983; *accepted* 5 *March* 1984)

Abstract. $M_r = 298·39$, monoclinic, $P2_1/n$, $a = 17·573$ (11), $b = 23·000$ (10), $c = 18·105$ (8) Å, $\beta = 113·89$ (4)°, $V = 6691$ (6) Å^3, $Z = 16$, $D_x = 1·19$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·820$ cm^{-1}, $F(000) = 2560$, $T = 291$ K. Final $R = 0·108$ for 4137 observed reflexions. None of the four independent molecules shows threefold symmetry. In spite of the absence of crystallographic symmetry between these four molecules, their conformations are very similar. There is an approximate inversion center. The helical conformation is in good agreement with published results for comparable molecules.

Introduction. This seems to be the first structure determination of a tris(azolyl)methane derivative. Compared to triphenylmethane, the particularity of this molecule is the asymmetry of the five-membered rings. Even in the case of a regular helical conformation, in addition to the two enantiomers corresponding to the left-handed and the right-handed helix, this asymmetry

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