The methoxy group O(4)—C(14) is found to be approximately in the phenyl plane; deviations for O(4) and C(14) are 0·044 (5) and 0·15 (1) Å respectively. The methyl C atom deviations of the methoxy groups bonded to quinone rings are 0·214 (5) Å for *R*-4-MD and 0·155 (6) Å for *S*-4,4′-DMD. In *R*-3,4-DMD, however, the C(16) methyl is twisted out of the plane of the quinone ring, as is the C(17) methyl group: deviations are −0·50 (3) and −0·84 (2) Å. The mean C—H distance for the title compound is 0·96 (5) Å. Intermolecular distances were calculated up to 3·6 Å with *ORFFE*. The shortest O···H distance between neighbouring molecules is found in the **b** direction: $O(1)\cdots H(3^{i})$ 2·43 (5), $O(1)\cdots C(3^{i})$ 3·45 (1), C(3)—H(3) 1·15 (5) Å, the angle $C(3)—H(3)\cdots O(1^{i})$ being 147 (3)°. This C—H···O interaction may be considered as a very weak hydrogen bond. Otherwise, the structure consists of discrete molecules like those in *R*-3,4-DMD and *R*-4-MD.

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Structure of *N*-Carboxy-L-valine Anhydride, $C_6H_9NO_3$

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Abstract. $M_r = 143·1$, orthorhombic, $P2_12_12_1$, $a = 5·787$ (1), $b = 22·740$ (3), $c = 5·395$ (1) Å, $V = 709·1$ (1) Å^3, $Z = 4$, $D_m = 1·33$, $D_x = 1·33$ g cm^{-3}, $T = 293$ K, $F(000) = 292$, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·29$ cm^{-1}, $R = 0·056$ for 845 observed reflections. The molecules are linked by intermolecular hydrogen bonds between N(1)—H(1) and O(1) along the *a* axis. The *N*-carboxy anhydride rings are arranged in a layer sandwiched by hydrophobic side chains, as observed in the crystal of *N*-carboxy-L-leucine anhydride.

Introduction. The polymerization of the *N*-carboxy anhydrides of α-amino acids (α-amino acid NCA's) has been useful in obtaining polypeptides with high molecular weight (Bamford, Elliott & Hanby, 1956). In a previous paper, it was revealed that polymerizability in the solid state was very different from that in solution (Kanazawa & Kawai, 1980). To elucidate the reaction mechanism in the solid state, the crystal structures of glycine NCA (Kanazawa, Matsuura, Tanaka, Kakudo, Komoto & Kawai, 1976*a*), L-alanine NCA (Kanazawa, Matsuura, Tanaka, Kakudo, Komoto & Kawai, 1976*b*), γ-benzyl-L-glutamate NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978*a*) and L-leucine NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978*b*) have been determined. The difference in polymerizability between L-leucine NCA and L-alanine NCA in the solid state was proved to be caused by the different molecular packing in the crystal (Kanazawa, Ohashi, Sasada & Kawai, 1982). In the present paper the crystal and molecular structure of L-valine NCA is compared with those of the related compounds so far determined.

Experimental. Colorless plate-like crystals obtained from an ethyl acetate solution in hexane vapor at 285 K, density by flotation in C_6H_{12}/CCl_4; systematic absences *h*00 $h = 2n + 1$, 0*k*0 $k = 2n + 1$, 00*l* $l = 2n + 1$; approximate crystal dimensions 0·3 × 0·4 × 0·5 mm, Rigaku AFC-4 diffractometer, graphite monochromator; cell parameters refined by least squares on the basis of 21 independent 2θ values, Mo $K\alpha$ radiation

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters*, B_{eq}, *for non*-H *atoms*

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å^2)
C(1)	4606 (5)	4673 (1)	7048 (6)	3·4 (1)
C(2)	2041 (5)	3954 (1)	6206 (6)	3·3 (1)
C(3)	3718 (5)	3980 (1)	4061 (6)	2·7 (1)
C(4)	5019 (6)	3397 (1)	3585 (6)	3·4 (1)
C(5)	6840 (7)	3493 (2)	1589 (8)	5·1 (1)
C(6)	3329 (8)	2917 (2)	2765 (9)	6·3 (1)
N(1)	5202 (5)	4455 (1)	4875 (5)	3·2 (1)
O(1)	5422 (4)	5067 (1)	8272 (5)	4·9 (1)
O(2)	2678 (4)	4372 (1)	7928 (4)	3·6 (1)
O(3)	449 (5)	3639 (1)	6570 (5)	5·3 (1)

Table 2. *Bond angles* (°) *of* L-*valine NCA*

N(1)–C(1)–O(1)	131·5 (3)	C(2)–C(3)–N(1)	100·2 (2)
N(1)–C(1)–O(2)	109·1 (3)	C(4)–C(3)–N(1)	113·7 (3)
O(1)–C(1)–O(2)	119·4 (3)	C(3)–C(4)–C(5)	109·4 (3)
C(3)–C(2)–O(2)	108·5 (2)	C(3)–C(4)–C(6)	110·4 (3)
C(3)–C(2)–O(3)	130·6 (3)	C(5)–C(4)–C(6)	109·9 (3)
O(2)–C(2)–O(3)	120·9 (3)	C(1)–N(1)–C(3)	113·3 (3)
C(2)–C(3)–C(4)	114·0 (2)	C(1)–O(2)–C(2)	108·9 (2)

($20° < 2\theta < 30°$); intensities collected up to $2\theta = 55°$ ($+h$, $+k$, $+l$ set), ω–2θ scan technique, scan speed 2° min^{-1} (θ); 991 reflections measured, 845 intensities with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for structure determination; corrections for Lorentz and polarization, absorption and secondary extinction ignored; direct methods [*MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)] and subsequent difference Fourier calculation, block-diagonal least squares (*HBLS*, Ohashi, 1975) with anisotropic thermal parameters for all non-H atoms; H atoms located on difference map, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = (1{\cdot}9959 – 0{\cdot}1335|F_o| + 0{\cdot}004488|F_o|^2)^{-1}$ for $2{\cdot}712 < |F_o| < 27{\cdot}12$ and $w = 0{\cdot}6$ for the other reflections; final $R = 0{\cdot}056$ for 845 observed reflections; $(\Delta/\sigma)_{\rm max} = 0{\cdot}1$; final difference-map excursions $\leq 0{\cdot}18$ e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations carried out on FACOM-HITAC system M-180 computer at this Institute.

Discussion. The final atomic parameters for non-H atoms are in Table 1.* A perspective view of the molecule and the bond distances are shown in Fig. 1. The atoms of the five-membered ring and the exocyclic O atoms are planar within ±0·01 Å. The conformation around the C(3)—C(4) bond is a stable staggered form; the torsion angles N(1)—C(3)—C(4)—C(5) and C(2)—C(3)—C(4)—C(6) are 59·7 (4)° and −65·3 (4)°, respectively. A stereoscopic drawing of the crystal structure viewed along **a** is shown in Fig. 2. The molecules are connected along **c** by the intermolecular hydrogen bond N(1)—H(1)···O(1). N(1)···O(1) and H(1)···O(1) are 2·888 (4) and 2·07 (3) Å, respectively. A similar N(1)—H(1)···O(1) bond is found in the glycine NCA and L-leucine NCA crystals.

Bond distances in the five-membered ring of the present crystal are in good agreement with the corresponding values in glycine NCA and L-leucine NCA, but deviate from those of L-alanine NCA, in which O(3) forms a hydrogen bond with N(1)—H(1) of the neighboring molecule; C(1)—O(2) and C(2)—O(2) in glycine NCA, L-leucine NCA and L-valine NCA are significantly shorter and longer, respectively, than the corresponding bonds in L-alanine NCA. This is probably due to the change in conjugation of the

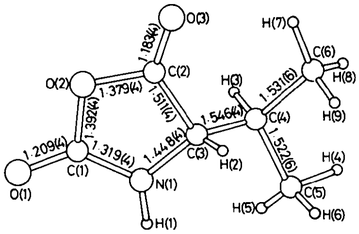

Fig. 1. A perspective view of L-valine NCA and the bond distances (Å).

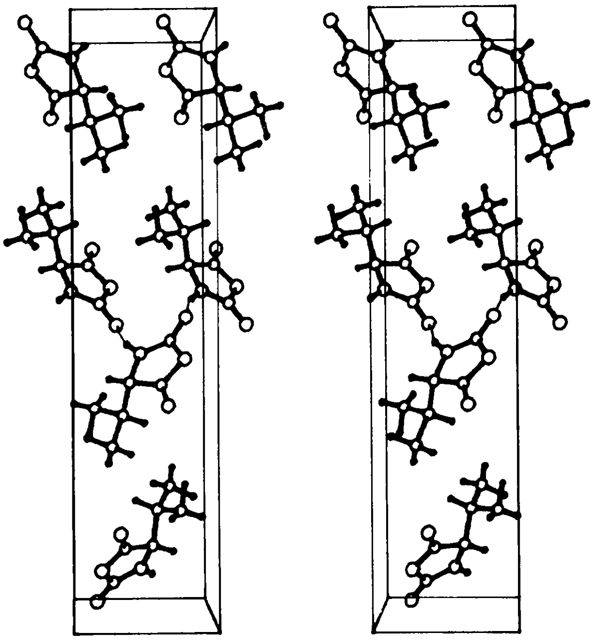

Fig. 2. Stereoview (Harata, 1978) showing the packing and hydrogen bonding (fine lines) in the crystal. The z axis is horizontal, the y axis vertical and the origin is in the lower, left front corner.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39275 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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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, $\theta = 3$–$70°$, $0 \le h \le 11$, $0 \le k \le 14$, $0 \le l \le 19$, $R_{\rm int} = 0{\cdot}02$, 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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