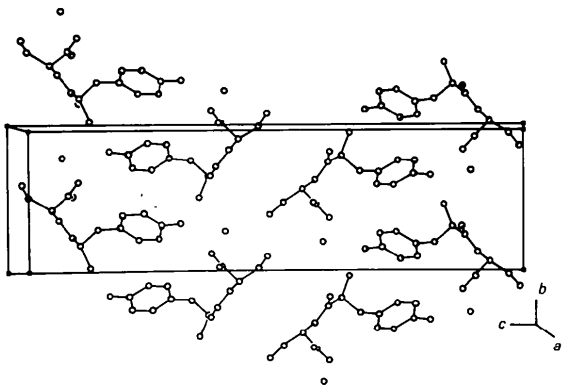

Fig. 2. View of crystal packing along **a**.

agreement with classical energy calculations (Ponnuswamy & Sasisekharan, 1971). As can be seen from Fig. 2, the tyrosine ring does not stack in the crystal lattice. The water molecule forms hydrogen bonds with the amino and carboxyl terminals of the dipeptide molecules (Fig. 2).

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Conformation and Structure of L-Valyl-L-glutamic Acid, $C_{10}H_{18}N_2O_5$

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Abstract. $M_r = 246{\cdot}3$, orthorhombic, $P2_12_12$, $a = 16{\cdot}781\ (7)$, $b = 13{\cdot}827\ (4)$, $c = 5{\cdot}367\ (4)$ Å, $V = 1245{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}313$, $D_m = 1{\cdot}30\ (2)$ Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 0{\cdot}099$ mm^{-1}, $F(000) = 528$, $T = 293$ K. Final $R = 0{\cdot}038$ for 1374 observations. The dipeptide crystallizes as a zwitterion with the main-chain carboxyl ionized and the amino terminus protonated. The configuration of the peptide bond is *trans* with an ω torsion angle of 175°. The peptide backbone is in an extended conformation as is the glutamyl side chain. There is extensive intermolecular hydrogen bonding in the crystal lattice.

Introduction. Acidic amino-acid residues are of primary importance in the binding of calcium and magnesium in proteins (Kretsinger & Nelson, 1976). In addition, the role of acidic amino acids in the molecular basis for the sweet taste has been well documented (Ariyoshi, 1976; Lelj, Tancredi, Temussi & Toniolo, 1976; Goodman & Gilon, 1975; Chorev, Willson & Goodman, 1977; Murai, Ajisaka, Nobuya, Takeuchi, Kamisaku & Masagaki, 1975). Thus, the conformational and structural properties of peptides containing acidic residues are of considerable interest.

Examination of the primary sequences of many known calcium-binding proteins reveals a virtual absence of valine preceding an acidic residue in regions known or proposed to be involved in calcium binding. The possible conformational influence(s) of the hydrophobic β-branched valine residue on an adjacent glutamic acid residue thus prompted the extension of our structural studies on the conformational properties of peptides containing acidic residues (Eggleston, Valente & Hodgson, 1981*a*,*b*; Eggleston & Hodgson, 1982*a*,*b*,*c*; Eggleston & Hodgson, 1983*a*,*b*) to examine the L-valyl-L-glutamic acid molecule.

Experimental. White powder from Vega Biochemicals, Inc., colorless rods grown by slow evaporation of an aqueous methanol solution, crystal 0·4 × 0·4 × 0·5 mm, D_m measured by flotation in methylene

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chloride/1,2-dichloroethane; Enraf–Nonius CAD-4 diffractometer; systematic absences $h00$ for h odd, $0k0$ for k odd, cell constants from least-squares analysis of 25 reflections with $30 \le 2\theta(\text{Mo}) \le 35°$ measured on the diffractometer; intensity data collected in a θ–2θ scan mode as suggested by peak-shape analysis; 1779 independent reflections, $2\theta \le 56°$, $0 \le h \le 22$, $0 \le k \le 18$, $0 \le l \le 7$; Lorentz–polarization correction, no absorption correction; data corrected for decay using the program *CHORT* of the Enraf–Nonius (1979) *SDP*, min. correction 0·961, max. correction 1·095, reflections $10,\bar{7},\bar{1}$, $11,\bar{2},\bar{2}$, $\bar{1},10,1$ monitored at the beginning, end, and each 3 h during data collection (23 times); max. deviations in F 2·9, 3·4 and 4·9%, respectively; mean values of F 129·1 (10), 115·2 (8), and 89·2 (9), respectively. Structure determined using the *RANTAN* feature (Yao Jia-xing, 1981) of *MULTAN* (*MULTAN*80, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); E map revealed positions for all non-H atoms; anisotropic least-squares refinement (on F) of these positions led to wR 0·097; weights $4F_o^2/\sigma^2(I)$; subsequent difference Fourier maps revealed positions for all H atoms which were allowed to vary in remaining least-squares cycles; five final cycles of full-matrix least-squares refinement [non-H atoms anisotropic, H atoms isotropic, the weighting scheme above with $\sigma(I)$ as defined by Corfield, Doedens & Ibers (1967) with $p = 0·05$], $R = 0·038$, $wR = 0·048$, $S = 1·36$, 1374 observations with $I \ge 3·0\sigma(I)$ and 227 variables; an extinction parameter included in the later stages refined to $2·3\,(2) \times 10^{-6}$; in the final least-squares cycle $(\Delta/\sigma)_{\max}$ 0·04; a final difference Fourier map contained no peak higher than 0·24 e Å^{-3}. One cycle using all data with $I \ge 0·01\sigma(I)$ gave $R = 0·046$, $wR = 0·050$.

Discussion. Positional parameters, along with their standard deviations as estimated from the inverse least-squares matrix, are listed in Table 1.* The structure of a single molecule of the dipeptide is shown in Fig. 1; the notation used in the labeling of atoms is that adopted by the IUPAC–IUB Commission on Biochemical Nomenclature (1970). The dipeptide crystallizes as a zwitterion with the main-chain carboxyl ionized and the amino terminus protonated. The glutamyl side chain is not ionized. The molecule adopts a *trans* configuration about the peptide bond. The side chains are disposed on opposite sides of the plane (see below) defined by the peptide linkage.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39336 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters*

	x	y	z	B_{eq}*(Å^2)
O_1'	0·7273 (1)	−0·0915 (1)	0·5493 (3)	3·48 (3)
O_2^{γ}	0·7413 (1)	0·1845 (1)	0·5590 (4)	3·15 (3)
O_2''	0·6756 (1)	0·1579 (1)	0·2058 (3)	3·10 (3)
$O_2^{\varepsilon 1}$	0·3896 (1)	0·2620 (2)	0·4127 (4)	4·14 (4)
$O_2^{\varepsilon 2}$	0·4143 (1)	0·2114 (2)	0·8007 (4)	4·20 (4)
N_1	0·7402 (1)	−0·1895 (1)	1·0166 (4)	2·57 (4)
N_2	0·6717 (1)	0·0268 (1)	0·7792 (3)	2·18 (4)
C_1'	0·7180 (1)	−0·0495 (2)	0·7483 (4)	2·32 (4)
C_1^{α}	0·7609 (1)	−0·0858 (2)	0·9836 (4)	2·51 (4)
C_1^{β}	0·8514 (2)	−0·0719 (2)	0·9616 (6)	3·54 (5)
C_2'	0·6884 (1)	0·1441 (2)	0·4346 (4)	1·99 (3)
C_2^{α}	0·6320 (1)	0·0740 (2)	0·5712 (5)	2·12 (4)
C_2^{β}	0·5584 (1)	0·1259 (2)	0·6717 (5)	2·56 (4)
C_2^{γ}	0·5088 (1)	0·1769 (2)	0·4763 (4)	2·96 (4)
C_2^{δ}	0·4329 (1)	0·2182 (2)	0·5829 (5)	2·90 (4)
$C_1^{\gamma 2}$	0·8706 (2)	0·0332 (3)	0·908 (1)	7·4 (1)
$C_1^{\gamma 1}$	0·8948 (2)	−0·1081 (3)	1·1906 (7)	5·23 (7)

* $B_{eq} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (ab\cos\gamma)\beta_{12} + (ac\cos\beta)\beta_{13} + (bc\cos\alpha)\beta_{23}]$.

Table 2. *Bond angles* (°)

O_1'–C_1'–N_2	124·2 (2)	C_1'–N_2–C_2^{α}	122·1 (2)
O_1'–C_1'–C_1^{α}	120·1 (2)	C_1^{α}–C_1^{β}–$C_1^{\gamma 2}$	110·2 (2)
N_2–C_1'–C_1^{α}	115·7 (2)	C_1^{α}–C_1^{β}–$C_1^{\gamma 1}$	111·8 (3)
N_1–C_1^{α}–C_1'	107·7 (2)	$C_1^{\gamma 1}$–C_1^{β}–$C_1^{\gamma 2}$	111·7 (3)
N_1–C_1^{α}–C_1^{β}	111·2 (2)	N_2–C_2^{α}–C_2^{β}	108·0 (2)
C_1'–C_1^{α}–C_1^{β}	111·0 (2)	N_2–C_2^{α}–C_2'	111·5 (2)
C_1^{α}–C_1^{β}–C_2^{γ}	114·8 (2)	C_2^{β}–C_2^{α}–C_2'	111·7 (2)
C_2^{β}–C_2^{γ}–C_2^{δ}	112·2 (2)	$O_2^{\varepsilon 1}$–C_2^{δ}–$O_2^{\varepsilon 2}$	124·2 (2)
$O_2^{\varepsilon 1}$–C_2^{δ}–C_2^{γ}	112·2 (2)	$O_2^{\varepsilon 2}$–C_2^{δ}–C_2^{γ}	123·6 (2)
$O_2^{\varepsilon 1}$–C_2^{δ}–C_2^{γ}	125·2 (2)	O_2'–C_2'–C_2^{α}	117·8 (2)
O_2'–C_2'–C_2^{α}	117·0 (2)		

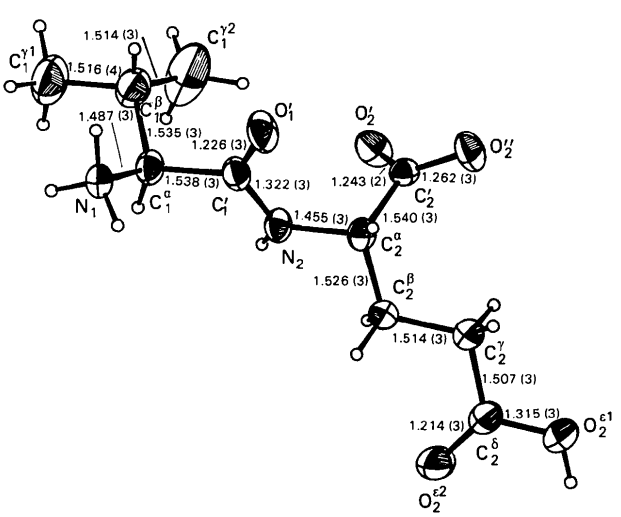

Fig. 1. An *ORTEP* view (Johnson, 1976) of the L-valyl-L-glutamic acid molecule showing atomic-numbering scheme and bond lengths (Å). Thermal ellipsoids are drawn at the 50% probability level, H atoms are shown as small spheres of arbitrary size.

The principal bond lengths are displayed in Fig. 1; the principal bond angles are in Table 2. Bond lengths within the peptide backbone compare favorably with averages recently compiled for peptides containing acidic amino acids (Eggleston, 1983). Bond lengths within both side chains are unexceptional for these residues. Bond angles within the Val-Glu structure are also quite normal, including the observed widening of the formally tetrahedral angle(s) about C_β in both the valyl and glutamyl side chains, *i.e.* for valine C_1^α–C_1^β–$C_1^{\gamma 1} = 111{\cdot}8$ (3), C_1^α–C_1^β–$C_1^{\gamma 2} = 110{\cdot}2$ (2)°; for glutamic acid C_2^α–C_2^β–$C_2^\gamma = 114{\cdot}8$ (2)°. In addition, there is a marked deviation from averages recently compiled by Benedetti (1977) in bond angles about the peptide carbonyl carbon, C_1'. The angles O_1'–C_1'–N_2 [124·2 (2)°] and C_1^α–C_1'–N_2 [115·7 (2)°] in Val-Glu show an approximate 1–2° deviation from such averages in keeping with trends recently noted for peptides containing acid residues in which both termini are unblocked (Eggleston, 1983).

The principal torsion angles in L-Val-L-Glu reflect an extended conformation for the molecule although neither the ψ [N_1–C_1^α–C_1'–$N_2 = 124{\cdot}5°$] nor the φ [C_1'–N_2–C_2^α–$C_2' = -81{\cdot}7°$] angle is fully extended thus suggesting a coiling of the molecule. The ω value of 175·2° is typical of a *trans* peptide linkage. The five principal atoms of the peptide bond [C_1^α–C_1'–O_1'–N_2–C_2^α] are virtually planar with the maximum deviation from the plane of 0·042 (2) Å at N_2. The torsion angles $\chi_1^{1,1}$ and $\chi_1^{1,2}$ of −59·6 and 175·6° for the valine residue are consistent with angles observed in 80% of all crystal structures containing this residue (Benedetti, 1977). The torsion angles χ_2^1 (−178·5°) and χ_2^2 (174·4°) describe a highly extended *trans–trans* conformation for the glutamyl side chain similar to the conformation observed for the glutamyl side-chain in α-L-Glu-L-Asp (Eggleston & Hodgson, 1983*b*) and in the structure of a fully blocked derivative of α-L-Glu-L-Glu (Benedetti, DiBlasio, Pavone, Pedone, Germain & Goodman, 1979). The torsion angles $\chi_2^{3,1}$ (−179·6°), $\chi_2^{3,2}$ (0·3°) and χ_2^4 (177·9°) are identical to commonly observed values for these angles of 180, 0 and 180°, respectively.

There is intermolecular but no intramolecular hydrogen bonding observed in the L-Val-L-Glu structure. All possible donors participate in the extensive hydrogen-bonding network. There is hydrogen bonding between the peptide N atom (donor) and O_2'' (acceptor) of the deprotonated carboxy terminus of molecules translated along **c** with associated distances of $N_2\cdots O_2'' = 2{\cdot}921$ (3), $H_2\cdots O_2'' = 2{\cdot}08$ (3) Å and angle N_2–$H_2\cdots O_2'' = 174$ (2)°. Hydrogen bonding between the protonated side-chain carboxyl $O_2^{\varepsilon 1}$ and the ionized carboxy-terminal oxygen O_2' of a different molecule also occurs with associated distances of $O_2^{\varepsilon 1}\cdots O_2' = 2{\cdot}601$ (2), $H_2^{\varepsilon 1}\cdots O_2' = 1{\cdot}83$ (3) Å and angle $O_2^{\varepsilon 1}$–$H_2^{\varepsilon 1}\cdots O_2' = 154$ (3)°. Each H atom on the protonated amino terminus participates in the hydrogen-bonding scheme which includes one bifurcated interaction involving H_1^3. The associated distances and angles are as follows: $N_1\cdots O_2^{\varepsilon 2} = 2{\cdot}856$ (3), $H_1^1\cdots O_2^{\varepsilon 2} = 1{\cdot}98$ (2) Å, N_1–$H_1^1\cdots O_2^{\varepsilon 2} = 156$ (2)°; $N_1\cdots O_2'' = 2{\cdot}806$ (3), $H_1^2\cdots O_2'' = 1{\cdot}86$ (3) Å, N_1–$H_1^2\cdots O_2'' = 157$ (3)°; $N_1\cdots O_1' = 3{\cdot}171$ (3), $H_1^3\cdots O_1' = 2{\cdot}66$ (3) Å, N_1–$H_1^3\cdots O_1' = 120$ (2)°; $N_1\cdots O_2^{\varepsilon 1} = 3{\cdot}204$ (3), $H_1^3\cdots O_2^{\varepsilon 1} = 2{\cdot}83$ (3) Å, N_1–$H_1^3\cdots O_2^{\varepsilon 1} = 109$ (2)°.

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