N(3*B'*)···O(*W*1), respectively. The remaining H atom of the carbamoyl group in *B* participates in a hydrogen bond with the water oxygen O(*W*2). Furthermore, additional hydrogen bonds with the water molecules link molecules *A* and *B* in the three-dimensional network.

The NH···N hydrogen bond between the carbamoyl group and adenine N(1) mentioned above is similar to that found in the complex 3-(9-adeninyl)propionamide–1-methylthymine dihydrate, in spite of the different crystal fields. This may suggest a strong affinity of the carbamoyl group in glutamine or asparagine residues for the adenine N(1) site.

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Conformation and Structure of α-L-Leucyl-L-glutamic Acid, $C_{11}H_{20}N_2O_5$

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Abstract. $M_r = 260{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 15{\cdot}042$ (4), $b = 15{\cdot}993$ (5), $c = 5{\cdot}517$ (2) Å, $V = 1327{\cdot}03$ Å^3, $Z = 4$, $D_x = 1{\cdot}303$, D_m (flotation in methylene chloride/1,2-dichloroethane) = 1·28 (2) Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0{\cdot}70926$, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 0{\cdot}11$ mm^{-1}, $T = 292$K, $R = 0{\cdot}066$, $wR = 0{\cdot}041$ for 1181 observations. The dipeptide crystallizes as a zwitterion with the main-chain carboxyl ionized and the amino terminus protonated. The dipeptide adopts a *trans* configuration with an ω torsion angle of 172°. The side chains adopt fully extended conformations on opposite sides of the peptide linkage. There is intermolecular, and possibly intramolecular, hydrogen bonding in the structure. Neither the peptide carbonyl O nor the amide N atoms are involved in the intermolecular hydrogen-bonding network.

Introduction. The conformational and structural properties of peptides containing the acidic residues glutamic acid (Glu), aspartic acid (Asp) or γ-carboxyglutamic acid (Gla) are of considerable interest, partly because of the importance of these residues in calcium-binding proteins (Kretsinger & Nelson, 1976). Recently, we have undertaken a systematic structural study of peptides containing acidic residues and have reported the structures of several of these molecules (Valente, Hiskey & Hodgson, 1979; Eggleston, Valente & Hodgson, 1981*a*,*b*; Eggleston & Hodgson, 1982*a*,*b*,*c*). In extending this study, we here report the structure of α-L-Leu-L-Glu. This peptide sequence, with Glu replaced by Gla, occurs three times in the γ-carboxyglutamic-acid-rich fragment of prothrombin (Davie & Hanahan, 1977).

Experimental. Colorless rods from Vega Biochemicals, Inc., grown by slow cooling of an aqueous solution, crystal 0·40 × 0·60 × 1·0 mm; Enraf–Nonius CAD-4 diffractometer; systematic absences $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, cell constants from a least-squares analysis of 25 reflections with $30° \le 2\theta(\text{Mo}) \le 38°$ measured on the diffractometer; $F(000) = 560{\cdot}0$; intensity data collected in a θ–ω scan mode, as suggested by examination of the shapes of several peaks; 1778 independent reflections, $2\theta \le 55°$, $0 \le h \le 19$, $0 \le k \le 20$, $0 \le l \le 7$; Lorentz–polarization correction, no absorption correction; no systematic fluctuations in reflections $\bar{4}50$, $1\bar{6}\bar{1}$, and $\bar{2}74$ monitored at the beginning and each 3 h during data collection (17 times); maximum deviations in F 2·2, 1·6, and 3·3%, respectively; mean values of F 63·5 (7), 83·0 (7), and 52·1 (8), respectively. Programs in the CAD-4 structure determination package; the structure determined using *MULTAN* (Germain, Main & Woolfson, 1971); E map revealed positions of all non-hydrogen atoms; anisotropic least-squares refinement (on F) of these positions led to wR 0·094; weights $4F_o^2/\sigma^2(I)$; subsequent difference Fourier maps revealed

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positions for all 20 H atoms; because of paucity of data, all methylene H atoms fixed at calculated positions with C–H 1·0 Å; positions of all other H atoms allowed to vary; three final cycles of full-matrix least-squares refinement [non-hydrogen atoms anisotropic, H atoms isotropic, the weighting scheme above with $\sigma(I)$ as defined by Corfield, Doedens & Ibers (1967) with $p = 0{\cdot}01$], $wR = 0{\cdot}041$, $S = 1{\cdot}70$, 1181 observations with $I \geq 1{\cdot}0\sigma(I)$ and 226 variables; an extinction parameter included in the later stages of refinement refined to $6{\cdot}8\,(4) \times 10^{-7}$; in the final least-squares cycle, the maximum ratio of the shift to error was 0·82; a final difference Fourier map contained no peak higher than 0·14 eÅ^{-3}.

Discussion. The positional parameters, along with their standard deviations as estimated from the inverse matrix, are listed in Table 1.*

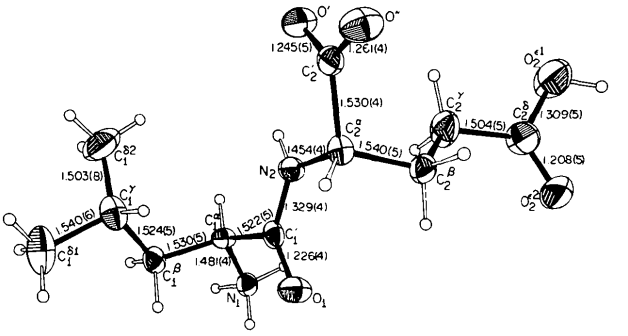

Fig. 1. View of a single molecule of α-L-Leu-L-Glu, showing atomic numbering scheme and bond lengths (Å). Thermal ellipsoids are drawn at the 50% probability level, but H atoms are shown as small spheres of arbitrary size. The C^{β}_2–C^{γ}_2 bond length, omitted for clarity, is 1·508 (5) Å.

* Lists of structure factors, H-atom positions, thermal parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38084 (13 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*

$U_{eq} = (6\pi^2)^{-1} \sum_i \sum_j \beta_{ij} \bar{\mathbf{a}}_i \bar{\mathbf{a}}_j$

	x	y	z	U_{eq}(Å^2)
O_1	0·0140 (2)	0·4333 (1)	0·8150 (5)	0·0465 (6)
O'	−0·0184 (2)	0·6451 (1)	0·2054 (5)	0·0453 (6)
O''	−0·0336 (2)	0·7320 (1)	0·5149 (6)	0·0471 (6)
$O^{\delta 1}_2$	0·3087 (2)	0·6894 (2)	0·4462 (6)	0·0799 (7)
$O^{\delta 2}_2$	0·2977 (2)	0·6249 (2)	0·7983 (6)	0·0741 (7)
N_1	0·0502 (2)	0·2962 (2)	0·5143 (6)	0·0327 (4)
N_2	0·0091 (2)	0·5126 (2)	0·4766 (6)	0·0336 (6)
C^{α}_1	−0·0122 (2)	0·3631 (2)	0·4407 (7)	0·0304 (6)
C^{β}_1	−0·1071 (2)	0·3315 (2)	0·4802 (8)	0·0356 (9)
C^{γ}_1	−0·1812 (3)	0·3920 (2)	0·4111 (8)	0·0464 (9)
$C^{\delta 1}_1$	−0·2705 (3)	0·3554 (3)	0·4975 (11)	0·0718 (12)
$C^{\delta 2}_1$	−0·1822 (3)	0·4088 (3)	0·1431 (10)	0·0867 (13)
C'_1	0·0066 (2)	0·4401 (2)	0·5945 (7)	0·0321 (7)
C^{α}_2	0·0154 (2)	0·5927 (2)	0·5998 (7)	0·0306 (9)
C^{β}_2	0·1097 (2)	0·6098 (2)	0·6967 (8)	0·0372 (9)
C^{γ}_2	0·1802 (3)	0·6101 (3)	0·5024 (9)	0·0555 (9)
C^{δ}_2	0·2681 (3)	0·6401 (3)	0·5996 (9)	0·0543 (9)
C'_2	−0·0157 (2)	0·6612 (2)	0·4261 (8)	0·0343 (9)

Table 2. *Bond angles* (°)

O_1–C'_1–C^{α}_1	119·9 (4)	N_2–C^{α}_2–C^{β}_2	112·3 (3)
O_1–C'_1–N_2	124·1 (4)	N_2–C^{α}_2–C'_2	108·6 (3)
N_2–C'_1–C^{α}_1	116·0 (3)	C^{β}_2–C^{α}_2–C'_2	111·9 (3)
C'_1–N_2–C^{α}_2	122·8 (3)	C^{α}_2–C^{β}_2–C^{γ}_2	113·4 (3)
N_1–C^{α}_1–C'_1	108·3 (3)	C^{β}_2–C^{γ}_2–C^{δ}_2	111·5 (4)
N_1–C^{α}_1–C^{β}_1	108·3 (3)	$O^{\delta 1}_2$–C^{δ}_2–$O^{\delta 2}_2$	122·4 (4)
C^{β}_1–C^{α}_1–C'_1	111·2 (3)	$O^{\delta 1}_2$–C^{δ}_2–C^{γ}_2	111·8 (4)
C^{α}_1–C^{β}_1–C^{γ}_1	115·9 (3)	$O^{\delta 2}_2$–C^{δ}_2–C^{γ}_2	125·7 (4)
C^{β}_1–C^{γ}_1–$C^{\delta 1}_1$	108·6 (4)	O'–C'_1–O''	124·0 (4)
C^{β}_1–C^{γ}_1–$C^{\delta 2}_1$	111·5 (5)	O'–C'_2–C^{α}_2	118·3 (4)
$C^{\delta 1}_1$–C^{γ}_1–$C^{\delta 2}_1$	111·4 (5)	O''–C'_2–C^{α}_2	117·7 (4)

The structure of a single molecule of the dipeptide is shown in Fig. 1; the notation used in the labeling of the 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 and the overall conformation of the dipeptide is highly extended with the two side chains disposed on opposite sides of the plane (see below) defined by the peptide linkage. Thus, hydrophobic and hydrophilic moieties within the molecule are as far apart as possible.

The principal bond lengths in the dipeptide are shown in Fig. 1; the principal bond angles are in Table 2. While the observed bond lengths and angles are quite typical of those found in linear peptides (Benedetti, 1977), C^{γ}_1–$C^{\delta 2}_1$ [1·503 (8) Å] and C^{β}_2–C^{γ}_2 [1·508 (5) Å] appear surprisingly short for sp^3–sp^3 bonds involving C atoms. Application of a riding-model correction for thermal motion (Busing & Levy, 1964), however, leads to the expected result that the C^{γ}_1–$C^{\delta 2}_1$ and C^{γ}_1–$C^{\delta 1}_1$ lengths are not different ['corrected' values of 1·564 (7) and 1·560 (8) Å, respectively] and that C^{β}_2–C^{γ}_2 is also normal [1·536 (7) Å] and slightly longer than the sp^2–sp^3 bond C^{γ}_2–C^{δ}_2 ['corrected' value 1·518 (8) Å]. Hence, it is apparent that these anomalously short bond lengths are due to the thermal motion of the atoms involved. We note, however, a widening of the formally tetrahedral angle about C^{β}_1 (C^{α}_1–C^{β}_1–C^{γ}_1), which is 115·9 (3)° in the present structure. Flexibility around C^{β} of the leucyl side chain has been noted before (Leung & Marsh, 1958) although the observed bond angles are typically 112·5–114°. Leung & Marsh (1958) reported an angle of 118° for the structure of L-Leu-L-Pro-Gly and attributed this large deviation to the steric effect of an O atom hydrogen bonding to the terminal N atom. Similar

hydrogen-bonding interactions occur in L-Leu-L-Glu (see below).

The principal torsion angles in L-Leu-L-Glu reflect the highly extended conformation of the dipeptide. Values of 172·0, 135·6 and −160·4° for ω [C_1^{α}–C_1'–N_2–C_2^{α}], ψ [N_1–C_1^{α}–C_1'–N_2] and φ [C_1'–N_2–C_2^{α}–C_2'], respectively, describe a *trans* extended peptide linkage. The torsion angles χ_1^1 [N_1–C_1^{α}–C_1^{β}–C_1^{γ}], $\chi_1^{2,1}$ [C_1^{α}–C_1^{β}–C_1^{γ}–$C_1^{\delta 1}$], and $\chi_1^{2,2}$ [C_1^{α}–C_1^{β}–C_1^{γ}–$C_1^{\delta 2}$] of −179·6, 171·8, and 65·3°, respectively, correspond to one of the idealized positions (180, 180, and 60°) noted by Ramachandran & Sasisekharan (1968), although this position is the least commonly observed of the three preferred positions (Benedetti, 1977). The torsion angles χ_2^1 [N_2–C_2^{α}–C_2^{β}–C_2^{γ}] and χ_2^2 [C_2^{α}–C_2^{β}–C_2^{γ}–C_2^{δ}] of 60·0 and 171·0°, respectively, describe an extended *cis-trans* conformation of the glutamyl side chain. The χ_2^1 angle of 60·0° corresponds precisely to one of the three (±60, 180°) preferred positions (Ramachandran & Sasisekharan, 1968) and is comparable to the values of 56·4, 60·3, and 72·1° in Gly-Asp (Eggleston & Hodgson, 1982*a*), Glu-Glu (Eggleston & Hodgson, 1982*b*), and Glu-Gly (Eggleston, Valente & Hodgson, 1981*b*) but different from values near −60° in Asp-Gly (Eggleston, Valente & Hodgson, 1981*a*), Boc-Ala-Glu (Dideberg, Lamotte, Dupont & Christiaens, 1981), a blocked derivative of Glu-Glu (Benedetti, DiBlasio, Pavone, Pedone, Germain & Goodman, 1979) and in Glu-Glu (Eggleston & Hodgson, 1982*b*) and those near 180° in the blocked Glu-Glu derivative (Benedetti *et al.*, 1979) and in Pro-Glu (Eggleston & Hodgson, 1982*c*). Similarly, the χ_2^2 angle of 171·0° is similar to values near 180° in Glu-Gly, the blocked Glu-Glu derivative and Glu-Glu but different from those in Boc-Ala-Glu (−62·3°) and Pro-Glu (70·6°). The torsion angles $\chi_2^{3,1}$ [C_2^{β}–C_2^{γ}–C_2^{δ}–$O_2^{\varepsilon 1}$] and $\chi_2^{3,2}$ [C_2^{β}–C_2^{γ}–C_2^{δ}–$O_2^{\varepsilon 2}$] of −139·1 and 37·6° differ markedly from the commonly observed values of 180 and 0°; this divergence may be due to the hydrogen-bonding requirements of $O_2^{\varepsilon 2}$ (see below). The torsional angle χ_2^4 [C_2^{γ}–C_2^{δ}–$O_2^{\varepsilon 1}$–$H_2^{\varepsilon 1}$] of 177° is very close to the value of 180° normally observed.

The disposition of the terminal carboxyl group in L-Leu-L-Glu is also worthy of note. Several authors (Dunitz & Robertson, 1952; Pasternak, 1956; Leung & Marsh 1958) pointed out the strong tendency for the amino or peptide N atoms to be as close as possible to the carboxyl or carbonyl O atoms of the same peptide residue and, hence, to be coplanar with the adjacent carboxyl or peptide groups. As can be seen in Fig. 1, in Leu-Glu the terminal carboxyl group is nearly coplanar with the planar peptide group The dihedral angle between these two planar groups is 21·8° and the carboxyl O atom (O′) to amide N atom (N_2) distance is only 2·627 (4) Å. Among the acidic peptides which we have characterized structurally this is the most nearly coplanar disposition of the terminal carboxyl group and peptide linkage. This close approach of O′ to N_2 presumably blocks the amide N atom from participation in the N_2–H_2···O_1 intermolecular hydrogen bonding which commonly occurs in peptides. It is noteworthy that associated with this short intramolecular contact are an H_2···O′ distance of 2·23 (3) Å and an N_2–H_2···O′ angle of 109 (3)°, which suggest that there may be an intramolecular N–H···O hydrogen bond here. In addition, we observe that O′ acts as an acceptor for only one intermolecular hydrogen bond [N_1···O′ = 2·745 (4) Å, N_1–H_1^3···O′ angle of 174 (3)°] while O″ acts as a double acceptor: from the terminal amino group [N_1···O″ distance 2·804 (5) Å and N_1–H_1^1···O″ angle 170 (3)°] and from the protonated glutamyl side chain [$O_2^{\varepsilon 1}$···O″ distance 2·694 (4) Å and $O_2^{\varepsilon 1}$–$H_2^{\varepsilon 1}$···O″ angle 150 (6)°]. The hydrogen-bonding scheme is completed by donation from the amino terminus to the side-chain carboxyl O atom $O_2^{\varepsilon 2}$ with associated N_1···$O_2^{\varepsilon 2}$ and H_1^2···$O_2^{\varepsilon 2}$ distances of 2·871 (4) and 1·94 (4) Å, respectively, and N_1–H_1^2···$O_2^{\varepsilon 2}$ angle of 163 (4)°. The peptide carbonyl O atom O_1 does not participate in the hydrogen-bonding network.

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1-Benzyloxy-3-methyl-4-nitrobenzene, $C_{14}H_{13}NO_3$: Apparent Red and Yellow Forms

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Abstract. $M_r = 243{\cdot}3$; lath (normally red) form (recrystallized from CH_2Cl_2–hexane): monoclinic, $P2_1/c$, $a = 7{\cdot}274$ (2), $b = 18{\cdot}379$ (4), $c = 9{\cdot}446$ (2) Å, $\beta = 97{\cdot}64$ (2)°, $U = 1251{\cdot}7$ (5) Å^3, $D_x = 1{\cdot}29$ g cm^{-3}, $Z = 4$, $R = 0{\cdot}049$ for 812 diffractometer-measured reflections, λ(Mo $K\alpha$) = 0·71069 Å. A prism (normally yellow) form can be produced by recrystallization from *n*-hexane or methanol. It has the same crystal structure as the lath form, but occurs as twinned crystals. An apparent photochemical isomerism is shown to be due to impurity.

Introduction. The title compound was found to show what appeared to be polymorphism of a rather unusual kind. On crystallization from CH_2Cl_2–hexane, it formed red lath-shaped crystals. These were photosensitive, turning yellow under illumination by sunlight. What appeared to be the same yellow form was also produced as prismatic crystals by recrystallization (either before or after irradiation) from methanol or hexane. This study aimed to clarify what appeared to be isomerism.

Experimental. 3-Methyl-4-nitrophenol (11 g, 72 mmol) was dissolved in NaOH (4 g)/H_2O (80 cm^3) at room temperature. To this clear, dark liquid, benzyltri(*n*-butyl)ammonium bromide (0·55 g) was added and the solution was heated to 363K with vigorous stirring. Benzyl chloride (11·5 cm^3, 100 mmol) was added in a single portion and the mixture was stirred for 2 h, after which time TLC showed the absence of phenolic material. The liquid was cooled to room temperature, water (100 cm^3) and 2 *M* aqueous NaOH (20 cm^3) were added, and the two-phase mixture was steam-distilled until the distillate became clear. The remaining contents of the flask were cooled to room temperature and acidified (HCl). The crude 1-benzyloxy-3-methyl-4-nitrobenzene was extracted with dichloromethane (3 × 50 cm^3), filtered through a small pad of silica gel (to remove dark coloured impurities) and dried ($MgSO_4$). Evaporation of solvent yielded a light brown-yellow solid (17·2 g), which was recrystallized from hot methanol (40 cm^3). The resulting yellow solid was filtered off, washed with a little cold methanol and finally dried at reduced pressure over calcium chloride. Yield 15·7 g, 90%, m.p. 339–341K; ^{1}H NMR ($CDCl_3$); δ 2·61 (*s*, 3*H*), 5·11 (*s*, 2*H*), 6·86 (*m*, 2*H*), 7·40 (*m*, 5*H*), 9·07 (*m*, 1*H*) p.p.m.

A sample of this yellow material on recrystallization from dichloromethane–hexane (1:3 v/v) deposited a mass of red-orange crystals, m.p. 341–343K, with a ^{1}H NMR spectrum identical to that of the yellow form. TLC (silica gel, CH_2Cl_2) showed that the yellow and the red forms were indistinguishable chromatographically (R_F 0·7) (dibenzyl ether: R_F 0·45; 3-methyl-4-nitrophenol: R_F 0·15). UV–visible spectra of dilute solutions in methanol of both forms were identical, and dominated by a strong peak at 305 nm ($\varepsilon = 9\,200 \pm 200$ dm^3 mol^{-1} cm^{-1}). Concentrated solutions of both forms (0·165 mol dm^{-3}) showed considerable differences in the blue region of the spectrum with the 'orange' form absorbing 2–3 times as much as the 'yellow' form at 415–420 nm. A sample of the crystalline red form on standing in direct sunlight turned yellow. Repeated recrystallization from methanol yielded almost white material, while recrystallization from CH_2Cl_2–hexane always yielded orange-red material.

^{1}H NMR spectra were recorded on a Perkin Elmer *R*34 instrument (220 MHz) at ambient temperature (*ca* 296 K). Melting points were determined in capillary tubes using an electrothermal apparatus and are uncorrected. TLC plates were 0·2 mm thick precoated silica gel F_{254} (Merck) and spots were visualized using a low-power UV lamp. UV spectra were run on a Shimadzu 365 instrument.

Red form: Syntex $P2_1$ four-circle diffractometer, maximum $2\theta = 50°$, scan range $\pm 1{\cdot}0°$ (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 2·5–29° min^{-1} (depending on the intensity of a 2 s pre-scan), backgrounds

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