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α -L-Aspartylglycine Monohydrate

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Abstract. $C_6H_{10}N_2O_5 \cdot H_2O$, orthorhombic, $P2_12_12_1$, $a = 4.844$ (5), $b = 9.916$ (3), $c = 18.070$ (4) Å, $V = 868.05$ Å³, $Z = 4$, $D_c = 1.59$, D_m (floatation in chloroform/iodoform) = 1.60 (1) Mg m⁻³; $R_1 = 0.040$, $R_2 = 0.033$ for 1088 observations. The dipeptide crystallizes as a zwitterion with the main-chain carboxyl ionized and the side-chain amino group protonated. The overall dipeptide conformation is highly extended and the molecule is extensively hydrogen bonded.

Introduction. Colorless rods of α -L-aspartylglycine monohydrate were grown from aqueous ethanol at pH 6–7. A crystal of dimensions 0.125 × 0.300 × 0.525 mm was used in the analysis. Preliminary cell constants were obtained with the *SEARCH* routine on an

Enraf–Nonius CAD-4 diffractometer. The crystals were assigned to the orthorhombic system; the observed systematic absences of $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd indicated the noncentrosymmetric space group $P2_12_12_1$. Final cell constants (Mo $K\alpha$) were determined from a least-squares analysis of 25 reflections with $30^\circ \leq 2\theta(\text{Mo } K\alpha) \leq 35^\circ$ measured on the diffractometer. Intensity data were collected on the diffractometer in a θ - ω scan mode, as suggested by the examination of the shapes of several peaks. A total of 1193 reflections with $2\theta \leq 55^\circ$ were collected and corrected for Lorentz–polarization effects but not for absorption since the small linear absorption coefficient ($\mu = 0.154 \text{ mm}^{-1}$) suggested to us that this effect is negligible. The programs used throughout the analysis were those provided by Enraf–Nonius with the CAD-4–SDP system.

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The structure was determined by *MULTAN* (Main, Woolfson & Germain, 1971) using 104 reflections with $E \geq 1.60$. An E map, calculated for the solution with the highest combined figure of merit, revealed 13 of the 14 non-hydrogen atoms. After one cycle of least-squares refinement using isotropic thermal parameters a difference Fourier map revealed the water O atom. All least-squares calculations in this analysis were run on F , the function minimized being $\sum w(|F_o| - |F_c|)^2$ where the weights w were initially assigned as unity but were eventually assigned (see below) as $4F_o^2/\sigma^2(I)$. Two additional cycles of least-squares refinement were succeeded by anisotropic refinement.

A subsequent difference Fourier map revealed the positions of all 12 H atoms. Three additional cycles of least-squares refinement using isotropic thermal parameters for H atoms and anisotropic thermal parameters for other atoms and the weighting scheme above with $\sigma(I)$ as defined by the expression of Corfield, Doedens & Ibers (1967) with $p = 0.01$ converged to final values of the standard agreement factors $R_1 = 0.040$ and R_2 (or weighted R factor) = 0.033, based on 1088 observations with $I \geq 0.01 \sigma(I)$ and 175 variables. The error on an observation of unit weight is 1.84. No correction for secondary extinction appeared necessary, so none was applied. The posi-

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

Discussion. As part of our ongoing research into the structural properties of peptides containing acidic amino acid residues (Valente, Hiskey & Hodgson, 1979), we are examining the crystal structures of peptides containing L-aspartyl residues. A survey of the literature reveals an absence of structure determinations for linear peptides containing this residue. We here report, therefore, the first such structure, that of α-L-Asp-Gly. H₂O

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 Cⁿ-C' distances of the Asp and Gly residues of 1.526 (2) and 1.504 (2) Å, respectively, are in close agreement with the average value of 1.51 Å as tabulated for free peptides by Marsh & Donohue (1967). Similarly, the N-C^α [1.480 (2) and 1.448 (2) Å], C'-N [1.322 (2) Å] and peptide carbonyl [1.233 (2) Å] distances are similar to their reported averages of 1.45, 1.32, and 1.24 Å, respectively. The torsional angles along the dipeptide chain are shown in Fig. 2; the definitions of the torsional angles are those of the IUPAC-IUB Commission on Biochemical Nomenclature (1970). These values are well within the allowed limits for the conformational angles in the extended structure in peptides (Anfinsen & Scheraga, 1975). As can be seen from these values, and also from an examination of Fig. 1, the dipeptide adopts an extended conformation in the crystal. The bond angles in the structure have been deposited.*

There is extensive hydrogen bonding in the structure, as is illustrated in Fig. 3. The amide function N₂ is a

Table 1. Positional parameters and thermal parameters for α-L-aspartylglycine monohydrate

	x	y	z	U_{eq}^*/B^{\dagger} (Å ²)
N ₁	0.3912 (4)	-0.1181 (2)	0.17654 (9)	0.0266
N ₂	0.1887 (4)	0.0638 (2)	0.01521 (9)	0.0234
O ₁	0.6084 (3)	-0.0346 (2)	0.06722 (8)	0.0292
O ₂ ¹	0.0839 (4)	0.1724 (2)	0.31483 (8)	0.0400
O ₂ ²	-0.1643 (3)	0.0105 (2)	0.26098 (8)	0.0317
O ⁺	0.1970 (4)	0.1593 (2)	-0.17680 (7)	0.0310
O ⁻	-0.0898 (3)	0.0236 (2)	-0.11517 (8)	0.0339
OW ₁	0.6336 (4)	0.2259 (2)	0.45909 (9)	0.0454
C ₁ ^α	0.2149 (5)	-0.0133 (2)	0.1421 (1)	0.0272
C ₁ ^β	0.1923 (5)	0.1124 (2)	0.1908 (1)	0.0279
C ₁ ^γ	0.0336 (5)	0.1004 (2)	0.2624 (1)	0.0269
C ₁ ^δ	0.3546 (4)	0.0286 (2)	0.0700 (1)	0.0219
C ₂ ^α	0.2927 (5)	0.1226 (2)	-0.0527 (1)	0.0289
C ₂ ^β	0.1182 (5)	0.0989 (2)	-0.1202 (1)	0.0240
H ₁ ¹	0.576 (6)	-0.091 (3)	0.1814 (13)	5.3 (7)
H ₁ ²	0.336 (6)	-0.136 (3)	0.2265 (14)	5.1 (7)
H ₁ ³	0.401 (6)	-0.190 (3)	0.1467 (13)	5.0 (7)
H ₁ ⁴	0.038 (4)	-0.052 (2)	0.1327 (9)	1.4 (4)
H ₁ ⁵	0.372 (5)	0.149 (2)	0.2006 (11)	2.9 (5)
H ₁ ⁶	0.072 (5)	0.188 (2)	0.1605 (11)	2.7 (5)
H ₁ ⁷	-0.250 (7)	-0.006 (3)	0.3154 (14)	6.0 (7)
H ₂ ¹	0.028 (4)	0.051 (2)	0.0223 (10)	2.2 (5)
H ₂ ²	0.464 (4)	0.084 (2)	-0.0623 (10)	2.3 (5)
H ₂ ³	0.315 (5)	0.220 (2)	-0.0461 (11)	3.3 (5)
HW ₁	0.626 (6)	0.155 (3)	0.4417 (14)	5.0 (7)
HW ₂	0.844 (9)	0.243 (8)	0.4927 (29)	13.4 (12)

* Calculated from the r.m.s. amplitudes in Å, where $U_{eq}^{\lambda} = U_1 U_2 U_3$; c.s.d.'s are 0.0007 Å².
† For H atoms.

* Lists of structure factors, anisotropic thermal parameters, and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35957 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

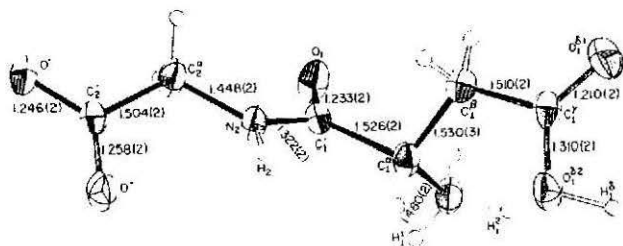


Fig. 1. View of the α-L-aspartylglycine molecule, showing principal bond lengths (Å) and associated c.s.d.'s. Thermal ellipsoids are drawn at the 50% probability level; H atoms are shown as small circles of arbitrary size. The water molecule is omitted.

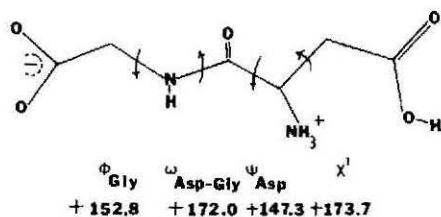


Fig. 2. Schematic showing the torsional angles ($^{\circ}$) in the peptide backbone as defined by the IUPAC-IUB Commission on Biochemical Nomenclature (1970).

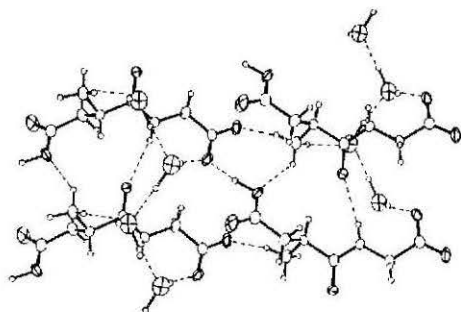


Fig. 3. The hydrogen-bonding network in crystals of α -L-aspartylglycine as viewed down c with b horizontal. O atoms are shown with principal ellipses.

donor to the peptide carboxyl O_1 along the a direction with $N_2 \cdots O_1$ and $H_2 \cdots O_1$ distances and associated $N_2-H_2 \cdots O_1$ angle of 2.977 (2) Å, 2.20 (2) Å and 166(2) $^{\circ}$, respectively. The ionized carboxyl is hydrogen bonded through O' to the protonated amino terminus N_1 with $N_1 \cdots O'$ and $H_1^2 \cdots O'$ distances and $N_1-H_1^2 \cdots O'$ angle of 2.715 (2) Å, 1.79 (2) Å, and 168(2) $^{\circ}$, respectively, and through O'' to the un-ionized side chain $O_1^{\delta 2}$ of a screw-related molecule along b with $O_1^{\delta 2} \cdots O''$ and $H_1^{\delta} \cdots O''$ distances and $O_1^{\delta 2}-H_1^{\delta} \cdots O''$ angle of 2.558 (2) Å, 1.49 (3) Å, and 171 (2) $^{\circ}$, respectively. The ionized carboxyl group is also hydrogen

bonded to an adjacent water molecule with $OW_1 \cdots O''$ and $HW_1 \cdots O''$ distances and $OW_1-HW_1 \cdots O''$ angle of 2.823 (2) Å, 2.04 (3) Å, and 173 (2) $^{\circ}$, respectively. The water molecules form channels through the structure along the a direction, each water molecule acting as a donor and an acceptor towards two adjacent water molecules along the chain with an $OW_1 \cdots OW_1$ distance of 2.874 (2) Å. The amino terminus also acts as a donor to an associated water molecule with an $N_1 \cdots OW_1$ distance of 2.904 (2) Å, and (relatively weakly) to the Asp carboxyl group with $N_1 \cdots O_1^{\delta 2}$ and $H_1^1 \cdots O_1^{\delta 2}$ distances, and $N_1-H_1^1 \cdots O_1^{\delta 2}$ angle of 2.932 (2) Å, 2.16 (2) Å, and 139 (2) $^{\circ}$, respectively.

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