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L-Tyrosyl-L-glutamic Acid Monohydrate, $C_{14}H_{18}N_2O_6.H_2O$

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Abstract. $M_r = 328{\cdot}32$, triclinic, $P1$, $a = 5{\cdot}801$ (1), $b = 7{\cdot}977$ (1), $c = 9{\cdot}110$ (2) Å, $\alpha = 102{\cdot}33$ (1), $\beta = 97{\cdot}92$ (1), $\gamma = 109{\cdot}82$ (1)°, $V = 377{\cdot}2$ (1) Å^3 at 293 K, $Z = 1$, $D_x = 1{\cdot}45$, $D_m = 1{\cdot}45$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}74$ cm^{-1}, $F(000) = 174{\cdot}0$. $R = 0{\cdot}046$ for 990 unique observed [$F_o > 4\sigma(F_o)$] reflections. The crystal structure is stabilized by extensive hydrogen bonding involving all N and O atoms.

Introduction. We report here the structure of L-tyrosyl-L-glutamic acid monohydrate as a part of our investigations on peptides which are possibly involved in specific interactions with nucleic acids.

Experimental. The dipeptide was purchased from Bachem Inc., and was used without further purification. Needle-like crystals by evaporation from aqueous solution; cell dimensions by least-squares analysis of 25 θ values, D_m by flotation in acetone/bromoform, intensity data collected up to $\theta_{max} = 26{\cdot}85°$, syntex $P2_1$ diffractometer, crystal $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}12$ mm; 1097 reflections considered observed [$F_o > 4\sigma(F_o)$] of which 990 were unique (index range h 0 to 6, k −9 to 8, l −10 to 10); two strong reflections monitored periodically during data collection showed negligible variation; Lorentz–polarization corrections but not for absorption; direct methods [*MULTAN*, Germain, Main & Woolfson, 1971], block-diagonal least-squares refinement (on F) with anisotropic thermal parameters (to $R = 0{\cdot}064$); all the H atoms (from a difference map) included with isotropic temperature factors; final $R = 0{\cdot}046$, $R_w = 0{\cdot}050$; function minimized in the final stages of refinement $\sum w(|F_o| - |F_c|)^2$ where $w = 1/(a + b|F_o| + |F_o|^2)^{1/2}$ with $a = 5{\cdot}16$, $b = 1{\cdot}0$, and $c = 0{\cdot}033$ (Cruickshank, 1961); scattering factors for H atoms from Stewart, Davidson & Simpson (1965), for the other atoms, computed from the function of Cromer & Waber (1965); maximum and minimum final $\Delta\rho$ excursions 0·19 and −0·26 e Å^{-3}, $(\Delta/\sigma)_{max} = 1{\cdot}0$; block-diagonal least-squares program of Shiono (1965).

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Table 1. *Final positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic temperature factors with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for non-hydrogen atoms.

	x	y	z	B_{eq} or B_{iso}(Å^2)
N(1)	9877 (13)	7504 (8)	12090 (7)	3·1 (2)
C(1)	11396 (13)	9513 (9)	12748 (7)	2·2 (2)
C(5)	12329 (13)	10390 (9)	11472 (8)	2·3 (2)
C(6)	10305 (12)	10033 (9)	10060 (7)	2·3 (2)
C(7)	10132 (15)	8794 (10)	8698 (9)	3·0 (2)
C(11)	8613 (13)	10930 (10)	10074 (8)	2·7 (2)
C(8)	8396 (16)	8458 (10)	7377 (8)	3·2 (2)
C(10)	6861 (15)	10585 (11)	8756 (9)	3·1 (3)
C(9)	6714 (14)	9335 (10)	7391 (8)	2·7 (2)
O(4)	4935 (10)	9073 (8)	6123 (6)	3·8 (2)
C(2)	9743 (12)	10380 (9)	13541 (7)	2·0 (2)
O(1)	7450 (9)	9583 (7)	13197 (6)	3·1 (1)
N(2)	10988 (10)	12005 (8)	14589 (6)	2·3 (2)
C(3)	9681 (12)	12980 (9)	15457 (7)	1·9 (2)
C(12)	11468 (15)	14523 (10)	16856 (8)	2·9 (2)
C(13)	12820 (15)	13821 (11)	17995 (8)	3·1 (3)
C(14)	13036 (14)	14842 (10)	19636 (8)	2·9 (2)
O(5)	11709 (17)	15660 (11)	19972 (7)	6·2 (3)
O(6)	14663 (11)	14670 (10)	20682 (6)	4·6 (2)
C(4)	8295 (12)	13887 (9)	14516 (7)	2·0 (2)
O(2)	9339 (10)	14667 (8)	13594 (6)	3·2 (2)
O(3)	6277 (9)	13902 (7)	14846 (6)	2·9 (2)
O(W)	14175 (10)	15778 (8)	23464 (6)	3·3 (2)
H1(N1)	847 (20)	723 (15)	1154 (12)	5·95 (1)
H2(N1)	1044 (17)	663 (13)	1136 (10)	4·5 (21)
H3(N1)	950 (17)	664 (13)	1289 (10)	6·0 (21)
H(C1)	1295 (12)	965 (10)	1345 (8)	1·4 (14)
H1(C5)	1317 (13)	1191 (10)	1207 (8)	1·6 (14)
H2(C5)	1366 (11)	981 (8)	1111 (6)	0·0 (11)
H(C7)	1128 (14)	818 (10)	865 (8)	2·5 (15)
H(C8)	837 (14)	768 (10)	648 (8)	2·8 (15)
H(C10)	575 (14)	1133 (11)	888 (9)	3·5 (16)
H(C11)	864 (16)	1174 (12)	1108 (9)	3·9 (18)
H(O4)	470 (18)	831 (14)	570 (11)	8·9 (22)
H(N2)	1260 (12)	1239 (9)	1481 (7)	1·0 (12)
H(C3)	840 (11)	1200 (8)	1574 (7)	1·1 (11)
H1(C12)	1289 (14)	1549 (10)	1663 (9)	1·9 (15)
H2(C12)	1030 (21)	1489 (16)	1737 (13)	6·34 (1)
H1(C13)	1149 (15)	1249 (12)	1810 (10)	4·3 (19)
H2(C13)	1450 (16)	1422 (12)	1793 (9)	3·9 (19)
H(O6)	1405 (23)	1497 (17)	2205 (14)	7·00 (1)
H1(W)	1464 (17)	1491 (13)	2369 (11)	4·8 (20)
H2(W)	1242 (17)	1519 (13)	2357 (10)	3·9 (20)

Table 2. *Conformational angles* (°)

N(1)–C(1)–C(2)–N(2)	ψ_1	159·6 (6)
C(2)–N(2)–C(3)–C(4)	φ_2	−74·1 (8)
C(1)–C(2)–N(2)–C(3)	ω	−178·9 (6)
N(1)–C(1)–C(5)–C(6)	χ_1^1	52·7 (8)
C(1)–C(5)–C(6)–C(7)	χ_1^{22}	−106·1 (8)
C(1)–C(5)–C(6)–C(11)	χ_1^{21}	74·7 (9)
N(2)–C(3)–C(12)–C(13)	χ_2^1	−60·2 (8)
C(3)–C(12)–C(13)–C(14)	χ_2^2	−140·8 (7)
C(12)–C(13)–C(14)–O(5)	χ_2^{31}	20·0 (11)
C(12)–C(13)–C(14)–O(6)	χ_2^{32}	−164·3 (7)

Discussion. The molecular structure and atomic numbering are shown in Fig. 1, and final positional and isotropic thermal parameters are listed in Table 1.* Bond lengths and angles are shown in Figs. 2 and 3, while conformational angles, following the convention of the IUPAC–IUB Commission on Biochemical Nomenclature (1970), are listed in Table 2.

The molecule exists as a zwitterion, with the N-terminal end protonated and the carboxyl terminal end deprotonated. The carboxyl group on the glutamic acid side chain is protonated. The conformational angles involving the tyrosine side chain are similar to those of other aromatic amino acid residues (Cody, Duax & Hauptman, 1973). The χ_1^1 angle of 52·7° (Table 2) for this structure puts it in class *A* (Cody *et al.*, 1973) and is close to the mean value for aromatic amino acid residues. The χ_1^{21} angle of 74·7° is also within the range observed in other structures.

According to classical energy calculations by Ponnuswamy & Sasisekharan (1971), the energetically favourable side-chain conformations in glutamic acid correspond to χ^1, χ^2 combinations of (60, 180°), (180, 60°), (180, 180°), (−60, 180°) and (−60, −60°). The combination (−60·2, −140·8°) seen in this structure falls in a region of the χ^1, χ^2 map predicted to be energetically unfavourable by these workers. Such a combination has not been reported for any other crystal structure containing glutamic acid.

Intermolecular hydrogen-bond parameters are listed in Table 3* and shown in the packing diagram (Fig. 4). There are no intramolecular H bonds. All available protons are involved in H-bonding interactions.

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* Lists of structure factors, anisotropic thermal parameters and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38895 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

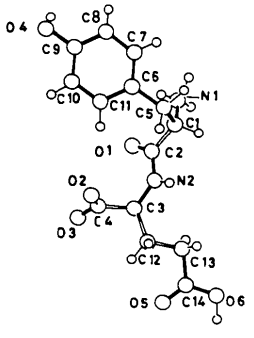

Fig. 1. Molecular structure and atomic numbering.

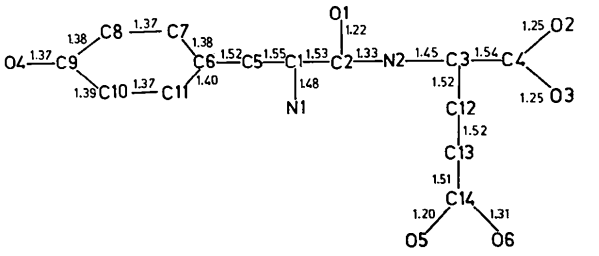

Fig. 2. Bond lengths. Average e.s.d. = 0·01 Å.

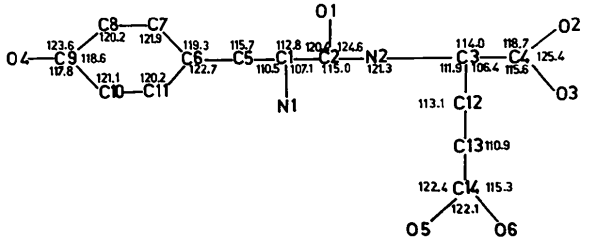

Fig. 3. Bond angles. Average e.s.d. = 0·6°.

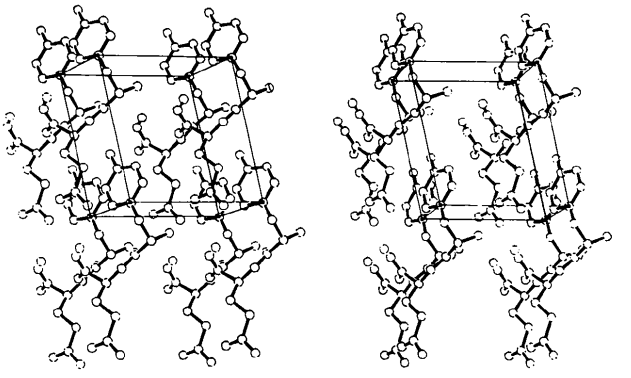

Fig. 4. Stereoview of crystal packing along **a**.

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