A stereoscopic view of the packing of the molecule is shown in Fig. 2. The amide nitrogen, N(1), forms a hydrogen bond with a carbonyl oxygen, O(1), related by a centre of symmetry [N(1)—H(N1) = 0·86 (3), N(1)···O(1)($-x$, $-y$, $-z$) = 2·853 (4), H(N1)···O(1)($-x$, $-y$, $-z$) = 2·00 (3) Å, N(1)—HN(1)···O(1) = 172°]. The molecules thus form an infinite hydrogen-bonded network.

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# Structure of L-Prolyl-L-tyrosine Monohydrate

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**Abstract.** $C_{14}H_{18}N_2O_4.H_2O$, $M_r = 296{\cdot}32$, triclinic, $P\bar{1}$, $a = 5{\cdot}524$ (3), $b = 6{\cdot}621$ (2), $c = 10{\cdot}307$ (2) Å, $\alpha = 78{\cdot}82$ (3), $\beta = 86{\cdot}82$ (4), $\gamma = 84{\cdot}96$ (4)°, $V = 368{\cdot}11$ Å$^3$, $Z = 1$, $D_x = 1{\cdot}34$ g cm$^{-3}$, $\lambda$(Mo $K\alpha_1$) = 0·70930 Å, $\mu = 1{\cdot}10$ cm$^{-1}$, $F(000) = 158$, $T = 298$ K, final $R = 0{\cdot}044$ for 2182 observed reflections. The molecule crystallizes as a zwitterion with the peptide backbone folded and a water molecule of hydration. The water molecule and the dipeptide molecule are involved in an extensive hydrogen-bond network.

**Introduction.** The crystal structure of the hydrate of the dipeptide L-prolyl-L-tyrosine is reported here as part of a research project involving the X-ray studies of crystalline samples of amino acids and small peptides. We are interested not only in the solid-state structure but also in the intermolecular interactions that occur between dipeptide molecules and those that result from any co-crystallized water.

**Experimental.** L-Prolyl-L-tyrosine obtained from Sigma Chemical Company, recrystallized from aqueous ethanol to give colorless crystals, approximate dimensions 0·50 × 0·30 × 0·20 mm. Enraf–Nonius CAD-4 diffractometer with graphite-crystal-monochromatized Mo $K\alpha$ radiation. Unit-cell dimensions, lack of systematic absences and successful solution of the structure determined space group as $P\bar{1}$. Unit-cell dimensions were determined by least-squares fit of 25 centered reflections with $43 \le 2\theta \le 60°$. Three-dimensional intensity data collected in $\omega$:$2\theta$ scan mode; total of 2256 independent reflections, 2182 observed with $I > 3\sigma(I)$; $1 \le 2\theta \le 60°$; $[(\sin\theta)/\lambda]_{max} = 0{\cdot}70$ Å$^{-1}$; $-7 \le h \le 7$, $-9 \le k \le 9$, $0 \le l \le 14$. Data corrected for Lorentz and polarization effects. Three standard reflections measured every 2 h during data collection (200, 040, 002) showed no significant change in intensity. Absorption as a function of $\psi$ was corrected empirically (maximum relative transmission 99·91%, minimum relative transmission 85·17%). Structure solved by direct methods using the *MULTAN*11/82 series of programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Initial $E$ map con-

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tained 20 non-H atoms. Remaining atoms including H atoms located in difference Fourier map. Full-matrix least-squares refinement on $F$ of 21 anisotropic non-H-atom and 20 isotropic H-atom (270 variables) coordinates and temperature factors and a scale factor. Final $R = 0{\cdot}044$, $wR = 0{\cdot}056$ where $w = 1/\sigma(F)^2$ and $\sigma(F)^2 = [\sigma(I)^2_{cs} + (0{\cdot}04)^2(F^2)^2]$, $S = 2{\cdot}46$ for 2182 observed reflections.

In the final least-squares cycle $(\Delta/\sigma)_{max} = 0{\cdot}06$. Maximum and minimum peaks in the difference Fourier map were $+0{\cdot}55$ and $-0{\cdot}31$ e Å$^{-3}$, respectively. Scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) are corrected for anomalous-scattering contributions, *CAD-4 SDP* programs used (Frenz, 1978).

**Discussion.** Final fractional coordinates for the non-H atoms are given in Table 1.* The numbering system for the molecule can be found in Fig. 1. Bond lengths and angles are given in Table 2. The title compound crystallized as a zwitterion with the proline nitrogen, N2, protonated and the carboxylate group unprotonated. There is one water of crystallization in the unit cell. There is an extensive hydrogen-bond network involving the water molecule, carboxylate group, the protonated proline nitrogen and the tyrosine amide nitrogen. The specific hydrogen-bond parameters can be found in Table 3. Although there is a close intramolecular contact distance between O3 and N1 and O4 and N2, these are not hydrogen-bonding interactions. [The O3···N1 contact distance is 2·780 (1) Å but the N1 hydrogen atom, HN1, points away from the O3 atom. Similarly, the O4···N2 distance is 2·644 (1) Å but the N2 hydrogen atoms point in the opposite direction from O4.]

The structure of the molecule can be described by the torsional angles along the peptide chain listed in Table 4. The definitions of the torsional angles are those of the IUPAC–IUB Commission on Biochemical Nomenclature (1971). The four-atom chain connecting the five-membered pyrrolidine ring of the proline and the six-membered aromatic ring of the tyrosine is extended in the crystal structure. The peptide backbone is folded with $\varphi_{Tyr} = -67{\cdot}9\ (2)°$, $\omega_{Tyr\text{-}Pro} = 174{\cdot}4\ (1)°$, $\psi_{Tyr} = -35{\cdot}0\ (2)°$ and $\psi_{Pro} = 162{\cdot}2\ (1)°$. It is interesting to compare the structure of the L-Pro-L-Tyr with the structure of the neurotensin tetrapeptide, L-Pro-L-Tyr-L-Ile-L-Leu (Cotrait,

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and temperature factors, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54253 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their estimated standard deviations*

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| *OW*1 | −0·2031 (4) | 0·4558 (4) | 1·5213 (2) | 6·13 (4) |
| O1 | 0·035 | 0·739 | 1·337 | 5·00 (3) |
| O2 | 0·4263 (2) | 0·4040 (2) | 0·8996 (1) | 3·00 (2) |
| O3 | 0·7666 (2) | 0·4905 (2) | 0·7845 (1) | 3·12 (2) |
| O4 | 0·8026 (2) | −0·0471 (2) | 0·8478 (1) | 3·30 (2) |
| N1 | 1·0179 (2) | 0·1569 (2) | 0·9407 (1) | 2·47 (2) |
| N2 | 1·1831 (2) | −0·2650 (2) | 0·7643 (1) | 2·47 (2) |
| C1 | 0·2367 (4) | 0·6457 (3) | 1·2849 (2) | 3·58 (3) |
| C2 | 0·3041 (4) | 0·4366 (3) | 1·3205 (2) | 3·66 (3) |
| C3 | 0·5094 (4) | 0·3496 (3) | 1·2604 (2) | 3·39 (3) |
| C4 | 0·6505 (3) | 0·4703 (2) | 1·1644 (1) | 2·83 (2) |
| C5 | 0·5802 (4) | 0·6794 (3) | 1·1322 (2) | 3·84 (3) |
| C6 | 0·3760 (5) | 0·7662 (3) | 1·1911 (2) | 4·17 (4) |
| C7 | 0·8677 (3) | 0·3755 (3) | 1·0966 (2) | 3·14 (3) |
| C8 | 0·7974 (2) | 0·2555 (2) | 0·9930 (1) | 2·25 (2) |
| C9 | 0·6536 (2) | 0·3945 (2) | 0·8819 (1) | 2·11 (2) |
| C10 | 0·9975 (2) | 0·0157 (2) | 0·8670 (1) | 2·27 (2) |
| C11 | 1·2317 (2) | −0·0675 (2) | 0·8042 (1) | 2·25 (2) |
| C12 | 1·3107 (3) | 0·0741 (3) | 0·6764 (2) | 3·58 (3) |
| C13 | 1·4145 (5) | −0·0782 (4) | 0·5909 (2) | 4·67 (4) |
| C14 | 1·2402 (4) | −0·2448 (3) | 0·6196 (2) | 3·98 (3) |

Table 2. *Bond distances* (Å) *and angles* (°) *and their estimated standard deviations*

| | | | |
|---|---|---|---|
| O1—C1 | 1·362 (2) | C3—C4 | 1·394 (2) |
| O2—C9 | 1·257 (1) | C4—C5 | 1·385 (2) |
| O3—C9 | 1·246 (1) | C4—C7 | 1·506 (1) |
| O4—C10 | 1·227 (1) | C5—C6 | 1·384 (2) |
| N1—C8 | 1·458 (1) | C7—C8 | 1·534 (1) |
| N1—C10 | 1·329 (1) | C8—C9 | 1·534 (1) |
| N2—C11 | 1·494 (1) | C10—C11 | 1·522 (1) |
| N2—C14 | 1·489 (2) | C11—C12 | 1·527 (2) |
| C1—C2 | 1·385 (2) | C12—C13 | 1·520 (2) |
| C1—C6 | 1·375 (2) | C13—C14 | 1·503 (3) |
| C2—C3 | 1·396 (2) | | |

| | | | |
|---|---|---|---|
| C8—N1—C10 | 118·86 (8) | N1—C8—C9 | 111·28 (7) |
| C11—N2—C14 | 108·27 (9) | C7—C8—C9 | 112·03 (8) |
| O1—C1—C2 | 123·0 (1) | O2—C9—O3 | 125·40 (9) |
| O1—C1—C6 | 117·8 (1) | O2—C9—C8 | 115·51 (9) |
| C2—C1—C6 | 119·2 (1) | O3—C9—C8 | 119·07 (8) |
| C1—C2—C3 | 120·1 (1) | O4—C10—N1 | 123·33 (9) |
| C2—C3—C4 | 121·0 (1) | O4—C10—C11 | 119·98 (9) |
| C3—C4—C5 | 117·4 (1) | N1—C10—C11 | 116·69 (8) |
| C3—C4—C7 | 121·1 (1) | N2—C11—C10 | 107·73 (7) |
| C5—C4—C7 | 121·5 (1) | N2—C11—C12 | 105·37 (9) |
| C4—C5—C6 | 121·7 (1) | C10—C11—C12 | 112·74 (8) |
| C1—C6—C5 | 120·5 (1) | C11—C12—C13 | 102·6 (1) |
| C4—C7—C8 | 112·91 (9) | C12—C13—C14 | 103·1 (1) |
| N1—C8—C7 | 108·69 (8) | N2—C14—C13 | 103·5 (1) |

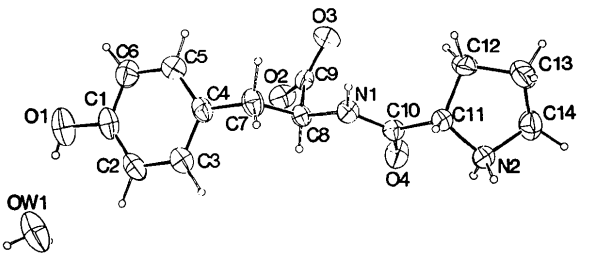


Fig. 1. *ORTEP* diagram of L-prolyl-L-tyrosine monohydrate drawn with 50% probability ellipsoids.

Table. 3. *Hydrogen-bond distances* (Å) *and angles* (°)

| Donor | Acceptor | Bond length | Symmetry operation |
|---|---|---|---|
| OW1 | O1 | 2·761 (3) | $x, y, z$ |
| OW1 | H1 | 2·01 (3) | $x, y, z$ |
| OW1···H1—O1 | 179· (3) | | |
| OW1 | O3 | 2·761 (2) | $x-1, y, z+1$ |
| HW1 | O3 | 1·95 (3) | $x-1, y, z+1$ |
| OW1—HW1···O3 | 161· (3) | | |
| N1 | O2 | 2·867 (1) | $x-1, y, z$ |
| HN1 | O2 | 1·99 (2) | $x-1, y, z$ |
| N1—HN1···O2 | 174· (2) | | |
| N2 | O2 | 2·657 (1) | $x-1, y+1, z$ |
| HN2′ | O2 | 1·77 (2) | $x-1, y+1, z$ |
| N2—HN2′···O2 | 172· (2) | | |
| N2 | O3 | 2·903 (1) | $x, y+1, z$ |
| HN2 | O3 | 2·15 (2) | $x, y+1, z$ |
| N2—HN2···O3 | 147· (2) | | |

Table 4. *Selected torsion angles* (°)

| | | |
|---|---|---|
| C10—N1—C8—C7 | 168·2 (1) | |
| C10—N1—C8—C9 | −67.9 (2) | $\varphi_{Tyr}$ |
| C8—N1—C10—C11 | 174·4 (1) | $\omega_{Tyr\text{-}Pro}$ |
| C4—C7—C8—C9 | 61.0 (2) | |
| C4—C7—C8—N1 | −175·6 (1) | |
| N1—C8—C9—O2 | 146·5 (1) | $\psi_{Tyr}$ |
| N1—C8—C9—O3 | −35.0 (2) | $\psi_{Tyr}$ |
| N1—C10—C11—N2 | 162·2 (1) | $\psi_{Pro}$ |
| N1—C10—C11—C12 | −82·0 (2) | |

Geoffre, Hospital & Precigoux, 1979). The torsion angles in the L-Pro-L-Tyr fragment of the tetrapeptide are very similar to those obtained in the dipeptide. These are $\varphi_{Tyr} = 71·4°$, $\omega_{Tyr\text{-}Pro} = 170·3°$ and $\psi_{Tyr} = -47·9°$. Proline is in the *cis* conformation ($\psi \simeq 180°$) in the dipeptide with $\psi_{Pro} = 162·2\ (1)°$ as it is in the tetrapeptide with $\psi_{Pro} = 169°$. The pyrrolidine ring is puckered with C13 −0·611 (3) Å out of the plane defined by C11, N2, C14 and C13. The plane of the carboxylate group in the tyrosine is 45·2 (2)° to the plane of the aromatic ring. The peptide bond C10—N1 is 1·329 (1) Å in length. This is shorter than other N—C bonds due to the partial double-bond character of CO═NH found in the peptide.

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# Structure of the 1:1 Complex Formed from 4-Nitropyridine *N*-Oxide and 2-Aminobenzoic Acid

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**Abstract.** $C_7H_7NO_2.C_5H_4N_2O_3$, $M_r = 277·2$, monoclinic, $Cc$, $a = 9·522\ (3)$, $b = 10·637\ (4)$, $c = 12·611\ (3)$ Å, $\beta = 104·31\ (2)°$, $V = 1237·7\ (4)$ Å$^3$, $Z = 4$, $D_m = 1·49\ (1)$, $D_x = 1·488$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $F(000) = 576$, $\mu = 0·111$ mm$^{-1}$, $T = 295$ K, $R = 0·0401$, $wR = 0·0392$, 834 observed reflections. The complex is formed by alternate stacking of 4-nitropyridine *N*-oxide and 2-aminobenzoic acid molecules. The resulting stacks follow the [$\bar{1}$10] and [110] directions and exhibit overlap between aromatic rings with interplanar distances equal to 3·32 (3) and 3·46 (3) Å. Besides an intramolecular hydrogen bond with an N···O distance of 2·675 (7) Å between amino and carbonyl groups, intermolecular hydrogen bonds with an O···O distance of 2·629 (5) Å and an N···O distance of 2·999 (6) Å are observed between the carboxyl and *N*-oxide groups, and the amino and *N*-oxide groups, respectively, from molecules in neighboring stacks.

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