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L-Proline Monohydrate at 100 K

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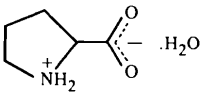
Abstract

A new crystalline modification of proline was identified by the present X-ray analysis as a monoclinic L-proline monohydrate, $C_5H_9NO_2.H_2O$. The pyrrolidine rings are in a C_2–C^γ-*exo*–C^δ-*endo* conformation. The C4 atom (C^γ) is in a *trans* position with respect to the carboxyl group. In the crystal lattice, columns of L-proline molecules are stabilized by intermolecular hydrogen bonds. These columns are interconnected by water molecules. The water molecules in the structure form non-linear hydrogen-bonded chains parallel to the *c* axis. One H atom of the water molecule chain is disordered.

Comment

L-Proline is a cyclic amino acid. It contains a pyrrolidine ring whose presence in a protein chain can disrupt the α-helix and can also give rise to the specific collagen spiral (Rich & Crick, 1961; Nagai & Noda, 1957; Miller & Wray, 1971; Stacey *et al.*, 1988; Kadler *et al.*, 1991; Horovitz, Matthews & Fersht, 1992; Bella *et al.*, 1994; Schulman & Kim, 1996; Fields & Prockop, 1996).

The crystal structure of L-proline monohydrate, (I), has not been determined previously, only the space group and unit-cell dimensions have been mentioned by Sasisekharan (1959). During attempts to recrystallize L-proline itself to obtain suitable crystals for a charge density determination, we obtained a monoclinic modification which previously has been mentioned by Sasisekharan (1959). Therefore, we determined the crystal structure and present here the full structural details of this modification.



(I)

At room temperature [a = 20.553 (5), b = 6.304 (2), c = 5.164 (2) Å and β = 93.61 (3)], the C4 atom (see Fig. 1) has unusually large vibrational amplitudes in the direction perpendicular to the pyrrolidine ring plane; therefore, this crystal was measured again at a lower temperature of 100 (2) K. A similar behaviour for the C^γ atom can be found in DL-proline hydrochloride (Mitsui, Tsuboi & Iitaka, 1969) and in some oligopeptides containing L-proline (Leung & Marsh, 1958; Ukei *et al.*, 1969). At low temperature, the anisotropic displacement parameters for the C4 atom are comparable with those of the other atoms. Geometric details of the room and low temperature analyses do not differ significantly so the following discussion of results can be based on the low-temperature data only.

The conformation of the pyrrolidine ring in the L-proline molecule (Fig. 1) may be described, in a similar manner to the ring in the crystal structure of DL-proline monohydrate (Padmanabhan, Suresh & Vijayan, 1995), as C_2–C^γ-*exo*–C^δ-*endo* or C_s–C^γ-*exo* or C_s–C^δ-*endo* (IUPAC–IUB Commission on Biochemical Nomenclature, 1970; Balasubramanian *et al.*, 1971;

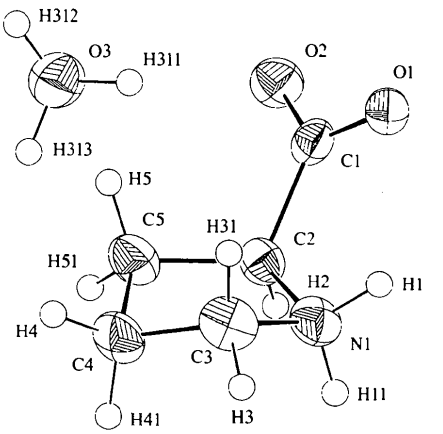


Fig. 1. *ORTEP*II (Johnson, 1971) drawing showing the molecular structure of the title compound and the crystallographic numbering scheme (50% probability displacement ellipsoids). The H312 and H313 atoms have an occupation factor of 0.5.

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Ashida & Kakudo, 1974; Nair & Vijayan, 1981). According to this classification, for comparision, the conformation of the pyrrolidine ring in the crystals of L-proline can be described as C_2–C^γ-*endo* (Kayushina & Vainshtein, 1966), in L-hydroxyproline (Donohue & Trueblood, 1952) and DL-proline hydrochloride (Mitsui, Tsuboi & Iitaka, 1969) as C_s–C^α-*exo*, in the dipeptide of L-Pro–L-Pro as C_2–C^γ-*exo* for Pro(1) and C_2–C^β-*exo* for Pro(2) (Aubry, Vitoux & Marraud, 1985), in the dipeptide L-Pro–L-Pro monohydrate as C_2–C^α-*endo* and C_2–C^β-*exo* (Panneerselvam & Chacko, 1989), and in the tripeptide of proline as C_s–C^γ-*exo*, C_2–C^β-*exo* and C_2–C^γ-*endo* (Bavoso *et al.*, 1982).

The carboxyl group (C1, O1 and O2) is almost symmetrical with respect to the C—O bond lengths, confirming, together with the rather long N—C bond lengths and the presence of two H atoms at the N1 atom, the expected zwitterionic form. The C2, C1, O1, O2 group is planar, the N1 atom being displaced by 0.028 (6) Å from this plane. The pyrrolidine ring fragment C2, C3, C5, N1 is nearly planar [mean deviation 0.077 (12) Å] and the ring C4 atom (C^γ) is in a *trans* position with respect to the carboxyl group, in contrast to the crystal structure of L-proline (Kayushina & Vainshtein, 1966) in which the C^γ atom is in a *cis* position.

In the crystal structure of the title compound (Fig. 2), the molecules of L-proline form molecular columns along the *c* axis, stabilized by an intermolecular hydrogen bond; N1—H11···O1(x, y, $z-1$) with N···O 2.723 (4) Å. In addition to this intermolecular hydrogen bond, an intramolecular hydrogen bond exists between the O1 and H1 atoms. The water molecules are interconnected by hydrogen bonds, forming zigzag chains. These chains of water molecules occupy the channels between the columns of L-proline molecules. One of the water H atoms statistically occupies two positions. These water chains interconnect two neighbouring L-proline molecular columns. Weaker N1—H1···O1($\frac{1}{2}-x$, $\frac{1}{2}+y$, $1-z$) hydrogen bonds [N···O 3.243 (5) Å] also exist. These weaker forces interconnect the double molecular columns to form a three-dimensional network.

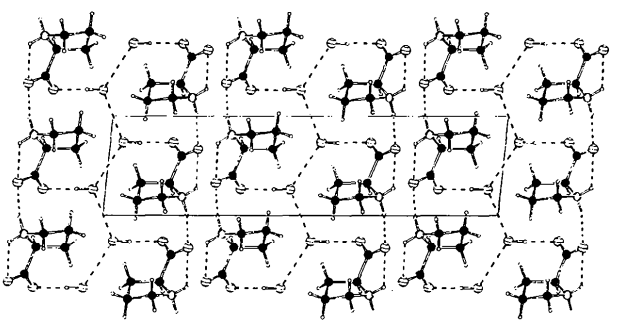

Fig. 2. The crystal structure as viewed along the *b* axis, with the *a* axis horizontal and the *c* axis vertical (*SCHAKAL92*; Keller, 1992). The disordered H atom has been omitted for clarity.

Experimental

The sample of L-proline was obtained from the Sigma Chemical Company and crystals of the monohydrate were grown by slow evaporation of a solution in 98% ethanol at room temperature.

Crystal data

$C_5H_9NO_2.H_2O$
M_r = 133.15
Monoclinic
*C*2
a = 20.431 (4) Å
b = 6.192 (1) Å
c = 5.136 (1) Å
β = 95.79 (2)°
V = 646.4 (2) Å^3
Z = 4
D_x = 1.368 Mg m^{-3}
D_m = 1.340 Mg m^{-3}
D_m measured by floation in benzene/carbon tetrachloride
Cu $K\alpha$ radiation
λ = 1.54179 Å
Cell parameters from 25 reflections
θ = 20–30°
μ = 0.954 mm^{-1}
T = 100 (2) K
Prism
0.37 × 0.28 × 0.23 mm
Colourless

Data collection

Stoe AED diffractometer
ω–2θ scans
Absorption correction: Gaussian (Hall & Stewart, 1990)
T_{min} = 0.753, T_{max} = 0.821
1012 measured reflections
945 independent reflections
945 reflections with $F > 2\sigma(F)$
R_{int} = 0.017
θ_{max} = 60.0°
$h = -22 \rightarrow 22$
$k = -6 \rightarrow 6$
$l = 0 \rightarrow 5$
3 standard reflections
frequency: 90 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.084
S = 1.207
945 reflections
83 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.2792P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.071
$\Delta\rho_{max}$ = 0.196 e Å^{-3}
$\Delta\rho_{min}$ = −0.122 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 7.2 (2) × 10^3
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.0 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.27712 (13)	0.3471 (5)	0.6677 (5)	0.0407 (8)
O2	0.34177 (13)	0.0596 (4)	0.7329 (5)	0.0366 (8)
N1	0.3059 (2)	0.4248 (6)	0.1884 (6)	0.0340 (8)
C1	0.3177 (2)	0.2107 (6)	0.5983 (7)	0.0301 (9)
C2	0.3395 (2)	0.2395 (7)	0.3262 (7)	0.0298 (9)
C3	0.3552 (2)	0.6047 (7)	0.1820 (9)	0.0459 (12)
C4	0.4167 (2)	0.4816 (7)	0.1499 (8)	0.0410 (11)
C5	0.4127 (2)	0.2895 (7)	0.3289 (8)	0.0398 (11)
O3	0.46711 (14)	−0.1299 (5)	0.7375 (5)	0.0458 (9)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.260 (5)	C1—C2	1.520 (5)
O2—C1	1.236 (5)	C2—C5	1.526 (6)
N1—C2	1.480 (5)	C3—C4	1.494 (7)
N1—C3	1.504 (6)	C4—C5	1.510 (6)
C2—N1—C3	107.8 (3)	N1—C2—C5	104.7 (3)
O2—C1—O1	125.9 (4)	C1—C2—C5	113.2 (3)
O2—C1—C2	117.8 (4)	C4—C3—N1	101.4 (3)
O1—C1—C2	116.4 (3)	C3—C4—C5	103.7 (3)
N1—C2—C1	111.4 (3)	C4—C5—C2	105.5 (4)
C3—N1—C2—C1	106.7 (3)	C2—N1—C3—C4	35.7 (4)
C3—N1—C2—C5	−16.1 (4)	N1—C3—C4—C5	−40.8 (4)
O2—C1—C2—N1	179.3 (3)	C3—C4—C5—C2	32.0 (4)
O1—C1—C2—N1	−1.9 (4)	N1—C2—C5—C4	−9.8 (4)
O2—C1—C2—C5	−63.0 (5)	C1—C2—C5—C4	−131.4 (3)
O1—C1—C2—C5	115.8 (4)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O1^{i}	0.900	1.841	2.723 (4)	165.7 (2)
N1—H1···O1	0.900	2.153	2.632 (4)	112.5 (2)
O3—H311···O2	0.996	1.833	2.815 (4)	168.3 (2)
O3—H312···O3^{ii}	0.886	2.158	2.889 (5)	139.4 (3)
O3—H313···O3^{iii}	0.902	2.035	2.902 (6)	160.7 (2)
N1—H1···O3^{iv}	0.900	2.581	3.243 (5)	130.9 (2)

Symmetry codes: (i) $x, y, z-1$; (ii) $1-x, y, 2-z$; (iii) $1-x, y, 1-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$.

All H atoms were located in difference Fourier maps and were not refined.

Data collection: Stoe AED diffractometer software. Cell refinement: Stoe AED diffractometer software. Data reduction: Stoe AED diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971) and *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1239). Services for accessing these data are described at the back of the journal.

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An Extended Imide Containing Two Methylene Meldrum's Acid Units

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Abstract

We report the crystal structure of the unusual imide 5,5′-(iminodimethylidene)bis(2,2-dimethyl-1,3-dioxane-4,6-dione), $C_{14}H_{15}NO_8$, which contains two Meldrum's acid (dioxanedione) substituents. The geometry of the imide moiety shows the effects of delocalization of the N-atom

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