Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis(L-proline) hydrogen nitrate

S. Pandiarajan,[a] B. Sridhar[b] and R. K. Rajaram[b]*

[a]Department of Physics, Devanga Arts College, Aruppukottai 626 101, India, and [b]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: sshiya@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.047
wR factor = 0.121
Data-to-parameter ratio = 7.7

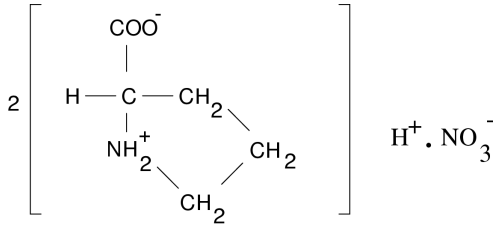
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 2 July 2002
Accepted 10 July 2002
Online 19 July 2002

In the title compound, $2C_5H_9NO_2\cdot H^+\cdot NO_3^-$, the two proline residues are linked by a strong O—H···O hydrogen bond, with an O···O distance of 2.414 (3) Å. In one of the residues, the pyrrolidine ring adopts an envelope conformation, while in the other it adopts a half-chair conformation. N—H···O hydrogen bonds link the two residues to form double-chain structures down the *a* axis, which are interlinked by N—H···O hydrogen bonds involving the O atoms of the nitrate ions.

Comment

In proline (2-pyrrolidinecarboxylate), the α-amino group is not free but is substituted by a portion of its *R* group to yield a cyclic structure; thus, this imino acid has a unique conformation. Proline, with the help of vitamin C, is essential in the manufacture of collagen. It enhances skin texture and strengthens body joints, tendon and heart muscle. The crystal structures of L-proline monohydrate (Kayushina & Vainshtein, 1965; Verbist *et al.*, 1972; Janczak & Luger, 1997), DL-proline hydrochloride (Mitsui *et al.*, 1969), DL-homoproline tetrahydrate (Bhattacharjee & Chacko, 1979), DL-proline monohydrate (Padmanabhan *et al.*, 1995) and bis(L-proline) hydrogen(1+) perchlorate (Pandiarajan *et al.*, 2002) have been reported. In the present study, the crystal structure determination of L-proline reacted with nitric acid was undertaken to study the effect of the inorganic acid on the conformation of the proline molecule and the hydrogen-bonding scheme.



(I)

The asymmetric unit of (I) contains two crystallographically independent proline residues (*A* and *B*) and hydrogen nitrate. The conformation angles ψ^1 for the proline residues are −8.3 (4) and −10.0 (5)°. The conformation angles χ^1, χ^2, χ^3, χ^4 and θ of the pyrrolidine ring for residues *A*/*B* are −41.6 (3)/−30.2 (4), 39.7 (3)/36.8 (5), −23.9 (4)/−27.7 (5), −2.1 (3)/8.0 (5) and 27.0 (3)/14.3 (4)°, respectively (Prasad & Vijayan, 1993). The conformation of the pyrrolidine ring, in general, is intermediate between half-chair and envelope (Prasad & Vijayan, 1993; Padmanabhan *et al.*, 1995). In the present structure, the pyrrolidine ring in residue *A* adopts an envelope conformation [q_2 = 0.411 (4) Å and φ_2 = 249.7 (5)°], while in

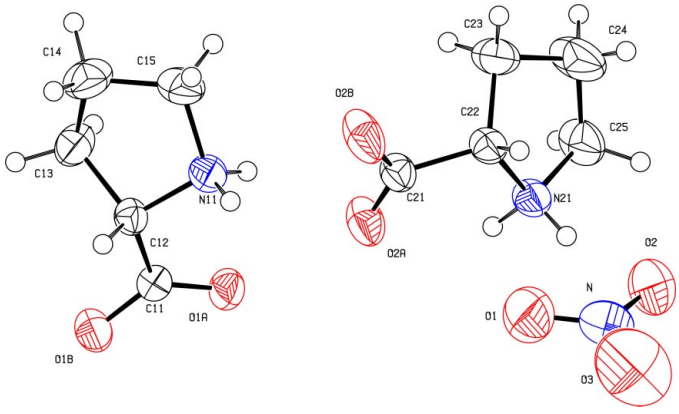


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

residue *B* it adopts a half-chair conformation [q_2 = 0.342 (4) Å and φ_2 = 264.5 (6)°] (Cremer & Pople, 1975; Nardelli, 1983).

The H atom liberated from the nitric acid links the two residues by a strong hydrogen bond [O2*B*—H2*B*···O1*B*^{i} 2.414 (3) Å; symmetry code: (i) *x*−1, *y*, *z*]. These pairs are also linked by strong N—H···O hydrogen bonds (N21—H21*B*···O1*B*) to form an infinite one-dimensional chain along the *a* direction. The symmetry-related chains are interlinked by three-centred N—H···O hydrogen bonds [N11—H11*B*···O1*A*^{iii} and N11—H11*B*···O2*A*^{iv}; symmetry codes: (iii) *x*−1/2, −*y*−1/2, 1−*z*; (iv) 1/2+*x*, −*y*−1/2, 1−*z*] to form double chains along the *a* axis. In the crystal, these double-chain structures are interlinked by N—H···O hydrogen bonds involving the nitrate O atoms. A zigzag (*Z*1) head-to-tail sequence involving residue *A* is observed. An intramolecular N—H···O hydrogen bond is present in residue *B*, as found in L-proline monohydrate at 100 K (Janczak & Luger, 1997).

Experimental

The title compound, (I), was crystallized at room temperature by slow evaporation of an aqueous solution of L-proline and nitric acid in a stoichiometric ratio of 2:1.

Crystal data

$2C_5H_9NO_2{\cdot}H^+{\cdot}NO_3^-$
M_r = 293.28
Orthorhombic, $P2_12_12_1$
a = 7.2006 (6) Å
b = 7.711 (1) Å
c = 24.060 (3) Å
V = 1335.9 (3) Å^3
Z = 4
D_x = 1.458 Mg m^{-3}
D_m = 1.454 Mg m^{-3}
D_m measured by flotation method in a mixture of carbon tetrachloride and xylene
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 11.3–13.9°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, colourless
0.5 × 0.5 × 0.5 mm

Data collection

Enraf–Nonis CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.916, T_{max} = 0.937
3718 measured reflections
1430 independent reflections
1276 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 25.5°
h = −1 → 8
k = −1 → 9
l = −29 → 29
3 standard reflections
frequency: 60 min
intensity decay: none

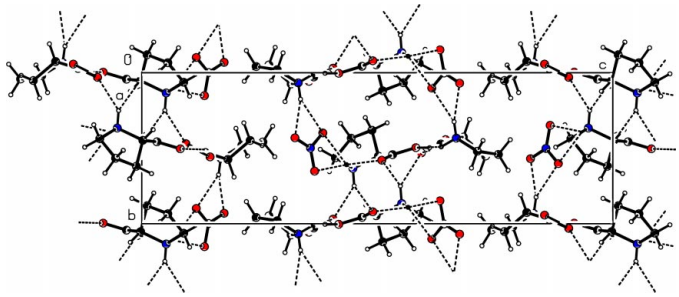


Figure 2
Packing of the molecules, viewed down the *a* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.121
S = 1.16
1430 reflections
186 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.319P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.102 (9)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.216 (3)	O2*A*—C21	1.188 (4)
O1*B*—C11	1.250 (3)	O2*B*—C21	1.282 (4)
O1*A*—C11—C12—N11	−8.3 (4)	O2*A*—C21—C22—N21	−10.0 (5)
C13—C12—N11—C15	27.0 (3)	C23—C22—N21—C25	14.3 (4)
N11—C12—C13—C14	−41.6 (3)	N21—C22—C23—C24	−30.2 (4)
C12—C13—C14—C15	39.7 (3)	C22—C23—C24—C25	36.8 (5)
C12—N11—C15—C14	−2.1 (3)	C23—C24—C25—N21	−27.7 (5)
C13—C14—C15—N11	−23.9 (4)	C22—N21—C25—C24	8.0 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*B*—H2*B*···O1*B*^{i}	1.11 (6)	1.40 (6)	2.414 (3)	148 (5)
N11—H11*A*···O1^{ii}	0.90	2.30	3.045 (4)	141
N11—H11*A*···O3^{ii}	0.90	2.42	3.231 (6)	151
N11—H11*B*···O1*A*^{iii}	0.90	2.12	2.825 (3)	135
N11—H11*B*···O2*A*^{iv}	0.90	2.25	2.932 (3)	132
N21—H21*B*···O2*A*	0.90	2.22	2.676 (3)	111
N21—H21*B*···O1*B*	0.90	2.14	2.792 (3)	128
N21—H21*A*···O2	0.90	2.01	2.879 (5)	161
N21—H21*A*···O1	0.90	2.39	2.982 (4)	124

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

The H atom linking the two proline residues was located and refined isotropically. All other H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation, with U_{iso} equal to 1.2U_{eq} of the carrier atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

BS and RKR thank the Department of Science and Technology (DST), Government of India, for financial support. One of the authors (SPR) thanks the management of Devanga Arts College, Aruppukottai, India, for permitting him to pursue his doctoral research work.

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