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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$ 

Disorder in main residue

R factor = 0.051

wR factor = 0.145

Data-to-parameter ratio = 7.0

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

## Bis(L-proline) hydrogen(1+) perchlorate

In the title compound,  $2\text{C}_5\text{H}_9\text{NO}_2 \cdot \text{H}^+ \cdot \text{ClO}_4^-$ , two proline residues are linked by a strong  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bond with an  $\text{O} \cdots \text{O}$  distance of  $2.474(6) \text{ \AA}$ . Conformational disorder is observed in the pyrrolidine rings of the two proline residues. In one of the residues, both the major and minor conformers adopt conformations intermediate between half-chair and envelope, whereas in the other residue, they adopt envelope conformations. The crystal structure is stabilized by a number of  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds.

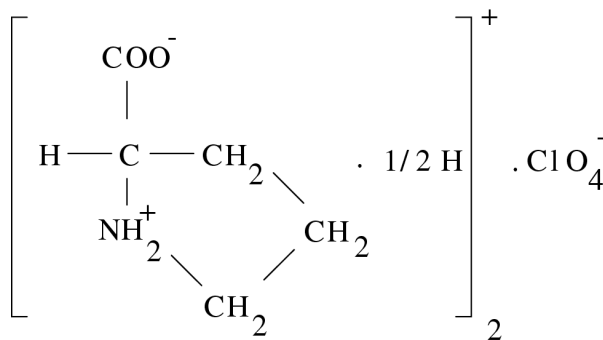
Received 29 August 2001

Accepted 11 December 2001

Online 22 December 2001

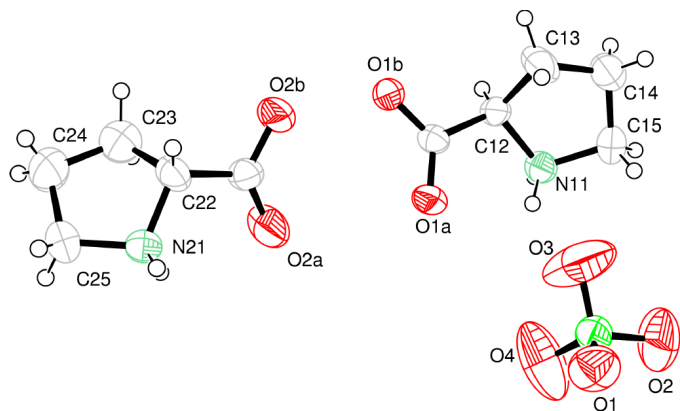
## Comment

Proline is a very important amino acid due to its unique conformation, which may affect the structure of proteins, in particular, collagen. The crystal structures of L-proline monohydrate (Kayushina & Vainshtein, 1965), DL-proline hydrochloride (Mitsui *et al.*, 1969), DL-homoproline tetrahydrate (Bhattacharjee & Chacko, 1979) and DL-proline monohydrate (Padmanabhan *et al.*, 1995) have been reported. The crystal structure determination of L-proline with perchloric acid was undertaken to study the effect of the inorganic acid on the conformation of the proline residue.



(I)

The asymmetric unit of the title compound, (I), consists of two crystallographically independent proline residues *A* and *B*, a  $\text{H}^+$  cation and a  $\text{ClO}_4^-$  ion. The conformation angles  $\psi^1$  for *A* and *B* are  $3.9(6)$  and  $7.8(9)^\circ$ , respectively. The twisting of the carboxyl plane away from the C–N bond is observed in various amino acids (Lakshminarayanan *et al.*, 1967). The conformation angles  $\chi^1$ ,  $\chi^2$ ,  $\chi^3$ ,  $\chi^4$  and  $\theta$  of the pyrrolidine ring for both *A* and *B*, respectively, are  $33.3(8)$  and  $40.7(10)$ ,  $-37.6(10)$  and  $-31.8(11)$ ,  $26.8(10)$  and  $10.0(10)$ ,  $-6.1(8)$  and  $16.8(9)$ , and  $-16.6(7)$  and  $-35.5(8)^\circ$  (Prasad & Vijayan, 1993).



**Figure 1**

The molecular structure of (I) showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976). For clarity, only the major conformers (76 and 72%) of the pyrrolidine rings are shown.

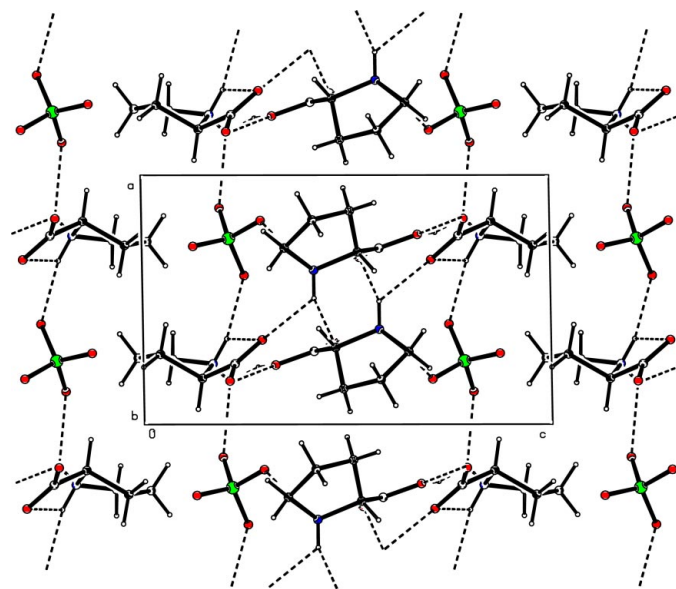
The conformation of the pyrrolidine ring, in general, is intermediate between half-chair and envelope (Prasad & Vijayan, 1993; Padmanabhan *et al.*, 1995). In the present case, the C<sup>γ</sup> atom of residue A and C<sup>β</sup> of residue B are disordered. Both the major and minor conformers of the pyrrolidine ring adopt conformations intermediate between half-chair and envelope in residue A, whereas in residue B they adopt half-chair conformations (Cremer & Pople, 1975; Nardelli, 1983).

The two proline residues in the asymmetric unit are linked through a strong O—H...O hydrogen bond [2.474 (6) Å]. The equality of the C—O distances within experimental error [1.219 (7) and 1.184 (7), and 1.283 (6) and 1.280 (8) Å] indicates that atom H2B is equally shared by residues A and B. Hence, this hydrogen bond may be termed a symmetric hydrogen bond. The O2B—H2B and O1B—H2B distances are 1.23 (10) and 1.34 (11) Å, respectively. This symmetrically hydrogen-bonded proline dimer is positively charged, as found in L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997) and L-lysine L-lysinium dichloride nitrate (Srinivasan *et al.*, 2001).

The perchlorate anion forms hydrogen bonds with the amino N atoms of both proline residues (Table 2). An intramolecular hydrogen bond, N11—H11A...O1A, is observed in residue A. The N atoms of both A and B are involved in three-centred hydrogen bonds with O atoms of the carboxyl groups and the perchlorate anion. Residues A and B are engaged in a head-to-tail sequence, since the N11—H11A...O1A(−x + 1, y + 1/2, −z + 1) (Z1 sequence), N11—H11A...O2A(−x + 1, y + 1/2, −z + 1) (as a three-centred hydrogen bond) and N21—H21A...O1B(x, y − 1, z) hydrogen bonds connect them (Vijayan, 1988).

## Experimental

The title compound was crystallized by slow evaporation from an aqueous solution of L-proline and perchloric acid in a 2:1 stoichiometric ratio.



**Figure 2**

Packing of the molecules viewed down the *b* axis (for clarity, only the major conformers of the pyrrolidine rings are shown).

## Crystal data

$2C_5H_9NO_2 \cdot H^+ \cdot ClO_4^-$   
 $M_r = 330.72$   
 Monoclinic,  $P2_1$   
 $a = 7.848$  (6) Å  
 $b = 7.3951$  (14) Å  
 $c = 12.834$  (5) Å  
 $\beta = 90.95$  (4)°  
 $V = 744.7$  (5) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 1.475$  Mg m<sup>−3</sup>  
 $D_m = 1.472$  Mg m<sup>−3</sup>

$D_m$  measured by flotation in a mixture of carbon tetrachloride and xylene  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 8.3$ – $11.6^\circ$   
 $\mu = 0.30$  mm<sup>−1</sup>  
 $T = 293$  (2) K  
 Needle, colorless  
 $0.5 \times 0.3 \times 0.2$  mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ – $2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.899$ ,  $T_{\max} = 0.942$   
 1528 measured reflections  
 1420 independent reflections  
 1181 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.009$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = 0 \rightarrow 9$   
 $k = 0 \rightarrow 8$   
 $l = -15 \rightarrow 15$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.145$   
 $S = 1.12$   
 1420 reflections  
 204 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.4916P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.29$  e Å<sup>−3</sup>  
 $\Delta\rho_{\text{min}} = -0.29$  e Å<sup>−3</sup>  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.07 (17)

**Table 1**

Selected geometric parameters (Å, °).

O1A—C11	1.219 (7)	O2A—C21	1.184 (7)
O1B—C11	1.283 (6)	O2B—C21	1.280 (8)
O1A—C11—C12—N11	3.9 (6)	O2A—C21—C22—N21	7.8 (9)
N11—C12—C13—C14	33.3 (8)	N21—C22—C23—C24	40.7 (10)
C12—C13—C14—C15	−37.6 (10)	C22—C23—C24—C25	−31.8 (11)
C13—C14—C15—N11	26.8 (10)	C23—C24—C25—N21	10.0 (10)
C14—C15—N11—C12	−6.1 (8)	C23—C22—N21—C25	−35.5 (8)
C13—C12—N11—C15	−16.6 (7)	C24—C25—N21—C22	16.8 (9)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2B—H2B...O1B	1.23 (10)	1.34 (11)	2.474 (6)	149 (8)
N11—H11B...O1A <sup>i</sup>	0.90	2.02	2.795 (6)	143
N11—H11B...O2A <sup>i</sup>	0.90	2.32	2.851 (7)	117
N11—H11A...O1A	0.90	2.19	2.645 (6)	110
N11—H11A...O3	0.90	2.35	3.083 (9)	139
N21—H21A...O1B <sup>ii</sup>	0.90	2.18	2.766 (6)	123
N21—H21A...O1 <sup>iii</sup>	0.90	2.41	3.108 (8)	134
N21—H21B...O4 <sup>iv</sup>	0.90	2.15	3.000 (9)	158

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

Atoms C14 and C23 were found to be disordered, suggesting conformational disorder in the pyrrolidine rings of both proline residues. The population of the major conformation was found to be 0.76 (2) for proline residue *A* and 0.72 (2) for residue *B*. The corresponding C—C distances in the major and minor conformers were restrained to be equal, with an effective standard deviation of 0.01 Å. Due to a large ADP max/min ratio, the disordered positions C23 and C23' were isotropically refined. Atom H2B was located in a difference Fourier map and refined isotropically; all other H atoms were geometrically fixed and allowed to ride on their attached atoms. Since the crystal belongs to a non-centrosymmetric space group and the diffracted intensities are rather low, the data-to-parameter ratio (7.00) is poor.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

BS and RKR thank the Department of Science and Technology (DST), Government of India, for financial support. SPR thanks the University Grants Commission, New Delhi, and the management of Devanga Arts College, Aruppukottai, India, for permitting him to pursue his doctoral research work under the Faculty Improvement Programme.

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