

L-Prolinium trichloroacetate at 105 K

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.026
wR factor = 0.069
Data-to-parameter ratio = 24.6

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

In the title compound, $\text{C}_5\text{H}_{10}\text{NO}_2^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^-$, the proline molecule exists as a cation with a positively charged amino group and a neutral carboxylic acid group. The trichloroacetic acid molecule is in the anionic state. The 3_1 -screw-related proline cations and trichloroacetate anions are linked by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to form molecular columns along the *c* axis. No head-to-tail hydrogen bonds are observed.

Comment

Systematic X-ray crystallographic investigations on the complexes of amino acids with carboxylic acids, being pursued in our laboratory, are aimed at providing useful information regarding the nature of intermolecular interactions involving the two distinct chemical species. Interestingly, amino acids and carboxylic acids form proton-transfer complexes and hence the ionization states and stoichiometry of individual molecules and their effect on aggregation patterns are of immense interest. The present study reports the crystal structure of a complex of L-proline with trichloroacetic acid, (I). While L-proline, an α -imino acid, is known to disrupt the α -helix in a protein, trichloroacetic acid possesses a variety of potential medicinal applications. The crystal structure of a complex of a dipeptide with trichloroacetic acid, namely L-phenylalanylglycine trichloroacetate (Mitra & Subramanian, 1993), has already been reported. Recently, the crystal structures of L-prolinium tartrate (Subha Nandhini *et al.*, 2001), DL-valinium trichloroacetate (Rajagopal *et al.*, 2002) and DL-methioninium trichloroacetate (Rajagopal *et al.*, 2003) have also been reported. It is interesting to note that the crystal structure of pure trichloroacetic acid is still unknown.

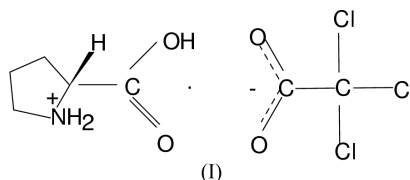


Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The proline molecule in (I) exists in the cationic form, with a positively charged amino group and a neutral carboxylic acid group. The trichloroacetic acid is in the anionic state. The conformation angles χ^1 , χ^2 , χ^3 , χ^4 and θ of the pyrrolidine ring are 38.0 (1), -35.3 (1), 19.2 (1), 4.6 (5) and -26.6 (2) $^\circ$, respectively. The corresponding values of two independent molecules of bis(L-proline)hydrogen nitrate (Pandiarajan *et al.*, 2002) are -41.6 (3)/ -30.2 (4), 39.7 (3)/

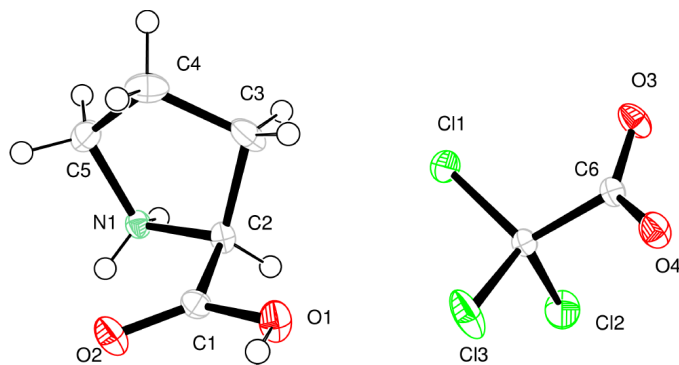


Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

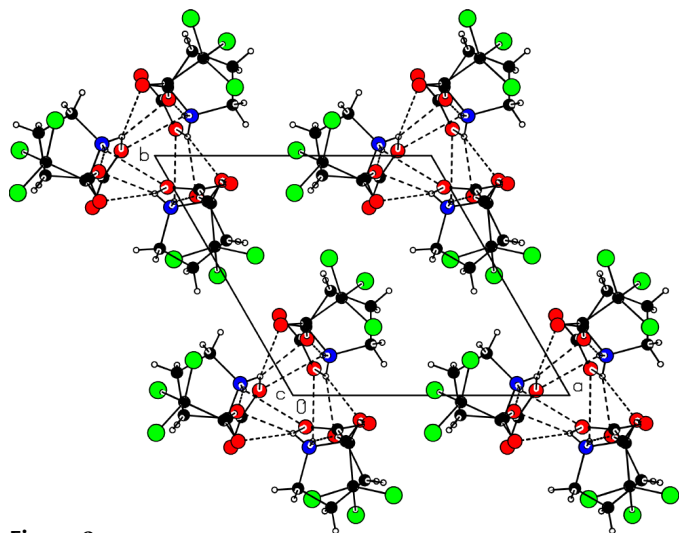


Figure 2
The packing of (I), viewed down the *c* axis.

36.8 (5), -23.9 (4)/ -27.7 (5), -2.1 (3)/ 8.0 (5) and 27.0 (3)/ 14.3 (4)°. In the case of DL-proline hemisuccinic acid (Prasad & Vijayan, 1993), these values are 11.4 (4), -33.2 (4), 42.0 (4), -34.9 (3) and 15.3 (3)°, respectively. The pyrrolidine ring adopts an envelope conformation. This is supported by both the puckering parameters (Cremer & Pople, 1975) $q_2 = 0.376$ (2) Å and $\varphi_2 = 66.0$ (2)°, and the deviation of C3 by 0.589 (1) Å from the N1/C2/C4/C5 mean plane. Interestingly, the pyrrolidine ring adopts a conformation intermediate between an envelope and a half-chair in L-proline monohydrate (Janczak & Luger, 1997), DL-proline monohydrate (Padmanabhan *et al.*, 1995) and DL-proline hemisuccinic acid (Prasad & Vijayan, 1993). In several other crystal structures containing proline, atom C4 exhibits higher displacement parameters, and in the case of L-prolinium tartrate, it is associated with a positional disorder. However, no such feature has been observed in the present case, possibly due to the fact that the study has been carried out at low temperature.

The packing of (I), viewed down the *c* axis, is shown in Fig. 2. The 3_1 -screw-related proline cations and trichloroacetate anions are linked by N—H···O and O—H···O hydrogen bonds to form molecular columns along the *c* axis (Table 2 and Fig. 2). No hydrogen bonds are observed between the ions of

adjacent columns, but they are interlinked through $\text{Cl2} \cdots \text{Cl3}(-y, x - y + 1, z + 1/3)$ short contacts [3.257 (1) Å]. The aggregation pattern is distinctly different from that found in L-prolinium tartrate. Strikingly, in the present structure and in L-prolinium tartrate, no head-to-tail hydrogen bonds are observed; in the case of DL-proline hemisuccinic acid, two DL-type head-to-tail sequences were observed. It is interesting to note that (I) crystallizes in the trigonal system with space group $P3_1$, which is quite unusual in complexes of amino acids with carboxylic acids.

Experimental

Colourless prismatic single crystals of (I) were grown from a saturated aqueous solution containing L-proline and trichloroacetic acid in a stoichiometric ratio of 1:1.

Crystal data

$\text{C}_5\text{H}_{10}\text{NO}_2^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^-$
 $M_r = 278.51$
 Trigonal, $P3_1$
 $a = 9.7541$ (14) Å
 $c = 10.089$ (2) Å
 $V = 831.3$ (2) Å³
 $Z = 3$
 $D_x = 1.669$ Mg m⁻³
 $D_m = 1.65$ Mg m⁻³

D_m , measured by flotation in a mixture of xylene and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 1024 reflections
 $\theta = 3\text{--}35^\circ$
 $\mu = 0.82$ mm⁻¹
 $T = 105$ (2) K
 Prism, colourless
 $0.5 \times 0.4 \times 0.3$ mm

Data collection

Bruker SMART diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.664$, $T_{\max} = 0.782$
 13374 measured reflections
 4363 independent reflections

4258 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 35.0^\circ$
 $h = -14 \rightarrow 15$
 $k = -15 \rightarrow 15$
 $l = -15 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.069$
 $S = 1.02$
 4363 reflections
 177 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.1873P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.008 (2)
 Absolute structure: Flack (1983), 1915 Friedel pairs
 Flack parameter = 0.00 (3)

Table 1

Selected geometric parameters (Å, °).

Cl1—C7	1.7689 (12)	O2—C1	1.2118 (14)
Cl2—C7	1.7764 (12)	O3—C6	1.2491 (14)
Cl3—C7	1.7674 (11)	O4—C6	1.2402 (14)
O1—C1	1.3171 (14)		
O2—C1—O1	126.00 (10)	O1—C1—C2	111.12 (9)
O2—C1—C2	122.85 (10)		
C5—N1—C2—C1	91.81 (11)	N1—C2—C3—C4	37.96 (11)
C5—N1—C2—C3	-26.62 (11)	C1—C2—C3—C4	-78.91 (11)
O2—C1—C2—N1	-2.43 (15)	C2—C3—C4—C5	-35.30 (13)
O1—C1—C2—N1	179.46 (9)	C2—N1—C5—C4	4.64 (13)
O2—C1—C2—C3	111.19 (13)	C3—C4—C5—N1	19.21 (13)
O1—C1—C2—C3	-66.92 (13)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1N \cdots O4^i$	0.79 (2)	2.15 (2)	2.8987 (14)	159 (2)
$O1-H1O \cdots O3^{ii}$	0.89 (3)	1.69 (3)	2.5775 (13)	175 (3)
$N1-H2N \cdots O4^{iii}$	0.87 (2)	2.06 (2)	2.9043 (14)	164 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $1-y, 1+x-y, z-\frac{2}{3}$; (iii) $1-y, 1+x-y, \frac{1}{3}+z$.

All H atoms were located in a difference Fourier map and were included in the refinement with isotropic displacement parameters. The ranges of C—H and N—H bond lengths are 0.92 (2)–1.05 (3) and 0.79 (2)–0.87 (2) Å, respectively, and the O—H distance is 0.89 (3) Å.

Data collection: *SMART-NT* (Bruker, 1999); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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