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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$
Disorder in main residue
R factor = 0.038
wR factor = 0.116
Data-to-parameter ratio = 9.7

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

L-Phenylalaninium trichloroacetate hemihydrate

In the title compound, $\text{C}_9\text{H}_{12}\text{NO}_2^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^- \cdot \frac{1}{2}\text{H}_2\text{O}$, the phenylalanine molecule exists as a cation with a positively charged amino group and a neutral carboxylic acid group. The trichloroacetic acid molecule is deprotonated as an anion and forms $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds with the phenylalaninium cations. Water molecules also mediate interactions with amino acid and trichloroacetate ions through $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. The aggregation pattern observed in the title salt has striking similarities with those observed in L-phenylalanine L-phenylalaninium formate and L-phenylalanine L-phenylalaninium perchlorate.

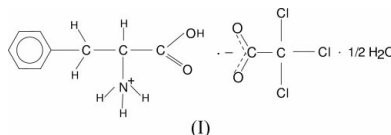
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Comment

Systematic investigations being pursued in our laboratory are concerned with the preparation and X-ray analysis of crystalline complexes involving amino acids with organic acids and inorganic salts. The results of these investigations will be useful in the understanding of ionization states, biomolecular interactions and characteristic aggregation patterns. The current focus of the programme is on complexes of amino acids with carboxylic acids, which are believed to have existed in the prebiotic milieu (Miller & Orgel, 1974). As a part of the proton-transfer study of the complexes of the type $A \cdot B$, where A is an amino acid and B is a halogenoacetic acid, the present study reports the crystal structure of the salt L-phenylalaninium trichloroacetate hemihydrate, (I).



Phenylalanine is an essential aromatic amino acid commonly found in proteins and plays a key role in the formation of a variety of physiologically important chemicals that transmit signals between nerve cells. It helps to increase memory and learning and has been used as an appetite suppressant. Trichloroacetic acid is a strong organic acid used in organic synthesis and is an excellent medicine for wrinkles formed in the skin. The crystal structure of trichloroacetic acid itself was determined only recently in our laboratory (Rajagopal, Mostad *et al.*, 2003). Previous studies on phenylalanine report only the unit-cell dimensions (Khawas & Murthy, 1968; Khawas, 1970, 1971, 1985) and the crystal structure of the D-form with a high R factor of 15% (Weissbuch *et al.*, 1990). The crystal structure L-phenylalanine, however, is yet to be reported. The crystal structure of a complex of a dipeptide

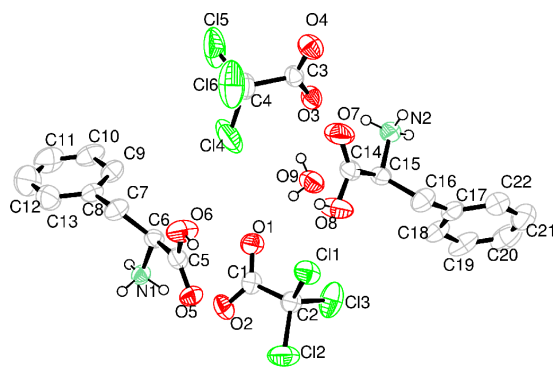


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. For clarity, only the major component of the disordered trichloroacetate ion is shown.

with trichloroacetic acid, L-phenylalanineglycinium trichloroacetate (Mitra & Subramanian, 1993) has already been reported. Recently, the crystal structures of DL-valinium trichloroacetate (Rajagopal *et al.*, 2002), DL-methionium trichloroacetate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2003), β -alaninium trichloroacetate (Rajagopal, Krishnakumar, Subha Nandhini *et al.*, 2003), L-phenylalanine L-phenylalaninium dihydrogenphosphate (Ravikumar *et al.*, 2002), L-phenylalaninium maleate (Alagar *et al.*, 2001), L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992) and L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997) have been reported.

The asymmetric unit of (I) comprises two crystallographically independent L-phenylalaninium cations, two trichloroacetate anions and a water molecule (Fig. 1 and Table 1). The conformation angles ψ^1 for the phenylalaninium cations are in agreement with the values reported for L-phenylalaninium maleate (Alagar *et al.*, 2001) and L-phenylalanine hydrochloride (Al-Karaghoulis & Koetzle, 1975). The branched-side-chain conformation angles χ^1 for the two cations correspond to the *gauche*-II form. They are different from those observed in L-phenylalanine L-phenylalaninium formate, where $\chi^1 = 72.3(4)$ and $70.8(4)^\circ$, respectively, for the zwitterion and cation, and in L-phenylalanine hydrochloride, where $\chi^1 = 60.7(6)^\circ$, indicating different side-chain conformations in different environments. The torsion angles χ^{21} and χ^{22} for both cations are distinctly different from those observed in L-phenylalanine hydrochloride [$84.2(7)$ and $-96.7(7)^\circ$]. The C—O distances of the carboxylic acid and carboxylate groups of (I) are in good agreement with the other similar carboxylic acid complexes, *viz.* DL-valinium trichloroacetate, DL-methionium trichloroacetate and L-phenylalaninium maleate.

The packing of molecules of (I) within the unit cell, viewed down the *b* axis, is shown in Fig. 2. The phenylalaninium cations and trichloroacetate anions form hydrogen-bonded double chains in which they alternate along the *a* axis and are held together by N—H \cdots O hydrogen bonds. The double

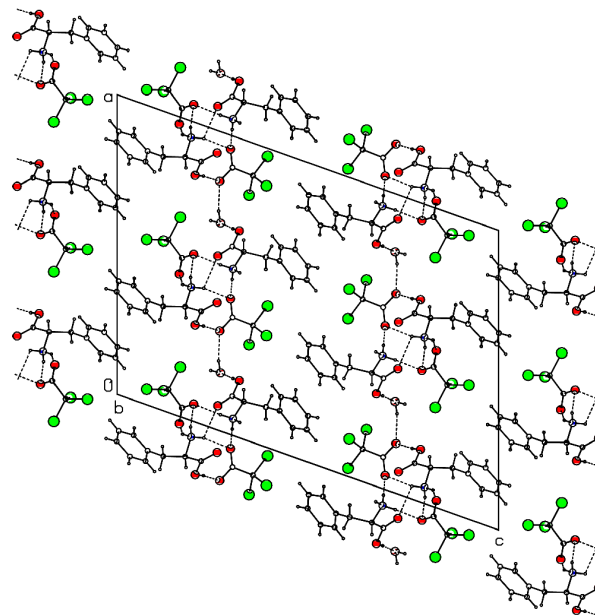


Figure 2

The molecular packing of (I), viewed down the *b* axis.

chain is flanked on either side by the hydrophobic side chains of phenylalanine, leading to alternating hydrophilic and hydrophobic zones along the *c* axis. These double chains are interconnected through O—H \cdots O and N—H \cdots O hydrogen bonds, to form two-dimensional networks parallel to the *ab* plane. Water molecules are also found to mediate hydrogen-bonded interactions with the cations and anions through O—H \cdots O hydrogen bonds (Table 2). A weak head-to-tail hydrogen bond between the symmetry-related phenylalaninium ions is present. A short Cl6 \cdots Cl9(*x*, *y* - 1, *z*) contact of 3.240(7) Å and Cl6 \cdots Cl12(*x*, *y* - 1, *z*) contact of 3.366(13) Å are also observed in the structure. The aggregation pattern observed in (I) has striking similarities to those observed in L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992), L-phenylalaninium maleate (Alagar *et al.*, 2001) and DL-phenylalaninium maleate (Alagar *et al.*, 2003).

Experimental

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

Crystal data

$C_9H_{12}NO_2^+ \cdot C_2Cl_3O_2^- \cdot \frac{1}{2}H_2O$
 $M_r = 337.76$
 Monoclinic, *C*2
 $a = 19.675(3)$ Å
 $b = 6.115(1)$ Å
 $c = 26.584(2)$ Å
 $\beta = 109.6(1)^\circ$
 $V = 3013(2)$ Å³
 $Z = 8$
 $D_x = 1.488$ Mg m⁻³
 $D_m = 1.50$ Mg m⁻³

D_m measured by flotation in a mixture of xylene and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 21 reflections
 $\theta = 20.5$ – 26.6°
 $\mu = 0.62$ mm⁻¹
 $T = 293(2)$ K
 Needle, colourless
 $0.50 \times 0.21 \times 0.15$ mm

Data collection

Rikagu AFC-5R diffractometer	$R_{\text{int}} = 0.013$
ω -2 θ scans	$\theta_{\text{max}} = 30.1^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 27$
$T_{\text{min}} = 0.855$, $T_{\text{max}} = 0.911$	$k = 0 \rightarrow 8$
4124 measured reflections	$l = -37 \rightarrow 32$
4030 independent reflections	3 standard reflections
2147 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 1.9550P]$
$R[F^2 > 2\sigma(F^2)] = 0.038$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.117$	$(\Delta/\sigma)_{\text{max}} < 0.002$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{\AA}^{-3}$
4030 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
416 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.251 (5)	O5—C5	1.210 (5)
O2—C1	1.230 (5)	O6—C5	1.300 (5)
O3—C3	1.242 (5)	O7—C14	1.194 (5)
O4—C3	1.225 (5)	O8—C14	1.294 (5)
O2—C1—C2	117.8 (4)	O5—C5—C6	121.8 (4)
O1—C1—C2	114.9 (3)	O6—C5—C6	113.0 (3)
O4—C3—C4	115.8 (4)	O7—C14—C15	122.9 (4)
O3—C3—C4	116.4 (3)	O8—C14—C15	112.2 (3)
O5—C5—C6—N1	17.1 (5)	O7—C14—C15—N2	-4.4 (6)
O6—C5—C6—N1	-163.8 (3)	O8—C14—C15—N2	173.8 (4)
N1—C6—C7—C8	-55.2 (5)	N2—C15—C16—C17	-65.2 (5)
C6—C7—C8—C13	127.5 (5)	C15—C16—C17—C18	-51.3 (6)
C6—C7—C8—C9	-55.3 (5)	C15—C16—C17—C22	134.9 (4)

Table 2
Hydrogen-bonding geometry (\AA , $^\circ$).

D—H...A	D—H	H...A	D...A	D—H...A
O6—H6...O1 ⁱ	0.82	1.83	2.642 (4)	172
O8—H8...O9 ^j	0.82	1.69	2.507 (5)	177
O9—H9A...O1	0.82 (4)	2.01 (3)	2.760 (4)	151 (6)
O9—H9A...C11	0.82 (4)	2.98 (5)	3.454 (5)	120 (4)
O9—H9B...O3	0.82 (4)	2.18 (6)	2.786 (5)	131 (7)
O9—H9B...C14	0.82 (4)	2.80 (8)	3.274 (6)	118 (7)
N1—H1A...O3 ⁱⁱ	0.89	2.09	2.971 (5)	172
N1—H1B...O2	0.89	2.12	2.984 (4)	163
N1—H1B...O7 ⁱⁱⁱ	0.89	2.40	2.869 (5)	113
N1—H1C...O4 ⁱⁱⁱ	0.89	2.02	2.814 (5)	147
N2—H2A...O2 ^{iv}	0.89	1.92	2.798 (5)	171
N2—H2B...O3	0.89	1.98	2.873 (4)	177

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

The H atoms of the phenylalaninium cations were placed at calculated positions and were allowed to ride on their respective parent atoms, with C—H = 0.96 (3)–0.98 (2) \AA , N—H = 0.84 (2)–0.90 (2) \AA and $U_{\text{iso}} = 0.05 \text{\AA}^2$. Water H atoms were located from a difference map and their positional and isotropic displacement parameters were refined, with the O—H distances restrained to

0.82 (3) \AA . A short H...H contact (2.05 \AA) involving one of these H atoms (H9B) and H8 is observed. In one of the trichloroacetate anions, the Cl atoms were found to have rotational disorder. It was modeled with three sets of three Cl atoms with the sum of their occupancies (0.559, 0.370 and 0.071, respectively) constrained to be equal to one. For the disordered trichloroacetate ion, the C—Cl bond distances and also the Cl...Cl distances were restrained to be equal. Intensities for nearly 400 reflections were not measured in the 2θ range 46–50 $^\circ$ and as a result the completeness of the data set is low (83.61%).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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