

## DL-Phenylalaninium trichloroacetate

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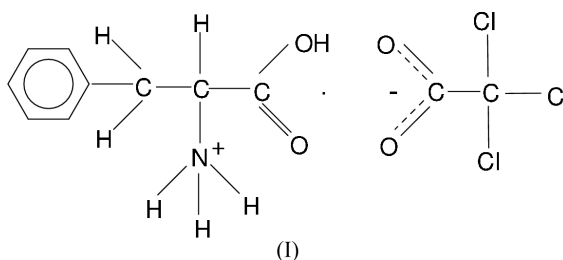
## Key indicators

Single-crystal X-ray study  
 $T = 273$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
 $R$  factor = 0.053  
 $wR$  factor = 0.154  
Data-to-parameter ratio = 14.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $\text{C}_9\text{H}_{12}\text{NO}_2^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^-$ , the amino acid molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The trichloroacetic acid molecule exists in the anionic state. The phenylalaninium cations and the trichloroacetate anions form hydrogen-bonded double chains, linked together by  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds, extending along the  $c$  axis.

## Comment

Phenylalanine, an essential amino acid commonly found in proteins, plays a key role in the formation of a variety of physiologically important chemicals that transmit signals between nerve cells. Interestingly, the crystal structures of the *L*- and racemic forms of phenylalanine remain unknown. However, the crystal structure of the *D*-form has been reported with a high  $R$  factor of 0.15 (Weissbuch *et al.*, 1990). Though phenylalanine is known to form innumerable complexes with inorganic acids, crystallographic data for their complexes with organic acids remain scarce.

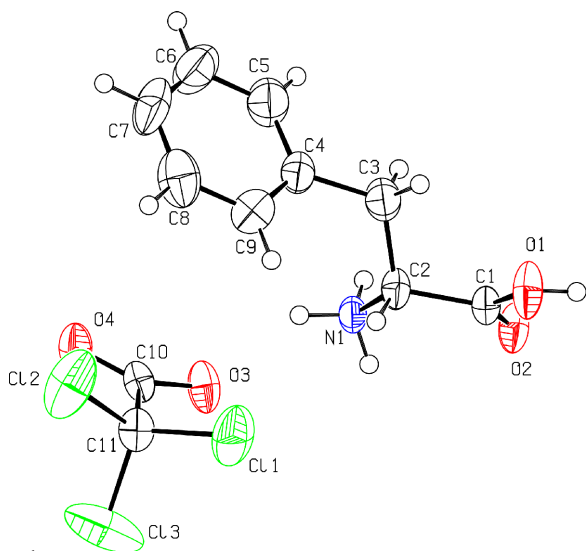


The present study, which reports the crystal structure of DL-phenylalaninium trichloroacetate, (I), is part of a series of X-ray investigations on proton transfer complexes of amino acids with trichloroacetic acid. The results of these investigations will be useful in the understanding of ionization states, biomolecular interactions and characteristic aggregation patterns. Recently, the crystal structures of DL-valinium trichloroacetate (Rajagopal *et al.*, 2002), DL-methioninium trichloroacetate (Rajagopal *et al.*, 2003a),  $\beta$ -alaninium trichloroacetate (Rajagopal, Krishnakumar, Subha Nandhini, Mostad & Natarajan, 2003), L-Proline trichloroacetate (Rajagopal *et al.*, 2003b), L-phenylalaninium trichloroacetate monohydrate (Rajagopal, Krishnakumar, Subha Nandhini, Cameron & Natarajan, 2003), DL-threoninium trichloroacetate (Rajagopal *et al.*, 2004), L-phenylalaninium maleate (Alagar *et al.*, 2001), DL-phenylalaninium maleate (Alagar *et al.*, 2003) and L-phenylalanine L-phenylalaninium formate (Görbitz & Etter, 1992) have been reported. The crystal

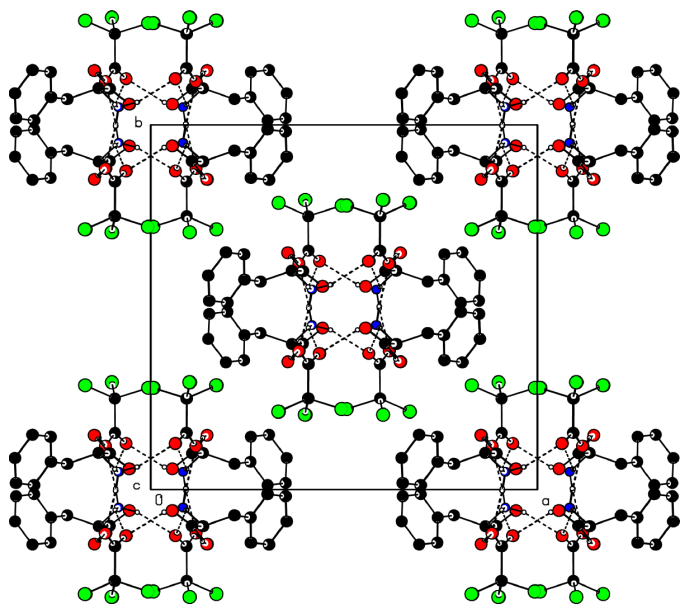
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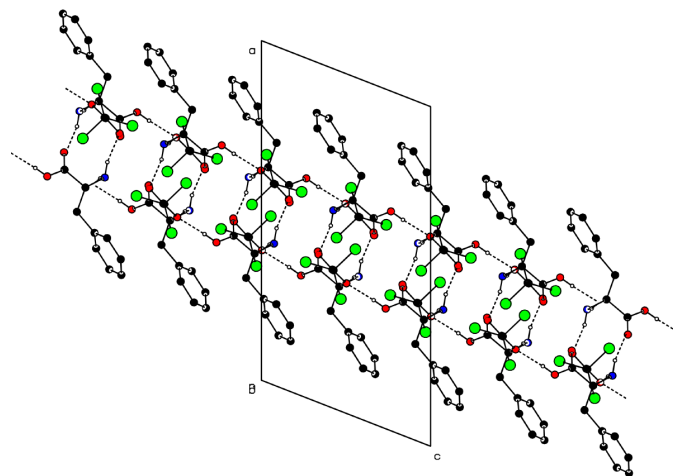
**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.



**Figure 2**  
Packing of cations and anions of (I), viewed along the *c* axis. H atoms not involved in hydrogen bonds have been omitted. Dashed lines indicate hydrogen bonds.

structure of trichloroacetic acid itself was determined only recently in our laboratory (Rajagopal, Mostad *et al.*, 2003).

Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The DL-phenylalanine molecule in (I) exists in the cationic form, with a positively charged amino group and an uncharged carboxylic acid group. The trichloroacetic acid is in the anionic state. The conformation angles  $\chi^1$  and  $\chi^2$  for the phenylalaninium cation are in agreement with the values reported for L-phenylalaninium maleate (Alagar *et al.*, 2001). The phenylalaninium cation has the *gauche*-II conformation with a  $\chi^1$  value of 67.6 (4)°. This is different from the values observed in L-phenylalanine L-phenylalaninium formate with  $\chi^1 = 72.3$  (4) and 70.8 (4)°,



**Figure 3**  
A view along the *b* axis, illustrating a column of molecules extending along the *c* axis. H atoms not involved in hydrogen bonds have been omitted. Dashed lines indicate hydrogen bonds.

respectively, for the zwitterion and the cation (Görbitz & Etter, 1992), and in DL-phenylalaninium maleate (Alagar *et al.*, 2003), where  $\chi^1 = 85.7$  (2)°, indicating different side chain conformations in different environments. The torsion angles  $\chi^{21}$  and  $\chi^{22}$  [−137.5 (4) and 48.6 (5)°, respectively] indicate a distorted folded conformation in the present case and are in good agreement with the values reported for DL-phenylalaninium maleate. These values are significantly different from those observed in L-phenylalaninium maleate [91.5 (3) and −88.8 (2)°, respectively].

Fig. 2 shows the packing of ions in (I), viewed along the *c* axis. It is clearly seen that the aggregation of phenylalaninium cations and trichloroacetate anions form columns along the *c* axis. These columns have no hydrogen-bonded contacts with each other, but are stabilized through van der Waals interactions. Fig. 3 illustrates how these columns extend along the *c* axis, forming hydrogen-bonded double chains flanked on either side by the hydrophobic side chains of phenylalaninium cations. No direct interactions between phenylalaninium cations in the form of head-to-tail hydrogen bonds are observed and trichloroacetate anions mediate interactions between amino acid cations. The aggregation pattern observed in (I) has striking similarities to those observed in L-phenylalaninium trichloroacetate (Rajagopal, Krishnakumar, Subha Nandhini, Cameron & Natarajan, 2003), L-phenylalanine phenylalaninium formate (Görbitz & Etter, 1992), L-phenylalaninium maleate (Alagar *et al.*, 2001) and DL-phenylalaninium maleate (Alagar *et al.*, 2003). A short Cl⋯Cl contact [Cl2⋯Cl2(−*x* + 1/2, −*y* + 1/2, −*z* + 2) = 3.509 (2) Å] is also observed in the structure; this is significantly less than the values [3.366 (13) Å and 3.320 (7) Å] observed in L-phenylalaninium trichloroacetate.

## Experimental

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

## Crystal data

$C_9H_{12}NO_2^+ \cdot C_2Cl_3O_2^-$   
 $M_r = 328.57$   
 Monoclinic,  $C2/c$   
 $a = 18.838$  (3) Å  
 $b = 16.557$  (2) Å  
 $c = 10.065$  (12) Å  
 $\beta = 111.354$  (14)°  
 $V = 2924$  (4) Å<sup>3</sup>  
 $Z = 8$   
 $D_x = 1.493$  Mg m<sup>-3</sup>  
 $D_m = 1.48$  (7) Mg m<sup>-3</sup>

$D_m$  measured by flotation in a liquid mixture of xylene and bromoform  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 11.3$ – $14.2^\circ$   
 $\mu = 0.63$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
 Prism, colorless  
 $0.35 \times 0.30 \times 0.20$  mm

## Data collection

Nonius MACH3 four-circle diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.815$ ,  $T_{\max} = 0.887$   
 2854 measured reflections  
 2560 independent reflections  
 1923 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 25.0^\circ$   
 $h = 0 \rightarrow 22$   
 $k = -1 \rightarrow 19$   
 $l = -11 \rightarrow 11$   
 3 standard reflections  
 frequency: 60 min  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.154$   
 $S = 1.03$   
 2560 reflections  
 174 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 8.3099P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.95$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.60$  e Å<sup>-3</sup>

**Table 1**  
 Selected geometric parameters (Å, °).

O1—C1	1.318 (4)	O3—C10	1.237 (4)
O2—C1	1.188 (4)	O4—C10	1.239 (4)
O2—C1—O1	125.6 (3)	O3—C10—O4	128.6 (3)
O2—C1—C2	123.2 (3)	O3—C10—C11	115.0 (3)
O1—C1—C2	111.2 (3)	O4—C10—C11	116.3 (3)
O2—C1—C2—N1	6.1 (4)	C2—C3—C4—C5	-137.5 (4)
O1—C1—C2—N1	-174.8 (3)	C2—C3—C4—C9	48.6 (5)
N1—C2—C3—C4	67.6 (4)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A <sup>i</sup> ...O3 <sup>i</sup>	0.89	2.08	2.847 (4)	144
O1—H1...O4 <sup>ii</sup>	0.82	1.81	2.630 (4)	175
N1—H1C...O4 <sup>iii</sup>	0.89	2.00	2.890 (3)	173
N1—H1B...O3 <sup>iv</sup>	0.89	2.04	2.887 (3)	159

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

The H atoms of the phenylalaninium cations were placed at calculated positions and were allowed to ride on their respective carrier atoms, with N—H = 0.89 Å, O—H = 0.82 Å, C—H = 0.93–0.98 Å and  $U_{\text{iso}} = 1.5U_{\text{eq}}$  of the carrier atom for the OH and NH<sub>3</sub> groups and  $1.2U_{\text{eq}}$  for CH<sub>2</sub> and CH groups.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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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