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## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.008$  Å  
Disorder in main residue  
 $R$  factor = 0.073  
 $wR$  factor = 0.255  
Data-to-parameter ratio = 11.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## DL-Valinium trifluoroacetate

In the title compound,  $\text{C}_5\text{H}_{12}\text{NO}_2^+ \cdot \text{C}_2\text{F}_3\text{O}_2^-$ , the valine molecule is in a cationic state, with a protonated amino group and an uncharged carboxylic acid group. The trifluoroacetic acid molecule is deprotonated and it displays rotational disorder. Inversion-related valinium residues are linked by  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds into a dimer. The dimers and the trifluoroacetate anions are alternately connected by  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds to form a layer parallel to the  $ab$  plane.

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## Comment

Valine, an essential amino acid, is required in human and animal diets for the maintenance of nitrogen equilibrium. It is hydrophobic, with a non-polar hydrocarbon chain, and plays a vital role in the stabilization of the structures of protein molecules. Trifluoroacetic acid is a very strong carboxylic acid, due to the charge-withdrawing effect of the F atoms on the  $\text{C}^\alpha$  atom. Our main interest in amino acid–trifluoroacetic acid compounds relates to their non-linear optic (NLO) properties. We report here the crystal structure of a salt of DL-valine with trifluoroacetic acid, the title compound, (I).

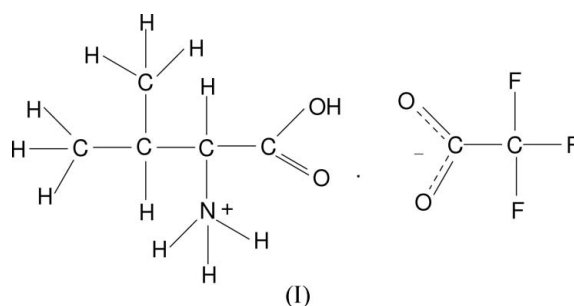


Fig. 1 illustrates the structure of the asymmetric unit of (I) and the atom-numbering scheme adopted. The valine molecule is in a cationic state, with a protonated amino group and an uncharged carboxylic acid group. The trifluoroacetic acid molecule is deprotonated. In the valinium residue, the carboxyl group ( $\text{O}3/\text{O}4/\text{C}3/\text{C}4$ ) is essentially planar, and atom N1 deviates from this plane by 0.359 (8) Å. The conformation of the valinium residue, determined by the torsion angles  $\varphi^1$  [ $-15.5$  (7)°],  $\varphi^2$  [ $165.7$  (4)°],  $\chi^{11}$  [ $71.4$  (5)°] and  $\chi^{12}$  [ $-160.5$  (4)°], agrees well with that observed for the monoclinic form of DL-valine (Mallikarjunan & Rao, 1969) and DL-valinium trichloroacetate (Rajagopal *et al.*, 2002). However, a comparison of  $\chi^{11}$  and  $\chi^{12}$  values, ignoring the differences in the ionization states, with those observed in the complexes DL-

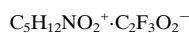
valinium maleate [57.1 (2) and  $-63.3$  (2) $^\circ$ ; Alagar *et al.*, 2001], DL-valine–fumaric acid (2/1) [ $-58.9$  (2) and  $68.5$  (2) $^\circ$ ; Alagar *et al.*, 2003] and DL-valine–succinic acid (2/1) [ $-59.9$  (2) and  $67.6$  (2) $^\circ$ ; Alagar *et al.*, 2004] possibly indicates the difference in the nature of the influence of the carboxylic acids on the conformation of DL-valine in these structures.

Fig. 2 shows the packing of (I). Amino acids are known to exhibit characteristic head-to-tail sequences in which hydrogen bonds occur between the  $\alpha$ -amino and  $\alpha$ -carboxylate groups of adjacent molecules (Suresh & Vijayan, 1983; Vijayan 1988). In the present structure, however, inversion-related valinium residues are linked to form a dimer by  $N1-H1C \cdots O4(-x, 1-y, 1-z)$  hydrogen bonds. The dimers and the trifluoroacetate anions are alternately linked by  $O-H \cdots O$  and  $N-H \cdots O$  hydrogen bonds (Table 1) to form a layer parallel to the *ab* plane.

## Experimental

Colourless prismatic single crystals of (I) were grown from a saturated solution of water containing DL-valine and trifluoroacetic acid in a 1:1 stoichiometric ratio. The density was determined by the flotation method using a liquid mixture of xylene and bromoform.

### Crystal data



$M_r = 231.18$

Triclinic, *P*1

$a = 6.7282$  (6) Å

$b = 9.0830$  (4) Å

$c = 9.2148$  (7) Å

$\alpha = 98.461$  (1) $^\circ$

$\beta = 91.990$  (1) $^\circ$

$\gamma = 101.052$  (1) $^\circ$

$V = 545.53$  (7) Å<sup>3</sup>

$Z = 2$

$D_x = 1.407$  Mg m<sup>-3</sup>

$D_m = 1.40$  Mg m<sup>-3</sup>

$D_m$  measured by flotation

Mo *K* $\alpha$  radiation

$\mu = 0.14$  mm<sup>-1</sup>

$T = 293$  (2) K

Prism, colourless

$0.3 \times 0.3 \times 0.3$  mm

### Data collection

Nonius MACH3 four-circle diffractometer

$\omega$  scans

Absorption correction:  $\psi$  scan (North *et al.*, 1968)

$T_{\min} = 0.958$ ,  $T_{\max} = 0.958$

2438 measured reflections

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.073$

$wR(F^2) = 0.255$

$S = 1.07$

1908 reflections

164 parameters

H-atom parameters constrained

1908 independent reflections

887 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 25.0^\circ$

3 standard reflections

frequency: 60 min

intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.1435P)^2$

$+ 0.0816P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.31$  e Å<sup>-3</sup>

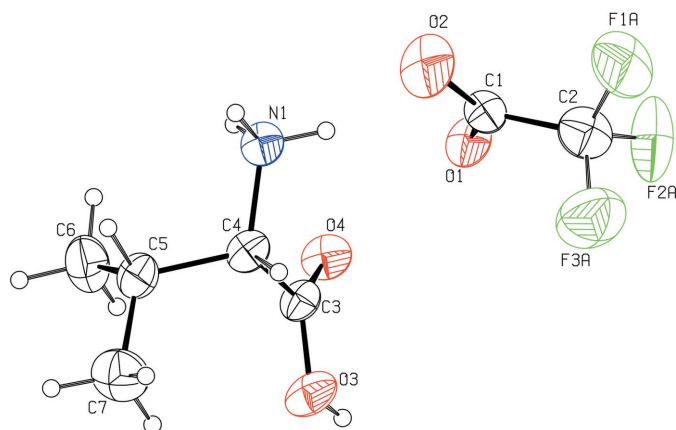
$\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å,  $^\circ$ ).

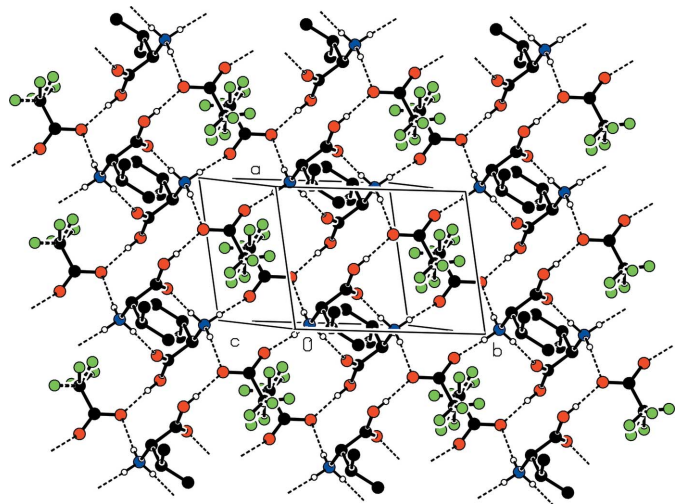
<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
$N1-H1B \cdots O2^i$	0.89	1.87	2.747 (5)	170
$N1-H1C \cdots O4^{ii}$	0.89	2.02	2.878 (5)	162
$O3-H3 \cdots O1^{iii}$	0.82	1.79	2.607 (4)	174
$N1-H1A \cdots O1$	0.89	1.97	2.827 (5)	161

Symmetry codes: (i)  $-x, -y, -z + 1$ ; (ii)  $-x, -y + 1, -z + 1$ ; (iii)  $-x + 1, -y + 1, -z + 1$ .



**Figure 1**

The asymmetric unit of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Only the major component of the disordered trifluoromethyl group is shown.



**Figure 2**

The packing of (I), with hydrogen bonds shown as dashed lines. H atoms that do not take part in the hydrogen bonding have been omitted for clarity.

The  $CF_3$  group is disordered over two different orientations, rotated about the  $C1-C2$  bond, with occupancy factors of 0.438 (14) and 0.562 (14). The  $C-F$  distances were restrained to 1.32 (1) Å and the  $U^{ij}$  components of the disordered F atoms were restrained to approximate isotropic behaviour. All H atoms were positioned geometrically and were allowed to ride on their respective parent atoms, with  $C-H = 0.96$  or  $0.98$  Å,  $N-H = 0.89$  Å and  $O-H = 0.82$  Å, and  $U_{\text{iso}}(H) = 1.2$  or  $1.5$  times  $U_{\text{eq}}(C,N)$ .

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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