

L-Argininium trifluoroacetate

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.060
wR factor = 0.150
Data-to-parameter ratio = 7.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title compound, $\text{C}_6\text{H}_{16}\text{N}_4\text{O}_2^+ \cdot \text{C}_2\text{F}_3\text{O}_2^-$, the amino acid exists as a zwitterionic argininium cation, with positively charged amino and guanidinium groups and a negatively charged carboxylate group. The trifluoroacetic acid molecule is deprotonated. The stoichiometry between the argininium ion and the trifluoroacetate anion is 1:1. The aggregation of argininium cations and trifluoroacetate anions is strikingly similar to those observed in the 1:2 stoichiometric analogue.

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Comment

Carboxylic acids are believed to have existed in the prebiotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971) and they are known to form complexes with amino acids involving proton transfer. A brief survey of the Cambridge Structural Database (Version 5.27; Allen, 2002) revealed a scarcity of precise crystallographic data on amino acid-halogenoacetic acid complexes. This motivated us to successfully crystallize and elucidate the crystal structure of trichloroacetic acid itself (Rajagopal *et al.*, 2003). We report here the crystal structure of a complex of L-arginine with trifluoroacetic acid, namely, L-argininium trifluoroacetate, (I), a compound with 1:1 stoichiometry. L-Argininium bis(trifluoroacetate), a complex with 1:2 stoichiometry, has already been reported (Silva *et al.*, 2003). Similar structures of interest and importance to the present study are complexes of arginine with oxalic acid (Chandra *et al.*, 1998), glutaric acid (Saraswathi & Vijayan, 2001), malonic acid (Saraswathi & Vijayan, 2002), pimelic acid (Saraswathi *et al.*, 2003) and adipic acid (Roy *et al.*, 2005).

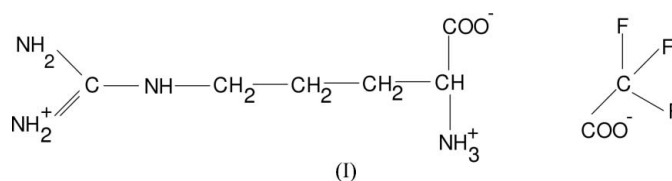


Fig. 1 illustrates the structure of the asymmetric unit of (I) and the atom-numbering scheme adopted. The amino acid exists as a zwitterionic argininium cation, with positively charged amino and guanidinium groups and a negatively charged carboxylate group. The trifluoroacetic acid molecule is deprotonated. The stoichiometry between the argininium ion and the trifluoroacetate anion is 1:1. The argininium cation may be thought of as made up of three nearly planar subgroups, *viz.* the carboxylate group along with the amino N atom, the central linear chain of C atoms and the tail fragment of the side chain involving the guanidyl N atoms, thus leading to an extended side-chain conformation. The trifluoroacetate

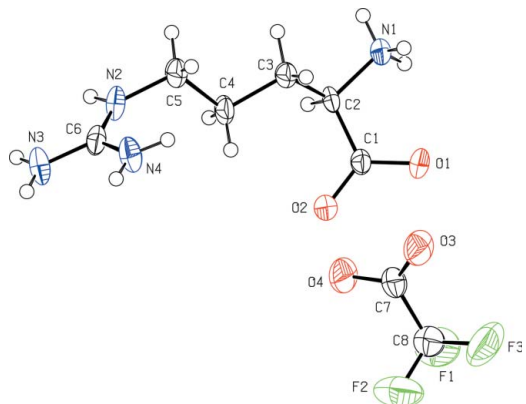


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom numbering scheme.

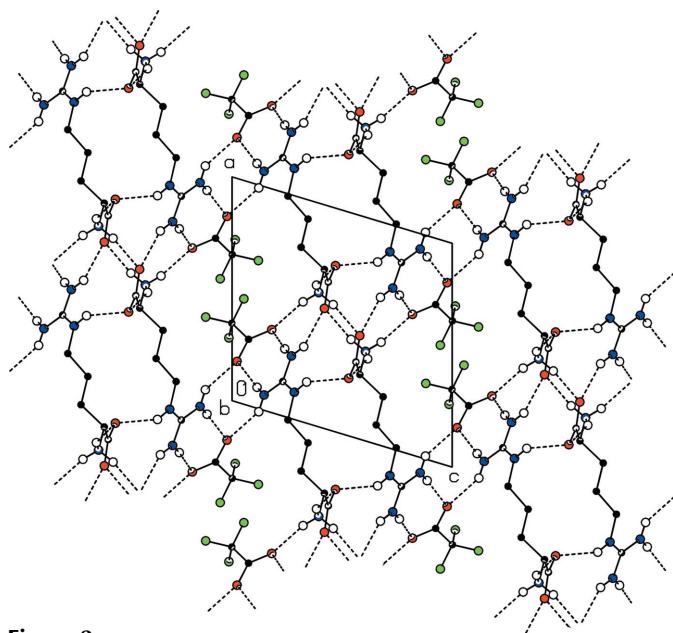


Figure 2
Packing of (I), viewed down the *b* axis, with hydrogen bonds shown as dashed lines. H atoms that do not take part in the hydrogen bonding have been omitted for clarity.

anion adopts the most favoured staggered conformation with typical bond lengths and angles.

Fig. 2 shows the packing of (I), viewed down the *b* axis. Amino acids are known to exhibit characteristic head-to-tail sequences in which hydrogen bonds occur between the α -amino and α -carboxylate groups of adjacent molecules (Suresh & Vijayan, 1983; Vijayan 1988). There are two head-to-tail-type hydrogen bonds observed in the complex three-dimensional network that stabilizes the crystal structure of (I), one straight [N1–H1A...O2 (*x*, *y* + 1, *z*)] and the other a zigzag [N1–H1B...O1 (–*x* + 1, *y* + $\frac{1}{2}$, –*z* + 1)], both of which occur in an arrangement similar to a double chain, forming a sub-unit of the complex intermolecular interaction pattern. These sub-units extend parallel to the shortest crystallographic axis and are bridged by guanidyl and carboxylate groups, leading to a three-dimensional hydrogen-bonding network.

Experimental

Colourless, prismatic single crystals of (I) were grown from a saturated solution of methanol–water containing L-arginine and trifluoroacetic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_6H_{15}N_4O_2^+ \cdot C_2F_3O_2^-$
 $M_r = 288.24$
Monoclinic, $P2_1$
 $a = 10.5860$ (6) Å
 $b = 5.6880$ (4) Å
 $c = 10.8780$ (7) Å
 $\beta = 106.770$ (1)°
 $V = 627.14$ (7) Å³

$Z = 2$
 $D_x = 1.526$ Mg m^{–3}
Mo $K\alpha$ radiation
 $\mu = 0.15$ mm^{–1}
 $T = 295$ (2) K
Block, colourless
 $0.26 \times 0.18 \times 0.12$ mm

Data collection

Nonius MACH3 four-circle diffractometer
 ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{min} = 0.97$, $T_{max} = 0.98$
1539 measured reflections

1223 independent reflections
1097 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.032$
 $\theta_{max} = 25.0^\circ$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.151$
 $S = 1.09$
1223 reflections
172 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1263P)^2 + 0.0434P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.30$ e Å^{–3}
 $\Delta\rho_{min} = -0.38$ e Å^{–3}

Table 1

Selected torsion angles (°).

N1–C2–C1–O2	–174.3 (3)	C5–C4–C3–C2	–164.5 (3)
C3–C2–C1–O2	62.5 (4)	C6–N2–C5–C4	93.6 (4)
N1–C2–C1–O1	4.7 (4)	C3–C4–C5–N2	177.6 (3)
C3–C2–C1–O1	–118.6 (3)	C5–N2–C6–N4	–0.8 (6)
N1–C2–C3–C4	164.5 (3)	C5–N2–C6–N3	–178.1 (3)
C1–C2–C3–C4	–71.7 (4)		

Table 2

Hydrogen-bond geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N1–H1A...O2 ⁱ	0.89	2.04	2.829 (4)	147
N1–H1B...O1 ⁱⁱ	0.89	1.96	2.835 (4)	167
N1–H1C...O3	0.89	2.01	2.832 (4)	152
N2–H2A...O2 ⁱⁱⁱ	0.86	2.14	2.902 (4)	148
N3–H3C...O3 ^{iv}	0.86	2.03	2.888 (6)	175
N3–H3D...O1 ^v	0.86	2.07	2.808 (4)	144
N4–H4C...O4 ^{vi}	0.86	2.09	2.872 (4)	151
N4–H4D...O4 ^{iv}	0.86	2.05	2.896 (5)	166
C5–H5A...O4 ^{vi}	0.97	2.49	3.426 (5)	161

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

All H atoms were positioned geometrically and were allowed to ride on their respective parent atoms, with C–H = 0.97 and 0.98 Å, N–H = 0.86 and 0.89 Å, and $U_{iso}(H)$ values of 1.2 or 1.5 times $U_{eq}(C, N)$. In the absence of significant anomalous scattering effects, Friedel pairs were averaged. The absolute configuration was assigned based on the known configuration of L-arginine.

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) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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