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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.038
 wR factor = 0.108
Data-to-parameter ratio = 5.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

L-Histidinium trifluoroacetate

The title compound, $\text{C}_6\text{H}_{10}\text{N}_3\text{O}_2^+ \cdot \text{C}_2\text{F}_3\text{O}_2^-$, crystallizes with two histidine cations and two trifluoroacetate anions in the asymmetric unit. The protonated cations and deprotonated anions are linked by a number of intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form a three-dimensional network.

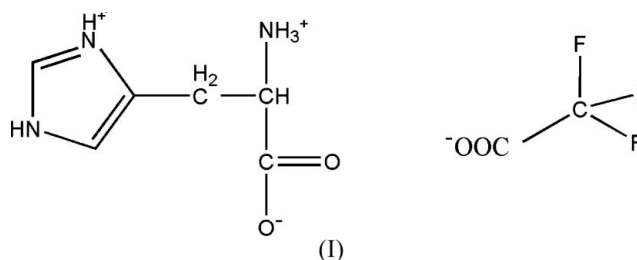
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Comment

Histidine is an interesting molecule from a crystal engineering point of view. It can act as a proton donor, a proton acceptor, a nucleophilic agent and a ligand for complexation with various metal ions. It exists as both orthorhombic and monoclinic polymorphic forms. The crystal structures of L-histidine (Madden, McGandy & Seeman, 1972; Madden, McGandy, Seeman, Harding & Hoy, 1972) and its complexes, such as L-histidinium hydrochloride (Fuess & Bartunik 1976; Donohue & Caron 1964), L-histidinium dinitrate (Benali-Cherif *et al.*, 2002), L-histidinium sulfate (Kumar *et al.*, 2005) and L-histidinium tetrafluorosuccinate (Akkurt *et al.*, 2004), have been reported, and recently the crystal structure of L-histidinium trichloroacetate (Gokul Raj *et al.*, 2005) has also been published. In the present study, we report the crystal structure of L-histidinium trifluoroacetate, (I).



The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. Compound (I) crystallizes with two histidinium cations (*A* and *B*) and two trifluoroacetate anions in the unit cell of the non-centrosymmetric triclinic space group *P*1. The α -amino and imidazole groups of the L-histidinium cations are protonated and positively charged, while the carboxyl groups are in the ionized state and are negatively charged. Moreover, the zwitterionic cation carries a net positive charge. The conformation angles of the histidine side chain (IUPAC-IUB Commission on Biochemical Nomenclature, 1970) are χ^1 [$-68.5(4)$ and $-69.9(4)^\circ$], χ^{21} [$-54.5(5)$ and $54.1(5)^\circ$] and χ^{22} [$126.2(4)$ and $132.0(4)^\circ$ for cations *A* and *B*, respectively]. The conformation ψ^1 is such that it is in a *gauche*-II form for both molecules, having a closed conformation (Pratap *et al.*, 2000) (see Table 1). The difference in the absolute values of

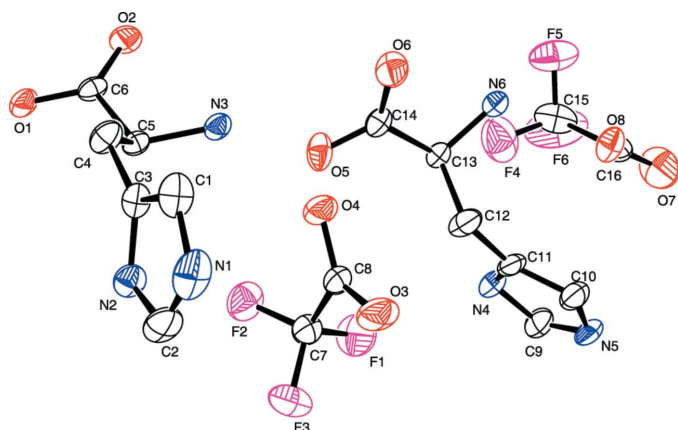


Figure 1
The structure of the asymmetric unit of (I), with the atomic numbering scheme and 50% probability displacement ellipsoids. H atoms have been omitted.

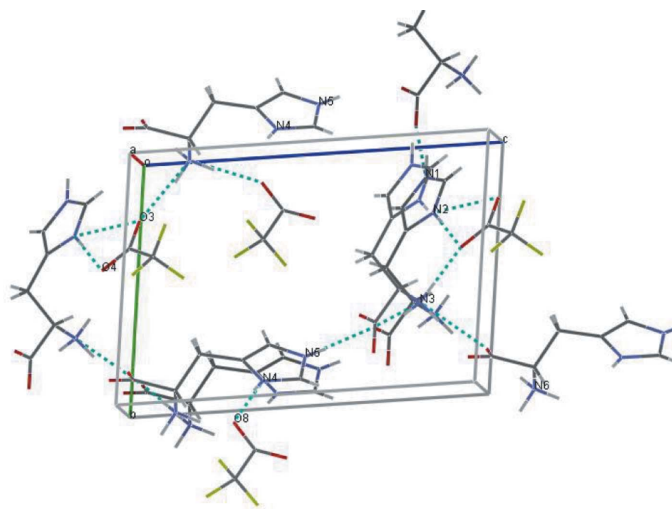


Figure 2
The crystal packing of (I), viewed approximately down the *a* axis. The intermolecular N–H...O bonds are shown as broken lines.

χ^{21} and χ^{22} is about 180° , indicating the planarity of the imidazole group. The deviations in the preferred torsion angles of χ^{21} at -90 and 90° are due to the interactions of the imidazole ring with other groups in the structure. The imidazole group of L-histidine is in a *trans* conformation, for both A [C3–C4–C5–C6 = $170.3(3)^\circ$] and B [C11–C12–C13–C14 = $168.9(3)^\circ$], with respect to the carboxylate group, and *gauche* with respect to the amino N atom. The corresponding *gauche*-II conformation angles observed in other complexes are -60 and -60.9° in L-histidinium formate formic acid, -60 and -67.5° in DL-histidinium formate monohydrate, 58.2 and -96.8° in L-histidinium glycolate, $-61.2(5)$ and $99.2(5)^\circ$ in monoclinic L-histidinium acetate and $37.1(6)$ and $-78.8(6)^\circ$ in L-histidinium trichloroacetate.

The trifluoroacetate anions play a vital role in the hydrogen bonding with the histidinium cation *via* the amine N atom and the N atom of the imidazole ring. The three-dimensional network of N–H...O bonds links the cations and trifluoro-

acetate anions, stabilizing the crystal packing as shown in Fig. 2.

Experimental

Crystals of the title compound, (I), were grown from a mixture of L-histidine and trifluoroacetic acid, in the stoichiometric ratio of 1:1, by slow evaporation at room temperature.

Crystal data

$C_6H_{10}N_3O_2^+ \cdot C_2F_3O_2^-$
 $M_r = 269.19$
 Triclinic, *P*1
 $a = 5.1724(6) \text{ \AA}$
 $b = 8.8183(12) \text{ \AA}$
 $c = 12.481(3) \text{ \AA}$
 $\alpha = 96.193(17)^\circ$
 $\beta = 99.853(13)^\circ$
 $\gamma = 102.106(13)^\circ$
 $V = 542.26(16) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.649 \text{ Mg m}^{-3}$
 Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 20\text{--}30^\circ$
 $\mu = 1.46 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, brown
 $0.2 \times 0.2 \times 0.1 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.790$, $T_{\max} = 0.864$
 2063 measured reflections
 2063 independent reflections

2053 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 68.0^\circ$
 $h = -6 \rightarrow 6$
 $k = -10 \rightarrow 10$
 $l = -14 \rightarrow 15$
 2 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.108$
 $S = 1.01$
 2063 reflections
 382 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0775P)^2 + 0.22P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.055(4)
 Absolute structure: Flack (1983), 97
 Friedel pairs
 Flack parameter: 0.04(2)

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

C1–N1	1.357 (6)	C6–O1	1.270 (4)
C2–N1	1.317 (7)	C7–F3	1.333 (5)
C2–N2	1.323 (5)	C7–F1	1.333 (5)
C3–N2	1.378 (5)	C7–F2	1.340 (5)
C5–N3	1.483 (4)	C8–O3	1.231 (5)
C6–O2	1.226 (4)	C8–O4	1.243 (5)
N1–C1–C3	107.6 (4)	F3–C7–F2	106.8 (3)
N1–C2–N2	108.7 (4)	F1–C7–F2	106.2 (3)
C1–C3–N2	105.8 (3)	F3–C7–C8	111.7 (3)
N2–C3–C4	124.3 (3)	F1–C7–C8	112.3 (3)
N3–C5–C6	109.6 (2)	F2–C7–C8	112.7 (3)
N3–C5–C4	111.1 (3)	O3–C8–O4	126.4 (4)
O2–C6–O1	125.9 (3)	O3–C8–C7	116.4 (3)
O2–C6–C5	119.4 (3)	O4–C8–C7	117.2 (3)
O1–C6–C5	114.6 (3)	C2–N1–C1	109.0 (3)
F3–C7–F1	106.8 (3)	C2–N2–C3	108.9 (3)
C1–C3–C4–C5	126.2 (4)	C3–C4–C5–C6	170.3 (3)
N2–C3–C4–C5	$-54.1(5)$	C11–C12–C13–C14	168.9 (3)
C3–C4–C5–N3	$-68.5(4)$		

Table 2
Hydrogen-bond geometry (Å, °).

<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—H1···O2 ⁱ	1.00 (6)	1.99 (6)	2.935 (4)	157 (5)
N2—H2···O4 ⁱⁱ	0.87 (5)	1.97 (6)	2.838 (4)	178 (4)
N3—H3A···O4	0.94 (1)	1.86 (1)	2.784 (4)	172 (4)
N3—H3B···O1 ⁱⁱⁱ	0.93 (5)	1.98 (2)	2.884 (4)	162 (5)
N3—H3C···O5	0.93 (1)	2.03 (3)	2.832 (4)	144 (5)
N4—H4···O8 ⁱⁱ	0.75 (7)	1.93 (7)	2.681 (5)	172 (6)
N5—H5···O1 ^{iv}	0.79 (6)	1.87 (6)	2.657 (4)	176 (6)
N6—H6A···O5 ⁱⁱⁱ	0.93 (1)	1.84 (2)	2.740 (4)	165 (4)
N6—H6B···O3 ^v	0.93 (1)	1.81 (1)	2.728 (4)	170 (4)
N6—H6C···O8	0.93 (5)	1.92 (2)	2.827 (4)	164 (7)

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

The tertiary CH and secondary CH₂ H atoms of the histidinium cations were included in calculated positions and treated as riding atoms, with C—H = 0.97–0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent C atom})$. All other H atoms were located in difference Fourier maps and refined freely [N—H = 0.75 (7)–1.00 (6) Å and C—H = 0.847 (11)–0.85 (6) Å].

Data collection: *CAD-4 Software* (Enraf–Nonius, 1997); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP32* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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