

L-Histidinium sulfate

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.010$ Å
 R factor = 0.047
 wR factor = 0.189
Data-to-parameter ratio = 8.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_6\text{H}_{11}\text{N}_3\text{O}_2^{2+} \cdot \text{SO}_4^{2-}$, crystallizes with two cations and two anions in the asymmetric unit. In both diprotonated histidinium cations, the C^{γ} atom has a *gauche*-II conformation with respect to the amine N atom and it is in a *trans* position to the C atom. An extensive three-dimensional network of intermolecular $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds links the histidinium cations and sulfate anions, forming a crystal structure in which zigzag (Z1) head-to-tail sequences are observed for both the cations.

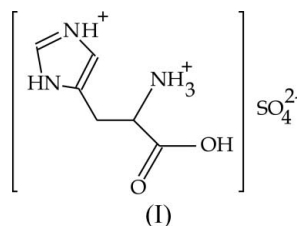
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Comment

The crystal structures of L-histidine (Madden *et al.*, 1972), L-histidine hydrochloride monohydrate (Fuess *et al.*, 1977), DL-histidine hydrochloride dihydrate (Bennett *et al.*, 1970), L-histidinium dinitrate (Asath Bahadur, 1992), DL-histidinium dinitrate (Bahadur *et al.*, 1991), DL-histidine sulfamate (Asath Bahadur, 1992) and bis(L-histidinium sulfate) trihydrate (Srinivasan *et al.*, 2001) have been reported previously. We present here the crystal structure of the title compound, (I), the anhydrous form of L-histidinium sulfate.



The asymmetric unit of (I) contains two crystallographically independent diprotonated histidinium cations, *A* and *B*, containing the atoms N11, N12 and N13, and N21, N22 and N23, respectively (Fig. 1), and two sulfate anions. In *A* and *B*, the deviations of the amine N atom from the carboxyl plane are 0.6913 (8) and 0.9273 (8) Å, respectively, while the dihedral angles between the imidazolium ring and carboxyl planes are 66.4 (2) and 19.5 (5)°, respectively. This difference in the twisting of the imidazolium rings leads to the difference in side-chain conformations in the two histidinium cations. The conformation angle ψ^1 is *cis* in both cations. The side-chain conformation angles χ^1 [−63.9 (5)° for *A* and −53.1 (8)° for *B*] are in a *gauche*-II form, resulting in a closed conformation (Pratap *et al.*, 2000). The C^{γ} atom has a *trans* conformation with respect to the C^{α} atom for both the cations. The conformations χ^{21} and χ^{22} are observed as −28.0 (12) and 156.3 (6)° for cation *A*, and 117.6 (9) and −62.7 (8)° for cation *B* (Table 1), respectively, corresponding to those observed in bis(L-histidinium sulfate) trihydrate (Srinivasan *et al.*, 2001).

The anions play a vital role in hydrogen bonding with the histidinium cations *via* the amine N atom and the N atom of the imidazolium ring. An extensive three-dimensional network of intermolecular N—H···O and O—H···O bonds (Table 2) links the cations and sulfate anions, stabilizing the crystal packing (Fig. 2). Separate zigzag (Z1) head-to-tail sequences of hydrogen-bonded cations *A* and *B* are formed along the *b* axis *via* the N11—H11A···O1Aⁱⁱ and N21—H21A···O2A^{viii} interactions (see Table 2 for symmetry codes).

Experimental

The title compound was crystallized from an L-histidine and sulfuric acid mixture in the stoichiometric ratio of 1:1 at room temperature by slow evaporation.

Crystal data

C₆H₁₁N₃O₂²⁺·SO₄²⁻
M_r = 253.25
 Monoclinic, *P*2₁
a = 6.8616 (6) Å
b = 5.8084 (6) Å
c = 25.6901 (18) Å
 β = 90.733 (8)°
V = 1023.79 (16) Å³
Z = 4
D_x = 1.643 Mg m⁻³
D_m = 1.642 Mg m⁻³

D_m measured by flotation in a liquid mixture of CCl₄ and bromoform
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 9.6–11.8°
 μ = 0.34 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.22 × 0.16 × 0.12 mm

Data collection

Nonius MACH-3 four-circle diffractometer
 ω–2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.774, *T_{max}* = 0.999
 2571 measured reflections
 2368 independent reflections
 2161 reflections with *I* > 2σ(*I*)

R_{int} = 0.094
 θ_{max} = 25.0°
h = 0 → 8
k = -1 → 6
l = -30 → 30
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.047
wR (*F*²) = 0.189
S = 1.15
 2368 reflections
 294 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.1269*P*)² + 1.9828*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.44 e Å⁻³
 Δρ_{min} = -0.51 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.131 (13)
 Absolute structure: Flack (1983), 370 Friedel pairs
 Flack parameter: -0.09 (18)

Table 1

Selected geometric parameters (Å, °).

O1A—C11	1.216 (10)	O1B—C11	1.305 (9)
O1A—C11—C12—N11	-30.1 (9)	O2A—C21—C22—N21	-41.6 (10)
N11—C12—C13—C14	-63.5 (9)	N21—C22—C23—C24	-53.1 (8)
C11—C12—C13—C14	177.9 (7)	C21—C22—C23—C24	-171.5 (6)
C12—C13—C14—C15	-28.0 (12)	C22—C23—C24—C25	117.6 (9)
C12—C13—C14—N13	156.3 (6)	C22—C23—C24—N23	-62.7 (8)

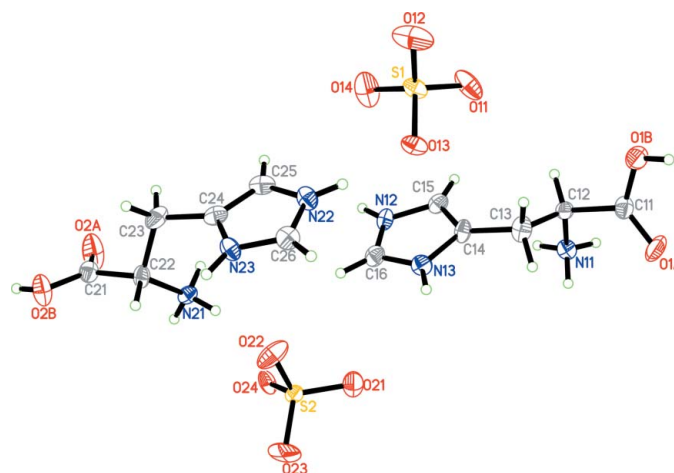


Figure 1

View of the asymmetric unit of the title compound, with the atom numbering scheme and 50% probability displacement ellipsoids.

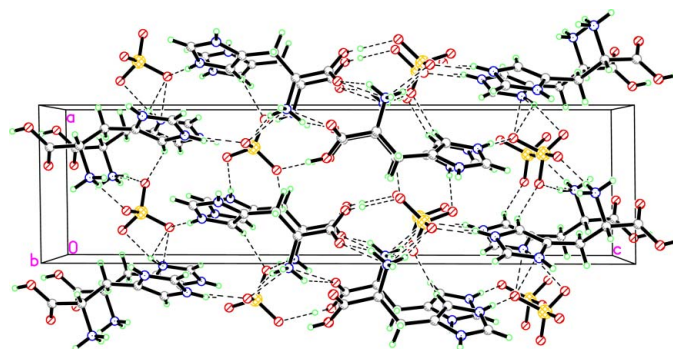


Figure 2

Packing diagram viewed down the *b* axis. The intermolecular hydrogen bonds are shown as dashed lines.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1B—H1B···O11 ⁱ	0.82	1.73	2.521 (7)	163
N11—H11A···O1A ⁱⁱ	0.89	2.15	2.834 (8)	133
N11—H11B···O13 ⁱⁱⁱ	0.89	1.88	2.721 (8)	157
N11—H11C···O12 ^{iv}	0.89	1.92	2.757 (10)	156
N12—H12A···O21 ^v	0.86	1.87	2.719 (8)	169
N13—H13···O14 ^{vi}	0.86	1.94	2.729 (8)	152
O2B—H2B···O24 ^{vii}	0.82	1.74	2.554 (7)	173
N21—H21A···O2A ^{viii}	0.89	1.93	2.790 (8)	161
N21—H21B···O22	0.89	1.83	2.708 (8)	168
N21—H21C···O23 ^v	0.89	1.86	2.679 (8)	152
N22—H22A···O13	0.86	1.85	2.694 (8)	168
N23—H23···O24 ^{ix}	0.86	1.99	2.811 (7)	160

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

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.98 Å, N—H = 0.86–0.89 Å, O—H = 0.82 Å and *U*_{iso}(H) = 1.2–1.5*U*_{eq}(parent atom).

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Bruker, 2000) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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