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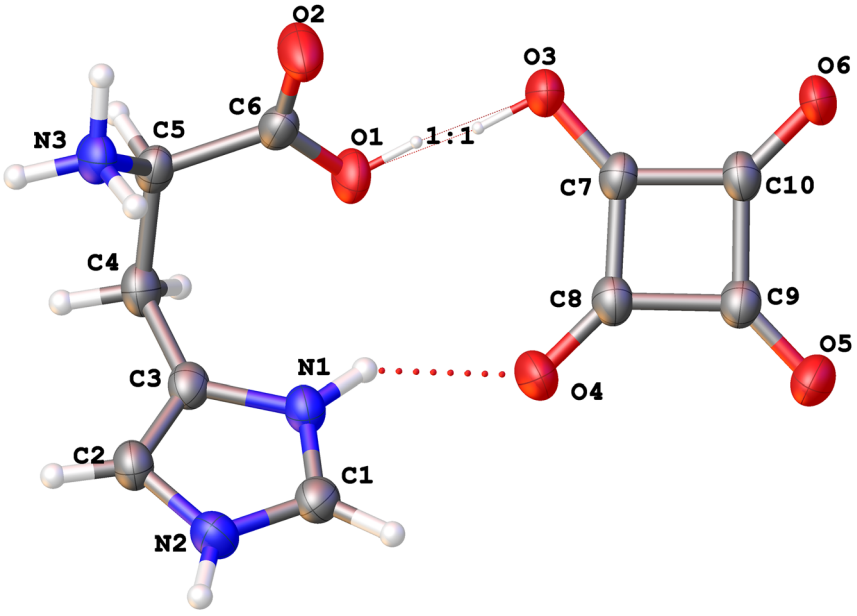
The crystal structure of Histidinium hydrogensquarate, $C_{10}H_{11}N_3O_6$



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Abstract

$C_{10}H_{11}N_3O_6$, monoclinic, $P2_1/c$ (no. 14), a = 7.4928(12) Å, b = 14.860(3) Å, c = 11.0593(18) Å, β = 109.465(5)°, V = 1161.0(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0439, w$R_{ref}(F^2)$ = 0.1060, T = 300.0(2) K.

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Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.50 × 0.20 × 0.14 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.13 mm^{-1}
Diffractometer, scan mode:	Bruker SMART X2S, ω
θ_{max}, completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7238, 2038, 0.061
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 1511
$N(param)_{refined}$:	222
Programs:	Bruker [1, 2], Olex2 [3], SHELX [4–6]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was obtained by adding of an aqueous solution of histidine free base to a water solution of squaric

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.5166 (2)	0.41853 (11)	0.40789 (15)	0.0383 (4)
H1[a]	0.487 (8)	0.435 (4)	0.328 (4)	0.05 (2)*
O2	0.7920 (2)	0.46850 (12)	0.39998 (15)	0.0542 (5)
N1	0.5610 (2)	0.22691 (12)	0.47788 (17)	0.0323 (5)
H1A	0.476 (3)	0.2631 (16)	0.417 (2)	0.052 (7)*
N2	0.7173 (3)	0.11023 (13)	0.57019 (18)	0.0365 (5)
H2	0.773 (4)	0.0497 (18)	0.582 (3)	0.074 (9)*
N3	0.9809 (2)	0.39328 (14)	0.62920 (19)	0.0344 (5)
H3A	1.045 (4)	0.4442 (19)	0.601 (3)	0.073 (9)*
H3B	1.042 (3)	0.3862 (17)	0.720 (3)	0.062 (8)*
H3C	0.993 (4)	0.3387 (19)	0.581 (3)	0.083 (10)*
C1	0.5924 (3)	0.14019 (15)	0.4629 (2)	0.0345 (5)
H1B	0.534 (3)	0.1043 (15)	0.383 (2)	0.039 (6)*
C2	0.7675 (3)	0.17971 (15)	0.6573 (2)	0.0346 (6)
H2A	0.853 (3)	0.1733 (14)	0.742 (2)	0.044 (6)*
C3	0.6706 (3)	0.25364 (14)	0.60051 (19)	0.0302 (5)
C4	0.6741 (3)	0.34658 (16)	0.6525 (2)	0.0348 (6)
H4A	0.539 (3)	0.3712 (14)	0.634 (2)	0.039 (6)*
H4B	0.736 (3)	0.3440 (14)	0.742 (2)	0.042 (6)*
C5	0.7788 (3)	0.41694 (14)	0.6011 (2)	0.0296 (5)
H5	0.781 (3)	0.4740 (14)	0.6442 (19)	0.037 (6)*
C6	0.6920 (3)	0.43687 (14)	0.4574 (2)	0.0324 (5)
O3	0.3825 (2)	0.46394 (10)	0.18179 (14)	0.0394 (4)
H3[a]	0.433 (7)	0.442 (3)	0.259 (4)	0.041 (19)*
O4	0.2771 (2)	0.25750 (10)	0.24150 (14)	0.0472 (5)
O5	−0.0117 (2)	0.24366 (11)	−0.04875 (14)	0.0460 (5)
O6	0.1226 (2)	0.44207 (10)	−0.11024 (13)	0.0430 (4)
C7	0.2759 (3)	0.39896 (14)	0.11818 (19)	0.0298 (5)
C8	0.2302 (3)	0.30902 (14)	0.1476 (2)	0.0327 (5)
C9	0.1001 (3)	0.30151 (15)	0.0127 (2)	0.0326 (5)
C10	0.1579 (3)	0.39213 (15)	−0.01332 (19)	0.0315 (5)

[a]Occupancy: 0.50 (6).

acid in a 1:1 molar ratio under continuous stirring at room temperature, as described previously by us [7, 8]. After completed addition of the amino acid the mixture was stirred for 24 h at 328–333 K. Then, the reaction mixture was slowly cooled to room temperature and left to crystillize at the same ambient conditions. Colourless clear crystals were obtained after recrystallization from doubly distilled water and crystallization over a period of several days at 268–270 K. The melting point of histidine hydrogensquarate is over 524–534 K under decomposition.

Experimental details

A single crystal of the title compound was examined on a Bruker SMART X2S benchtop diffractometer [1, 2] using Mo *K*α (λ = 0.71073 Å) radiation. The crystal was kept at 300.0(2) K during data collection. Using Olex2 [3], the structure was solved with the ShelXT [4] structure solution program and refined with the ShelXL [5] refinement package. Functional 1:1 disorder of the H1/H3 atoms can be obtained at each of the two molecules inside the unit. These O–H distances were restrained to be same. Hydrogen atoms were taken into account using a riding model.

Comment

The title structure was prepared following our previous studies for obtaining non-linear optically active single crystals of good quality and large size [7–9]. Within these investigations, a series of suitable organic molecules were used to generate optically active organic materials incorporating hydrogensquarate moieties with improved nonlinear optical (NLO) properties due to their possibility to alter the molecular structure [7–9]. In addition, several amino acids and their stable, crystalline complexes with squaric acid free base (H_2SQ) and the conjugated base of squaric acid (hydrogensquarete anion, HSQ^-) have been synthesized in order to investigate their biological effects [10] and the interaction between the zwitterionic compounds (amino acid) and the proton-donor (H_2SQ) [11].

The title compound crystallizes centrosymmetrically and the asymmetric unit contains one histidium zwitterion (His–H+) and one hydrogensquarate anion (HSQ^-). The squarate anion is nearly planar, the root mean square deviation from the plane of these eight atoms is calculated to be 0.045 Å with a maximum deviation of 0.065 Å. All nitrogen and oxygen atoms are involved in N···O hydrogen bonds with distances in the range between 2.743(2) Å and 2.814(2) Å except the one O···O hydrogen bond between O1 and O3 with a distance of 2.458(2) Å. The position of the hydrogen atom in this bond shows a positional disorder with a ratio of 1:1. As a result, the distances of O1 and O3 to the attached carbon atoms are significantly longer (1.274(2) Å to 1.300(2) Å) than the other C–O distances within the carboxylate groups (1.226(3) Å to 1.257(2) Å). All hydrogen atoms were refined isotropically, the disordered ones were restrained to have equivalent O–H distances.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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