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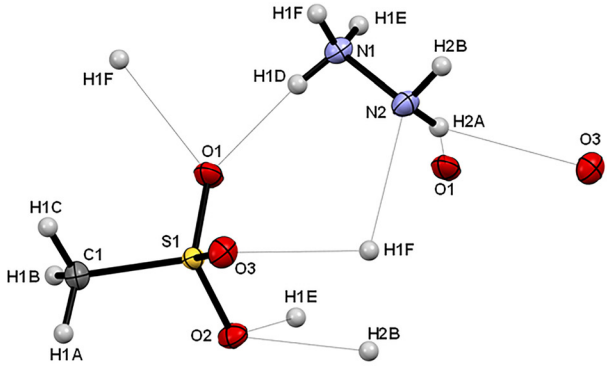
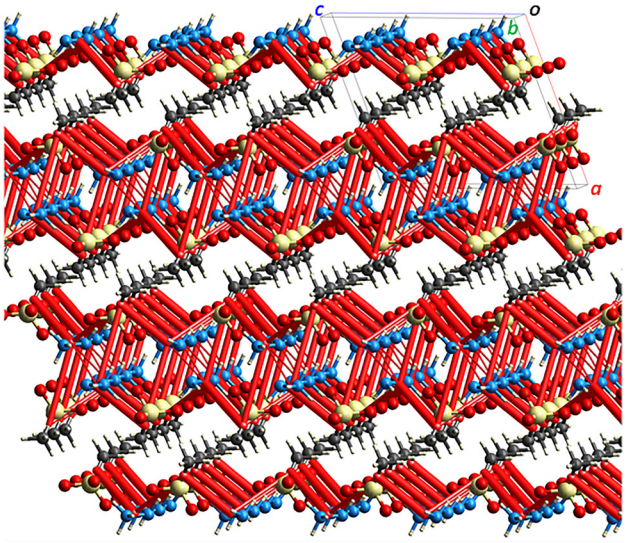
Crystal structure of hydrazinium methanesulfonate, $CH_8N_2O_3S$





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Abstract

$CH_8N_2O_3S$, monoclinic, $P2_1/c$ (no. 14), a = 9.7583 (16) Å, b = 5.4033 (9) Å, c = 10.4729 (17) Å, β = 110.483 (4)°, V = 517.29 (15) Å^3, Z = 1, $R_{gt}(F)$ = 0.0225, w$R_{ref}(F^2)$ = 0.0649, T = 150 K.

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Table 1: Data collection and handling.

Crystal:	Colourless plate
Size:	0.62 × 0.32 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.38 mm^{-1}
Diffractometer, scan mode:	Bruker APEX II, φ and ω
θ_{max}, completeness:	36.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23,772, 2531, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2245
$N(param)_{refined}$:	80
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4], CystalExplorer [5], Mercury [6]

The molecular structure, unique hydrogen bonds, a part of the title crystal structure and the energy framework are shown in the Figure. Tables 1 and 2 contain details on the crystal structure as well as measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of materials

To a solution of 97 µL (2 mmol) 99% hydrazine hydrate in 3 mL 95% EtOH were added 2 mL (2 mmol) of 1 M methanesulfonic acid in 95% EtOH. The resulting solution was brought to 4 °C and left for a week in a tube loosely covered with a screwcap. Slow evaporation of the solvent resulted in formation of crystals as colourless plates.

Experimental details

The hydrazine H atoms were treated by a mixture of independent and constrained refinement while the methylene hydrogen atoms were initially placed in calculated positions. All N-bound hydrogen atom coordinates were allowed to refine freely, while thermal parameters were constrained to ride on the carrier atoms (U_{iso}(methyl H) = 1.5 U_{eq}).

Comment

Hydrazine is an important commodity and, for decades, it has been used in many industries [7], from production of

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.71636 (2)	0.12650 (3)	0.48535 (2)	0.01256 (5)
O2	0.69367 (6)	−0.13439 (9)	0.44676 (6)	0.01809 (10)
O3	0.72696 (6)	0.16513 (11)	0.62597 (5)	0.01927 (10)
O1	0.84081 (6)	0.23025 (11)	0.45613 (5)	0.01989 (11)
C1	0.56118 (8)	0.28516 (14)	0.38064 (7)	0.01894 (12)
H1A	0.473405	0.211923	0.390222	0.028*
H1B	0.555234	0.272640	0.285498	0.028*
H1C	0.568072	0.459692	0.407629	0.028*
N2	1.11484 (8)	0.13258 (11)	0.77002 (7)	0.01833 (11)
N1	1.10890 (7)	0.31492 (11)	0.66790 (6)	0.01603 (10)
H1D	1.0287 (14)	0.303 (2)	0.6074 (13)	0.024*
H1E	1.1756 (13)	0.293 (2)	0.6316 (12)	0.024*
H2A	1.1430 (13)	−0.006 (2)	0.7415 (13)	0.024*
H2B	1.1887 (13)	0.171 (2)	0.8438 (13)	0.024*
H1F	1.1113 (13)	0.455 (2)	0.7015 (12)	0.024*

blowing agents to rocketry, as a propellant, to agriculture, as a precursor of synthetic pesticides, to medicine, as a building block of therapeutic drugs. For example, hydrazide-hydrazone based drugs are clinically used for treatment tuberculosis [8] or intestinal infections [9]. Our lab has been evaluating chelators for inhibition of iron-dependent cytotoxic virulence factors from drug-resistant bacteria [10, 11] and, in the course of the study, has prepared a series of hydrazine derivatives and salts, including the title compound.

Hydrazinium mesylate crystallizes in the monoclinic $P2_1/c$ space group, with one ion pair per asymmetric unit. The valence bond lengths and angles are in the expected ranges; geometries of the three S–O bonds in the mesylate anion are very similar: differences between the bond lengths are within 0.09 Å, the C–S–O valence angles are within the 0.7° range from the average 107°. The conventional hydrogen bonding in crystal structure of hydrazinium mesylate is extensive and multicentered, and includes the shortest heteroatom contact a (see the figure; N1···O2′ = 2.7793 (10) Å, H1E···O2′ = 1.941 (13) Å, N1–H1E···O2′ = 161.6 (10)°, ′ = 2 − *x*, −*y*, 1 − *z*), one bifurcated H-bond (N2···O1′ = 3.2183 (10) Å, H2A···O1′ = 2.451 (12) Å, N2–H2A···O1′ = 145.4 (11)° and N2···O3″ = 2.9618 (10) Å, H2A···O3″ = 2.337 (12) Å, N2–H2A···O3″ = 127.7 (11)°, ″ = 2 − *x*, −1/2 + *y*, 3/2 − *z*) and one trifurcated hydrogen bond (N1···O1‴ = 2.9007 (10) Å, H1F···O1‴ = 2.525 (12) Å, N1–H1F···O1‴ = 108.7 (10)°, ‴ = 2 − *x*, 1 − *y*, 1 − *z*; N1···O3⁗ = 2.8960 (9) Å, H1F···O3⁗ = 2.247 (12) Å, N1–H1F···O3⁗ = 135.1 (11)°, ⁗ = 2 − *x*, 1/2 + *y*, 3/2 − *z* and N1···N2⁗ = 3.0214 (11) Å, H1F···N2⁗ = 2.518 (13) Å, N1–H1F···N2⁗ = 120.1 (11)°) shown in the Figure. In addition, a short intermolecular contact, the C1–H1C···O2⁗⁗, which satisfies to the distance and directionality conditions (C11···O2⁗⁗ = 3.3706 (11) Å, H11···O2⁗⁗ = 2.48 Å, C11–H11···O2⁗⁗ = 152°, ⁗⁗ = *x*, 1 + *y*, *z*), may contribute to the stability of the molecular packing in the HMAIH crystal, as well. To account for all interactions involved in the build-up of the crystal structure, we have performed DFT calculations, at the B3LYP/6–31G(d,p) theory level [5, 12], of the electrostatic, dispersion, polarization, and repulsion energies in the hydrazinium mesylate crystal structure. According to the calculations, the interactions between hydrogen-bonded pairs of ions located within the unit cell and shown in Figure provided the largest contribution to the lattice energy, with the electrostatic energy contributing the most for the attractive forces between neighbouring cation-anion pairs of hydrazinium mesylate (E_{elstat} = −69.7 kJ/mol, $E_{polarization}$ = −1.5 kJ/mol, $E_{dispersion}$ = −12.4 kJ/mol). The spatial distribution of the energetically most significant interactions is illustrated in the Figure, showing the Coulomb energy framework as red cylinders penetrating the crystal lattice of hydrazinium mesylate. The cylinders connect centroids of the interacting molecules, and their diameters are proportional to Coulomb energies of the interactions, with the 13 kJ/mol cut-off, for clarity. The most extensive intermolecular interactions occur in the directions parallel to (102) (see the Figure).

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

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