

Supramolecular hydrogen-bonding network in bis[1-(diaminomethylene)thiouron-1-ium] naphthalene-1,5-disulfonate

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Intermolecular interactions are important for the understanding of molecular self-organization of new solids with desired physical and chemical properties [1]. In this work crystals of bis[1-(diaminomethylene)thiouron-1-ium] naphthalene-1,5-disulfonate were grown using solution growth technique. A single-crystal sample was characterized by X-ray diffraction and FTIR spectroscopy. The compound crystallizes in centrosymmetric group C2/c of the monoclinic system. The conformations of the cation bis[1-(diaminomethylene)thiouron-1-ium] and the anion naphthalene 1,5-disulfonate are shown in figure 1.

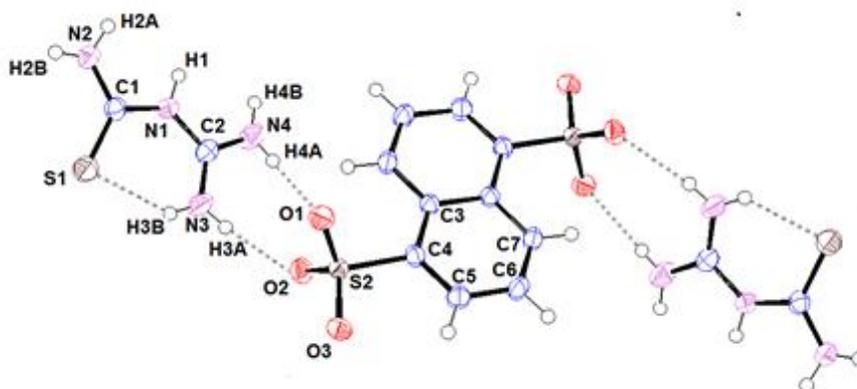
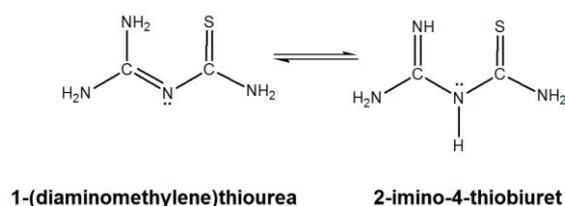


Figure 1: Atomic labels for the asymmetric unit of the title compound (inversion center on the middle of the naphthalene ring). N-H...O intermolecular and N-H...S intramolecular hydrogen bondings are represented by dashed lines.

Experimental:

Commercially available 2-imino-4-thiobiuret, which is in the fact the tautomeric form (scheme 1), 1-(diaminomethylene)thiourea [2] and the 1,5-naphthalenedisulfonic acid tetrahydrate were added to hot water in a molar proportion of 2:1. After several days, transparent colourless crystals were formed. The crystals have been separated by filtration and dried in air. Analysis: Calculated for C₁₄H₂₀N₈O₆S₄: C, 32.05; N, 21.26; O, 18.30; S, 24.45 and H, 3.84%. Found: C, 31.88; N, 21.32; O, 18.63; S, 24.39 and H, 3.78%. A colourless 0.05 mm x 0.02 mm x 0.05 mm sample was mounted on a Gemini Oxford CCD Diffractometer provided with a liquid nitrogen low-temperature device. IR data measured with an ABB Bomen MB 3000 FTIR spectrometer using KBr pellets.



Scheme 1: Tautomeric equilibrium forms of 1-(diaminomethylene)thiourea and 2-imino-4-thiobiuret

Table 1: Crystallographic data and refinement parameters for the title compound

Empirical formula	(C ₁₀ H ₆ O ₆ S ₂) (C ₂ H ₇ N ₄ S) ₂	
Molecular weight (g.mol ⁻¹)	524.62	
Crystal system / Space group	Monoclinic C2/c	
Radiation type, Wavelength (Å)	Mo Kα, λ= 0.71073	
Z	4	
Temperature	293 K	110 K
a(Å)	32.4476(6)	32.2303(2)
b(Å)	8.1602(2)	8.1523(4)
c(Å)	8.3878(2)	8.3096(4)
β	104.098(2)	104.358(4)
V(Å ³)	2154.02(9)	2115.2(2)
Absorption coefficient μ(mm ⁻¹)	0.49	0.50
R[F ² >2σ(F ²)]	0.0368	0.0305

Comments:

The X-ray analysis shows that the sulfonate group is deprotonated and the protons are transferred to the central nitrogen atom of 1-(diaminomethylene)thiourea molecule. The asymmetric unit (figure 1) is formed by one unit of cation 1-(diaminomethylene)thiuron-1-ium and a half of the anion naphthalene-1,5 disulfonate, the other half of the compound is obtained by inversion at the centre of the naphthalene ring. At room and low temperature, the system remains isostructural. The conformation of the cation is not strictly planar, but twisted, stabilized by one intramolecular hydrogen bond N3-H3B...S1 in a S(6) graph set (table 2). Both arms of the 1-(diaminomethylene)thiuron-1-ium are rotated around C-N bond involving the central N1 atom. Compared to neutral 1-(diaminomethylene)thiourea, where the observed dihedral angle is 22.2(1)°[2], the protonation on N1 reduces the steric effect of lone pair of electrons and the dihedral angle decreases to 6.0(3)°. The conformation of the anion compares to bis(dihydronium) naphthalene-1,5-disulfonate [3], with one oxygen (O3) laying on the ring.

In the crystal (figures 2 and 3) the opposite charges interact via almost linear hydrogen bonds forming three graph sets $R_2^2(8)$ and one $R_2^1(6)$ (table 2). The hydrogen bonding interactions (five N-H...O between cation-anion and one N2-H2B...S1ⁱⁱ between cation-cation) lead to formation of infinite zig-zag arrangements parallel to *ab* plane (figure 3). These arrangements are linked by *c* glide-plane symmetries via the N4-H4B...O2ⁱⁱⁱ hydrogen bonds (figure 2).

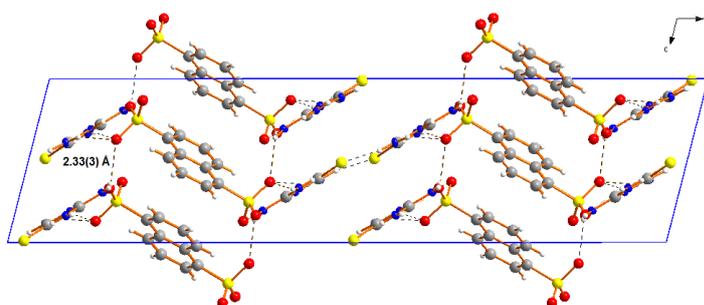


Figure 2: Unit cell of bis[1-(diaminomethylene)thiuron-1-ium] naphthalene-1,5-disulfonate viewed along *b* axis; zig-zag layers are linked via N4-H4B...O2ⁱⁱⁱ (table 2).

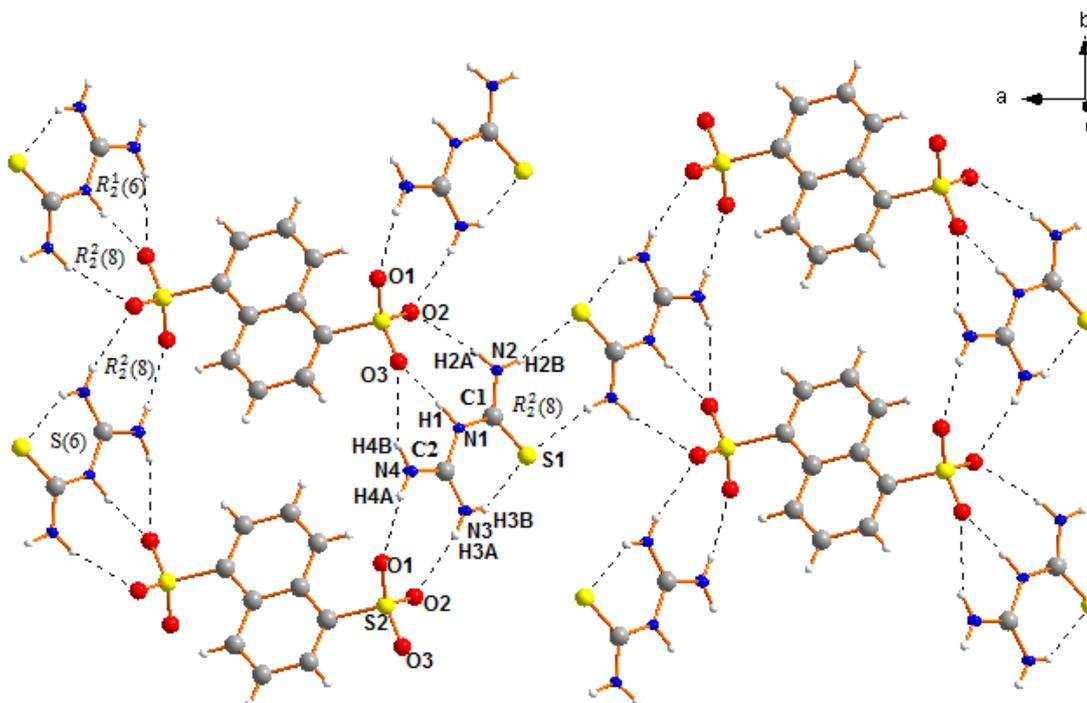


Figure 3: One layer viewed along *c* axis with N-H...O and N-H...S hydrogen bonds forming S(6), R₂²(8) and R₂¹(6) graph sets.

Table 2: Hydrogen bonds

Bonds	Distance (Å)			Angle (°)
	<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>H</i> ... <i>A</i>
N3—H3B...S1	0.84(3)	2.30(3)	2.991(2)	140(2)
N3—H3A...O2	0.79(3)	2.10(3)	2.865(2)	162(3)
N4—H4A...O1	0.79(3)	2.15(3)	2.934(3)	175(3)
N2—H2A...O2 ⁱ	0.87(3)	2.16(3)	2.983(2)	158(2)
N1—H1...O3 ⁱ	0.86(2)	1.97(2)	2.813(2)	170(2)
N4—H4B...O3 ⁱ	0.87(3)	2.41(3)	3.122(3)	139(3)
N2—H2B...S1 ⁱⁱ	0.80(3)	2.59(3)	3.383(2)	168(2)
N4—H4B...O2 ⁱⁱⁱ	0.87(3)	2.33(3)	2.926(2)	126(2)

Symmetry codes: (i) *x*, 1+*y*, *z*; (ii) 1-*x*, 3-*y*, 1-*z* (iii) *x*, 2-*y*, -0.5+*z*

The FTIR spectrum is shown in figure 4. The functional and skeletal groups are: C=S, SO₃⁻, N-C-N, C-N-C and N-C-S of the cation, naphthalene ring and SO₃⁻ of the anion. A band on spectral range of 3400-3100 cm⁻¹ can be attributed to asymmetric and symmetric stretching of NH₂ groups. A band on region of 2900 cm⁻¹ are assigned to C-H stretching. The broad absorption on FTIR region of 2800-2200 cm⁻¹ is attributed to N-H...O hydrogen bonds overlapped to C=N-H⁺ stretching of cation 1-(diaminomethylene)thiuron-1-ium. The stretching of sulfonate groups appeared on spectral range of 1230-1150 cm⁻¹ and the out of plane vibrations of three adjacent hydrogen atoms of the naphthalene ring occurred on 790 cm⁻¹. The C=S stretching is observed on 730 cm⁻¹. Skeletal deformations C-N-C, N-C-N and SO₃⁻ asymmetric deformation are observed on 564 cm⁻¹ [2,4].

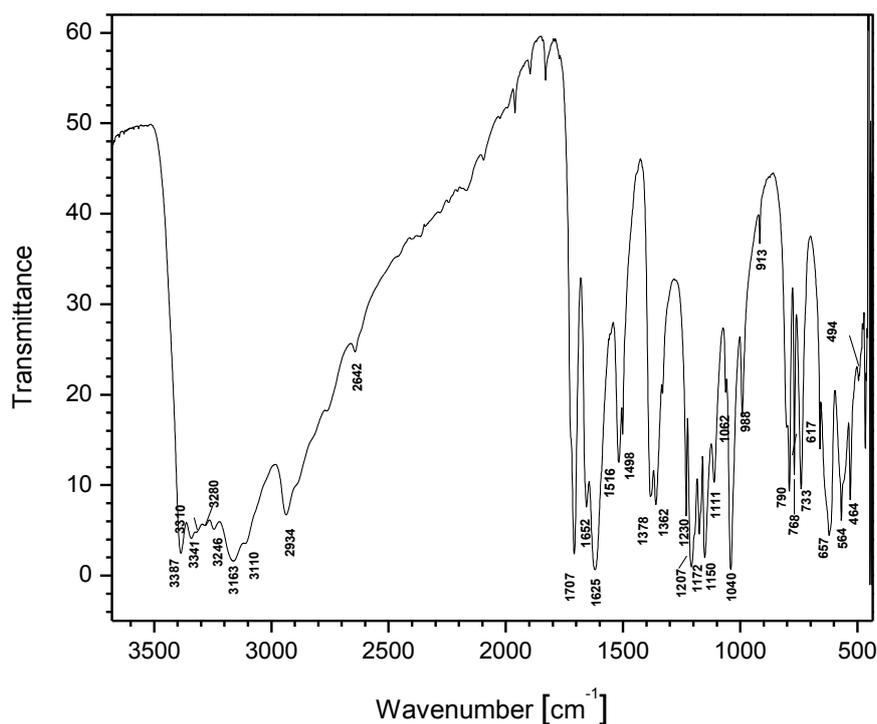


Figure 4: Spectrum FTIR of bis[1-(diaminomethylene)thiourea-1-ium] naphthalene-1,5-disulfonate

This work shows the applicability of diaminomethylene thiourea derivatives to build supramolecular structures. The arrangement of the oppositely charged components (bis[1-(diaminomethylene)thiourea-1-ium] and naphthalene-1,5-disulfonate) is mainly determined by ionic and hydrogen bonding interactions in crystal. The N-H \cdots O and N-H \cdots S intermolecular hydrogen bonds form $R_2^2(8)$ and $R_2^1(6)$ graph sets stabilizing the crystal structure.

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