

Salt forms of a thioamide: protonation of 1-(2,6-dimethylphenyl)thiourea

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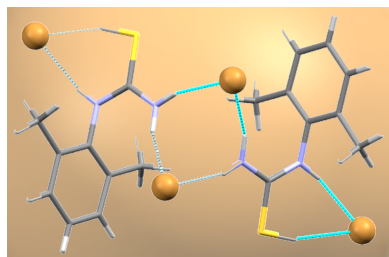
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Treating the thioamide 1-(2,6-dimethylphenyl)thiourea ($C_9H_{12}N_2S$, **DMPT**) with concentrated aqueous strong acids gave three salt forms with protonation at the thioamide S atom. The structures of 1-(2,6-dimethylphenyl)thiuronium chloride, $C_9H_{13}N_2S^+ \cdot Cl^-$ or **[DMPT(H)][Cl]**, 1-(2,6-dimethylphenyl)thiuronium bromide, $C_9H_{13}N_2S^+ \cdot Br^-$ or **[DMPT(H)][Br]**, and 1-(2,6-dimethylphenyl)thiuronium hydrogen sulfate, $C_9H_{13}N_2S^+ \cdot HSO_4^-$ or **[DMPT(H)][HSO₄]**, are compared with that of neutral **DMPT**. Protonation at the S atom results in a systematic lengthening of the C=S bond and a shortening of the C—N bonds, with a larger effect found for the bonds involving the secondary amine rather than the primary amine function. The **[DMPT(H)]⁺** cations are found to adopt one of two possible conformations, with the halide species having secondary N—H *syn* to S—H, whilst in the hydrogen sulfate structure, this relationship is *anti*. The change in cation conformation is related to a change in the hydrogen-bonding motif, but all three salt forms form layered structures with two-dimensional hydrogen-bonded units separated by layers of hydrophobic arene rings. An alternative product type was isolated on adding **DMPT** to concentrated sulfuric or tetrafluoroboric acid. Structures of the dicarbocationic disulfide species (disulfane-1,2-diyl)bis[*N*-(2,6-dimethylphenyl)methanediaminium] bis(tetrafluoroborate), $C_{18}H_{24}N_4S_2^{2+} \cdot 2BF_4^-$ or **[Dimer][BF₄]₂**, and (disulfane-1,2-diyl)bis[*N*-(2,6-dimethylphenyl)methanediaminium] bis(hydrogen sulfate) monohydrate, $C_{18}H_{24}N_4S_2^{2+} \cdot 2HSO_4^- \cdot H_2O$ or **[Dimer][HSO₄]₂·H₂O**, are also described.

1. Introduction

Study of protonated small molecules from chemical classes often thought of as non-basic (or neutral or non-ionizable) is often undertaken to aid understanding of acid-catalysed reaction mechanisms. Crystallographic studies of such reactive species include those on protonated ketones (Uran & Lozinšek, 2025; Stuart *et al.*, 2017), protonated aldehydes (Stuart *et al.*, 2017; Hayatifar *et al.*, 2014), protonated esters (Hollenwäger *et al.*, 2025), protonated carboxylic acids (Hollenwäger *et al.*, 2024) and protonated nitriles (Haiges *et al.*, 2016). When it comes to the protonation of amides, similar studies have also been carried out and are often performed with a view to gaining an understanding of salt formation for the pharmaceutical industry. Salt forms of active pharmaceutical ingredients (APIs) are commonly generated in an attempt to access a phase of an acidic or basic API which has idealized material properties (Stahl & Wermuth, 2008). More rarely, similar studies are carried out on formally neutral APIs. Nanubolu and co-workers surveyed known crystal structures of protonated amides in 2012. Since then, systematic API-relevant work on the solid-state structures of protonated amides has concentrated on simple amides such as paracetamol cognates (Perumalla & Sun, 2012; Perumalla *et al.*,



2012; Trzybiński *et al.*, 2016; Kennedy *et al.*, 2018; Suzuki *et al.*, 2020; Jaconelli & Kennedy, 2024) and on the urea-containing carbamazepine and its relatives (Perumalla & Sun, 2012; Perumalla & Sun, 2013; Buist *et al.*, 2013; Buist *et al.*, 2015; Eberlin *et al.*, 2013; Buist & Kennedy, 2016). These amides have been shown to protonate at the O atom and to feature patterns of elongated C=O and shortened C—N bonds consistent with the resonance forms shown in Fig. 1. However, little similar structural work has been undertaken for comparable thioamide compounds. A search of the Cambridge Structural Database (Version 6.01, with updates to November 2025; Groom *et al.*, 2016) found 18 structures that contained protonated thiourea [HSC(NH₂)₂], but in all structures this cation was associated with small inorganic anions or MX_x anions (M = transition metal and X = halide) and so relevance to APIs is low (for typical examples, see Biesiada *et al.*, 2014; Daub & Hillebrecht, 2021; Li & Li, 2014). Structures of larger organic fragments that could reliably be described as protonated thioamide anions are restricted to CSD refcodes MUSDAI, PAJLIY, VOZGUP, WEXGUB, XEYVUW and XEYVOQ (Ho *et al.*, 2020; Liu *et al.*, 2017; Eichele *et al.*, 2019; Gladii *et al.*, 1994; Golovnev *et al.*, 2023).

To obtain a series of salt forms of protonated thioamides, we investigated protonation of 1-(2,6-dimethylphenyl)thiourea (**DMPT**). This compound was of interest partly as it is a simple model compound containing an aromatic thiourea function-

ality and partly as it is a crucial intermediate in the synthesis of the veterinary tranquilizer and drug of abuse xylazine (Ruiz-Colón *et al.*, 2014; Chang *et al.*, 2025). The structure of **DMPT** was reported by Sarojini and co-workers in 2007. Herein we re-elucidate this structure and present the new crystal structures of three protonated or salt forms of **DMPT**, namely, [DMPT(H)][Cl], [DMPT(H)][Br] and [DMPT(H)][HSO₄]. Also described are the structures of two disulfide compounds recovered from acidic solutions of **DMPT**; these are [Dimer][BF₄]₂ and [Dimer][HSO₄]₂·H₂O.

2. Experimental

2.1. Synthesis and crystallization

The synthesis of **DMPT** was based on the method of Burke & Fitzgerald (1989). Acetone (25 ml) was dried over calcium chloride and ammonium thiocyanate was dried in a vacuum oven at 80 °C. Ammonium thiocyanate (5.30 g, 0.07 mol) was added to a two-necked flask fitted with a condenser and dropping funnel, and then dissolved in the dry acetone. Benzoyl chloride (6.7 ml, 0.06 mol) was added at a fast rate, *via* the dropping funnel, to the stirred reaction mixture. Once the addition was complete, the dropping funnel was used to add 2,6-dimethylaniline (6.2 ml, 0.05 mol) at a rate which caused the reaction mixture to reflux gently. After addition, the mixture was refluxed for a further 5 min. Cooling the reaction mixture to 10 °C gave a solid that was recovered by filtration and washed with water. The crude solid was added to an aqueous solution of 2.8 *M* sodium hydroxide (7.5 g in 67.5 ml), heated to boiling and left for 5 min. After allowing the mixture to cool to room temperature, the resulting solid was filtered off and washed with water. Drying the product under vacuum gave a free-flowing pale-yellow powder (typical yield 6.04 g, 66.5%). Large crystals of **DMPT** were obtained upon recrystallization from hot acetone (m.p. 179–180 °C).

Crystals of [DMPT(H)][Cl] and [DMPT(H)][Br] were produced by first forming slurries from 0.1 g (0.55 mmol) of **DMPT** and 3 ml of deionized water. 2 ml of the appropriate concentrated acid were then added slowly and the solutions warmed to aid dissolution. After filtration, the clear solutions obtained were left to evaporate slowly, giving suitable colourless crystals within 4 d. The melting points were 167–168 and 145–146 °C for the chloride and bromide salt, respectively.

Using the same method with concentrated sulfuric acid initially gave crystals of the expected product [DMPT(H)][HSO₄] after approximately six weeks of slow evaporation. However, on rechecking the same acidic-aqueous sample after approximately six months, the crystals isolated were found to be [Dimer][HSO₄]₂·H₂O. Similar checks on the halide salt samples (above) observed no such disulfide products, with crystals of both [DMPT(H)][Cl] and [DMPT(H)][Br] still being present despite being in contact with the original acidic-aqueous mother liquors.

Using a similar method with concentrated HBF₄ did not give any of the desired [DMPT(H)]⁺-containing product. Instead, only large colourless crystals of the disulfide product

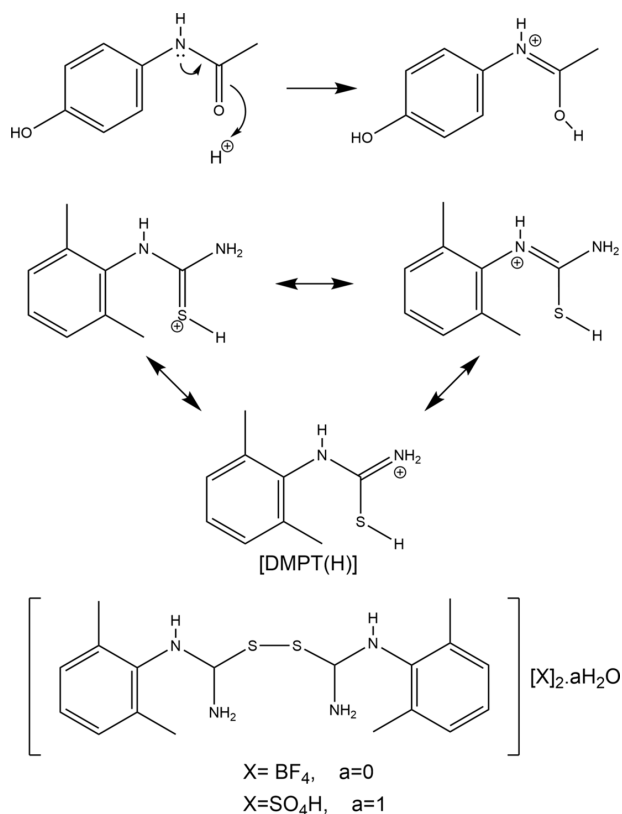


Figure 1

(Top) C=O bond lengthening and C—N bond shortening on protonation of the simple API paracetamol. (Middle) Potential resonance forms of the protonated cation [DMPT(H)]⁺. (Bottom) The structures of [Dimer][BF₄]₂ and [Dimer][HSO₄]₂·H₂O.

Table 1
Experimental details.

Experiments were carried out with Cu $K\alpha$ radiation using a Rigaku Synergy-i diffractometer. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Rigaku OD, 2025). H atoms were treated by a mixture of independent and constrained refinement.

	DMPT	[DMPT(H)][Cl]	[DMPT(H)][Br]
Crystal data			
Chemical formula	C ₉ H ₁₂ N ₂ S	C ₉ H ₁₃ N ₂ S ⁺ ·Cl [−]	C ₉ H ₁₃ N ₂ S ⁺ ·Br [−]
M_r	180.27	216.72	261.18
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature (K)	180	180	100
a, b, c (Å)	9.8193 (1), 8.3655 (3), 11.7827 (2)	11.7848 (2), 10.3644 (2), 19.2687 (3)	13.3544 (2), 8.7556 (1), 20.5020 (2)
β (°)	91.696 (1)	105.844 (2)	112.485 (1)
V (Å ³)	967.45 (4)	2264.11 (7)	2214.97 (5)
Z	4	8	8
μ (mm ^{−1})	2.54	4.37	6.48
Crystal size (mm)	0.25 × 0.18 × 0.06	0.20 × 0.15 × 0.10	0.17 × 0.14 × 0.08
Data collection			
$T_{\min}, T_{\max}$	0.758, 1.000	0.758, 1.000	0.770, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10267, 1887, 1811	6924, 2189, 1949	11782, 2157, 2119
R_{int}	0.016	0.028	0.020
($\sin \theta/\lambda$) _{max} (Å ^{−1})	0.617	0.616	0.616
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.077, 1.09	0.031, 0.089, 1.05	0.018, 0.048, 1.05
No. of reflections	1887	2189	2157
No. of parameters	123	136	137
No. of restraints	0	1	0
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.23, −0.25	0.24, −0.19	0.33, −0.30

	[DMPT(H)][HSO ₄]	[Dimer][BF ₄] ₂	[Dimer][HSO ₄] ₂ ·H ₂ O
Crystal data			
Chemical formula	C ₉ H ₁₄ N ₂ O ₄ S ₂ ⁺ ·HSO ₄ [−]	C ₁₈ H ₂₄ N ₄ S ₂ ²⁺ ·2BF ₄ [−]	C ₁₈ H ₂₄ N ₄ S ₂ ²⁺ ·2HSO ₄ [−] ·H ₂ O
M_r	278.34	534.15	572.68
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
Temperature (K)	100	180	120
a, b, c (Å)	11.9033 (2), 13.3341 (3), 8.0321 (2)	15.6877 (2), 10.4883 (2), 14.8569 (2)	15.7786 (1), 10.5384 (1), 15.1791 (1)
β (°)	102.842 (2)	98.972 (1)	102.694 (1)
V (Å ³)	1242.96 (5)	2414.60 (6)	2462.31 (3)
Z	4	4	4
μ (mm ^{−1})	3.97	2.71	4.05
Crystal size (mm)	0.40 × 0.12 × 0.12	0.22 × 0.15 × 0.07	0.09 × 0.08 × 0.07
Data collection			
$T_{\min}, T_{\max}$	0.428, 1.000	0.732, 1.000	0.793, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11118, 2361, 2209	10154, 2347, 2180	25961, 4797, 4387
R_{int}	0.044	0.020	0.039
($\sin \theta/\lambda$) _{max} (Å ^{−1})	0.615	0.616	0.617
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.049, 0.127, 1.10	0.033, 0.089, 1.08	0.029, 0.088, 1.04
No. of reflections	2361	2347	4797
No. of parameters	176	168	361
No. of restraints	3	0	11
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.41, −0.72	0.31, −0.21	0.38, −0.42

Computer programs: *CrysAlis PRO* (Rigaku OD, 2025), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *SHELXL* in *WinGX* (Farrugia, 2012).

[Dimer][BF₄]₂ were isolated. These became apparent after approximately 7 d of slow evaporation.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms bonded to C atoms

were observed in difference electron-density calculations, but were added in expected positions and refined as riding on their parent C atoms. All H atoms bonded to S atoms were refined freely and isotropically. Similar free refinement was used for most H atoms bonded to either O or N atoms. However, N—H distances in both [DMPT(H)][Cl] and [DMPT(H)][HSO₄] were restrained to 0.88 (1) Å, as were both the N—H and the

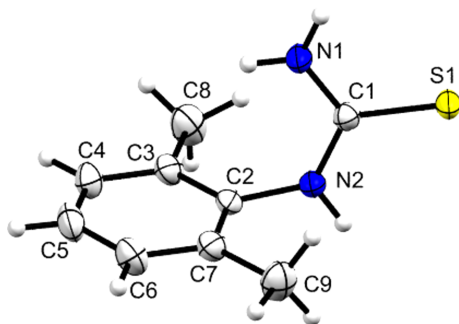


Figure 2

The molecular structure of **DMPT**, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary size. Disordered H-atom positions on C8 have been omitted for clarity.

O—H distances in **[Dimer][HSO₄]₂·H₂O**. The H atoms of the methyl group at C8 of **DMPT** were modelled as rotationally disordered over two sites.

3. Results and discussion

The molecular structure of **DMPT** is shown in Fig. 2 and is in agreement with that reported earlier by Sarojini *et al.* (2007). This structure is used herein largely as a comparison for the species with protonated **[DMPT(H)]⁺** cations, but some salient points to note are that there is an 80.82 (5)° angle between the plane of the thioamide group and the aromatic ring plane (here and later defined by the N1/C1/S1/N2 plane and the six C atoms C2–C7, respectively) and that both the N atoms adopt essentially *sp*² geometries coplanar with the thioamide plane, although there is a small nonplanar deviation of the secondary amine (N2), with atom C2 lying 0.3246 (17) Å from the thioamide plane. The main intermolecular feature is the one-dimensional hydrogen-bonded ribbon shown in Fig. 3. This extends parallel to the crystallographic *b* direction and is formed from *R*₂²(8) motifs utilizing sulfur as the acceptor and two of the three N—H atoms as donors; see Table 2 for further details (Etter *et al.*, 1990).

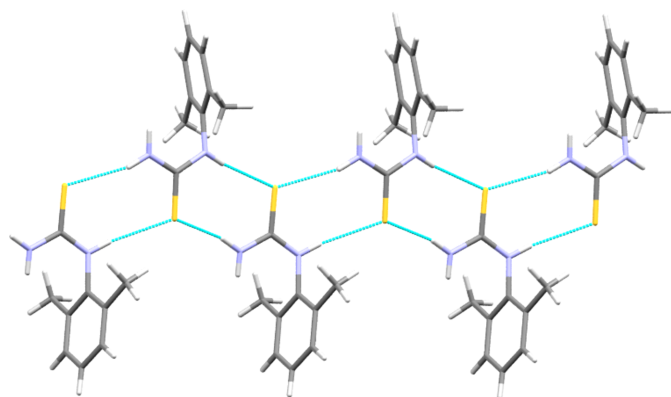


Figure 3

Section of the hydrogen-bonded (dashed lines) one-dimensional ribbon found in the structure of **DMPT**.

Table 2

Selected hydrogen-bond parameters (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>
DMPT				
N1—H1N...S1 ⁱ	0.856 (19)	2.464 (19)	3.2961 (12)	164.2 (15)
N2—H3N...S1 ⁱⁱ	0.849 (17)	2.576 (18)	3.4183 (11)	171.6 (14)
[DMPT(H)][Cl]				
S1—H1S...Cl1 ⁱⁱⁱ	1.26 (2)	2.39 (2)	3.6064 (6)	162.4 (14)
N1—H1N...Cl1 ^{iv}	0.87 (2)	2.33 (2)	3.1685 (15)	162.9 (19)
N1—H2N...Cl1 ^v	0.94 (2)	2.42 (2)	3.2649 (15)	149.4 (19)
N2—H3N...Cl1 ⁱⁱⁱ	0.863 (9)	2.296 (10)	3.1467 (13)	168.7 (18)
[DMPT(H)][Br]				
S1—H1S...Br1	1.23 (2)	2.52 (2)	3.7176 (4)	162.9 (16)
N1—H1N...Br1 ^{vi}	0.82 (2)	2.56 (2)	3.3363 (14)	160.1 (19)
N1—H2N...Br1 ^{vii}	0.89 (2)	2.58 (2)	3.3725 (14)	148.4 (18)
N2—H3N...Br1	0.88 (2)	2.47 (2)	3.3298 (13)	165.4 (19)
[DMPT(H)][HSO₄]				
S1—H1S...O3	1.18 (5)	2.54 (4)	3.645 (3)	154 (3)
S1—H1S...O4	1.18 (5)	2.60 (5)	3.678 (3)	150 (3)
N1—H1N...O3	0.874 (10)	1.935 (11)	2.807 (4)	175 (4)
N1—H2N...O4 ^{viii}	0.877 (10)	1.985 (12)	2.859 (4)	174 (4)
N2—H3N...O1 ^{viii}	0.878 (10)	1.968 (11)	2.845 (4)	178 (5)
O2—H2S...O1 ^{ix}	0.84 (6)	1.79 (6)	2.627 (3)	173 (6)
[Dimer][BF₄]₂				
N1—H1N...F2 ^x	0.91 (2)	1.90 (2)	2.8128 (17)	173 (2)
N1—H2N...F1 ⁱⁱ	0.85 (2)	1.99 (2)	2.8105 (18)	161.3 (19)
N2—H3N...F4	0.84 (2)	2.02 (2)	2.8396 (18)	166 (2)
N2—H3N...S1 ^{xi}	0.84 (2)	2.76 (2)	3.1502 (14)	110.1 (16)
[Dimer][HSO₄]₂·H₂O				
N1—H1N...O1	0.877 (9)	1.951 (10)	2.8256 (16)	175 (2)
N1—H2N...O2 ^{xii}	0.878 (10)	1.962 (11)	2.8172 (16)	164 (2)
N2—H3N...O3 ^{xiii}	0.868 (9)	1.947 (10)	2.8125 (16)	175.2 (18)
N3—H4N...O7 ^{xiv}	0.879 (9)	1.976 (10)	2.8440 (16)	169.3 (19)
N3—H5N...O8	0.877 (9)	2.132 (12)	2.9596 (16)	157.0 (19)
N4—H6N...O6 ^{xv}	0.868 (9)	2.058 (12)	2.8703 (16)	155.5 (19)
O4—H1H...O1W	0.891 (10)	1.673 (11)	2.5571 (15)	171 (3)
O6—H2H...O3 ^{xvi}	0.884 (10)	1.717 (10)	2.5966 (15)	173 (2)
O1W—H1W...O5 ^{xvii}	0.865 (10)	2.36 (2)	2.9801 (16)	129 (2)
O1W—H2W...O8 ^{xvii}	0.874 (10)	2.017 (13)	2.8515 (16)	159 (2)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 2, -y, -z + 1$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (v) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (vii) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (viii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ix) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (x) $x, -y, z - \frac{1}{2}$; (xi) $-x + 1, y, -z + \frac{1}{2}$; (xii) $-x, -y + 1, -z + 1$; (xiii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (xiv) $-x + 1, -y + 1, -z + 2$; (xv) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (xvi) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (xvii) $-x + 1, -y + 1, -z + 1$.

Notably, this arrangement does not allow the third N—H atom, on the primary amine, to act as a hydrogen-bond donor.

Addition of concentrated HCl to a slurry of **DMPT** gave colourless crystals identified as **[DMPT(H)][Cl]**. It was noted that at temperatures below 170 K, these crystals did not diffract – and that often the mounted single crystal shattered. This is suggestive of the chloride salt displaying a temperature-induced phase change. Reactions with HBr and H₂SO₄ also gave crystals that contained the **[DMPT(H)]⁺** cation and the structures of all three species **[DMPT(H)][Cl]**, **[DMPT(H)][Br]** and **[DMPT(H)][HSO₄]** are displayed in Figs. 4–6.

In all cases, the protonation site of **DMPT** is identified as the S atom. Electron-density contour maps in support of these protonation sites are available in the supporting information. For the halide salts, the protonated S—H group is *syn* to the N—H group of the secondary amide at N2 and neutral **DMPT** has a similar *syn* conformation. Conversely, in the hydrogen sulfate salt, the S—H group is orientated *anti* to the N2 N—H

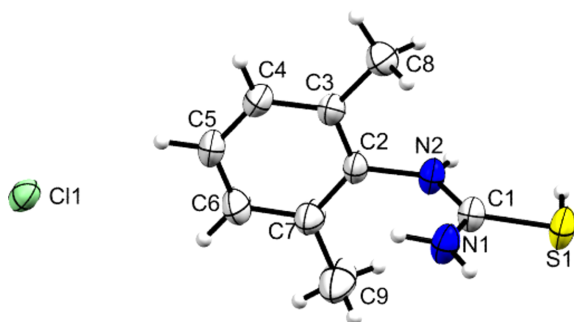


Figure 4

Contents of the asymmetric unit of **[DMPT(H)][Cl]**, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary size.

moiety. In terms of the dihedral angles between the thioamide plane and the aromatic plane, there is no systematic change observed between the **[DMPT(H)]⁺** cations and **DMPT**, with the value of 80.81 (5)° for the latter falling within the range [75.10 (4)–89.94 (5)°] found for the cations. A small difference is that the slight pyramidalization of the secondary amine seen for **DMPT** is not present in any of the cationic forms. In all cases, the C1–S1–H1S angle of the cation is somewhat narrow [range 92 (2)–95.9 (11)°]. However, this is supported by the internal consistency of the three reported **[DMPT(H)]⁺** structures and by similar angles being observed in other protonated thioamides (Ho *et al.*, 2020; Liu *et al.*, 2017; Golovnev *et al.*, 2023). From consideration of resonance structures (Fig. 1) and by comparison to known O-protonated amide structures, it is expected that the C1=S1 bond lengths will increase upon protonation at S and that the N–C1 bonds should correspondingly shorten. Table 3 shows that this effect is indeed observed here, with protonation leading to the C1=S1 distances increasing by 0.052 (2) to 0.054 (2) Å, C1–N1 decreasing by 0.007 (4) to 0.015 (3) Å and C1–N2 decreasing by 0.026 (3) to 0.032 (3) Å. These values indicate that the increase in double-bond character is much larger for the C1–N2 bond of the secondary amine moiety bonded to the aryl ring, than it is for the C1–N1 bond to the primary

Table 3

Selected bond lengths (Å) for **DMPT** and protonated **[DMPT(H)]⁺** species.

DMPT			
S1–C1	1.6992 (12)	N2–C1	1.3447 (15)
N1–C1	1.3225 (16)	N2–C2	1.4429 (14)
[DMPT(H)][Cl]			
S1–C1	1.7530 (15)	N2–C1	1.312 (2)
N1–C1	1.308 (2)	N2–C2	1.4442 (18)
[DMPT(H)][Br]			
S1–C1	1.7508 (15)	N2–C1	1.318 (2)
N1–C1	1.313 (2)	N2–C2	1.4476 (19)
[DMPT(H)][HSO₄]			
S1–C1	1.751 (3)	N2–C1	1.317 (4)
N1–C1	1.316 (4)	N2–C2	1.444 (4)

amine. Similar effects were seen in the protonated urea functionality of carbamazepine derivatives [$R_2NC(OH)NH_2$], where bond-length shortening was more pronounced for the N–C bond of the tertiary amine than for the primary amine (Buist *et al.*, 2013). At approximately 0.05 Å, the increase in the C=S bond lengths is greater in absolute terms than that seen for hemi-protonated amides (*e.g.* for acetanilide, **ACT**, the C=O bond lengths increase by approximately 0.02 to 0.04 Å on forming **[ACT(H)·ACT]** pairs), but at the low end for the typical increase seen for fully protonated amide species (*e.g.* for carbamazepine and paracetamol, C=O bond lengths typically increase by 0.05 to 0.07 Å and, in all cases, these changes are at least an order of magnitude greater than the associated error) (Jaconelli & Kennedy, 2024; Buist *et al.*, 2013; Kennedy *et al.*, 2018). This is interesting as C=S bonds are of course longer than C=O bonds and thus the observed increase in bond length between neutral and protonated states is smaller in percentage terms (approximately 3% compared to 5%) for C=S *versus* C=O. It is suggested that the relatively small effect may be related to the poorer 2*p*–3*p* orbital overlap between C and S in forming the π -bond, as compared to the more energy matched 2*p*–2*p* orbital overlap in the O and C π -bond. Overall this renders the ‘double-bond’ description of C=S somewhat less relevant than it is for C=O.

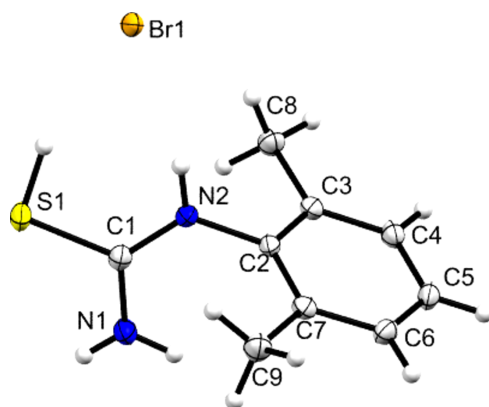


Figure 5

Contents of the asymmetric unit of **[DMPT(H)][Br]**, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary size.

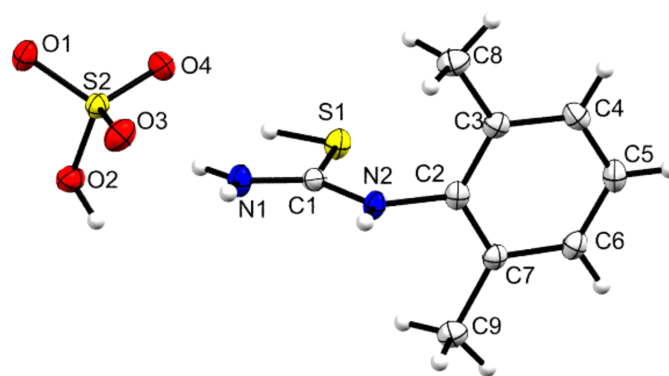


Figure 6

Contents of the asymmetric unit of **[DMPT(H)][HSO₄]**, with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary size.

Table 4

Selected bond angles ($^{\circ}$) and the dihedral angles ($^{\circ}$) between the planes of thioamide group and the C_6 ring for the DMPT-containing structures.

DMPT		[DMPT(H)][Cl]	
C1—N2—C2	120.47 (10)	C1—S1—H1S	94.5 (9)
N1—C1—N2	117.96 (11)	C1—N2—C2	122.45 (13)
N1—C1—S1	120.39 (9)	N1—C1—N2	122.01 (14)
N2—C1—S1	121.64 (9)	N1—C1—S1	117.69 (12)
Dihedral	80.82 (5)	N2—C1—S1	120.29 (12)
		Dihedral	89.94 (5)
[DMPT(H)][Br]		[DMPT(H)][HSO ₄]	
C1—S1—H1S	95.9 (11)	C1—S1—H1S	92 (2)
C1—N2—C2	122.33 (13)	C1—N2—C2	123.0 (3)
N1—C1—N2	121.70 (14)	N1—C1—N2	122.1 (3)
N1—C1—S1	117.21 (12)	N1—C1—S1	121.1 (2)
N2—C1—S1	121.08 (12)	N2—C1—S1	116.8 (2)
Dihedral	75.10 (4)	Dihedral	87.44 (10)

The $C=S$ bond lengths observed here fit with those found for compounds containing the thiourea hydrogen ion ($HSCNH_2$)₂, albeit at the long end of the observed range (*e.g.* Biesiada *et al.*, 2014; Daub & Hillebrecht, 2021; Li & Li, 2014).

Table 4 illustrates that protonation also results in a systematic change to the bond angles of the thioamide. The $C1-N2-C2$ and $N1-C1-N2$ angles both increase on protonation, by approximately $2.0-2.5$ and $3.7-4.1^{\circ}$, respectively, with all error values an order of magnitude lower. The change in the angle at C1 is matched by similar increases in the equivalent amide species (Jaconelli & Kennedy, 2024; Buist *et al.*, 2013). However, the other angles present more complex behaviour. For both paracetamol and acetanilide, the equivalent of the $C1-N2-C2$ angle was found to change in different ways depending on the conformation of the cation (Jaconelli & Kennedy, 2024; Kennedy *et al.*, 2018). When the amide was coplanar with the aryl ring, this angle systematically widened on protonation, but narrowed when the amide group was twisted out of the plane of the ring. All the current protonated thioamide fragments are twisted (see Table 4), but in contrast to the amide examples all show widening of

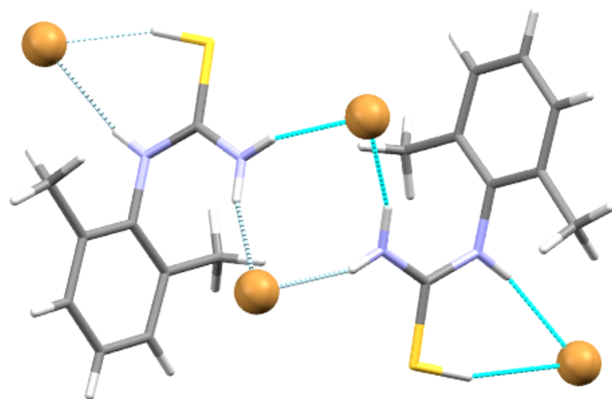


Figure 7

Section illustrating the main hydrogen-bonding interaction types (dashed lines) found in [DMPT(H)][Br]. The same structural motifs are found in [DMPT(H)][Cl]. Cations are drawn in stick format and bromide anions are shown as large balls.

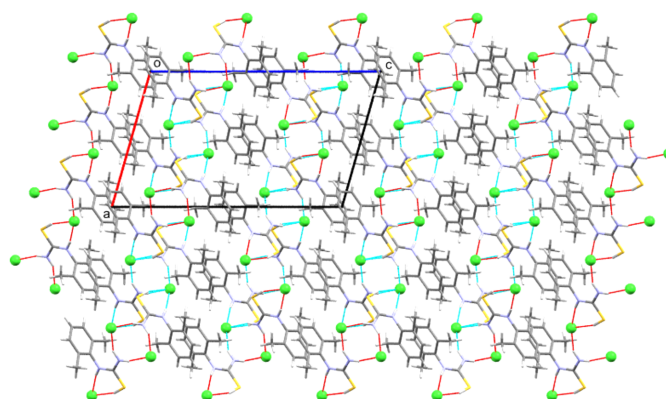


Figure 8

Packing array found in [DMPT(H)][Cl], viewed along the b direction. Note the hydrophobic layers consisting of aromatic groups that separate the hydrogen-bonded hydrophilic zones. Both layer types lie parallel to the ab plane.

$C1-N2-C2$. The angular changes that seem to depend on conformation here are those involving the S atom. For the two halide species where the protonated $S-H$ group is *syn* to the $N-H$ group of the secondary amide, $N1-C1-S1$ decreases on protonation [from 120.35 (10) to 117.69 (12) and 117.21 (12) $^{\circ}$], as do the $N2-C1-S1$ angles, albeit by a smaller amount [from 121.66 (10) to 120.29 (12) and 121.08 (12) $^{\circ}$]. In contrast in the *anti* species, [DMPT(H)][HSO₄], $N1-C1-S1$ increases to 121.1 (2) $^{\circ}$ and $N2-C1-S1$ shows a large decrease to 116.8 (2) $^{\circ}$. Thus, angular changes on protonation of this thioamide are found to depend upon conformation, as well as on the act of protonation itself.

The *syn* arrangement of the protonated $S-H$ group and the $N-H$ group of the secondary amide allow these two groups to form a six-membered hydrogen-bonded ring, $R_2^1(6)$, with the halide anions of [DMPT(H)][Cl] and [DMPT(H)][Br]. In both structures, the two H atoms of the NH_2 groups also act as

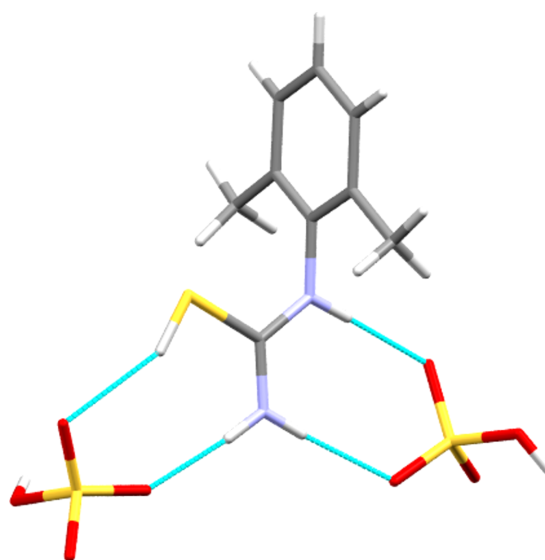


Figure 9

Hydrogen-bonded contacts (dashed lines) formed by the cation in [DMPT(H)][HSO₄].

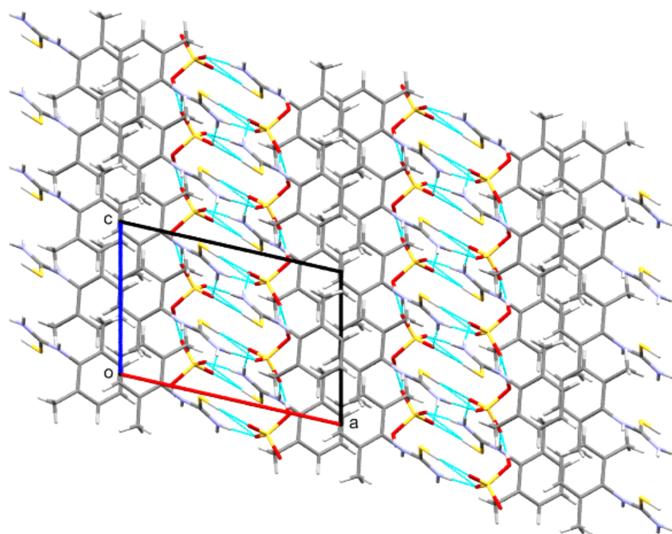


Figure 10
Packing diagram of the **[DMPT(H)][HSO₄]** structure, viewed along the direction of the *b* axis.

single hydrogen-bond donors to two further halide anions. The action of the crystallographic twofold axis forms $[\text{NH}_2\text{--}X\text{--}\text{NH}_2\text{--}X]$ dimers of type $R_2^2(8)$ from these latter interactions (see Table 2 and Fig. 7). Combining these interaction types gives two-dimensional hydrogen-bonded layers that lie perpendicular to the *c* axis. Each such two-dimensional motif is separated from its neighbours by the aromatic groups, giving layered structures, such as that seen for **[DMPT(H)][Cl]** in Fig. 8.

The *anti* conformer of the cation in **[DMPT(H)][HSO₄]** forms one hydrogen bond from each donor atom to four O atoms of two neighbouring hydrogen sulfate anions. This gives two $R_2^2(8)$ rings, one with S—H and N—H donors, and the other with two N—H donors, as shown in Fig. 9 and detailed in

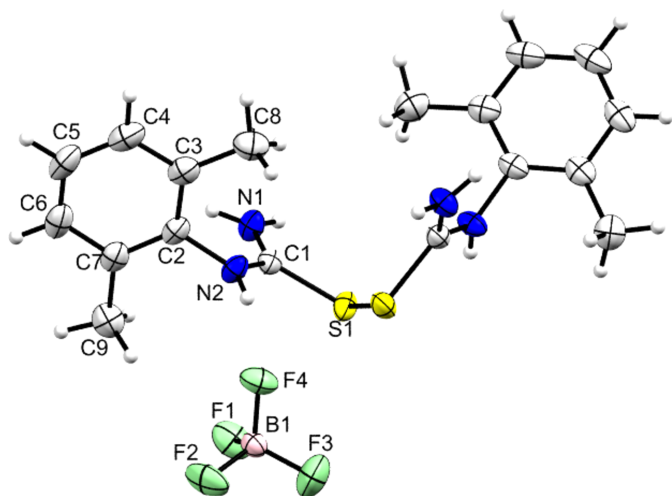


Figure 11
The asymmetric unit of **[Dimer][BF₄]₂**, with the cation expanded to show its full atomic connectivity. The unnumbered atoms are related to the named atoms by the operation $(-x + 1, y, -z + \frac{1}{2})$. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary size.

Table 2. These interactions combine with anion-to-anion O—H...O hydrogen bonds to give a two-dimensional hydrogen-bonded construct that forms layers perpendicular to the crystallographic *a* direction (see Fig. 10). As with the halide structures above, these layers are separated by layers formed by the hydrophobic aromatic groups.

Two further products were isolated from addition of strong acids to **DMPT**, as described in the *Experimental* section. These were the disulfide species **[Dimer][BF₄]₂** and **[Dimer][HSO₄]₂·H₂O**, whose structures are illustrated in Figs. 11 and 12. The asymmetric unit of the BF_4^- salt contains one anion and half of the cation – with the other half generated by the action of a crystallographic twofold axis. Although these are clearly decomposition products and not the expected salt forms of **DMPT**, their structures are reported here as there are surprisingly few structural reports of carbocations with a CSNN core in the CSD. A search found only five structures with acyclic CSNN cores and of these only that of $[(\text{Me}_2\text{N})_2\text{C}(\text{SSC}(\text{NMe}_2)_2)][\text{Fe}_2\text{OCl}_6]$ contained a dication as described here (Senda *et al.*, 2000). Note that the synthesis of disulfides is of perennial interest in medically-relevant organic synthesis (*e.g.* Hou *et al.*, 2025; Hunter *et al.*, 2006).

The S—S disulfide bonds of 2.0364 (8) and 2.0431 (5) Å are indistinguishable from similar bond lengths found in neutral species [a search found 1656 C—S—S—C fragments, in high-quality structures with $R < 5\%$, that gave an average S—S bond length of 2.05 (4) Å]. Table 5 shows that the two salts of the disulfide species also have similar C—N and C—S bonds at the carbocation centres, and that both C—S—S—C torsion angles deviate only slightly from a perpendicular conformation. Further indications of the conformational similarity of the two dicarbocations are that the aromatic ring planes and

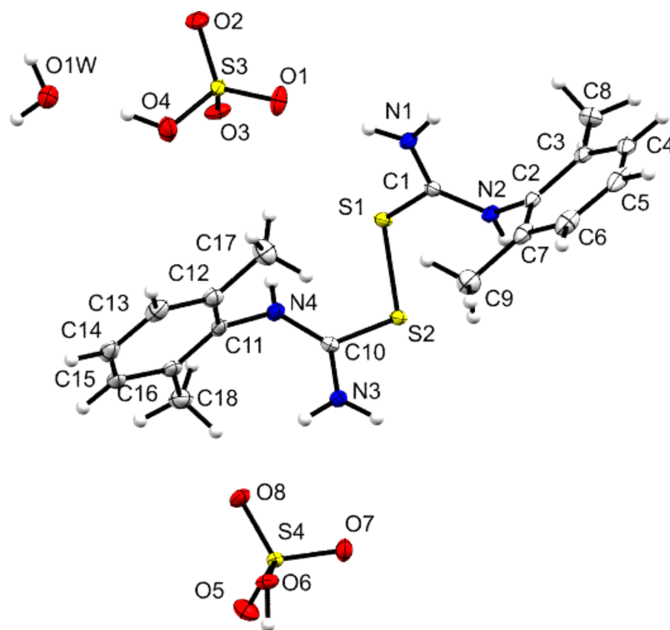


Figure 12
Contents of the asymmetric unit of **[Dimer][HSO₄]₂·H₂O**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary size.

Table 5

Selected geometric parameters (Å, °) for the disulfide species.

[Dimer][BF₄]₂			
N1—C1	1.305 (2)	C1—S1	1.7792 (15)
N2—C1	1.307 (2)	S1—S1 ⁱ	2.0364 (8)
C1—S1—S1 ⁱ —C1 ⁱ	−95.78 (11)		
[Dimer][HSO₄]₂·H₂O			
S1—C1	1.7879 (14)	N2—C1	1.3107 (18)
S1—S2	2.0431 (5)	N3—C10	1.3097 (19)
S2—C10	1.7804 (14)	N4—C10	1.3076 (18)
N1—C1	1.3106 (19)	C1—S1—S2—C10	97.20 (10)

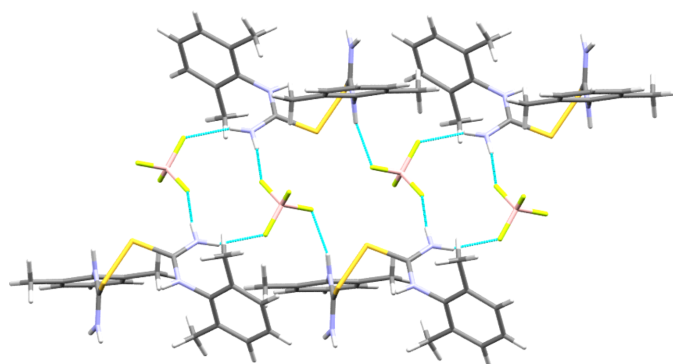
Symmetry code: (i) $-x + 1, y, -z + \frac{1}{2}$.

Figure 13

Representation of the hydrogen bonding (dashed lines) found in **[Dimer][BF₄]₂**, showing both the $R_4^4(12)$ rings common to the BF_4^- and HSO_4^- salt forms, and the $R_4^4(22)$ rings found only in the BF_4^- salt.

their adjacent CSN_2 carbocation planes are essentially perpendicular (range 86.95 – 87.23°), and that both have broadly similar dihedral angles of 50.42 and 46.32° between the planes of their two aromatic rings.

There are some differences in structure between the two disulfide structures related to details of the hydrogen bonding present. Similarities are that both cations form one hydrogen bond from every NH atom to an F or O atom of the appro-

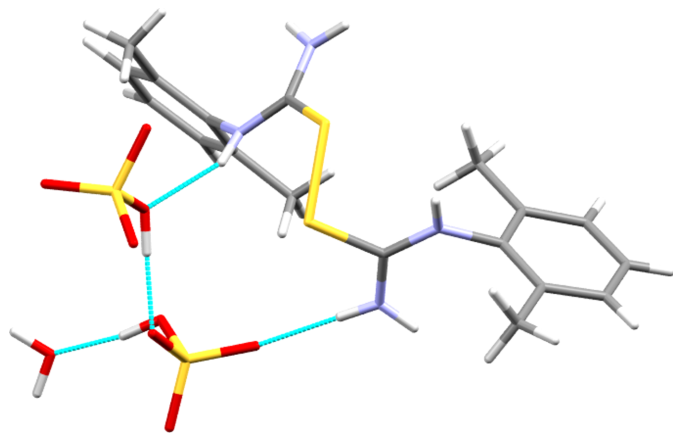


Figure 14

Illustration of the $R_3^3(13)$ hydrogen-bonding motif found in the structure of **[Dimer][HSO₄]₂·H₂O**. Hydrogen bonds are represented by dashed lines.

priate anion, and that in both structures the primary amines form $R_4^4(12)$ rings involving two NH_2 groups and two anions. However, the motifs formed by the secondary amine differ. In the BF_4^- salt, the principle motif is $R_4^4(22)$ rings formed from two cations and two anions, but the hydrogen-bond donor OH group of the hydrogen sulfate anion ensures a different outcome in **[Dimer][HSO₄]₂·H₂O**. Here, an $R_3^3(13)$ motif is formed from a single cation and two anions. These hydrogen-bonding contacts are illustrated in Figs. 13 and 14, and detailed in Table 2. A final point with respect to intermolecular contacts is that none of the **[DMPT(H)]⁺**-cation-containing structures show any significant cation-to-cation interactions. However, both structures with **[Dimer]⁺** cations do so. Both feature short $\text{C}\cdots\text{C}$ contacts that indicate that all the C_6 aryl rings are involved in π – π interactions [minimum $\text{C}\cdots\text{C}$ distances of 3.343 (3) and 3.224 (4) Å for **[Dimer][BF₄]₂** and **[Dimer][HSO₄]₂·H₂O**, respectively].

4. Summary

Three salt forms with S-protonated thioamide groups were characterized crystallographically, as were two disulfide carbocation species formed from the neutral parent thioamide. The **[DMPT(H)]⁺** cations were found to have elongated $\text{C}=\text{S}$ distances and shortened $\text{C}—\text{N}$ distances compared to the structure of neutral **DMPT**. These deviations are in line with changes found previously in O-protonated amide species. Systematic changes to the bond angles of the protonated thioamide groups were also observed, but these seemed to be sensitive to the conformation of the group. The species with *syn* conformations gave different narrowing/widening behaviour to that with the *anti* cation conformation. This illustrates that not all structural changes observed on protonation can be simply attributed to the act of protonation itself, subtleties of conformation can alter what may be expected. In all three **[DMPT(H)][X]** species, hydrogen bonding between the polar thioamide group and the anions gave two-dimensional hydrogen-bonded constructs. These layers were separated from one another by layers of non-polar dimethylphenyl groups.

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supporting information

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Salt forms of a thioamide: protonation of 1-(2,6-dimethylphenyl)thiourea

Kristin Donnachie, Bethany Gibson, Alan R. Kennedy, Connor MacCall and Marc Reid

Computing details

1-(2,6-Dimethylphenyl)thiourea (DMPT)

Crystal data

$C_9H_{12}N_2S$

$M_r = 180.27$

Monoclinic, $P2_1/n$

$a = 9.8193$ (1) Å

$b = 8.3655$ (3) Å

$c = 11.7827$ (2) Å

$\beta = 91.696$ (1)°

$V = 967.45$ (4) Å³

$Z = 4$

$F(000) = 384$

$D_x = 1.238$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 9109 reflections

$\theta = 3.7\text{--}71.9^\circ$

$\mu = 2.54$ mm⁻¹

$T = 180$ K

Large spar cut to size, colourless

$0.25 \times 0.18 \times 0.06$ mm

Data collection

Rigaku Synergy-i
diffractometer

Radiation source: microsource tube

ω scans

Absorption correction: multi-scan
(CrysAlis PRO; Rigaku OD, 2025)

$T_{\min} = 0.758$, $T_{\max} = 1.000$

10267 measured reflections

1887 independent reflections

1811 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 71.9^\circ$, $\theta_{\min} = 5.8^\circ$

$h = -11 \rightarrow 12$

$k = -7 \rightarrow 10$

$l = -14 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.077$

$S = 1.09$

1887 reflections

123 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.3242P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.25$ e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0019 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.19532 (3)	0.05410 (4)	0.22241 (3)	0.03216 (13)	
N1	0.43366 (11)	−0.08919 (13)	0.23004 (10)	0.0299 (3)	
N2	0.44286 (10)	0.18349 (13)	0.24003 (9)	0.0244 (2)	
C1	0.36828 (12)	0.04895 (14)	0.23188 (10)	0.0229 (3)	
C2	0.58479 (11)	0.17674 (14)	0.27506 (10)	0.0238 (3)	
C3	0.68354 (12)	0.14742 (15)	0.19473 (11)	0.0288 (3)	
C4	0.81727 (13)	0.12300 (17)	0.23477 (12)	0.0351 (3)	
H4	0.886321	0.100088	0.182371	0.042*	
C5	0.85061 (13)	0.13159 (18)	0.34888 (13)	0.0379 (3)	
H5	0.941803	0.112575	0.374539	0.045*	
C6	0.75198 (14)	0.16779 (18)	0.42659 (12)	0.0363 (3)	
H6	0.776684	0.177584	0.504847	0.044*	
C7	0.61705 (13)	0.18990 (15)	0.39076 (11)	0.0287 (3)	
C8	0.64851 (15)	0.1413 (2)	0.06950 (12)	0.0437 (4)	
H8A	0.731101	0.119455	0.027441	0.066*	0.5
H8B	0.581711	0.056244	0.054534	0.066*	0.5
H8C	0.609915	0.244113	0.045033	0.066*	0.5
H8D	0.550717	0.160420	0.057231	0.066*	0.5
H8E	0.700107	0.223631	0.030138	0.066*	0.5
H8F	0.671903	0.035762	0.039639	0.066*	0.5
C9	0.50760 (15)	0.2252 (2)	0.47431 (11)	0.0407 (3)	
H9A	0.462779	0.326351	0.453994	0.061*	
H9B	0.548669	0.233538	0.550907	0.061*	
H9C	0.440239	0.138763	0.472328	0.061*	
H1N	0.3882 (17)	−0.176 (2)	0.2319 (14)	0.044 (5)*	
H2N	0.5199 (19)	−0.093 (2)	0.2363 (14)	0.042 (4)*	
H3N	0.4002 (15)	0.271 (2)	0.2470 (13)	0.035 (4)*	

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01803 (18)	0.02117 (18)	0.0572 (2)	0.00040 (10)	−0.00096 (13)	−0.00239 (12)
N1	0.0196 (5)	0.0202 (5)	0.0500 (7)	−0.0004 (4)	0.0018 (4)	−0.0003 (5)
N2	0.0202 (5)	0.0192 (5)	0.0338 (5)	0.0002 (4)	0.0012 (4)	−0.0011 (4)
C1	0.0221 (6)	0.0224 (6)	0.0243 (5)	−0.0002 (4)	0.0025 (4)	0.0003 (4)
C2	0.0200 (5)	0.0193 (5)	0.0323 (6)	−0.0026 (4)	0.0024 (4)	−0.0002 (4)
C3	0.0247 (6)	0.0286 (6)	0.0335 (6)	−0.0062 (5)	0.0057 (5)	−0.0018 (5)
C4	0.0225 (6)	0.0377 (8)	0.0457 (8)	−0.0043 (6)	0.0101 (5)	−0.0013 (6)
C5	0.0209 (6)	0.0418 (8)	0.0508 (8)	−0.0038 (6)	−0.0018 (5)	0.0043 (6)

C6	0.0311 (7)	0.0427 (8)	0.0346 (7)	−0.0048 (6)	−0.0048 (5)	0.0008 (6)
C7	0.0270 (6)	0.0271 (6)	0.0319 (6)	−0.0031 (5)	0.0031 (5)	−0.0012 (5)
C8	0.0368 (8)	0.0617 (10)	0.0332 (7)	−0.0070 (7)	0.0087 (6)	−0.0054 (7)
C9	0.0378 (7)	0.0536 (9)	0.0309 (7)	0.0039 (7)	0.0066 (6)	−0.0046 (6)

Geometric parameters (Å, °)

S1—C1	1.6992 (12)	C5—H5	0.9500
N1—C1	1.3225 (16)	C6—C7	1.3909 (18)
N1—H1N	0.856 (19)	C6—H6	0.9500
N1—H2N	0.848 (18)	C7—C9	1.5080 (17)
N2—C1	1.3447 (15)	C8—H8A	0.9800
N2—C2	1.4429 (14)	C8—H8B	0.9800
N2—H3N	0.849 (17)	C8—H8C	0.9800
C2—C7	1.3948 (17)	C8—H8D	0.9800
C2—C3	1.3966 (16)	C8—H8E	0.9800
C3—C4	1.3971 (18)	C8—H8F	0.9800
C3—C8	1.5060 (19)	C9—H9A	0.9800
C4—C5	1.376 (2)	C9—H9B	0.9800
C4—H4	0.9500	C9—H9C	0.9800
C5—C6	1.386 (2)		
C1—N1—H1N	119.3 (11)	C5—C6—C7	120.43 (12)
C1—N1—H2N	120.7 (12)	C5—C6—H6	119.8
H1N—N1—H2N	119.4 (17)	C7—C6—H6	119.8
C1—N2—C2	120.47 (10)	C6—C7—C2	118.22 (12)
C1—N2—H3N	117.4 (10)	C6—C7—C9	121.25 (12)
C2—N2—H3N	118.8 (10)	C2—C7—C9	120.52 (11)
N1—C1—N2	117.96 (11)	C3—C8—H8A	109.5
N1—C1—S1	120.39 (9)	C3—C8—H8B	109.5
N2—C1—S1	121.64 (9)	H8A—C8—H8B	109.5
C7—C2—C3	122.28 (11)	C3—C8—H8C	109.5
C7—C2—N2	117.77 (10)	H8A—C8—H8C	109.5
C3—C2—N2	119.81 (11)	H8B—C8—H8C	109.5
C2—C3—C4	117.47 (12)	H8D—C8—H8E	109.5
C2—C3—C8	121.80 (12)	H8D—C8—H8F	109.5
C4—C3—C8	120.73 (12)	H8E—C8—H8F	109.5
C5—C4—C3	121.09 (12)	C7—C9—H9A	109.5
C5—C4—H4	119.5	C7—C9—H9B	109.5
C3—C4—H4	119.5	H9A—C9—H9B	109.5
C4—C5—C6	120.41 (12)	C7—C9—H9C	109.5
C4—C5—H5	119.8	H9A—C9—H9C	109.5
C6—C5—H5	119.8	H9B—C9—H9C	109.5
C2—N2—C1—N1	−15.77 (17)	C8—C3—C4—C5	178.69 (14)
C2—N2—C1—S1	165.01 (9)	C3—C4—C5—C6	−1.2 (2)
C1—N2—C2—C7	−90.53 (14)	C4—C5—C6—C7	2.5 (2)
C1—N2—C2—C3	85.40 (14)	C5—C6—C7—C2	−0.9 (2)

C7—C2—C3—C4	3.26 (18)	C5—C6—C7—C9	178.43 (14)
N2—C2—C3—C4	−172.48 (11)	C3—C2—C7—C6	−2.06 (19)
C7—C2—C3—C8	−177.03 (13)	N2—C2—C7—C6	173.76 (11)
N2—C2—C3—C8	7.23 (19)	C3—C2—C7—C9	178.65 (13)
C2—C3—C4—C5	−1.6 (2)	N2—C2—C7—C9	−5.53 (18)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1N $\cdots$ S1 ⁱ	0.856 (19)	2.464 (19)	3.2961 (12)	164.2 (15)
N2—H3N $\cdots$ S1 ⁱⁱ	0.849 (17)	2.576 (18)	3.4183 (11)	171.6 (14)

Symmetry codes: (i) $-x+1/2, y-1/2, -z+1/2$; (ii) $-x+1/2, y+1/2, -z+1/2$.

1-(2,6-Dimethylphenyl)thiuronium chloride (DMPTHCl)*Crystal data*

C₉H₁₃N₂S⁺·Cl[−]

M_r = 216.72

Monoclinic, *C*2/*c*

a = 11.7848 (2) Å

b = 10.3644 (2) Å

c = 19.2687 (3) Å

β = 105.844 (2)°

V = 2264.11 (7) Å³

Z = 8

F(000) = 912

D_x = 1.272 Mg m^{−3}

Cu *K*α radiation, λ = 1.54184 Å

Cell parameters from 9109 reflections

θ = 3.7–71.9°

μ = 4.37 mm^{−1}

T = 180 K

Fragment, colourless

0.20 × 0.15 × 0.10 mm

Data collection

Rigaku Synergy-i
diffractometer

Radiation source: microsource tube

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2025)

T_{min} = 0.758, *T_{max}* = 1.000

6924 measured reflections

2189 independent reflections

1949 reflections with *I* > 2σ(*I*)

R_{int} = 0.028

$\theta_{\max}$ = 71.8°, $\theta_{\min}$ = 4.8°

h = −14→13

k = −12→11

l = −22→23

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.031

wR (*F*²) = 0.089

S = 1.05

2189 reflections

136 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.050*P*)² + 0.799*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 0.24 e Å^{−3}

Δρ_{min} = −0.19 e Å^{−3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.33300 (4)	0.18533 (5)	0.77782 (2)	0.04816 (15)
Cl1	0.60589 (3)	0.03080 (4)	0.35418 (2)	0.04156 (14)
N1	1.13222 (14)	0.30459 (15)	0.72088 (8)	0.0448 (3)
N2	1.19064 (11)	0.16667 (13)	0.64431 (7)	0.0363 (3)
C1	1.20737 (13)	0.22185 (15)	0.70757 (8)	0.0364 (3)
C2	1.08503 (13)	0.18685 (15)	0.58619 (8)	0.0335 (3)
C3	1.08327 (14)	0.28558 (16)	0.53733 (8)	0.0374 (3)
C4	0.98220 (15)	0.30085 (18)	0.48026 (9)	0.0443 (4)
H4	0.979195	0.366795	0.445563	0.053*
C5	0.88693 (16)	0.2212 (2)	0.47386 (9)	0.0507 (4)
H5	0.818556	0.232052	0.434549	0.061*
C6	0.88959 (16)	0.1261 (2)	0.52378 (10)	0.0560 (5)
H6	0.822304	0.072734	0.518913	0.067*
C7	0.98921 (15)	0.10611 (17)	0.58157 (9)	0.0454 (4)
C8	1.18615 (17)	0.3758 (2)	0.54587 (10)	0.0544 (5)
H8A	1.174323	0.428899	0.502388	0.082*
H8B	1.258904	0.325587	0.553026	0.082*
H8C	1.192256	0.431698	0.587749	0.082*
C9	0.9918 (2)	0.0024 (2)	0.63679 (13)	0.0719 (7)
H9A	0.929473	−0.060770	0.616996	0.108*
H9B	0.978838	0.041345	0.680352	0.108*
H9C	1.068660	−0.040771	0.648939	0.108*
H1S	1.3740 (18)	0.107 (2)	0.7411 (12)	0.056 (6)*
H1N	1.1391 (18)	0.341 (2)	0.7623 (13)	0.053 (6)*
H2N	1.067 (2)	0.333 (2)	0.6843 (13)	0.065 (6)*
H3N	1.2404 (14)	0.1092 (15)	0.6387 (10)	0.046 (5)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0421 (2)	0.0588 (3)	0.0326 (2)	0.00971 (18)	−0.00825 (17)	−0.00862 (17)
Cl1	0.0420 (2)	0.0511 (3)	0.0304 (2)	0.01382 (16)	0.00783 (16)	0.00814 (15)
N1	0.0438 (8)	0.0517 (8)	0.0330 (7)	0.0113 (6)	0.0004 (6)	−0.0092 (6)
N2	0.0323 (6)	0.0407 (7)	0.0301 (6)	0.0074 (5)	−0.0013 (5)	−0.0054 (5)
C1	0.0338 (8)	0.0391 (8)	0.0315 (7)	0.0003 (6)	0.0010 (6)	−0.0025 (6)
C2	0.0295 (7)	0.0400 (8)	0.0266 (7)	0.0009 (6)	0.0001 (5)	−0.0047 (6)
C3	0.0341 (8)	0.0460 (9)	0.0301 (7)	−0.0051 (6)	0.0052 (6)	−0.0029 (6)
C4	0.0426 (9)	0.0545 (10)	0.0308 (8)	−0.0020 (7)	0.0016 (7)	0.0070 (7)
C5	0.0369 (9)	0.0727 (12)	0.0342 (8)	−0.0067 (8)	−0.0045 (7)	0.0053 (8)
C6	0.0413 (9)	0.0712 (13)	0.0469 (10)	−0.0231 (9)	−0.0027 (7)	0.0047 (9)
C7	0.0456 (9)	0.0477 (9)	0.0368 (8)	−0.0112 (7)	0.0009 (7)	0.0039 (7)
C8	0.0501 (10)	0.0639 (12)	0.0445 (9)	−0.0207 (9)	0.0052 (8)	0.0041 (9)
C9	0.0775 (15)	0.0648 (13)	0.0592 (13)	−0.0259 (12)	−0.0055 (11)	0.0213 (11)

Geometric parameters (Å, °)

S1—C1	1.7530 (15)	C4—H4	0.9500
S1—H1S	1.26 (2)	C5—C6	1.372 (3)
N1—C1	1.308 (2)	C5—H5	0.9500
N1—H1N	0.87 (2)	C6—C7	1.395 (2)
N1—H2N	0.94 (2)	C6—H6	0.9500
N2—C1	1.312 (2)	C7—C9	1.507 (3)
N2—C2	1.4442 (18)	C8—H8A	0.9800
N2—H3N	0.863 (9)	C8—H8B	0.9800
C2—C3	1.387 (2)	C8—H8C	0.9800
C2—C7	1.389 (2)	C9—H9A	0.9800
C3—C4	1.392 (2)	C9—H9B	0.9800
C3—C8	1.504 (2)	C9—H9C	0.9800
C4—C5	1.372 (3)		
C1—S1—H1S	94.5 (9)	C4—C5—H5	119.7
C1—N1—H1N	124.7 (14)	C6—C5—H5	119.7
C1—N1—H2N	121.2 (14)	C5—C6—C7	121.27 (16)
H1N—N1—H2N	114 (2)	C5—C6—H6	119.4
C1—N2—C2	122.45 (13)	C7—C6—H6	119.4
C1—N2—H3N	118.8 (13)	C2—C7—C6	117.01 (15)
C2—N2—H3N	118.3 (13)	C2—C7—C9	121.69 (16)
N1—C1—N2	122.01 (14)	C6—C7—C9	121.29 (16)
N1—C1—S1	117.69 (12)	C3—C8—H8A	109.5
N2—C1—S1	120.29 (12)	C3—C8—H8B	109.5
C3—C2—C7	122.68 (14)	H8A—C8—H8B	109.5
C3—C2—N2	118.90 (13)	C3—C8—H8C	109.5
C7—C2—N2	118.42 (14)	H8A—C8—H8C	109.5
C2—C3—C4	118.11 (14)	H8B—C8—H8C	109.5
C2—C3—C8	121.48 (14)	C7—C9—H9A	109.5
C4—C3—C8	120.40 (15)	C7—C9—H9B	109.5
C5—C4—C3	120.36 (16)	H9A—C9—H9B	109.5
C5—C4—H4	119.8	C7—C9—H9C	109.5
C3—C4—H4	119.8	H9A—C9—H9C	109.5
C4—C5—C6	120.53 (15)	H9B—C9—H9C	109.5
C2—N2—C1—N1	−3.9 (3)	C8—C3—C4—C5	−177.83 (19)
C2—N2—C1—S1	175.80 (12)	C3—C4—C5—C6	0.4 (3)
C1—N2—C2—C3	91.59 (19)	C4—C5—C6—C7	−1.0 (3)
C1—N2—C2—C7	−88.5 (2)	C3—C2—C7—C6	1.5 (3)
C7—C2—C3—C4	−2.1 (2)	N2—C2—C7—C6	−178.45 (16)
N2—C2—C3—C4	177.87 (14)	C3—C2—C7—C9	−177.9 (2)
C7—C2—C3—C8	176.83 (17)	N2—C2—C7—C9	2.2 (3)
N2—C2—C3—C8	−3.2 (2)	C5—C6—C7—C2	0.1 (3)
C2—C3—C4—C5	1.1 (3)	C5—C6—C7—C9	179.4 (2)

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
$S1\cdots H1S\cdots Cl1^i$	1.26 (2)	2.39 (2)	3.6064 (6)	162.4 (14)
$N1\cdots H1N\cdots Cl1^{ii}$	0.87 (2)	2.33 (2)	3.1685 (15)	162.9 (19)
$N1\cdots H2N\cdots Cl1^{iii}$	0.94 (2)	2.42 (2)	3.2649 (15)	149.4 (19)
$N2\cdots H3N\cdots Cl1^i$	0.86 (1)	2.30 (1)	3.1467 (13)	169 (2)

Symmetry codes: (i) $-x+2, -y, -z+1$; (ii) $x+1/2, -y+1/2, z+1/2$; (iii) $-x+3/2, -y+1/2, -z+1$.

1-(2,6-Dimethylphenyl)thiuronium bromide (DMPTHBr)

Crystal data

$C_9H_{13}N_2S^+\cdot Br^-$

$M_r = 261.18$

Monoclinic, $C2/c$

$a = 13.3544$ (2) $\text{\AA}$

$b = 8.7556$ (1) $\text{\AA}$

$c = 20.5020$ (2) $\text{\AA}$

$\beta = 112.485$ (1) $^\circ$

$V = 2214.97$ (5) $\text{\AA}^3$

$Z = 8$

$F(000) = 1056$

$D_x = 1.566$ Mg m^{-3}

$\text{Cu K}\alpha$ radiation, $\lambda = 1.54184$ $\text{\AA}$

Cell parameters from 10519 reflections

$\theta = 4.7\text{--}71.7^\circ$

$\mu = 6.48$ mm^{-1}

$T = 100$ K

Chip cut from block, colourless

$0.17 \times 0.14 \times 0.08$ mm

Data collection

Rigaku Synergy-i

diffractometer

Radiation source: microsource tube

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2025)

$T_{\min} = 0.770$, $T_{\max} = 1.000$

11782 measured reflections

2157 independent reflections

2119 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 71.8^\circ$, $\theta_{\min} = 4.7^\circ$

$h = -16 \rightarrow 16$

$k = -10 \rightarrow 9$

$l = -24 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.048$

$S = 1.05$

2157 reflections

137 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.025P)^2 + 3.2341P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 0.33$ $\text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.30$ $\text{e \AA}^{-3}$

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00016 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.10952 (2)	0.48512 (2)	0.85726 (2)	0.01839 (8)
S1	0.19210 (3)	0.65744 (5)	0.71974 (2)	0.02242 (11)
N1	0.39098 (11)	0.76307 (17)	0.77511 (7)	0.0204 (3)
N2	0.33780 (10)	0.62667 (16)	0.85209 (6)	0.0162 (3)
C1	0.31770 (12)	0.68462 (18)	0.78902 (8)	0.0166 (3)
C2	0.43763 (12)	0.65686 (18)	0.91173 (7)	0.0152 (3)
C3	0.43310 (12)	0.76442 (18)	0.96089 (8)	0.0164 (3)
C4	0.52787 (13)	0.79266 (19)	1.01960 (8)	0.0183 (3)
H4	0.527402	0.864530	1.054202	0.022*
C5	0.62282 (12)	0.71600 (19)	1.02759 (8)	0.0196 (3)
H5	0.687034	0.736094	1.067661	0.024*
C6	0.62503 (12)	0.61077 (19)	0.97790 (8)	0.0192 (3)
H6	0.690837	0.559501	0.984348	0.023*
C7	0.53192 (12)	0.57850 (18)	0.91827 (8)	0.0169 (3)
C8	0.32969 (13)	0.8470 (2)	0.95086 (8)	0.0211 (3)
H8A	0.308734	0.911144	0.908539	0.032*
H8B	0.340603	0.911372	0.992142	0.032*
H8C	0.272254	0.772542	0.945357	0.032*
C9	0.53569 (14)	0.4645 (2)	0.86420 (9)	0.0228 (3)
H9A	0.462396	0.426630	0.837140	0.034*
H9B	0.582586	0.378823	0.888142	0.034*
H9C	0.564555	0.513829	0.832162	0.034*
H1S	0.1461 (19)	0.604 (3)	0.7565 (12)	0.044 (6)*
H1N	0.3762 (17)	0.805 (3)	0.7370 (12)	0.028 (6)*
H2N	0.4539 (19)	0.790 (3)	0.8091 (12)	0.031 (6)*
H3N	0.2858 (17)	0.578 (3)	0.8596 (11)	0.026 (5)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01543 (10)	0.02569 (11)	0.01400 (10)	−0.00487 (6)	0.00555 (7)	−0.00426 (6)
S1	0.01756 (19)	0.0307 (2)	0.01393 (18)	−0.00340 (15)	0.00036 (14)	0.00252 (15)
N1	0.0193 (7)	0.0253 (7)	0.0147 (6)	−0.0035 (6)	0.0044 (6)	0.0041 (6)
N2	0.0129 (6)	0.0206 (7)	0.0139 (6)	−0.0029 (5)	0.0038 (5)	0.0009 (5)
C1	0.0156 (7)	0.0173 (7)	0.0152 (7)	0.0007 (6)	0.0040 (6)	−0.0009 (6)
C2	0.0135 (7)	0.0189 (7)	0.0119 (7)	−0.0026 (6)	0.0033 (6)	0.0023 (6)
C3	0.0152 (7)	0.0191 (7)	0.0152 (7)	−0.0002 (6)	0.0062 (6)	0.0028 (6)
C4	0.0195 (7)	0.0202 (8)	0.0137 (7)	−0.0014 (6)	0.0046 (6)	−0.0010 (6)
C5	0.0158 (7)	0.0235 (8)	0.0150 (7)	−0.0012 (6)	0.0008 (6)	0.0014 (6)
C6	0.0135 (7)	0.0226 (8)	0.0202 (7)	0.0017 (6)	0.0049 (6)	0.0032 (6)
C7	0.0171 (7)	0.0180 (8)	0.0158 (7)	−0.0008 (6)	0.0063 (6)	0.0018 (6)
C8	0.0177 (8)	0.0256 (8)	0.0198 (7)	0.0027 (6)	0.0068 (6)	−0.0016 (6)
C9	0.0204 (8)	0.0266 (9)	0.0212 (8)	0.0022 (7)	0.0078 (7)	−0.0024 (7)

Geometric parameters (Å, °)

S1—C1	1.7508 (15)	C4—H4	0.9500
S1—H1S	1.23 (2)	C5—C6	1.382 (2)
N1—C1	1.313 (2)	C5—H5	0.9500
N1—H1N	0.82 (2)	C6—C7	1.399 (2)
N1—H2N	0.89 (2)	C6—H6	0.9500
N2—C1	1.318 (2)	C7—C9	1.507 (2)
N2—C2	1.4476 (19)	C8—H8A	0.9800
N2—H3N	0.88 (2)	C8—H8B	0.9800
C2—C7	1.395 (2)	C8—H8C	0.9800
C2—C3	1.397 (2)	C9—H9A	0.9800
C3—C4	1.395 (2)	C9—H9B	0.9800
C3—C8	1.502 (2)	C9—H9C	0.9800
C4—C5	1.388 (2)		
C1—S1—H1S	95.9 (11)	C6—C5—H5	119.6
C1—N1—H1N	121.1 (15)	C4—C5—H5	119.6
C1—N1—H2N	121.6 (14)	C5—C6—C7	121.08 (15)
H1N—N1—H2N	116 (2)	C5—C6—H6	119.5
C1—N2—C2	122.33 (13)	C7—C6—H6	119.5
C1—N2—H3N	118.8 (14)	C2—C7—C6	116.90 (14)
C2—N2—H3N	118.4 (13)	C2—C7—C9	122.56 (14)
N1—C1—N2	121.70 (14)	C6—C7—C9	120.53 (14)
N1—C1—S1	117.21 (12)	C3—C8—H8A	109.5
N2—C1—S1	121.08 (12)	C3—C8—H8B	109.5
C7—C2—C3	123.28 (14)	H8A—C8—H8B	109.5
C7—C2—N2	119.82 (14)	C3—C8—H8C	109.5
C3—C2—N2	116.89 (13)	H8A—C8—H8C	109.5
C4—C3—C2	117.81 (14)	H8B—C8—H8C	109.5
C4—C3—C8	121.06 (14)	C7—C9—H9A	109.5
C2—C3—C8	121.13 (13)	C7—C9—H9B	109.5
C5—C4—C3	120.15 (15)	H9A—C9—H9B	109.5
C5—C4—H4	119.9	C7—C9—H9C	109.5
C3—C4—H4	119.9	H9A—C9—H9C	109.5
C6—C5—C4	120.76 (14)	H9B—C9—H9C	109.5
C2—N2—C1—N1	5.8 (2)	C8—C3—C4—C5	−179.46 (15)
C2—N2—C1—S1	−175.17 (11)	C3—C4—C5—C6	−0.2 (2)
C1—N2—C2—C7	−78.6 (2)	C4—C5—C6—C7	0.0 (2)
C1—N2—C2—C3	102.08 (17)	C3—C2—C7—C6	0.6 (2)
C7—C2—C3—C4	−0.7 (2)	N2—C2—C7—C6	−178.70 (13)
N2—C2—C3—C4	178.58 (13)	C3—C2—C7—C9	−179.11 (15)
C7—C2—C3—C8	179.24 (15)	N2—C2—C7—C9	1.6 (2)
N2—C2—C3—C8	−1.5 (2)	C5—C6—C7—C2	−0.2 (2)
C2—C3—C4—C5	0.5 (2)	C5—C6—C7—C9	179.48 (15)

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D\cdots H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$S1-H1S\cdots Br1$	1.23 (2)	2.52 (2)	3.7176 (4)	162.9 (16)
$N1-H1N\cdots Br1^i$	0.82 (2)	2.56 (2)	3.3363 (14)	160.1 (19)
$N1-H2N\cdots Br1^{ii}$	0.89 (2)	2.58 (2)	3.3725 (14)	148.4 (18)
$N2-H3N\cdots Br1$	0.88 (2)	2.47 (2)	3.3298 (13)	165.4 (19)

Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $x+1/2, y+1/2, z$.

1-(2,6-Dimethylphenyl)thiuronium hydrogen sulfate (DMPH SO_4H)

Crystal data

$C_9H_{14}N_2O_4S_2^+\cdot HSO_4^-$	$F(000) = 584$
$M_r = 278.34$	$D_x = 1.487 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 11.9033 (2) \text{ \AA}$	Cell parameters from 9501 reflections
$b = 13.3341 (3) \text{ \AA}$	$\theta = 3.8-71.2^\circ$
$c = 8.0321 (2) \text{ \AA}$	$\mu = 3.97 \text{ mm}^{-1}$
$\beta = 102.842 (2)^\circ$	$T = 100 \text{ K}$
$V = 1242.96 (5) \text{ \AA}^3$	Bar, colourless
$Z = 4$	$0.40 \times 0.12 \times 0.12 \text{ mm}$

Data collection

Rigaku Synergy-i diffractometer	2361 independent reflections
Radiation source: microsource tube	2209 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.044$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2025)	$\theta_{\text{max}} = 71.4^\circ$, $\theta_{\text{min}} = 3.8^\circ$
$T_{\text{min}} = 0.428$, $T_{\text{max}} = 1.000$	$h = -14 \rightarrow 14$
11118 measured reflections	$k = -13 \rightarrow 16$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 4.5398P]$
$wR(F^2) = 0.127$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2361 reflections	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
176 parameters	$\Delta\rho_{\text{min}} = -0.71 \text{ e \AA}^{-3}$
3 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.35965 (7)	0.22607 (6)	0.47150 (11)	0.0221 (2)
S2	0.66476 (7)	0.30899 (6)	0.32475 (10)	0.0183 (2)

O1	0.7232 (2)	0.34039 (18)	0.1903 (3)	0.0244 (5)
O2	0.7642 (2)	0.30229 (19)	0.4861 (3)	0.0249 (5)
O3	0.6155 (2)	0.21000 (18)	0.2939 (3)	0.0281 (6)
O4	0.5838 (2)	0.38371 (19)	0.3547 (3)	0.0261 (5)
N1	0.4410 (2)	0.0727 (2)	0.3178 (4)	0.0228 (6)
N2	0.2808 (2)	0.0420 (2)	0.4267 (3)	0.0182 (6)
C1	0.3619 (3)	0.1027 (2)	0.3980 (4)	0.0178 (6)
C2	0.1851 (3)	0.0761 (2)	0.4951 (4)	0.0184 (6)
C3	0.0858 (3)	0.1082 (2)	0.3801 (4)	0.0195 (7)
C4	−0.0069 (3)	0.1403 (3)	0.4465 (4)	0.0219 (7)
H4	−0.075760	0.162485	0.371624	0.026*
C5	0.0012 (3)	0.1399 (3)	0.6211 (4)	0.0234 (7)
H5	−0.061919	0.162666	0.665344	0.028*
C6	0.1004 (3)	0.1067 (2)	0.7316 (4)	0.0209 (7)
H6	0.104267	0.106902	0.851023	0.025*
C7	0.1944 (3)	0.0730 (2)	0.6713 (4)	0.0177 (6)
C8	0.0787 (3)	0.1063 (3)	0.1908 (4)	0.0278 (8)
H8A	0.133627	0.154540	0.162350	0.042*
H8B	0.000446	0.124214	0.129983	0.042*
H8C	0.097280	0.038827	0.156611	0.042*
C9	0.2995 (3)	0.0319 (3)	0.7904 (4)	0.0224 (7)
H9A	0.292182	0.040527	0.908624	0.034*
H9B	0.367905	0.067859	0.773355	0.034*
H9C	0.307248	−0.039617	0.766882	0.034*
H1S	0.443 (4)	0.248 (3)	0.422 (6)	0.041 (12)*
H2S	0.751 (5)	0.261 (5)	0.558 (7)	0.069 (18)*
H1N	0.497 (2)	0.113 (2)	0.307 (5)	0.023 (10)*
H2N	0.438 (4)	0.0134 (17)	0.270 (5)	0.042 (13)*
H3N	0.278 (4)	−0.0199 (15)	0.389 (6)	0.058 (16)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0237 (4)	0.0173 (4)	0.0274 (4)	−0.0026 (3)	0.0104 (3)	−0.0025 (3)
S2	0.0182 (4)	0.0165 (4)	0.0216 (4)	−0.0012 (3)	0.0072 (3)	0.0010 (3)
O1	0.0271 (12)	0.0219 (12)	0.0278 (13)	−0.0027 (10)	0.0138 (10)	0.0008 (10)
O2	0.0216 (12)	0.0273 (13)	0.0249 (13)	−0.0032 (10)	0.0030 (10)	0.0066 (10)
O3	0.0333 (14)	0.0230 (13)	0.0292 (13)	−0.0096 (11)	0.0097 (11)	−0.0009 (10)
O4	0.0239 (12)	0.0277 (13)	0.0280 (13)	0.0072 (10)	0.0082 (10)	0.0034 (10)
N1	0.0226 (14)	0.0184 (14)	0.0303 (15)	−0.0023 (12)	0.0122 (12)	−0.0029 (12)
N2	0.0208 (13)	0.0148 (13)	0.0217 (13)	−0.0006 (11)	0.0102 (11)	−0.0027 (11)
C1	0.0186 (15)	0.0177 (15)	0.0167 (15)	0.0004 (12)	0.0032 (12)	0.0021 (12)
C2	0.0194 (15)	0.0136 (15)	0.0236 (16)	−0.0021 (12)	0.0078 (13)	−0.0030 (13)
C3	0.0218 (16)	0.0152 (15)	0.0217 (16)	−0.0018 (13)	0.0056 (13)	−0.0007 (12)
C4	0.0173 (15)	0.0201 (16)	0.0273 (17)	0.0009 (13)	0.0029 (13)	−0.0008 (13)
C5	0.0195 (16)	0.0231 (17)	0.0303 (18)	−0.0016 (14)	0.0115 (14)	−0.0032 (14)
C6	0.0235 (16)	0.0193 (16)	0.0219 (16)	−0.0017 (13)	0.0093 (13)	−0.0019 (13)
C7	0.0183 (15)	0.0145 (15)	0.0207 (16)	−0.0029 (12)	0.0054 (12)	0.0000 (12)

C8	0.0331 (19)	0.0278 (19)	0.0220 (17)	−0.0002 (15)	0.0055 (14)	0.0005 (14)
C9	0.0263 (17)	0.0190 (16)	0.0219 (16)	−0.0009 (14)	0.0050 (13)	−0.0005 (13)

Geometric parameters (Å, °)

S1—C1	1.751 (3)	C3—C4	1.395 (5)
S1—H1S	1.18 (5)	C3—C8	1.505 (5)
S2—O4	1.443 (2)	C4—C5	1.384 (5)
S2—O3	1.443 (2)	C4—H4	0.9500
S2—O1	1.470 (2)	C5—C6	1.383 (5)
S2—O2	1.551 (2)	C5—H5	0.9500
O2—H2S	0.84 (6)	C6—C7	1.389 (4)
N1—C1	1.316 (4)	C6—H6	0.9500
N1—H1N	0.874 (10)	C7—C9	1.500 (4)
N1—H2N	0.877 (10)	C8—H8A	0.9800
N2—C1	1.317 (4)	C8—H8B	0.9800
N2—C2	1.444 (4)	C8—H8C	0.9800
N2—H3N	0.878 (10)	C9—H9A	0.9800
C2—C3	1.395 (5)	C9—H9B	0.9800
C2—C7	1.396 (4)	C9—H9C	0.9800
C1—S1—H1S	92 (2)	C5—C4—H4	119.9
O4—S2—O3	113.52 (15)	C3—C4—H4	119.9
O4—S2—O1	111.62 (14)	C6—C5—C4	120.6 (3)
O3—S2—O1	112.03 (14)	C6—C5—H5	119.7
O4—S2—O2	108.34 (14)	C4—C5—H5	119.7
O3—S2—O2	107.22 (15)	C5—C6—C7	121.2 (3)
O1—S2—O2	103.45 (14)	C5—C6—H6	119.4
S2—O2—H2S	113 (4)	C7—C6—H6	119.4
C1—N1—H1N	121 (3)	C6—C7—C2	117.1 (3)
C1—N1—H2N	122 (3)	C6—C7—C9	121.3 (3)
H1N—N1—H2N	117 (4)	C2—C7—C9	121.7 (3)
C1—N2—C2	123.0 (3)	C3—C8—H8A	109.5
C1—N2—H3N	119 (3)	C3—C8—H8B	109.5
C2—N2—H3N	117 (3)	H8A—C8—H8B	109.5
N1—C1—N2	122.1 (3)	C3—C8—H8C	109.5
N1—C1—S1	121.1 (2)	H8A—C8—H8C	109.5
N2—C1—S1	116.8 (2)	H8B—C8—H8C	109.5
C3—C2—C7	123.0 (3)	C7—C9—H9A	109.5
C3—C2—N2	117.9 (3)	C7—C9—H9B	109.5
C7—C2—N2	119.0 (3)	H9A—C9—H9B	109.5
C4—C3—C2	117.8 (3)	C7—C9—H9C	109.5
C4—C3—C8	121.3 (3)	H9A—C9—H9C	109.5
C2—C3—C8	120.9 (3)	H9B—C9—H9C	109.5
C5—C4—C3	120.2 (3)		
C2—N2—C1—N1	−172.1 (3)	C8—C3—C4—C5	179.0 (3)
C2—N2—C1—S1	7.8 (4)	C3—C4—C5—C6	−0.8 (5)

C1—N2—C2—C3	88.9 (4)	C4—C5—C6—C7	0.1 (5)
C1—N2—C2—C7	−92.8 (4)	C5—C6—C7—C2	1.3 (5)
C7—C2—C3—C4	1.3 (5)	C5—C6—C7—C9	−176.7 (3)
N2—C2—C3—C4	179.5 (3)	C3—C2—C7—C6	−2.0 (5)
C7—C2—C3—C8	−177.5 (3)	N2—C2—C7—C6	179.9 (3)
N2—C2—C3—C8	0.6 (5)	C3—C2—C7—C9	176.0 (3)
C2—C3—C4—C5	0.1 (5)	N2—C2—C7—C9	−2.1 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
S1—H1S $\cdots$ O3	1.18 (5)	2.54 (4)	3.645 (3)	154 (3)
S1—H1S $\cdots$ O4	1.18 (5)	2.60 (5)	3.678 (3)	150 (3)
N1—H1N $\cdots$ O3	0.87 (1)	1.94 (1)	2.807 (4)	175 (4)
N1—H2N $\cdots$ O4 ⁱ	0.88 (1)	1.99 (1)	2.859 (4)	174 (4)
N2—H3N $\cdots$ O1 ⁱ	0.88 (1)	1.97 (1)	2.845 (4)	178 (5)
O2—H2S $\cdots$ O1 ⁱⁱ	0.84 (6)	1.79 (6)	2.627 (3)	173 (6)

Symmetry codes: (i) $-x+1, y-1/2, -z+1/2$; (ii) $x, -y+1/2, z+1/2$.

(Disulfane-1,2-diyl)bis[*N*-(2,6-dimethylphenyl)methanediaminium] bis(tetrafluoroborate) (DimerBF42)*Crystal data*

C₁₈H₂₄N₄S₂²⁺·2BF₄[−]

M_r = 534.15

Monoclinic, C2/*c*

a = 15.6877 (2) Å

b = 10.4883 (2) Å

c = 14.8569 (2) Å

β = 98.972 (1)°

V = 2414.60 (6) Å³

Z = 4

F(000) = 1096

D_x = 1.469 Mg m^{−3}

Cu *Kα* radiation, λ = 1.54184 Å

Cell parameters from 8054 reflections

θ = 5.1–71.7°

μ = 2.71 mm^{−1}

T = 180 K

Fragment, colourless

0.22 × 0.15 × 0.07 mm

Data collection

Rigaku Synergy-i

diffractometer

Radiation source: microsource tube

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2025)

*T*_{min} = 0.732, *T*_{max} = 1.000

10154 measured reflections

2347 independent reflections

2180 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.020

θ_{max} = 71.9°, θ_{min} = 5.1°

h = −19→19

k = −12→12

l = −18→14

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.033

wR(*F*²) = 0.089

S = 1.08

2347 reflections

168 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F*_o²) + (0.0424*P*)² + 2.2827*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.31 e Å^{−3}

Δρ_{min} = −0.21 e Å^{−3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.33083 (7)	−0.16788 (13)	0.33745 (7)	0.0548 (3)
F2	0.35541 (10)	−0.22140 (12)	0.48583 (7)	0.0609 (4)
F3	0.45751 (9)	−0.25523 (15)	0.39770 (12)	0.0765 (4)
F4	0.42489 (7)	−0.05355 (10)	0.43436 (7)	0.0445 (3)
N1	0.33264 (9)	0.21941 (14)	0.16990 (9)	0.0328 (3)
N2	0.36765 (9)	0.15583 (13)	0.31949 (9)	0.0305 (3)
C1	0.37719 (9)	0.15054 (14)	0.23370 (10)	0.0263 (3)
B1	0.39376 (12)	−0.17581 (18)	0.41412 (12)	0.0291 (4)
S1	0.45030 (2)	0.03945 (4)	0.19698 (3)	0.03333 (13)
C2	0.31496 (10)	0.24998 (15)	0.35613 (10)	0.0294 (3)
C3	0.35429 (12)	0.36456 (16)	0.38734 (10)	0.0349 (4)
C4	0.30426 (14)	0.45104 (17)	0.42751 (12)	0.0421 (4)
H4	0.328221	0.530518	0.449234	0.050*
C5	0.21985 (14)	0.42175 (19)	0.43593 (11)	0.0439 (5)
H5	0.187084	0.480662	0.465052	0.053*
C6	0.18244 (12)	0.30901 (18)	0.40295 (11)	0.0399 (4)
H6	0.124088	0.291799	0.408733	0.048*
C7	0.22929 (11)	0.21967 (16)	0.36111 (10)	0.0330 (4)
C8	0.44680 (13)	0.3935 (2)	0.37960 (14)	0.0490 (5)
H8A	0.456086	0.380212	0.316561	0.074*
H8B	0.484862	0.336784	0.420103	0.074*
H8C	0.459700	0.482337	0.397099	0.074*
C9	0.18837 (13)	0.0972 (2)	0.32438 (13)	0.0445 (4)
H9A	0.129633	0.091760	0.338854	0.067*
H9B	0.222490	0.025032	0.352168	0.067*
H9C	0.186271	0.094702	0.258132	0.067*
H3N	0.3927 (13)	0.100 (2)	0.3542 (14)	0.040 (5)*
H1N	0.3426 (14)	0.214 (2)	0.1110 (16)	0.047 (6)*
H2N	0.2884 (14)	0.261 (2)	0.1793 (14)	0.041 (6)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0505 (6)	0.0685 (8)	0.0405 (6)	−0.0196 (6)	−0.0084 (5)	0.0007 (5)
F2	0.0977 (10)	0.0557 (7)	0.0356 (6)	−0.0267 (7)	0.0299 (6)	−0.0005 (5)
F3	0.0627 (8)	0.0682 (9)	0.1034 (11)	0.0254 (7)	0.0275 (8)	−0.0062 (8)
F4	0.0487 (6)	0.0377 (6)	0.0436 (6)	−0.0137 (5)	−0.0036 (5)	0.0044 (4)
N1	0.0355 (7)	0.0393 (8)	0.0236 (7)	0.0075 (6)	0.0049 (5)	−0.0004 (5)
N2	0.0355 (7)	0.0314 (7)	0.0243 (6)	0.0104 (6)	0.0036 (5)	0.0021 (5)

C1	0.0236 (7)	0.0276 (7)	0.0272 (7)	−0.0006 (6)	0.0022 (5)	−0.0036 (6)
B1	0.0310 (8)	0.0301 (9)	0.0272 (8)	−0.0041 (7)	0.0075 (7)	−0.0001 (7)
S1	0.0241 (2)	0.0353 (2)	0.0404 (2)	0.00052 (14)	0.00444 (15)	−0.01378 (16)
C2	0.0376 (8)	0.0313 (8)	0.0191 (7)	0.0105 (7)	0.0037 (6)	0.0025 (6)
C3	0.0463 (9)	0.0343 (9)	0.0233 (7)	0.0057 (7)	0.0031 (6)	0.0035 (6)
C4	0.0653 (12)	0.0323 (9)	0.0274 (8)	0.0114 (8)	0.0036 (8)	0.0000 (6)
C5	0.0618 (12)	0.0451 (10)	0.0257 (8)	0.0267 (9)	0.0097 (8)	0.0043 (7)
C6	0.0415 (9)	0.0513 (11)	0.0279 (8)	0.0185 (8)	0.0086 (7)	0.0109 (7)
C7	0.0374 (8)	0.0386 (9)	0.0224 (7)	0.0095 (7)	0.0032 (6)	0.0064 (6)
C8	0.0508 (11)	0.0448 (11)	0.0504 (11)	−0.0056 (9)	0.0046 (9)	−0.0027 (9)
C9	0.0420 (9)	0.0509 (11)	0.0401 (9)	−0.0026 (8)	0.0053 (8)	0.0012 (8)

Geometric parameters (Å, °)

F1—B1	1.389 (2)	C3—C8	1.504 (3)
F2—B1	1.388 (2)	C4—C5	1.384 (3)
F3—B1	1.353 (2)	C4—H4	0.9500
F4—B1	1.388 (2)	C5—C6	1.376 (3)
N1—C1	1.305 (2)	C5—H5	0.9500
N1—H1N	0.91 (2)	C6—C7	1.395 (2)
N1—H2N	0.85 (2)	C6—H6	0.9500
N2—C1	1.307 (2)	C7—C9	1.500 (3)
N2—C2	1.447 (2)	C8—H8A	0.9800
N2—H3N	0.84 (2)	C8—H8B	0.9800
C1—S1	1.7792 (15)	C8—H8C	0.9800
S1—S1 ⁱ	2.0364 (8)	C9—H9A	0.9800
C2—C7	1.394 (2)	C9—H9B	0.9800
C2—C3	1.397 (2)	C9—H9C	0.9800
C3—C4	1.393 (3)		
C1—N1—H1N	120.7 (13)	C5—C4—H4	119.8
C1—N1—H2N	121.5 (14)	C3—C4—H4	119.8
H1N—N1—H2N	117.0 (19)	C6—C5—C4	121.30 (16)
C1—N2—C2	123.67 (13)	C6—C5—H5	119.3
C1—N2—H3N	117.2 (14)	C4—C5—H5	119.3
C2—N2—H3N	119.1 (14)	C5—C6—C7	120.71 (18)
N1—C1—N2	123.71 (14)	C5—C6—H6	119.6
N1—C1—S1	115.96 (12)	C7—C6—H6	119.6
N2—C1—S1	120.26 (12)	C2—C7—C6	116.72 (16)
F3—B1—F2	110.34 (16)	C2—C7—C9	122.49 (15)
F3—B1—F4	111.28 (15)	C6—C7—C9	120.79 (17)
F2—B1—F4	109.39 (14)	C3—C8—H8A	109.5
F3—B1—F1	109.87 (15)	C3—C8—H8B	109.5
F2—B1—F1	108.21 (14)	H8A—C8—H8B	109.5
F4—B1—F1	107.66 (14)	C3—C8—H8C	109.5
C1—S1—S1 ⁱ	102.43 (5)	H8A—C8—H8C	109.5
C7—C2—C3	123.93 (15)	H8B—C8—H8C	109.5
C7—C2—N2	118.43 (15)	C7—C9—H9A	109.5

C3—C2—N2	117.60 (15)	C7—C9—H9B	109.5
C4—C3—C2	116.95 (17)	H9A—C9—H9B	109.5
C4—C3—C8	121.06 (17)	C7—C9—H9C	109.5
C2—C3—C8	121.98 (16)	H9A—C9—H9C	109.5
C5—C4—C3	120.34 (18)	H9B—C9—H9C	109.5
C2—N2—C1—N1	−8.4 (2)	C2—C3—C4—C5	0.5 (2)
C2—N2—C1—S1	174.83 (12)	C8—C3—C4—C5	−178.55 (16)
N1—C1—S1—S1 ⁱ	145.85 (11)	C3—C4—C5—C6	−1.8 (3)
N2—C1—S1—S1 ⁱ	−37.15 (13)	C4—C5—C6—C7	1.0 (2)
C1—N2—C2—C7	92.81 (19)	C3—C2—C7—C6	−2.3 (2)
C1—N2—C2—C3	−89.33 (19)	N2—C2—C7—C6	175.41 (13)
C7—C2—C3—C4	1.5 (2)	C3—C2—C7—C9	178.15 (15)
N2—C2—C3—C4	−176.18 (14)	N2—C2—C7—C9	−4.1 (2)
C7—C2—C3—C8	−179.36 (16)	C5—C6—C7—C2	1.0 (2)
N2—C2—C3—C8	2.9 (2)	C5—C6—C7—C9	−179.46 (15)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ F2 ⁱⁱ	0.91 (2)	1.90 (2)	2.8128 (17)	173 (2)
N1—H2N $\cdots$ F1 ⁱⁱⁱ	0.85 (2)	1.99 (2)	2.8105 (18)	161.3 (19)
N2—H3N $\cdots$ F4	0.84 (2)	2.02 (2)	2.8396 (18)	166 (2)
N2—H3N $\cdots$ S1 ⁱ	0.84 (2)	2.76 (2)	3.1502 (14)	110.1 (16)

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $x, -y, z-1/2$; (iii) $-x+1/2, y+1/2, -z+1/2$.

(Disulfane-1,2-diyl)bis[*N*-(2,6-dimethylphenyl)methanediaminium] bis(hydrogen sulfate) monohydrate (DimerSO₄H₂.H₂O)

Crystal data

C₁₈H₂₄N₄S₂²⁺·2HSO₄[−]·H₂O

$M_r = 572.68$

Monoclinic, $P2_1/c$

$a = 15.7786$ (1) $\text{\AA}$

$b = 10.5384$ (1) $\text{\AA}$

$c = 15.1791$ (1) $\text{\AA}$

$\beta = 102.694$ (1) $^\circ$

$V = 2462.31$ (3) $\text{\AA}^3$

$Z = 4$

$F(000) = 1200$

$D_x = 1.545$ Mg m^{−3}

Cu $K\alpha$ radiation, $\lambda = 1.54184$ $\text{\AA}$

Cell parameters from 15106 reflections

$\theta = 2.8\text{--}71.8^\circ$

$\mu = 4.05$ mm^{−1}

$T = 120$ K

Block cut from larger crystal, colourless

$0.09 \times 0.08 \times 0.07$ mm

Data collection

Rigaku Synergy-i
diffractometer

Radiation source: microsource tube

ω scans

Absorption correction: multi-scan
(CrysAlis PRO; Rigaku OD, 2025)

$T_{\min} = 0.793$, $T_{\max} = 1.000$

25961 measured reflections

4797 independent reflections

4387 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 71.9^\circ$, $\theta_{\min} = 2.9^\circ$

$h = -19 \rightarrow 19$

$k = -11 \rightarrow 12$

$l = -18 \rightarrow 18$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.029$ $wR(F^2) = 0.088$ $S = 1.03$

4797 reflections

361 parameters

11 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.7585P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00021 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.20197 (2)	0.69958 (3)	0.71069 (2)	0.01420 (10)
S2	0.30516 (2)	0.67971 (3)	0.81778 (2)	0.01436 (10)
S3	0.14923 (2)	0.58714 (3)	0.42153 (2)	0.01334 (11)
S4	0.65213 (2)	0.41196 (3)	0.92440 (2)	0.01307 (11)
O1	0.12143 (8)	0.53680 (11)	0.49870 (7)	0.0247 (3)
O2	0.08416 (7)	0.58389 (11)	0.33799 (7)	0.0229 (3)
O3	0.18528 (7)	0.71616 (10)	0.43786 (7)	0.0196 (2)
O4	0.22560 (7)	0.49973 (11)	0.41108 (8)	0.0245 (3)
O5	0.73406 (7)	0.47758 (11)	0.93852 (8)	0.0258 (3)
O6	0.67386 (7)	0.26563 (10)	0.94233 (7)	0.0178 (2)
O7	0.59806 (7)	0.44880 (10)	0.98567 (7)	0.0205 (2)
O8	0.60336 (7)	0.41264 (10)	0.83078 (7)	0.0212 (2)
O1W	0.26627 (8)	0.49649 (13)	0.25705 (7)	0.0267 (3)
N1	0.08181 (8)	0.52086 (12)	0.67108 (8)	0.0168 (3)
N2	0.11674 (8)	0.58325 (11)	0.82169 (8)	0.0146 (3)
N3	0.42842 (8)	0.50792 (12)	0.83741 (8)	0.0167 (3)
N4	0.37225 (8)	0.56770 (12)	0.68940 (8)	0.0174 (3)
C1	0.12625 (9)	0.58822 (13)	0.73812 (9)	0.0131 (3)
C2	0.06607 (9)	0.48823 (14)	0.85545 (9)	0.0156 (3)
C3	−0.01728 (9)	0.52074 (15)	0.86535 (9)	0.0183 (3)
C4	−0.06144 (10)	0.43138 (17)	0.90596 (10)	0.0239 (3)
H4	−0.117665	0.450607	0.915214	0.029*
C5	−0.02411 (12)	0.31465 (16)	0.93297 (10)	0.0265 (4)
H5	−0.055271	0.254716	0.960305	0.032*
C6	0.05783 (12)	0.28405 (16)	0.92077 (10)	0.0251 (3)
H6	0.081937	0.203060	0.938835	0.030*
C7	0.10524 (10)	0.37151 (15)	0.88207 (9)	0.0196 (3)
C8	−0.05773 (10)	0.64657 (17)	0.83360 (11)	0.0252 (3)

H8A	−0.077739	0.645263	0.767747	0.038*
H8B	−0.014600	0.714107	0.850954	0.038*
H8C	−0.107220	0.662305	0.861421	0.038*
C9	0.19610 (11)	0.34172 (16)	0.87134 (11)	0.0259 (3)
H9A	0.198037	0.346469	0.807334	0.039*
H9B	0.212266	0.256047	0.894049	0.039*
H9C	0.236917	0.403321	0.905674	0.039*
C10	0.37475 (9)	0.57337 (13)	0.77599 (9)	0.0134 (3)
C11	0.42201 (9)	0.47852 (14)	0.64873 (9)	0.0164 (3)
C12	0.38358 (10)	0.36209 (15)	0.61971 (10)	0.0197 (3)
C13	0.43068 (11)	0.27974 (15)	0.57658 (10)	0.0231 (3)
H13	0.407102	0.199290	0.556175	0.028*
C14	0.51169 (11)	0.31467 (16)	0.56332 (10)	0.0230 (3)
H14	0.542959	0.257699	0.533765	0.028*
C15	0.54775 (10)	0.43123 (16)	0.59247 (10)	0.0209 (3)
H15	0.603132	0.453512	0.582223	0.025*
C16	0.50354 (9)	0.51631 (15)	0.63675 (9)	0.0181 (3)
C17	0.29443 (11)	0.32683 (16)	0.63239 (12)	0.0279 (4)
H17A	0.279395	0.241603	0.608107	0.042*
H17B	0.251766	0.387986	0.600428	0.042*
H17C	0.294169	0.327976	0.696893	0.042*
C18	0.54115 (10)	0.64408 (15)	0.66861 (10)	0.0233 (3)
H18A	0.593703	0.658991	0.645671	0.035*
H18B	0.555826	0.645835	0.734777	0.035*
H18C	0.498376	0.710466	0.646104	0.035*
H1N	0.0941 (14)	0.531 (2)	0.6179 (9)	0.038 (6)*
H2N	0.0350 (10)	0.4797 (19)	0.6770 (15)	0.040 (6)*
H3N	0.1408 (12)	0.6441 (14)	0.8569 (11)	0.027 (5)*
H4N	0.4261 (13)	0.5148 (19)	0.8945 (7)	0.032 (5)*
H5N	0.4717 (10)	0.4669 (18)	0.8228 (14)	0.034 (5)*
H6N	0.3437 (12)	0.6263 (15)	0.6550 (12)	0.033 (5)*
H1H	0.2342 (17)	0.501 (2)	0.3550 (9)	0.063 (8)*
H2H	0.7229 (9)	0.255 (2)	0.9831 (12)	0.060 (7)*
H1W	0.2324 (14)	0.492 (3)	0.2039 (10)	0.089 (11)*
H2W	0.3141 (10)	0.525 (2)	0.2441 (16)	0.062 (8)*

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.00939 (16)	0.01777 (19)	0.01458 (18)	−0.00065 (12)	0.00076 (12)	0.00381 (12)
S2	0.00963 (17)	0.01924 (19)	0.01325 (18)	0.00140 (12)	0.00042 (12)	−0.00419 (13)
S3	0.01339 (18)	0.01565 (19)	0.01121 (18)	−0.00263 (12)	0.00321 (13)	−0.00115 (12)
S4	0.01139 (18)	0.01710 (19)	0.01037 (18)	0.00151 (12)	0.00162 (13)	0.00041 (12)
O1	0.0367 (6)	0.0233 (6)	0.0188 (5)	−0.0018 (5)	0.0163 (5)	0.0014 (4)
O2	0.0183 (5)	0.0311 (6)	0.0167 (5)	−0.0078 (4)	−0.0019 (4)	−0.0040 (4)
O3	0.0201 (5)	0.0171 (5)	0.0173 (5)	−0.0053 (4)	−0.0054 (4)	0.0020 (4)
O4	0.0262 (6)	0.0277 (6)	0.0221 (6)	0.0097 (5)	0.0112 (5)	0.0042 (5)
O5	0.0161 (5)	0.0268 (6)	0.0338 (6)	−0.0053 (4)	0.0043 (5)	−0.0012 (5)

O6	0.0166 (5)	0.0169 (5)	0.0163 (5)	0.0038 (4)	−0.0041 (4)	−0.0020 (4)
O7	0.0232 (5)	0.0246 (6)	0.0158 (5)	0.0070 (4)	0.0089 (4)	0.0019 (4)
O8	0.0232 (5)	0.0286 (6)	0.0105 (5)	0.0056 (4)	0.0005 (4)	0.0025 (4)
O1W	0.0250 (5)	0.0380 (7)	0.0182 (6)	0.0038 (5)	0.0068 (5)	0.0008 (5)
N1	0.0153 (6)	0.0233 (7)	0.0110 (6)	−0.0049 (5)	0.0016 (5)	−0.0005 (5)
N2	0.0147 (6)	0.0171 (6)	0.0113 (6)	−0.0052 (5)	0.0011 (5)	−0.0023 (4)
N3	0.0153 (6)	0.0229 (6)	0.0116 (6)	0.0049 (5)	0.0023 (5)	0.0006 (5)
N4	0.0187 (6)	0.0211 (6)	0.0120 (6)	0.0079 (5)	0.0022 (5)	0.0019 (5)
C1	0.0093 (6)	0.0153 (7)	0.0142 (7)	0.0014 (5)	0.0018 (5)	0.0015 (5)
C2	0.0175 (7)	0.0201 (7)	0.0089 (6)	−0.0061 (6)	0.0021 (5)	−0.0021 (5)
C3	0.0167 (7)	0.0263 (8)	0.0107 (6)	−0.0057 (6)	0.0004 (5)	−0.0038 (6)
C4	0.0176 (7)	0.0404 (9)	0.0136 (7)	−0.0125 (7)	0.0031 (6)	−0.0053 (7)
C5	0.0337 (9)	0.0316 (9)	0.0142 (7)	−0.0192 (7)	0.0052 (6)	−0.0022 (6)
C6	0.0367 (9)	0.0213 (8)	0.0164 (7)	−0.0083 (7)	0.0038 (7)	−0.0002 (6)
C7	0.0248 (8)	0.0200 (7)	0.0131 (7)	−0.0044 (6)	0.0020 (6)	−0.0026 (6)
C8	0.0175 (7)	0.0354 (9)	0.0217 (8)	0.0021 (7)	0.0021 (6)	0.0005 (7)
C9	0.0284 (8)	0.0224 (8)	0.0268 (8)	0.0034 (7)	0.0059 (7)	−0.0003 (6)
C10	0.0098 (6)	0.0160 (7)	0.0141 (6)	−0.0002 (5)	0.0019 (5)	−0.0003 (5)
C11	0.0188 (7)	0.0212 (7)	0.0089 (6)	0.0090 (6)	0.0022 (5)	0.0015 (5)
C12	0.0214 (7)	0.0225 (8)	0.0148 (7)	0.0048 (6)	0.0033 (6)	0.0038 (6)
C13	0.0316 (8)	0.0201 (8)	0.0160 (7)	0.0073 (7)	0.0019 (6)	−0.0009 (6)
C14	0.0261 (8)	0.0289 (8)	0.0132 (7)	0.0145 (7)	0.0027 (6)	0.0009 (6)
C15	0.0175 (7)	0.0320 (8)	0.0128 (7)	0.0087 (6)	0.0022 (6)	0.0027 (6)
C16	0.0177 (7)	0.0240 (8)	0.0108 (6)	0.0058 (6)	−0.0008 (5)	0.0024 (6)
C17	0.0261 (8)	0.0265 (9)	0.0324 (9)	−0.0007 (7)	0.0091 (7)	0.0006 (7)
C18	0.0208 (7)	0.0260 (8)	0.0206 (7)	0.0030 (6)	−0.0006 (6)	0.0004 (6)

Geometric parameters (Å, °)

S1—C1	1.7879 (14)	C4—C5	1.386 (3)
S1—S2	2.0431 (5)	C4—H4	0.9500
S2—C10	1.7804 (14)	C5—C6	1.384 (3)
S3—O1	1.4395 (11)	C5—H5	0.9500
S3—O2	1.4460 (11)	C6—C7	1.395 (2)
S3—O3	1.4737 (11)	C6—H6	0.9500
S3—O4	1.5523 (11)	C7—C9	1.511 (2)
S4—O5	1.4399 (11)	C8—H8A	0.9800
S4—O7	1.4465 (10)	C8—H8B	0.9800
S4—O8	1.4598 (10)	C8—H8C	0.9800
S4—O6	1.5902 (11)	C9—H9A	0.9800
O4—H1H	0.891 (10)	C9—H9B	0.9800
O6—H2H	0.884 (10)	C9—H9C	0.9800
O1W—H1W	0.865 (10)	C11—C16	1.396 (2)
O1W—H2W	0.874 (10)	C11—C12	1.396 (2)
N1—C1	1.3106 (19)	C12—C13	1.396 (2)
N1—H1N	0.877 (9)	C12—C17	1.508 (2)
N1—H2N	0.878 (10)	C13—C14	1.387 (2)
N2—C1	1.3107 (18)	C13—H13	0.9500

N2—C2	1.4438 (18)	C14—C15	1.385 (2)
N2—H3N	0.868 (9)	C14—H14	0.9500
N3—C10	1.3097 (19)	C15—C16	1.396 (2)
N3—H4N	0.879 (9)	C15—H15	0.9500
N3—H5N	0.877 (9)	C16—C18	1.508 (2)
N4—C10	1.3076 (18)	C17—H17A	0.9800
N4—C11	1.4470 (18)	C17—H17B	0.9800
N4—H6N	0.868 (9)	C17—H17C	0.9800
C2—C7	1.396 (2)	C18—H18A	0.9800
C2—C3	1.399 (2)	C18—H18B	0.9800
C3—C4	1.393 (2)	C18—H18C	0.9800
C3—C8	1.504 (2)		
C1—S1—S2	101.76 (5)	C6—C7—C9	121.15 (15)
C10—S2—S1	103.12 (5)	C2—C7—C9	121.48 (14)
O1—S3—O2	114.85 (7)	C3—C8—H8A	109.5
O1—S3—O3	112.24 (6)	C3—C8—H8B	109.5
O2—S3—O3	110.05 (6)	H8A—C8—H8B	109.5
O1—S3—O4	104.28 (6)	C3—C8—H8C	109.5
O2—S3—O4	108.30 (6)	H8A—C8—H8C	109.5
O3—S3—O4	106.57 (6)	H8B—C8—H8C	109.5
O5—S4—O7	114.36 (7)	C7—C9—H9A	109.5
O5—S4—O8	113.99 (7)	C7—C9—H9B	109.5
O7—S4—O8	111.43 (6)	H9A—C9—H9B	109.5
O5—S4—O6	106.71 (6)	C7—C9—H9C	109.5
O7—S4—O6	106.60 (6)	H9A—C9—H9C	109.5
O8—S4—O6	102.66 (6)	H9B—C9—H9C	109.5
S3—O4—H1H	112.0 (17)	N4—C10—N3	124.29 (13)
S4—O6—H2H	111.2 (16)	N4—C10—S2	120.15 (11)
H1W—O1W—H2W	101.2 (17)	N3—C10—S2	115.52 (11)
C1—N1—H1N	117.6 (14)	C16—C11—C12	123.93 (14)
C1—N1—H2N	120.4 (14)	C16—C11—N4	118.18 (13)
H1N—N1—H2N	121 (2)	C12—C11—N4	117.81 (13)
C1—N2—C2	124.15 (12)	C13—C12—C11	117.08 (14)
C1—N2—H3N	116.1 (13)	C13—C12—C17	120.97 (15)
C2—N2—H3N	119.7 (13)	C11—C12—C17	121.94 (14)
C10—N3—H4N	119.8 (13)	C14—C13—C12	120.39 (15)
C10—N3—H5N	119.8 (14)	C14—C13—H13	119.8
H4N—N3—H5N	119.6 (19)	C12—C13—H13	119.8
C10—N4—C11	124.00 (12)	C15—C14—C13	121.08 (14)
C10—N4—H6N	118.0 (13)	C15—C14—H14	119.5
C11—N4—H6N	117.6 (13)	C13—C14—H14	119.5
N1—C1—N2	125.05 (13)	C14—C15—C16	120.65 (15)
N1—C1—S1	116.46 (11)	C14—C15—H15	119.7
N2—C1—S1	118.44 (10)	C16—C15—H15	119.7
C7—C2—C3	123.49 (14)	C15—C16—C11	116.86 (14)
C7—C2—N2	117.99 (13)	C15—C16—C18	121.67 (14)
C3—C2—N2	118.38 (13)	C11—C16—C18	121.46 (13)

C4—C3—C2	117.09 (15)	C12—C17—H17A	109.5
C4—C3—C8	121.28 (14)	C12—C17—H17B	109.5
C2—C3—C8	121.62 (14)	H17A—C17—H17B	109.5
C5—C4—C3	120.61 (15)	C12—C17—H17C	109.5
C5—C4—H4	119.7	H17A—C17—H17C	109.5
C3—C4—H4	119.7	H17B—C17—H17C	109.5
C6—C5—C4	121.06 (15)	C16—C18—H18A	109.5
C6—C5—H5	119.5	C16—C18—H18B	109.5
C4—C5—H5	119.5	H18A—C18—H18B	109.5
C5—C6—C7	120.36 (16)	C16—C18—H18C	109.5
C5—C6—H6	119.8	H18A—C18—H18C	109.5
C7—C6—H6	119.8	H18B—C18—H18C	109.5
C6—C7—C2	117.37 (15)		
C2—N2—C1—N1	10.6 (2)	C11—N4—C10—N3	6.9 (2)
C2—N2—C1—S1	−172.25 (11)	C11—N4—C10—S2	−175.71 (11)
S2—S1—C1—N1	−139.70 (10)	S1—S2—C10—N4	26.79 (13)
S2—S1—C1—N2	42.92 (12)	S1—S2—C10—N3	−155.57 (10)
C1—N2—C2—C7	83.26 (18)	C10—N4—C11—C16	−92.25 (18)
C1—N2—C2—C3	−100.91 (16)	C10—N4—C11—C12	90.89 (18)
C7—C2—C3—C4	1.5 (2)	C16—C11—C12—C13	0.2 (2)
N2—C2—C3—C4	−174.12 (12)	N4—C11—C12—C13	176.89 (13)
C7—C2—C3—C8	−178.49 (14)	C16—C11—C12—C17	−178.60 (14)
N2—C2—C3—C8	5.9 (2)	N4—C11—C12—C17	−1.9 (2)
C2—C3—C4—C5	−1.5 (2)	C11—C12—C13—C14	−0.5 (2)
C8—C3—C4—C5	178.49 (14)	C17—C12—C13—C14	178.37 (14)
C3—C4—C5—C6	0.3 (2)	C12—C13—C14—C15	0.1 (2)
C4—C5—C6—C7	1.0 (2)	C13—C14—C15—C16	0.5 (2)
C5—C6—C7—C2	−1.0 (2)	C14—C15—C16—C11	−0.8 (2)
C5—C6—C7—C9	177.71 (14)	C14—C15—C16—C18	−179.62 (13)
C3—C2—C7—C6	−0.2 (2)	C12—C11—C16—C15	0.4 (2)
N2—C2—C7—C6	175.37 (12)	N4—C11—C16—C15	−176.27 (12)
C3—C2—C7—C9	−178.97 (13)	C12—C11—C16—C18	179.25 (13)
N2—C2—C7—C9	−3.4 (2)	N4—C11—C16—C18	2.6 (2)

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1N $\cdots$ O1	0.88 (1)	1.95 (1)	2.8256 (16)	175 (2)
N1—H2N $\cdots$ O2 ⁱ	0.88 (1)	1.96 (1)	2.8172 (16)	164 (2)
N2—H3N $\cdots$ O3 ⁱⁱ	0.87 (1)	1.95 (1)	2.8125 (16)	175 (2)
N3—H4N $\cdots$ O7 ⁱⁱⁱ	0.88 (1)	1.98 (1)	2.8440 (16)	169 (2)
N3—H5N $\cdots$ O8	0.88 (1)	2.13 (1)	2.9596 (16)	157 (2)
N4—H6N $\cdots$ O6 ^{iv}	0.87 (1)	2.06 (1)	2.8703 (16)	156 (2)
O4—H1H $\cdots$ O1W	0.89 (1)	1.67 (1)	2.5571 (15)	171 (3)
O6—H2H $\cdots$ O3 ^v	0.88 (1)	1.72 (1)	2.5966 (15)	173 (2)

O1 <i>W</i> —H1 <i>W</i> ···O5 ^{vi}	0.87 (1)	2.36 (2)	2.9801 (16)	129 (2)
O1 <i>W</i> —H2 <i>W</i> ···O8 ^{vi}	0.87 (1)	2.02 (1)	2.8515 (16)	159 (2)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, -y+3/2, z+1/2$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x+1, y+1/2, -z+3/2$; (v) $-x+1, y-1/2, -z+3/2$; (vi) $-x+1, -y+1, -z+1$.