Redetermination of the structure of 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate

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The reaction of β-(thiomorpholin-1-yl)propioamidoxime with tosyl chloride in CHCl₃ in the presence of DIPEA when heated at 343 K for 8 h afforded the title hydrated salt, C₇H₁₄N₃S⁺Cl⁻H₂O, in 84% yield. This course of the tosylation reaction differs from the result of tosylation obtained for this substrate at room temperature, when only 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-ene-5-ammonium tosylate was isolated in 56% yield. The structure of the reaction product was established by physicochemical methods, spectroscopy, and X-ray diffraction. The single-crystal data demonstrated that the previously reported crystal structure of this compound [Kayukova et al. (2021). Chem. J. Kaz, 74, 21–31] had been refined in a wrong space group. In the extended structure, the chloride anions, water molecules and amine groups of the cations form two-periodic hydrogen-bonded networks with the fe₃ toplogy.

1. Chemical context

Sulfochlorination of amidoximes is known to afford stable products of acylation at the oxygen atom of the amidoxime group; at the same time, the sulfochlorination reaction of derivatives of primary amidoximes can, depending on the structure of the starting amidoxime and reaction conditions, lead to rearranged products with the formation of ureas and substituted cyanamides (Tiemann, 1891; Bakunov et al., 2000; Doulou et al., 2014).

Previously, in our studies of the acylation of β-aminopropioamidoximes with acid chlorides of substituted benzoic acids, only O-acyl-β-aminopropioamidoximes were identified as acylation reaction products. Their structures have been determined by the complex use of spectroscopic methods, as well as X-ray structural analysis (Kayukova, 2003; Beketov et al., 2004; Kayukova et al., 2010a). The dehydration of the products of the O-acylation of β-aminopropioamidoximes allows for 3,5-disubstituted 1,2,4-oxadiazoles to be obtained, which under conditions of acid hydrolysis and in the presence of moisture are capable of undergoing a Boulton–Katritsky rearrangement to 2-amino-1,5-diazaspiro[4.5]dec-1-ene-5-ium salts (Kayukova et al., 2010b, 2018, 2021a).

Recently, we found that the arylsulfochlorination reaction of β-aminopropioamidoximes at room temperature afforded 2-amino-8-(hetera)-1,5-diazaspiro[4.5]dec-1-ene-5-ium arylsulfonates as the main products (Kayukova et al., 2020, 2021b). Herein we report on the result of β-(thiomorpholin-1-yl)propioamidoxime tosylation at the boiling point of the solvent. By means of such a high-temperature process, the
formation of the most stable reaction product is expected. Under such conditions of thermodynamic control of the tosylation reaction of \( \beta \)-(thiomorpholin-1-yl)propioamidoxime (1) upon prolonged heating for 8 h at the boiling point of the solvent [CHCl\(_3\), 8 h, 343 K (bath temperature)], in the presence of DIPEA, the title hydrated salt, 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate (3) was obtained in good yield (84%). In our opinion, the source of hydrate formation was air moisture, since the formation of single crystals took place over a long time under conditions of natural evaporation of the solvent for crystallization with air access. This result of the amidoxime (1) tosylation differs from the result of the same reaction performed at room temperature, when the main kinetic product of the reaction was 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium tosylate (2) (Yergaliyeva et al., 2021).

Spiropyrazolinium chloride monohydrate 3 is a white opaque precipitate, poorly soluble in chloroform. When the reaction was complete, it was filtered off from the reaction mixture and recrystallized from propanol-2 solution over three weeks in the form of transparent prisms with a melting point of 575 K. We previously isolated a compound with the same chemical composition and melting point during the acid hydrolysis of 5-aryl-3-(\( \beta \)-thiomorpholin-1-yl)-1,2,4-oxadiazoles (Kayukova et al., 2010b). Not only the composition, but also the orthorhombic unit-cell parameters were similar for 3 and the previously reported structure; however, the space groups were different: \( P_{2_1}2_12_1 \) at room temperature (Kayukova et al., 2010b) and \( Pbca \) at 120.0 (2) K for 3, thus a single crystal of the reaction product was also determined at 295.0 (2) K and the resulting crystal structures were compared with the previously reported one.

2. Structural commentary

The molecular structure of 3 is shown in Fig. 2. The C3—N1 and N1—N2 bonds are elongated as compared with typical single bonds at 1.521 (1) and 1.463 (1) Å, respectively, which can be related to the anomic effect of the lone pair of atom N2. The six- and five-membered rings of the \( C_7H_{14}N_3S^+ \) cation adopt chair and envelope conformations, respectively. It may be noted that in respect to a chair conformation of the six-membered ring, atom N2 can be situated in the equatorial and axial positions of the N1 atom; however, in this and previously reported salts, only the axial disposition of the N2 atom is observed. This is in accord with our B3LYP/6-31++G(d,p) calculations of standard Gibbs free energies of reactions leading to the formation of various products. We established that the axial stereoisomer is more stable than the equatorial one (\( \Delta G = -144.29 \) and \( -124.23 \) kJ mol\(^{-1}\), respectively; Yergaliyeva et al., 2021).

The envelope conformation of the C1/C2/C3/N1/N2 five-membered ring in 3 is expressed as the deviation of C3 from the mean plane formed by atoms N1/N2/C1/C2 (r.m.s. deviation = 0.005 Å): it is equal to 0.401 (1) Å, and the two molecular conformers (corresponding to different directions of this carbon atom shifted in respect to the N—N—C—C mean plane) are equally present in this centrosymmetric crystal. However, the previously reported crystal structure (Kayukova et al., 2010b) [refcode APOBOX in the Cambridge Crystallographic Database (CSD; Groom et al., 2016)] contains two independent spiro-cations in the asymmetric unit with two different conformations of the five-membered ring (Fig. 3). A
question arises as to whether these structures are polymorphs of the same salt, or if the previously reported structure was incorrectly solved and refined. Our study of the same single crystal of 3 at room temperature confirmed that no phase transition occurs between 120 and 295 K. Unfortunately, crystallographic data for APOBOX stored in the CSD could not be re-refined. Thus, we compared the crystal packing and the system of hydrogen bonds for the two models refined in different space groups.

3. Supramolecular features

First, the system of hydrogen bonds was compared for the two solids at 120.0 (2) and 295.0 (2) K (Tables 1 and 2) and they are essentially the same, apart from a slight lengthening of the H···X contacts at the higher temperature. In both cases, the amine acts as a donor of hydrogen bonds with a water molecule, an anion and the water molecules act as acceptors of N—H···O bonds and as donors in two O—H···Cl interactions, and the chloride anion is an acceptor of three hydrogen bonds. As a result, infinite layers parallel to the (001) plane are observed (Fig. 4). A topological analysis of the system of hydrogen bonds, where the spiro-cations act as linkers and water molecules and anions are three-connected nodes, indicates that both layers are isoreticular and have the fes topology (the three-letter code is given in terms of the RSCCR notation; O’Keeffe et al., 2008).

Additional analysis of the crystal packing by means of the PLATON package (Spek, 2020) suggests that the Pbca space group is correct for both solids, and by means of the ‘Crystal Packing Similarity’ tool implemented within Mercury (Macrae et al., 2020) as described by Childs et al. (2009) or by Vologzhanina (2019) denotes that the packings of 30-molecule clusters for the two solids are also very close to each other (the average r.m.s. deviation of 0.15 Å can be explained by the different experimental temperatures). Thus, we propose that 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate crystallizes in the Pbca space group both at low and room temperatures in contrast with the data given previously in space group P2_12_2_1(Kayukova et al., 2010b).

4. Synthesis and crystallization

IR spectra were obtained on a Thermo Scientific Nicolet 5700 FTIR instrument in KBr pellets. 1H and 13C NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer (500 and 126 MHz, respectively). Melting points were determined on a TPL apparatus (Khimlabpribor, Russia). The progress of the reaction was monitored using Sorbil TLC plates (Sorbopolymer, Russia) coated with CTX-1A silica gel, grain size 5–17 μm, UV-254 indicator. The spots were developed in I2 vapours and in the UV light of a chromatoscope (λ = 254 nm) TSX 254/365 (PETROLASER). The eluent for the analysis was a mixture of EtOH:benzene = 1:1 + a few drops of a 25% aqueous solution of NH3. Microanalysis according to the Pregl method was carried out on an elemental analyser with the absorption of CO2 and O2 isolated during combustion with a two-degree repetition of combustion.

The tosylation of -(thiomorpholin-1-yl)propioamidoxime (1) was performed in dried CHCl3 with tosyl chloride in the presence of DIPEA, purchased from Sigma–Aldrich and used without purification. Solvents for synthesis, recrystallization

| Table 1 | Hydrogen-bond geometry (Å, °) for the low-temperature structure. |
|---------|---------------------------------------------------------------|
| D—H···A | D—H | H···A | D—H···A | D—H···A |
| N3···Cl | 0.88 | 2.38 | 3.2560 (9) | 175 |
| N3···Cl | 0.88 | 1.95 | 2.7970 (11) | 161 |
| O1···Cl | 0.85 | 2.26 | 3.1042 (9) | 175 |
| O1···Cl | 0.85 | 2.27 | 3.1152 (9) | 176 |
| C5···N3 | 0.99 | 2.58 | 3.3778 (12) | 138 |
| C6···N3 | 0.99 | 2.55 | 3.3346 (12) | 136 |

Symmetry codes: (i) x, y+1, z; (ii) x−1, y, z+1; (iii) −x−1, y−1, z; (iv) −x+1, y−1, z.

| Table 2 | Hydrogen-bond geometry (Å, °) for the room-temperature structure. |
|---------|---------------------------------------------------------------|
| D—H···A | D—H | H···A | D—H···A | D—H···A |
| N3···Cl | 0.87 | 2.42 | 3.2786 (18) | 174 |
| N3···Cl | 0.86 | 1.99 | 2.821 (2) | 162 |
| O1···Cl | 0.85 | 2.28 | 3.1244 (17) | 173 |
| O1···Cl | 0.85 | 2.29 | 3.1343 (17) | 175 |
| C6···Cl | 0.97 | 2.61 | 3.391 (2) | 138 |

Symmetry codes: (i) x, y+1, z; (ii) x+1,−y+1, z+1; (iii) −x+1,−y,−z+1; (iv) −x+1, y−1, z.
and TLC analysis (EtOH, 2-PrOH, benzene, CHCl₃) were purified according to the standard procedures described for each solvent.

Synthesis of 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride hydrate (3):

To a solution of 1.00 g (0.0053 mol) of β-(thiomorpholin-1-yl)propioamidoxime (1) in 40 ml of CHCl₃, 0.92 ml (0.0053 mol) of DIPEA were added. The reaction mixture was cooled to 272 K, and a solution of 1.01 g (0.0053 mol) of tosyl chloride in 4 ml of CHCl₃ was added dropwise under stirring. The reaction mixture was stirred for 1 h at room temperature and was then heated and stirred at the reflux temperature of CHCl₃ for 8 h until the completion of the reaction, the progress of the reaction being monitored by TLC. The formed white precipitate of the chloride hydrate 3 was filtered off and recrystallized from 2-PrOH solution. The yield of 3 was 1.01 g (84%), m.p. 78–88 K, Rp 0.08. Found, %: C 37.24, H 7.14. IR, cm⁻¹: 3230, 3380, 3384 (br s, C—N; d, C—H); 2150.4 (6), 19.291 (3), 1760.4 (8), 748 (8), ν(S—C); 3135, 3065, 1670, 1580, 1500, 1380, 1260 (s, C—N). 1H NMR, δ, ppm (J, Hz): 2.88 [m, 2H, S(CH₃)₂], 3.14 [m, 2H, S(CH₃)₂], 3.14 [m, 2H, N+(CH₂CH₂)₃], 3.37 (br s, 2H, H₂O), 3.62 [m, 2H, N+(CH₂H₂)], 3.74 [m, 2H, N+(CH₃)], 3.88 [s, 2H, J = 7.0, N+(CH₂CH₂)], 7.48 (br s, 2H, NH₂).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The positions of hydrogen atoms were calculated and included in the refinement in isotropic approximation using a riding model with U(eq)(H) = 1.5U(eq)(O) and 1.2U(eq)(X) for the other atoms.

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supporting information

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Computing details
For both structures, data collection: APEX2 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

2-Amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate (3_LT)

Crystal data
C₇H₁₄N₃S⁺·Cl⁻·H₂O  
Mr = 225.74  
Orthorhombic, Pbcn  
a = 11.0360 (18) Å  
b = 10.1005 (16) Å  
c = 19.291 (3) Å  
V = 2150.4 (6) Å³  
Z = 8  
F(000) = 960

Data collection
Bruker APEXII CCD diffractometer  
φ and ω scans  
Absorption correction: multi-scan  
(SADABS; Bruker, 2016)  
Tmin = 0.633, Tmax = 0.747  
29600 measured reflections

Refinement
Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.030  
wR(F²) = 0.087  
S = 1.06  
5145 reflections  
121 parameters  
0 restraints

Hydrogen site location: mixed  
H-atom parameters constrained  
\( w = 1/\left[ \sigma^2(F_c^2) + (0.050P)^2 \right] \)  
where P = (F_c² + 2F_e²)/3  
(Δσ)max = 0.002  
Δρmax = 0.44 e Å⁻³  
Δρmin = -0.34 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 (Å²)**

|        | x      | y      | z      | Uiso*/Ueq |
|--------|--------|--------|--------|-----------|
| Cl1    | -0.00746 (2) | 0.63396 (2) | 0.39143 (2) | 0.02000 (6) |
| S1     | 0.70833 (2)  | 0.12361 (2)  | 0.74087 (2)  | 0.02033 (6)  |
| N1     | 0.55731 (6)  | 0.31961 (6)  | 0.64122 (3)  | 0.01183 (11) |
| N2     | 0.53333 (6)  | 0.45906 (6)  | 0.62609 (4)  | 0.01348 (12) |
| N3     | 0.38623 (7)  | 0.57594 (7)  | 0.56713 (4)  | 0.02087 (15) |
| H3A    | 0.4200      | 0.6520      | 0.5782      | 0.025*      |
| H3B    | 0.3199      | 0.5747      | 0.5418      | 0.025*      |
| C1     | 0.43545 (7)  | 0.46295 (7)  | 0.58861 (4)  | 0.01473 (14) |
| C2     | 0.38062 (8)  | 0.33120 (8)  | 0.57138 (5)  | 0.02009 (16) |
| H2A    | 0.3594      | 0.3249      | 0.5216      | 0.024*      |
| H2B    | 0.3077      | 0.3134      | 0.5997      | 0.024*      |
| C3     | 0.48341 (7)  | 0.23868 (8)  | 0.58991 (4)  | 0.01713 (15) |
| H3C    | 0.5320      | 0.2156      | 0.5485      | 0.021*      |
| C4     | 0.51885 (7)  | 0.29562 (8)  | 0.71514 (4)  | 0.01528 (14) |
| H4A    | 0.4304      | 0.3102      | 0.7189      | 0.018*      |
| H4B    | 0.5595      | 0.3611      | 0.7454      | 0.018*      |
| C5     | 0.54806 (8)  | 0.15791 (8)  | 0.74105 (4)  | 0.01851 (16) |
| H5A    | 0.5063      | 0.0922      | 0.7114      | 0.022*      |
| H5B    | 0.5166      | 0.1479      | 0.7888      | 0.022*      |
| C6     | 0.73185 (8)  | 0.16153 (8)  | 0.65050 (4)  | 0.01875 (16) |
| H6A    | 0.8190      | 0.1519      | 0.6393      | 0.022*      |
| H6B    | 0.6862      | 0.0975      | 0.6217      | 0.022*      |
| C7     | 0.69134 (7)  | 0.30023 (8)  | 0.63285 (4)  | 0.01590 (14) |
| H7A    | 0.7345      | 0.3637      | 0.6632      | 0.019*      |
| H7B    | 0.7141      | 0.3200      | 0.5843      | 0.019*      |
| O1     | 0.16762 (6)  | 0.51532 (7)  | 0.50099 (3)  | 0.02415 (14) |
| H1A    | 0.1157      | 0.5460      | 0.4727      | 0.036*      |
| H1B    | 0.1256      | 0.4764      | 0.5318      | 0.036*      |

**Atomic displacement parameters (Å²)**

|        | U¹¹  | U¹²  | U¹³  | U²²  | U²³  | U³³  |
|--------|------|------|------|------|------|------|
| Cl1    | 0.02624 (11) | 0.01477 (9) | 0.01898 (10) | 0.00288 (7) | 0.00057 (7) | 0.00344 (7) |
| S1     | 0.02337 (11) | 0.01616 (10) | 0.02145 (11) | 0.00301 (7) | −0.00515 (8) | 0.00290 (7) |
| N1     | 0.0134 (3)  | 0.0084 (2)  | 0.0137 (3)  | −0.0004 (2) | −0.0002 (2)  | −0.0008 (2) |
| N2     | 0.0158 (3)  | 0.0082 (3)  | 0.0165 (3)  | 0.0001 (2)  | −0.0017 (2)  | 0.0006 (2)  |
| N3     | 0.0217 (3)  | 0.0126 (3)  | 0.0283 (4)  | 0.0003 (3)  | −0.0115 (3)  | 0.0011 (3)  |
| C1     | 0.0149 (3)  | 0.0123 (3)  | 0.0171 (3)  | −0.0004 (3) | −0.0010 (3)  | −0.0010 (3) |
### Geometric parameters (Å, °)

| S1—C5 | 1.8054 (9) | C3—H3C | 0.9900 |
| S1—C6 | 1.8038 (9) | C3—H3D | 0.9900 |
| N1—N2 | 1.4626 (9) | C4—H4A | 0.9900 |
| N1—C3 | 1.5210 (10) | C4—H4B | 0.9900 |
| N1—C4 | 1.5074 (10) | C4—C5 | 1.5128 (11) |
| N1—C7 | 1.5007 (10) | C5—H5A | 0.9900 |
| N2—C1 | 1.3003 (10) | C5—H5B | 0.9900 |
| N3—H3A | 0.8800 | C6—H6A | 0.9900 |
| N3—H3B | 0.8800 | C6—H6B | 0.9900 |
| N3—C1 | 1.3301 (10) | C6—C7 | 1.5093 (11) |
| C1—C2 | 1.4992 (11) | C7—H7A | 0.9900 |
| C2—H2A | 0.9900 | C7—H7B | 0.9900 |
| C2—H2B | 0.9900 | O1—H1A | 0.8501 |
| C2—C3 | 1.5125 (11) | O1—H1B | 0.8499 |

| C5—S1—C6 | 95.87 (4) | N1—C4—H4A | 108.8 |
| N2—N1—C3 | 106.89 (6) | N1—C4—H4B | 108.8 |
| N2—N1—C4 | 107.01 (5) | N1—C4—C5 | 113.60 (6) |
| N2—N1—C7 | 106.41 (6) | H4A—C4—H4B | 107.7 |
| C4—N1—C3 | 112.23 (6) | C5—C4—H4A | 108.8 |
| C7—N1—C3 | 112.85 (6) | C5—C4—H4B | 108.8 |
| C7—N1—C4 | 111.00 (6) | S1—C5—H5A | 109.1 |
| C1—N2—N1 | 106.89 (6) | S1—C5—H5B | 109.1 |
| H3A—N3—H3B | 120.0 | C4—C5—S1 | 112.66 (6) |
| C1—N3—H3A | 120.0 | C4—C5—H5A | 109.1 |
| C1—N3—H3B | 120.0 | C4—C5—H5B | 109.1 |
| N2—C1—N3 | 122.58 (7) | H5A—C5—H5B | 107.8 |
| N2—C1—C2 | 115.57 (7) | S1—C6—H6A | 109.2 |
| N3—C1—C2 | 121.84 (7) | S1—C6—H6B | 109.2 |
| C1—C2—H2A | 111.5 | H6A—C6—H6B | 107.9 |
| C1—C2—H2B | 111.5 | C7—C6—S1 | 111.87 (6) |
| C1—C2—C3 | 101.15 (6) | C7—C6—H6A | 109.2 |
| H2A—C2—H2B | 109.4 | C7—C6—H6B | 109.2 |
| C3—C2—H2A | 111.5 | N1—C7—C6 | 112.88 (6) |
| C3—C2—H2B | 111.5 | N1—C7—H7A | 109.0 |
| N1—C3—H3C | 111.2 | N1—C7—H7B | 109.0 |
| N1—C3—H3D | 111.2 | C6—C7—H7A | 109.0 |
| C2—C3—N1 | 102.94 (6) | C6—C7—H7B | 109.0 |
C2—C3—H3C  111.2  H7A—C7—H7B  107.8
C2—C3—H3D  111.2  H1A—O1—H1B  104.5
H3C—C3—H3D  109.1
S1—C6—C7—N1 −64.89 (8)  C3—N1—C4—C5  68.11 (8)
N1—N2—C1—N3  178.26 (7)  C3—N1—C7—C6 −66.08 (9)
N1—N2—C1—C2 −1.35 (10)  C4—N1—C3—C2  91.71 (8)
N1—C4—C5—S1  61.65 (8)  C4—N1—C7—C6  60.89 (8)
N2—N1—C3—C2 −25.32 (8)  C5—S1—C6—C7  56.71 (7)
N2—N1—C4—C5 −174.93 (6)  C6—S1—C5—C4 −55.24 (7)
N2—N1—C7—C6  176.99 (6)  C7—N1—C3—C2 −141.97 (7)
N3—C1—C2—C3 −14.59 (10)  C7—N1—C4—C5 −59.21 (8)
C1—C2—C3—N1  22.86 (8)  C7—N1—N2—C1  137.87 (7)
N2—N1—C4—C5 −174.93 (6)  C7—N1—C3—C2 −141.97 (7)
C1—C2—C3—N1  22.86 (8)  C7—N1—C4—C5 −59.21 (8)
C3—N1—N2—C1 −17.04 (8)

Hydrogen-bond geometry (Å, °)

\[
\begin{array}{cccc}
D & H \cdots A & D \cdots H & H \cdots A \\
N3 & H3A \cdots Cl1 & 0.88 & 2.38 & 3.2560 (9) & 175 \\
N3 & H3B \cdots O1 & 0.88 & 1.95 & 2.7970 (11) & 161 \\
O1 & H1A \cdots Cl1 & 0.85 & 2.26 & 3.1042 (9) & 175 \\
O1 & H1B \cdots Cl1 & 0.85 & 2.27 & 3.1152 (9) & 176 \\
C5 & H5B \cdots N2 & 0.99 & 2.58 & 3.3778 (12) & 138 \\
C6 & H6A \cdots N2 & 0.99 & 2.55 & 3.3346 (12) & 136 \\
\end{array}
\]

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

2-Amino-8-thia-1,5-diazaspiro[4.5]deca-1-en-5-ium chloride monohydrate (3_RT)

Crystal data

C7H14N3S+·Cl−·H2O  
Mr = 225.74  
Orthorhombic, Pbca  
a = 11.0924 (4) Å  
b = 10.1898 (4) Å  
c = 19.6434 (8) Å  
V = 2220.28 (15) Å³  
Z = 8  
F(000) = 960  

Data collection

Bruker D8 Quest PHOTON area detector  
Graphite monochromator  
phi and omega scans  
Absorption correction: multi-scan  
(SADABS; Bruker, 2016)  
T_range = 0.518, T_max = 0.746  
29622 measured reflections  

\[
\begin{array}{c}
D_\text{c} = 1.351 \text{ Mg m}^{-3} \\
\text{Mo } K\alpha\text{ radiation, } \lambda = 0.71073 \text{ Å} \\
\theta = 2.8–28.8° \ 
\mu = 0.50 \text{ mm}^{-1} \ 
T = 295 \text{ K} \ 
\text{Prism, colourless} \ 
0.41 \times 0.36 \times 0.32 \text{ mm} \ 
2969 \text{ independent reflections} \\
2269 \text{ reflections with } I > 2 \sigma(I) \ 
R_{\text{int}} = 0.106 \ 
\theta_{\text{max}} = 29.1°, \theta_{\text{min}} = 2.1° \ 
h = -15 \rightarrow 14 \ 
k = -11 \rightarrow 13 \ 
l = -26 \rightarrow 26
\end{array}
\]
Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.124$

$S = 1.05$

2969 reflections

118 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0532 P)^2 + 0.7125 P]$

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

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

$\Delta \rho_{max} = 0.29 \text{ e} \AA^{-3}$

$\Delta \rho_{min} = -0.34 \text{ e} \AA^{-3}$

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 ($\AA^2$)

| X    | Y    | Z    | U_{eq} |
|------|------|------|--------|
| C11  | 0.50712 (5) | −0.13596 (5) | 0.60611 (3) | 0.04965 (17) |
| S1   | 0.28950 (5) | 0.12409 (5) | 0.73957 (3) | 0.04811 (17) |
| N1   | 0.44413 (12) | 0.31778 (13) | 0.64306 (7) | 0.0269 (3) |
| N2   | 0.46759 (13) | 0.45621 (14) | 0.62725 (8) | 0.0308 (3) |
| N3   | 0.61220 (16) | 0.57229 (17) | 0.56826 (10) | 0.0481 (5) |
| H3A  | 0.5789 | 0.6458 | 0.5787 | 0.058* |
| H3B  | 0.6764 | 0.5712 | 0.5437 | 0.058* |
| C1   | 0.52107 (19) | 0.23660 (19) | 0.59441 (11) | 0.0433 (5) |
| H1A  | 0.5539 | 0.1599 | 0.6170 | 0.052* |
| H1B  | 0.4746 | 0.2086 | 0.5552 | 0.052* |
| C2   | 0.61951 (18) | 0.32998 (19) | 0.57400 (12) | 0.0463 (5) |
| H2A  | 0.6923 | 0.3153 | 0.6003 | 0.056* |
| H2B  | 0.6382 | 0.3225 | 0.5259 | 0.056* |
| C3   | 0.56420 (16) | 0.45980 (17) | 0.59016 (9) | 0.0325 (4) |
| C4   | 0.47724 (18) | 0.29721 (19) | 0.71662 (9) | 0.0364 (4) |
| H4A  | 0.4345 | 0.3610 | 0.7442 | 0.044* |
| H4B  | 0.5629 | 0.3132 | 0.7222 | 0.044* |
| C5   | 0.4484 (2) | 0.1611 (2) | 0.74256 (11) | 0.0438 (5) |
| H5A  | 0.4764 | 0.1533 | 0.7892 | 0.053* |
| H5B  | 0.4918 | 0.0972 | 0.7154 | 0.053* |
| C6   | 0.27154 (18) | 0.1587 (2) | 0.65017 (11) | 0.0442 (5) |
| H6A  | 0.3183 | 0.0961 | 0.6240 | 0.053* |
| H6B  | 0.1875 | 0.1479 | 0.6378 | 0.053* |
| C7   | 0.31144 (16) | 0.2961 (2) | 0.63200 (10) | 0.0384 (4) |
| H7A  | 0.2924 | 0.3128 | 0.5846 | 0.046* |
| H7B  | 0.2666 | 0.3585 | 0.6594 | 0.046* |
| O1   | 0.33147 (14) | −0.01611 (18) | 0.49843 (8) | 0.0577 (5) |
| H1C  | 0.3755 | −0.0450 | 0.5305 | 0.087* |
| H1D  | 0.3711 | 0.0261 | 0.4686 | 0.087* |
### Atomic displacement parameters (Å²)

|    | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|----|------------|------------|------------|------------|------------|------------|
| Cl1| 0.0635 (4) | 0.0357 (3) | 0.0498 (3) | 0.0080 (2) | 0.0013 (2) | 0.0113 (2) |
| S1 | 0.0550 (3) | 0.0369 (3) | 0.0524 (3) | -0.0082 (2)| 0.0144 (2) | 0.0064 (2) |
| N1 | 0.0311 (7) | 0.0193 (6) | 0.0302 (7) | 0.0009 (5) | 0.0013 (5) | -0.0024 (5)|
| N2 | 0.0360 (8) | 0.0194 (7) | 0.0370 (8) | 0.0012 (6) | 0.0059 (6) | 0.0009 (6) |
| N3 | 0.0517 (10)| 0.0287 (8) | 0.0640 (12)| -0.0021 (7)| 0.0241 (8) | 0.0024 (8) |
| C1 | 0.0537 (12)| 0.0260 (9) | 0.0500 (11)| 0.0012 (8) | 0.0201 (9) | -0.0096 (8)|
| C2 | 0.0443 (11)| 0.0301 (10)| 0.0644 (13)| 0.0043 (8) | 0.0196 (9) | -0.0042 (9)|
| C3 | 0.0358 (9) | 0.0261 (8) | 0.0355 (9) | 0.0005 (7) | 0.0015 (7) | -0.0037 (7)|
| C4 | 0.0446 (10)| 0.0318 (9) | 0.0326 (9) | -0.0055 (7)| -0.0092 (7)| 0.0090 (7) |
| C5 | 0.0549 (12)| 0.0363 (10)| 0.0401 (10)| -0.0013 (9)| -0.0076 (9)| 0.0111 (8) |
| C6 | 0.0400 (11)| 0.0384 (11)| 0.0540 (12)| -0.0131 (8)| -0.0035 (9)| -0.0026 (9)|
| C7 | 0.0319 (9) | 0.0390 (10)| 0.0444 (10)| -0.0051 (8)| -0.0081 (7)| 0.0061 (8) |
| O1 | 0.0387 (8) | 0.0872 (13)| 0.0473 (8) | -0.0039 (8)| -0.0054 (6)| 0.0084 (8) |

### Geometric parameters (Å, º)

|    | S1—C5 | 1.804 (2) | C2—H2B | 0.9700 |
|----|-------|----------|--------|--------|
| S1 | 1.802 (2) | C2—C3 | 1.492 (2) |
| N1 | 1.4676 (19) | C4—H4A | 0.9700 |
| N1 | 1.525 (2) | C4—H4B | 0.9700 |
| N1 | 1.506 (2) | C4—C5 | 1.512 (3) |
| N1 | 1.504 (2) | C5—H5A | 0.9700 |
| N2 | 1.296 (2) | C5—H5B | 0.9700 |
| C3 | 0.8600 | C6—H6A | 0.9700 |
| C3 | 0.8600 | C6—H6B | 0.9700 |
| C3 | 1.335 (2) | C6—C7 | 1.511 (3) |
| C1 | 0.9700 | C7—H7A | 0.9700 |
| C1 | 0.9700 | C7—H7B | 0.9700 |
| C1 | 1.503 (3) | O1—H1C | 0.8500 |
| C2 | 0.9700 | O1—H1D | 0.8499 |
| C6—S1—C5 | 95.67 (9) | N1—C4—H4A | 108.9 |
| N2—N1—C1 | 106.83 (13) | N1—C4—H4B | 108.9 |
| N2—N1—C4 | 107.07 (13) | N1—C4—C5 | 113.56 (15) |
| N2—N1—C7 | 106.50 (13) | H4A—C4—H4B | 107.7 |
| C4—N1—C1 | 112.92 (15) | C5—C4—H4A | 108.9 |
| C7—N1—C1 | 112.18 (14) | C5—C4—H4B | 108.9 |
| C7—N1—C4 | 110.91 (14) | S1—C5—H5A | 109.0 |
| C3—N2—N1 | 107.02 (13) | S1—C5—H5B | 109.0 |
| H3A—N3—H3B | 120.0 | C4—C5—S1 | 112.80 (14) |
| C3—N3—H3A | 120.0 | C4—C5—H5A | 109.0 |
| C3—N3—H3B | 120.0 | C4—C5—H5B | 109.0 |
| N1—C1—H1A | 111.1 | H5A—C5—H5B | 107.8 |
| N1—C1—H1B | 111.1 | S1—C6—H6A | 109.1 |
| H1A—C1—H1B | 109.1 | S1—C6—H6B | 109.1 |
C2—C1—N1 103.32 (15) H6A—C6—H6B 107.9
C2—C1—H1A 111.1 C7—C6—S1 112.28 (14)
C2—C1—H1B 111.1 C7—C6—H6A 109.1
C1—C2—H2A 111.4 C7—C6—H6B 109.1
C1—C2—H2B 111.4 N1—C7—C6 112.86 (15)
H2A—C2—H2B 109.3 N1—C7—H7A 109.0
C3—C2—C1 101.88 (15) N1—C7—H7B 109.0
C3—C2—H2A 111.4 C6—C7—H7A 109.0
C3—C2—H2B 111.4 C6—C7—H7B 109.0
N2—C3—N3 122.34 (16) H7A—C7—H7B 107.8
N2—C3—C2 115.74 (16) H1C—O1—H1D 112.9
N3—C3—C2 121.91 (16)

Hydrogen-bond geometry (Å, °)

| D—H⋯A   | D—H | H⋯A | D⋯A      | D—H⋯A |
|---------|------|-----|----------|--------|
| N3—H3A···Cl1i | 0.86 | 2.42 | 3.2786 (18) | 174     |
| N3—H3B···O1ii  | 0.86 | 1.99 | 2.821 (2)   | 162     |
| O1—H1C···Cl1    | 0.85 | 2.28 | 3.1244 (17) | 173     |
| O1—H1D···Cl1ii  | 0.85 | 2.29 | 3.1343 (17) | 175     |
| C6—H6B···N2iv   | 0.97 | 2.61 | 3.391 (2)   | 138     |

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