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CRYSTAL AND MOLECULAR STRUCTURE OF 2,4-DIMETHYLTHIENO[3,4-*b*]-1,5-DIAZEPINIUM CHLORIDE

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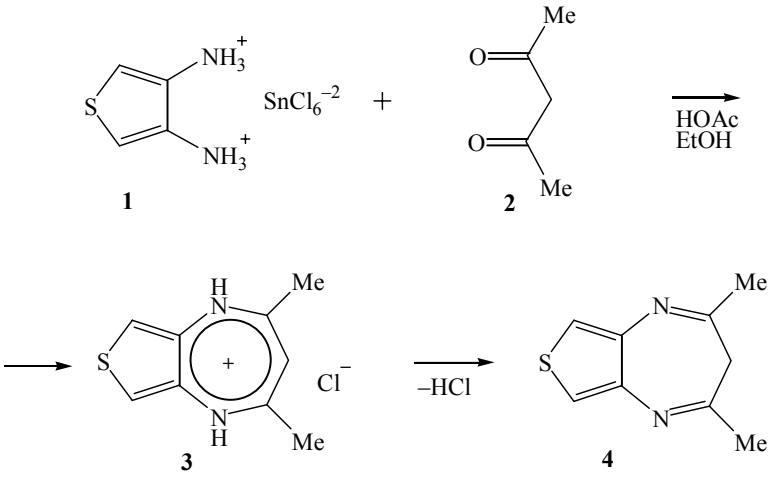
2,4-Dimethylthieno[3,4-b]-1,5-diazepinium chloride was obtained from 3,4-diaminothiophene hexachlorostannate and acetylacetone. Its molecular structure was established by X-ray crystallography.

Keywords: 3,4-diaminothiophene, diazatropylium cation, X-ray crystallography.

Thieno[2,3-*c*]-1,5-diazepins are interesting heterocyclic systems which contain both a π-excess and a π-deficient ring [1]. The synthesis of these compounds by reaction of 3,4-diaminothiophene with β-diketones is difficult, in the first place because of the instability of the diamine starting material.

We have carried out the reaction of the stable 3,4-diaminothiophene hexachlorostannate (**1**) with acetylacetone **2** in ethanol in the presence of a catalytic amount of acetic acid to give 2,4-dimethylthieno[3,4-*b*]-1,5-diazepinium chloride (**3**).



The IR spectrum of the diazatropylium salt **3** contains the characteristic bands at 1625 (superposition of the C=C and C=N double bonds, 3390 (the N–H bond), and 2957 cm^{-1} (the N^+–H bond). Maxima are observed at λ_{max} 269, 279, 330, and 460 nm in the UV spectrum of compound **3**.

The proposed structure of the product **3** was confirmed by X-ray crystallography (Fig. 1, 2, Tables 1-3).

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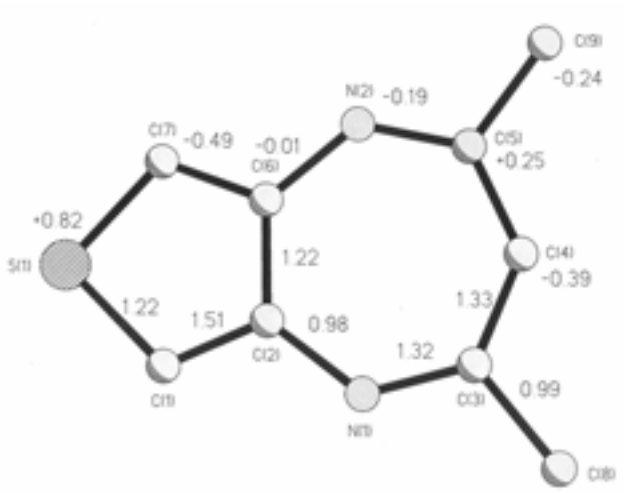

Fig.1. Structure of compound 3. Atomic charges and bond orders in compound **3**.

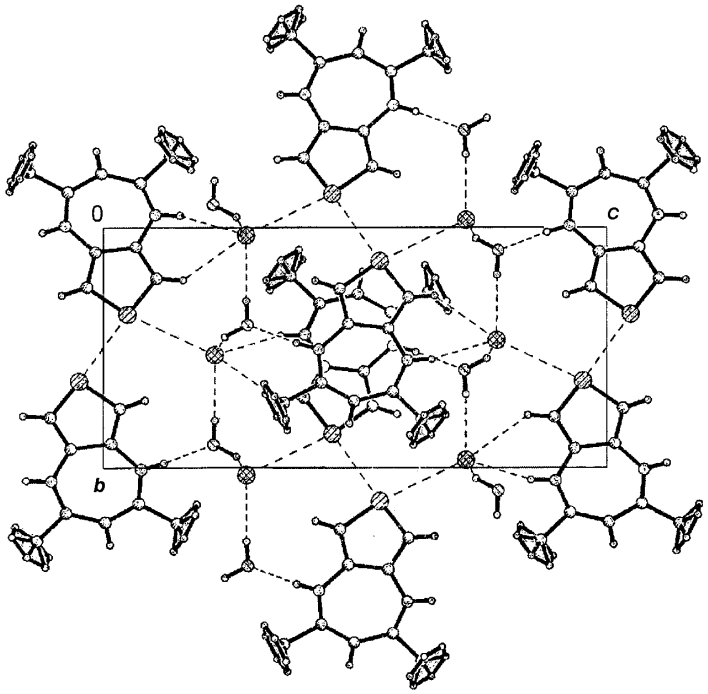

Fig. 2. Crystal structure of compound **3**.

The molecule of compound **3** is a planar cation. The deviation of atoms from the least mean squares plane does not exceed 0.02 Å. It should be noted that there is one molecule of crystallization water for each salt molecule.

The bond lengths in the diazepine unit are equalized to a considerable extent, i.e., there is considerable delocalisation of the π-electron density as a result of which the cation has C_{2v} symmetry with a precision of 3σ. Similar delocalisation was observed in the 2,4-dimethyl-1,5-benzodiazepinium cation [2-4], whereas in the corresponding diazepine [5] the seven-membered ring is distinctly non-planar and the bond lengths are close to

normal [6]. Quantum chemical calculations on the molecule **3** using the AM1 method [7] showed that the bond orders in the N–C–C–C–N unit are equalized (Fig. 1) which also confirms the presence of strong conjugative interactions in the seven-membered ring. However, the bond lengths in the thiophene ring do not differ from standard lengths [6].

In the crystal the molecules of **3** form a three-dimensional network (Fig. 2) as a result of intermolecular hydrogen bonds O(1W)' (0.5 – x, -0.5 + y, -0.5 – z) (O···H 1.96 Å, O···H–N 174.5°); H(1WA)···Cl(1S)'(-x, 1 – y, -1 – z) (Cl···H 2.36 Å, Cl···H–O 171.0°); H(1WB)···Cl(1S)' (-0.5 + x, 0.5 – y, 0.5 + z) (Cl···H 2.23 Å, Cl···H–O

TABLE 1. Bond Lengths (d) in Compound **3**

Bond	d, Å	Bond	d, Å	Bond	d, Å
S(1)–C(7)	1.705(4)	N(2)–C(6)	1.401(5)	C(4)–C(5)	1.392(6)
S(1)–C(1)	1.716(4)	C(1)–C(2)	1.351(6)	C(5)–C(9)	1.497(6)
N(1)–C(3)	1.326(5)	C(2)–C(6)	1.424(6)	C(6)–C(7)	1.352(6)
N(1)–C(2)	1.403(5)	C(3)–C(4)	1.395(6)		
N(2)–C(5)	1.322(5)	C(3)–C(8)	1.513(6)		

TABLE 2. Bond Angles (ω) in Compound **3**

Angle	ω, deg.	Angle	ω, deg.
C(7)–S(1)–C(1)	90.6(2)	C(4)–C(3)–C(8)	117.4(4)
C(3)–N(1)–C(2)	128.3(4)	C(5)–C(4)–C(3)	131.1(4)
C(5)–N(2)–C(6)	129.1(4)	N(2)–C(5)–C(4)	127.2(4)
C(2)–C(1)–S(1)	112.5(3)	N(2)–C(5)–C(9)	114.6(4)
C(1)–C(2)–N(1)	120.2(4)	C(4)–C(5)–C(9)	118.2(4)
C(1)–C(2)–C(6)	112.1(4)	C(7)–C(6)–N(2)	120.4(4)
N(1)–C(2)–C(6)	127.8(4)	C(7)–C(6)–C(2)	111.7(4)
N(1)–C(3)–C(4)	128.0(4)	N(2)–C(6)–C(2)	127.8(4)
N(1)–C(3)–C(8)	114.6(4)	C(6)–C(7)–S(1)	113.0(3)

TABLE 3. Coordinates of Non-hydrogen Atoms ($x\cdot10^4$, $y\cdot10^4$, $z\cdot10^4$) in Compound **3**

Atom	x	y	z
S(1)	3863(2)	8603(2)	-5475(1)
N(1)	3045(5)	4915(5)	-4259(2)
N(2)	1608(5)	4464(5)	-6018(2)
C(1)	3915(6)	7451(5)	-4679(2)
C(2)	3148(5)	6001(5)	-4845(2)
C(3)	2189(6)	3523(6)	-4308(3)
C(4)	1246(6)	2761(6)	-4960(3)
C(5)	1031(6)	3157(6)	-5728(3)
C(6)	2488(5)	5799(5)	-5641(2)
C(7)	2815(6)	71`01(5)	-6040(2)
C(8)	2260(7)	2693(6)	-3553(3)
C(9)	42(7)	2009(6)	-6305(3)
Cl(1S)	935(2)	5310(1)	-7808(1)
O(1W)	-21(4)	951(4)	-2163(2)

143.6°); Cl(1S)···H(2N) (Cl···H 2.39 Å, Cl···H–N 165.4°) and considerably shortened contacts Cl(1S)···S(1)' (0.5 – *x*, -0.5 + *y*, -1.5 – z) 3.4 Å (the sum of the van der Waals radii is 3.74 Å [8]); S(1)···S(1)' (1 – *x*, 2 – *y*, -1 – *z*) 3.18 Å (3.68 Å), explained by donation of unshared electron pairs from the chlorine and sulfur atoms into the antibonding orbitals of the S(1)–C(7) and S(1)–C(1) bonds (C–S···Cl and C–S···S bond angles 169.8° and 174.0° respectively).

The deviation of the chlorine atom from the direction of the S(1)–C(1) bond is probably a result of the short contact Cl(1S)···H(7) of 2.77 Å (3.06 Å). A shortened intramolecular is observed in the crystal: Cl(1S)···H(1)' (-0.5 + *x*, 1.5 – *y*, -0.5 + *z*) 2.97 Å.

The diazatropylium salt **3** was converted into 2,4-dimethylthieno[3,4-*b*]1,5-diazepine (**4**) by a standard method [9]. The physicochemical properties of the thienodiazepine **4** correspond to published values [1].

EXPERIMENTAL

IR spectra of KBr discs were recorded with an IR-75 spectrometer while electronic absorption spectra of methanol solutions ($c = 1.5 \cdot 10^{-5}$ mol/l) were recorded with a Specord Uv-vis machine.

3,4-Diaminothiophene was synthesized by a known method [10] and the required diamine was isolated as its hexachlorostannate.

X-ray Structural Study of a Monocrystal of Compound 3. Crystals of compound **3** ($C_9H_{10}N_2S \cdot HCl \cdot H_2O$) are monoclinic. At 20°C $a = 7.579(2)$, $b = 8.358(2)$, $c = 17.934(4)$ Å; $\beta = 101.76(3)°$; $V = 1112.2(4)$ Å^3; $d_{calc} = 1.390$ g/cm^3; space group $P2_1/n$; $Z = 4$. Elementary cell parameters and the intensities of 1949 independent reflexions ($R_{int} = 0.065$) were measured on a CAD-4 automatic diffractometer (λMo$K\alpha$, graphite monochromator, $\omega/2\theta$ scanning, $2\theta_{max} = 50°$).

The structure was solved by direct methods using the SHELXTL 7PLUS set of programs [11]. The positions of the hydrogen atoms (except those of the methyl groups) were revealed from an electron density difference synthesis and were refined by a "riding" model with fixed $U_{iso} = 1.2\ U_{eq}$ for non-hydrogen atoms bonded to the given hydrogen atom. The positions of the hydrogen atoms of the methyl groups were calculated geometrically for two disordered orientations with 0.5 occupancy and refined by the "riding" model with fixed $U_{iso} = 1.5\ U_{eq}$ for the corresponding carbon atom and additional refining of the angle of rotation relative to the bicyclic fragment. Refinement in F^2 in the full matrix least squares analysis in the anisotropic approximation for nonhydrogen atoms for 1546 reflexions gave $wR_2 = 0.133$ ($R_1 = 0.040$ for 838 reflexions with $F > 4s(F)$, $S = 0.924$). The coordinates of non-hydrogen atoms are given in Table 3.

2,4-Dimethylthieno[3,4-*b*]-1,5-diazepinium Chloride (3). A mixture of the salt **1** (1.6 g, 4 mmol) and acetylacetone (0.8 g, 8 mmol) was boiled in ethanol (5 ml), containing 1 drop of glacial acetic acid, for 45 min. After cooling the reaction mixture, the crystals formed were filtered off to give violet crystals of salt **3** (0.6 g, 65% yield); mp 232°C (decomp.) (ethanol). IR spectrum, ν, cm^{-1}: 1625 (C=C), 3390 (N–H), 2957 (N^+–H). UV spectrum (MeOH), λ_{max}, nm (log ε): 460 (2.88), 330 (3.09), 279 (4.49), 269 (4.45). Found, %: N 11.9. $C_9H_{10}N_2S \cdot HCl \cdot H_2O$. Calculated, %: N 12.0.

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