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Structure of 5-Imino-4-methyl-3-methylamino-4,5-dihydro-1,2,4-thiadiazolium Chloride Monohydrate

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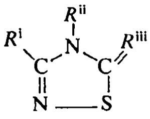
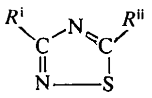
Abstract. $C_4H_9N_4S^+.Cl^-.H_2O$, $M_r = 198{\cdot}7$, monoclinic, $P2_1/n$, $a = 12{\cdot}153\ (8)$, $b = 11{\cdot}338\ (9)$, $c = 6{\cdot}421\ (5)$ Å, $\beta = 91{\cdot}69\ (4)°$, $V = 884{\cdot}4$ Å^3, $Z = 4$, $D_m = 1{\cdot}49$, $D_x = 1{\cdot}49$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}394$ mm^{-1}, $F(000) = 416$, $T = 298$ K, final $R = 0{\cdot}060$ for 1368 significant reflections. The cation is almost planar with maximum deviation by N(3) of the methylamino side chain (0·068 Å) from the five-membered-ring plane except for H atoms. From the bond lengths, the π conjugation would seem to include the d electrons of the S atom. The ions and water of crystallization are held together by hydrogen bonds.

Introduction. The title compound was obtained by oxidation of methylthiourea with iron(III) chloride. In this salt-like compound, the cation is a protonated 4,5-dihydro-1,2,4-thiadiazole derivative [(I*a*): $R^{\rm i} =$ MeNH, $R^{\rm ii} =$ Me, $R^{\rm iii} = H_2N^+$]. Butler, Glidewell & Liles (1978) showed that the oxidation of phenylthiourea produces a similar dihydrothiadiazole derivative [(I*b*): $R^{\rm i} =$ PhNH, $R^{\rm ii} =$ Ph, $R^{\rm iii} =$ PhN], which is known as Hector's base (Hector, 1889). Recently, we reported the formation of the 1,2,4-thiadiazole ring compound [(II): $R^{\rm i} = R^{\rm ii} = Ph_2N$] from *N,N*-diphenylthiourea on oxidation with iron(III) chloride (Senda & Maruha, 1985). It is also known that several *N,N'*-arylalkylthioureas change to thiadiazolidine derivatives (III) on oxidation [for example, $R^{\rm i} = R^{\rm iii} =$ Me, $R^{\rm ii} = R^{\rm iv} =$ PhN (Christophersen, Øttersen, Seff & Treppendahl, 1975; Kinoshita, Sato & Tamura, 1976)]. It seems that the substitution pattern affects the structure of the oxidation product.



(I)



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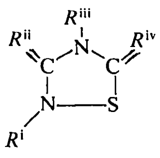

(III)

Experimental. Methylthiourea and anhydrous iron(III) chloride were reacted in ethanol. Green complex $[FeL_2Cl_2]$ (L = methylthiourea) was formed, filtered off, and red filtrate allowed to stand until red crystals precipitated. To aqueous solution of this red crystal, aqueous ammonia was added dropwise. $Fe(OH)_3$ formed was removed and solution allowed to stand. Colorless crystals obtained, purified by recrystallization from aqueous solution. Elemental analyses showed stoichiometry $C_4H_{11}ClN_4OS$. D_m by flotation. ^{1}H NMR in d_6-Me_2SO, δ 10·38 (NH_2, *s*, 2H), 7·88 (NH, *q*, 1H, $J = 4{\cdot}4$ Hz), 3·54 (CH_3, *s*, 3H), 3·44 (H_2O, *s*, 2H), 2·80 (amino-CH_3, *d*, 3H, $J = 4{\cdot}4$ Hz).

Crystal dimensions approximately 0·2 × 0·2 × 0·3 mm, lattice parameters determined by least-squares refinement of 20 reflections. JEOL JCX-4AB diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan mode, $\theta \leq 25°$; during data collection three standard reflections showed only statistical variation. Data corrected for Lp, no absorption correction. 1573 reflections measured, 1368 independent with $|F_o| > 3\sigma(|F_o|)$ used in calculations. Structure solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) and refined (on F) by block-diagonal least squares (*UNICS*; Sakurai, 1967) with anisotropic thermal parameters for non-H atoms. H atoms located from ΔF synthesis, refined isotropically, final $R = 0{\cdot}060$ and $wR = 0{\cdot}056$, $w = 1/[\sigma^2(|F_o|) + 0{\cdot}0043|F_o| + 0{\cdot}0027|F_o|^2]$ for $|F_o| > 0$ and $w = 2{\cdot}5742$ for $|F_o| = 0$, $S = 0{\cdot}62$. $(\Delta/\sigma)_{\rm max} = 0{\cdot}26$ for non-H atoms and 0·88 for H atoms; final ΔF synthesis showed no peak $> 0{\cdot}16$ e Å^{-3}. Atomic scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974) and for H atoms from Stewart, Davidson & Simpson (1965). All calculations performed on a FACOM F-170F computer.

Discussion. Final atomic coordinates and bond distances and bond angles are given in Tables 1 and 2.* The crystal consists of a protonated heterocyclic cation, chloride ion and water of crystallization as indicated in Fig. 1. These species seem to be held

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* Lists of structure factors, atomic coordinates for H atoms, bond distances involving H atoms and details of the thermal parameters and least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42363 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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together with hydrogen bonds. The possible hydrogen-bond distances and angles are given in Table 3. The structure of the cation and the atom numbering scheme for the crystallographic study are given in Fig. 2. The heterocyclic ring is nearly planar with a maximum deviation of 0·014 Å at C(1). The exocyclic C and N atoms also lie on this plane with a maximum deviation of 0·068 Å for N(3). The geometry of the cation is similar to those of several compounds containing dihydro-1,2,4-thiadiazole rings. For comparison, the skeletal structures of the three compounds (I*a*), (I*b*), (I*c*) are listed in Table 4. C(1)—N(1), 1·308 (3) Å, and exocyclic C(2)—N(4), 1·304 (3) Å, are close to the double-bond distance, 1·272 Å (Iwasaki & Akiba, 1981). Two H_3C—N bonds, 1·459 (3) and 1·439 (4) Å, are in agreement with a C—N single bond, 1·458 Å (Fischer-Hjalmers & Sundbom, 1968). The remaining three C—N bonds are intermediate between single and double bonds. The C(2)—S distance, 1·715 (3) Å, is shorter than that of the other 4,5-dihydro-1,2,4-thiadiazole compounds and the C(sp^2)—S distance of 1·759 Å (Sato, Kinoshita, Hata & Tamura, 1980). These results suggest that the π conjugation probably includes the *d* electrons of the S atom. The bond angles of the ring are comparable with the corresponding angles in other 4,5-dihydro-1,2,4-thiadiazoles.

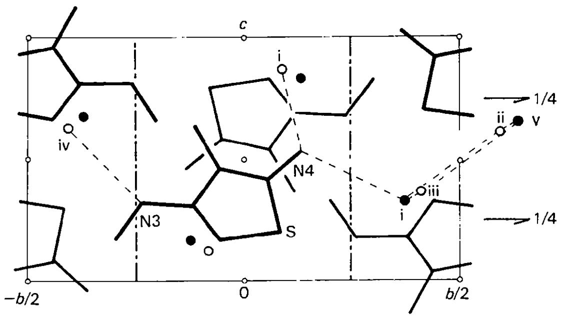

Fig. 1. Crystal structure projected on the *bc* plane (●: Cl^-, ○: O atom of H_2O). Hydrogen bonds are shown by broken lines. Symmetry codes are: (i) x, y, z; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iv) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (v) $2-x, 1-y, 1-z$.

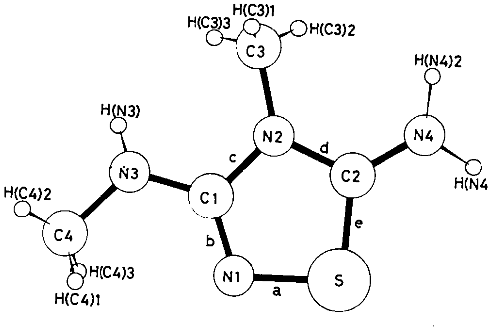

Fig. 2. Projection of the cation on the five-membered-ring plane with atom numbering scheme.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$)

	x	*y*	*z*	B_{eq}*
S	0·91250 (5)	0·08381 (6)	0·2023 (1)	3·15
N(1)	0·9444 (2)	−0·0590 (2)	0·1653 (3)	3·05
N(2)	0·8452 (2)	−0·0606 (2)	0·4638 (3)	2·54
N(3)	0·9088 (2)	−0·2392 (2)	0·3187 (3)	3·29
N(4)	0·7924 (2)	0·1337 (2)	0·5371 (4)	3·38
C(1)	0·9013 (2)	−0·1224 (2)	0·3122 (4)	2·61
C(2)	0·8420 (2)	0·0554 (2)	0·4242 (4)	2·55
C(3)	0·7906 (2)	−0·1155 (3)	0·6385 (4)	3·53
C(4)	0·9715 (2)	−0·3018 (3)	0·1676 (5)	3·68
Cl	0·86859 (5)	0·37547 (6)	0·3401 (1)	3·86
O	0·6273 (2)	0·0884 (2)	0·8486 (3)	3·69

$$* B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j B_{ij}a_i.a_j.$$

Table 2. *Bond distances* (Å) *and angles* (°) *for non*-H *atoms*

S—N(1)	1·683 (3)	S—C(2)	1·715 (3)
N(1)—C(1)	1·308 (3)	C(1)—N(2)	1·393 (3)
N(2)—C(2)	1·340 (3)	C(1)—N(3)	1·328 (4)
N(3)—C(4)	1·439 (4)	N(2)—C(3)	1·459 (3)
C(2)—N(4)	1·304 (3)		
C(2)—S—N(1)	93·4 (1)	S—N(1)—C(1)	109·2 (2)
N(1)—C(1)—N(2)	116·2 (2)	C(1)—N(2)—C(2)	111·9 (2)
N(2)—C(2)—S	109·2 (2)	N(1)—C(1)—N(3)	122·8 (2)
N(2)—C(1)—N(3)	120·9 (2)	C(1)—N(3)—C(4)	120·6 (2)
C(1)—N(2)—C(3)	124·5 (2)	C(2)—N(2)—C(3)	123·5 (2)
N(2)—C(2)—N(4)	125·0 (2)	S—C(2)—N(4)	125·8 (2)

Table 3. *Possible hydrogen-bond distances* (Å) *and angles* (°)

Cl···N(4)	3·169 (3)	Cl···H(N4)1	2·39 (4)	Cl···H(N4)—N(4)	163 (4)
O···N(4)	2·919 (4)	O···H(N4)2	2·07 (3)	O···H(N4)2—N(4)	172 (3)
Cl···O^i	3·134 (3)	Cl···H(O^i)1	2·30 (4)	Cl···H(O^i)1—O^i	173 (4)
Cl···O^{ii}	3·170 (3)	Cl···H(O^{ii})2	2·45 (4)	Cl···H(O^{ii})2—O^{ii}	168 (4)
N(3)···O^{iii}	2·938 (3)	H(N3)···O^{iii}	2·18 (3)	N(3)—H(N3)···O^{iii}	165 (3)

Symmetry code: none x, y, z; (i) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$.

Table 4. *Comparison of* 4,5-*dihydro*-1,2,4-*thiadiazole rings* (Å, °)

	(I*a*)	(I*b*)	(I*c*)
a	1·683 (3)	1·691 (3)	1·672 (7)
b	1·308 (3)	1·294 (4)	1·286 (9)
c	1·393 (3)	1·386 (4)	1·372 (8)
d	1·340 (3)	1·402 (4)	1·355 (7)
e	1·715 (3)	1·761 (4)	1·721 (5)
ae	93·4 (1)	95·3 (2)	94·6 (3)
ab	109·2 (2)	108·9 (2)	108·9 (5)
bc	116·2 (2)	117·6 (3)	116·7 (6)
cd	111·9 (2)	113·7 (3)	113·5 (5)
de	109·2 (2)	104·5 (2)	106·3 (4)

a, b, c etc. are indicated in Fig. 2. (I*a*): R^i = MeNH, R^{ii} = Me, R^{iii} = H_2N^+ (present work); (I*b*): R^i = PhNH, R^{ii} = Ph, R^{iii} = HN (Butler *et al.*, 1978); (I*c*): R^i = Me, R^{ii} = Me, R^{iii} = MeHN$^+$C(Me)N (Iwasaki & Akiba, 1981).

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Structure of *cis*-Bicyclo[3.3.0]oct-3-ene-2,7-dione 7-(2,2-Dimethyltrimethylene Acetal)

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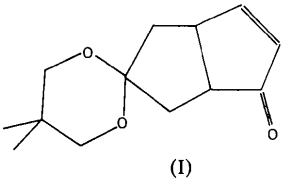
Abstract. $C_{13}H_{18}O_3$, $M_r = 222{\cdot}28$, orthorhombic, $Pbca$, $a = 19{\cdot}633\,(3)$, $b = 12{\cdot}211\,(2)$, $c = 10{\cdot}147\,(2)$ Å, $V = 2433\,(1)$ Å^3, $D_x = 1{\cdot}214\,(1)$ Mg m^{-3}, $Z = 8$, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 0·091 mm^{-1}, $F(000) = 976$, room temperature, $R = 0{\cdot}048$ for 1045 observed reflections. The six-membered ring has a chair conformation. The two five-membered rings have a skew-envelope and an envelope form. Most of the bond distances and angles are normal; deviations are due to electronic conjugations and steric effects.

Introduction. The title compound (I) was synthesized by Carceller, Moyano & Serratosa (1984) and it is a synthetic intermediate in which all eight C atoms are properly activated. This compound can undergo a series of chemo-, regio- and stereoselective reactions useful for the synthesis of either natural or non-natural polyfused cyclopentanoid systems.



(I)

Experimental. Colourless prism (0·1 × 0·1 × 0·2 mm). Philips PW 1100 diffractometer. Unit-cell parameters from 25 reflections ($4 \leq \theta \leq 11°$). Mo $K\alpha$, graphite monochromator, ω-scan technique, scan width 1°, scan speed 0·03° s^{-1}. 1076 independent reflections ($2 \leq \theta \leq 25°$); 1045 with $I \geq 2{\cdot}5\sigma(I)$. Max. h,k,l = 20,13,12. Three reflections every 2 h as control, significant variations not observed. Lorentz–polarization correction; no absorption or extinction correction. Attempts to solve the structure by direct methods failed. A model was derived from a Patterson synthesis using *SHELX*76 (Sheldrick, 1976) and *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, van der Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). This model was introduced into *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), using the Debye normalization. Refinements by full-matrix least-squares method, using *SHELX*76 and minimizing $\sum w||F_o| - |F_c||^2$, with $w = [\sigma^2(F_o) + 0{\cdot}026|F_o|^2]^{-1}$. H from $\Delta\rho$ map and refined with an overall isotropic temperature factor; non-hydrogen atoms refined as anisotropically vibrating; f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974). Final $R = 0{\cdot}048$ ($wR = 0{\cdot}054$). $(\Delta/\sigma)_{\max} = 0{\cdot}13$ for x coordinate of C(4). Max. and min. peaks in final $\Delta\rho$ map 0·1 [0·93 Å from H(C14)′] and −0·2 e Å^{-3}, respectively.

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