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(4-Chloromethyl-4-hydroxy-3-phenylthiazolidin-2-ylidene)ammonium chloride acetone solvate

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Key indicators

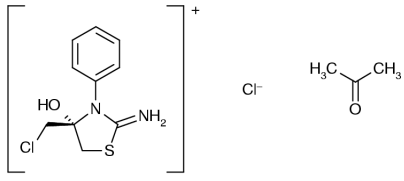
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.108
Data-to-parameter ratio = 23.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

At 150 K, the title compound, $C_{10}H_{12}ClN_2OS^+\cdot Cl^-\cdot C_3H_6O$, exists as discrete hydrogen-bonded [2 + 2]-dimers of cations and chloride anions. Of the two possible thiazolidin-2-ylideneammonium cations that may be formed by the reaction of 1,3-dichloroacetone with *N*-phenylthiourea, the reported isomer is unable to eliminate water to form the corresponding thiazole.

Comment

The acetone-solvated title compound, (I), was obtained as the major product formed by the attempted preparation of 4-chloromethylthiazol-2-ylphenylamine, (2), from *N*-phenylthiourea and 1,3-dichloroacetone in acetone at room temperature (Simiti *et al.*, 1962).



(I)

The precipitation of a mixture of (2) and another product under these conditions was noted by the authors, but the constitution of the latter was not determined, either analytically or spectroscopically; the only data reported were the observation of two melting points (for the mixture) and the solubility of the non-identified product in water, from which it was deduced that it was probably a hydrochloride salt.

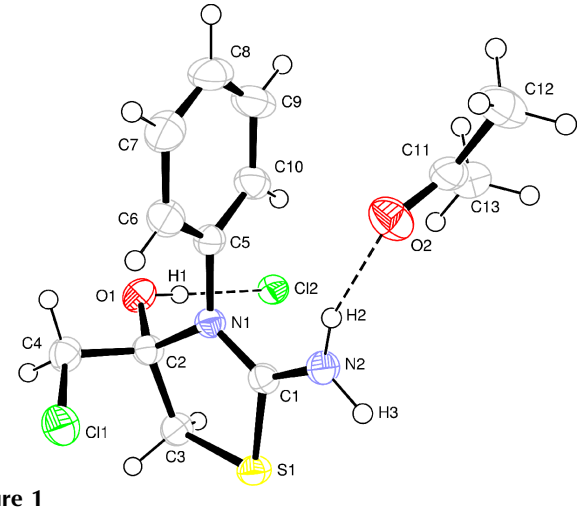
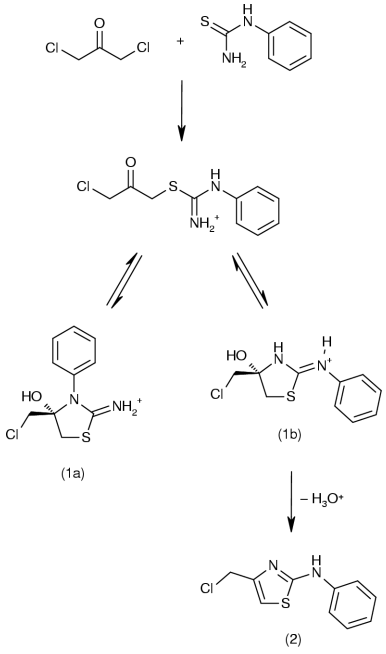


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitary size.



Under the reported reaction conditions, we obtained a colourless precipitate that comprised powder and colourless crystals. The presence of (I) and (2) in the ratio 3.4:1 was determined by ^{1}H NMR (immediately following dissolution of the precipitated product in DMSO) and the melting points were in agreement with those of Simiti *et al.* (1962). Unfortunately, a bulk sample of (I) could not be further purified due to the ease with which it rearranged to (2) in solution. The two products arise from the possibility of ring closure with either of the two thiourea N atoms. The major kinetic product is (1*a*) and it is sufficiently stable under the reaction conditions to crystallize, but the putative alternative (minor) kinetic product (1*b*) can eliminate water irreversibly to form the expected aromatic thiazole derivative (2). This is consistent with the observation that, in solution, (1*a*) readily undergoes ring-opening and ultimately rearranges to the thermodynamic product (2).

Within the heterocyclic ring of (I), the exocyclic C1—N2 bond distance is slightly shorter than the endocyclic C1—N1 distance (Table 1). Delocalization within the cationic isothiouronium moiety also results in C1—S1 being substantially shorter than C3—S1. Electrostatic attraction between this group and the chloride anions also results in a close S1···Cl2 non-bonded contact distance of 3.4411 (9) Å. Of the two formal C—N single bonds, C2—N1 is significantly the longer, which is consistent with the observed ease of ring-opening and rearrangement to (2).

The puckering parameters (Cremer & Pople, 1975) for the five-membered heterocyclic ring are: q_2 = 0.163 (3) Å and φ_2 = 123.5 (7)°. These are consistent with a relatively small distortion away from planar, and the puckering is closer to a twist than an envelope conformation. The angle between the respective normals of the least-squares planes of the five-membered ring and its phenyl substituent is 85.54 (10)°.

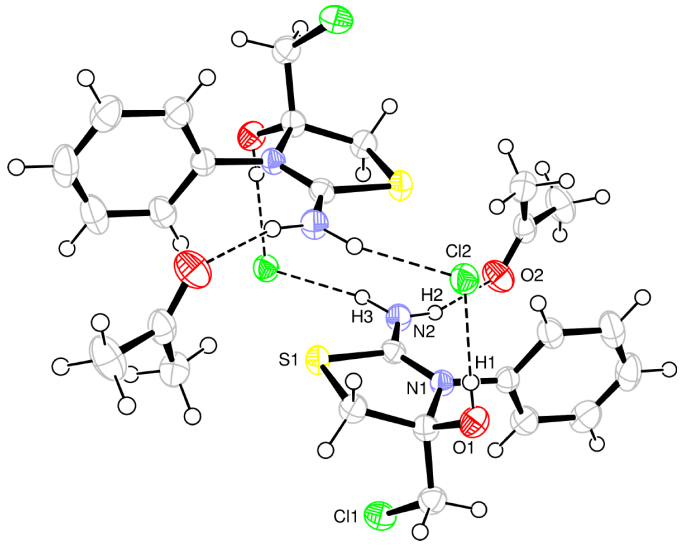


Figure 2
The intermolecular hydrogen bonding of (I).

There are hydrogen bonds from the hydroxyl and amine groups to the chloride anion, forming discrete [2+2]-dimers (Table 2). The O atom of the acetone molecule acts as the acceptor for the remaining amine hydrogen-bond donor.

Experimental

The reaction of *N*-phenylthiourea and 1,3-dichloroacetone in acetone at room temperature gave a mixture of the expected product, (2), and suitable colourless crystals of the title compound, (I), in the molar ratio 1:3.4 (by ^{1}H NMR). A pure bulk sample of (1*a*) for analysis could not be obtained as it readily converts into (2) in solution. Suitable crystals of (2) could not be obtained. Spectroscopic analysis: ^{1}H NMR (DMSO, p.p.m.): (1*a*), 10.17 (*s*, 1H, NH), 8.83 (*s*, 1H, NH), 8.32 (*s*, 1H, OH), 7.62 (*m*, 3H, ArH), 7.42 (*m*, 2H, ArH), 4.01 (*d*, 1H, *J* = 12.5 Hz, CH_2Cl), 3.73 (*d*, 1H, *J* = 11.8 Hz, CH_2S), 3.68 (*d*, 1H, *J* = 12.5 Hz, CH_2Cl), 3.55 (*d*, 1H, *J* = 11.8 Hz, CH_2S); (2), 10.29 (*s*, 1H, NH), 7.62 (*m*, 2H, ArH), 7.31 (*t*, 2H, ArH), 6.96 (*s*, 1H, HetArH), 6.95 (*t*, 1H, ArH), 4.66 (*s*, 2H, CH_2Cl).

Crystal data

$C_{10}H_{12}ClN_2OS^+\cdot Cl^-\cdot C_3H_6O$
M_r = 337.25
Triclinic, $P\overline{1}$
a = 8.5384 (19) Å
b = 9.477 (2) Å
c = 10.420 (2) Å
α = 97.115 (17)°
β = 96.380 (17)°
γ = 95.024 (17)°
V = 827.1 (3) Å^3
Z = 2
D_x = 1.354 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7613 reflections
θ = 2.0–29.8°
μ = 0.52 mm^{-1}
T = 150 (2) K
Needle, colourless
0.40 × 0.15 × 0.10 mm

Data collection

Stoe IPDS–II diffractometer
ω scans
Absorption correction: none
12 767 measured reflections
4668 independent reflections
2591 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 29.8°
h = −11 → 9
k = −13 → 13
l = −14 → 14

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.109$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
$S = 0.83$	$\Delta\rho_{min} = -0.54$ e Å^{-3}
4668 reflections	Extinction correction: *SHELXL*97
196 parameters	Extinction coefficient: 0.018 (3)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cl1—C4	1.791 (3)	N1—C5	1.445 (3)
S1—C1	1.741 (2)	N1—C2	1.493 (3)
S1—C3	1.817 (3)	N2—C1	1.308 (3)
O1—C2	1.391 (3)	C2—C4	1.511 (4)
N1—C1	1.324 (3)	C2—C3	1.544 (3)
C1—S1—C3	91.66 (11)	O1—C2—C4	103.7 (2)
C1—N1—C5	121.9 (2)	N1—C2—C4	110.77 (19)
C1—N1—C2	117.01 (19)	O1—C2—C3	113.15 (19)
C5—N1—C2	120.9 (2)	N1—C2—C3	105.67 (19)
N2—C1—N1	125.0 (2)	C4—C2—C3	113.1 (2)
N2—C1—S1	120.65 (19)	C2—C3—S1	108.77 (16)
N1—C1—S1	114.36 (18)	C2—C4—Cl1	111.56 (18)
O1—C2—N1	110.61 (19)		
N1—C2—C3—S1	16.2 (2)	C2—N1—C5—C6	89.5 (3)
O1—C2—C4—Cl1	−176.82 (15)	C1—N1—C5—C10	93.9 (3)
C1—N1—C5—C6	−85.4 (3)	C2—N1—C5—C10	−91.2 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl2	0.84 (4)	2.19 (4)	3.028 (2)	176 (4)
N2—H2···O2	0.91 (3)	1.98 (3)	2.854 (3)	161 (2)
N2—H3···Cl2^{i}	0.98 (4)	2.19 (4)	3.121 (2)	159 (3)

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

All H atoms were initially located in a difference Fourier map. The methyl H atoms were constrained to an ideal geometry, with C—H distances of 0.98 Å, but each group was allowed to rotate freely about its *X*—C bond. The hydroxyl and amine H-atom positional parameters were refined freely, along with an isotropic displacement parameter. All other H atoms were placed in geometrically idealized positions with C—H distances of 0.95–0.99 Å. U_{iso}(H) values were set at $1.2U_{eq}$(C) for all H atoms on carbon.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *X-STEP*32 (Stoe & Cie, 2001) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *WinGX* (Farrugia, 1999) and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

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