A triclinic polymorph of 1,3-thiazolidine-2-thione (2-mercaptothiazoline)

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A planar conformation of 1,3-thiazolidine-2-thione (TZDTH), $C_3H_5NS_2$, was crystallized for the first time. The new triclinic polymorph ($P\bar{1}$) obtained was compared in terms of its intra- and intermolecular geometry with three previous reports of a monoclinic polymorph ($P2_1/n$). The packing is based on centrosymmetric dimers of TZDTH, linked by N—H⋯S hydrogen bonds.

Comment

The heterocyclic thioamide 1,3-thiazolidine-2-thione, (2), exists in tautomeric equilibrium with its thiol form, 2-mercaptothiazoline, (1) (Raper *et al.*, 1983). Besides the thiol–thione tautomerism, this molecular system can also be deprotonated to form the thiolate anion, (5). In the solid state, the most stable form is the thione, (2), as evidenced either by IR spectroscopy (Flakus *et al.*, 2002) or by X-ray diffraction (Raper *et al.*, 1983; Zhou *et al.*, 1984; Flakus *et al.*, 2002).
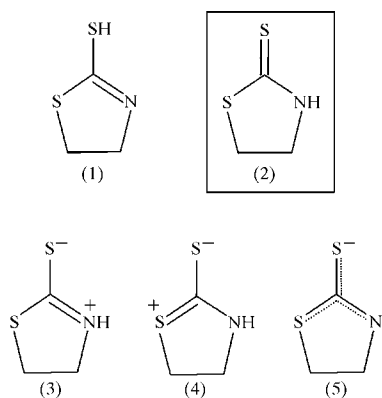

The tautomeric and canonic forms (1)–(5) are versatile ligands, as highlighted by the fact that 81 metal complex structures containing these ligands are deposited in the Cambridge Structural Database (CSD; updated August 2005; Allen, 2002). It is important to emphasize the pH-dependent coordination chemistry of these ligands. In neutral and acid media, where (2) is the most stable form, usually the exocyclic S atom and the N atom are available as donor atoms (see, for example, Rajalingam *et al.*, 2001; Bell *et al.*, 2001; Popovic *et al.*, 2002), whereas in alkaline media, it is the S—C—N component of the thiolate anion that is involved in coordination to metals (see, for example, Shi & Jiang, 2002; Du *et al.*, 2002; Brandt & Sheldrick, 1998). An interesting complex with copper containing both forms (2) and (5) as donors has been observed by Raper *et al.* (1998). Form (3) has been observed by Abram *et al.* (1998) in an Au^{3+} complex.

The 1,3-thiazolidine-2-thione structure has been determined previously by X-ray diffraction as belonging to space group $P2_1/n$ (Raper *et al.*, 1983; Zhou *et al.*, 1984; Flakus *et al.*, 2002) and in the present study as a new $P\bar{1}$ triclinic polymorph. The cell parameters observed by Flakus *et al.* (2002) for the $P2_1/n$ polymorph are a = 13.484 (5) Å, b = 5.452 (2) Å, c = 13.644 (5) Å and β = 94.71 (2)°. These values are very similar to those observed by Raper *et al.* (1983) and Zhou *et al.* (1984).

Fig. 1 shows an *ORTEP-3* (Farrugia, 1997) view of (2). Pairs of centrosymmetrically related molecules linked by N—H⋯S hydrogen bonds are formed, as observed also for the $P2_1/n$ polymorph. However, the new $P\bar{1}$ polymorph has just one molecule in the asymmetric unit (Z = 2), whereas for the $P2_1/n$ polymorph, there are two molecules in the asymmetric unit.

The main geometric parameters are given in Table 1. The intramolecular conformation was analyzed using *MOGUL* (Bruno *et al.*, 2004), a knowledge base of molecular geometry derived from the CSD. This study showed that all bond lengths and angles are in agreement with the expected values. Using Raper's arguments (Raper *et al.*, 1983), the C—S1 bond distance and the localization of the H atom at the N position both agree with the presence of (2), the thione form, rather than (1). Although the geometric parameters of the two polymorphs are very similar in terms of bond lengths and angles, comparison of these polymorphs by the Kabsch (1976) method showed them to be significantly different in terms of torsion angles. Fig. 2 shows the superposition of the two
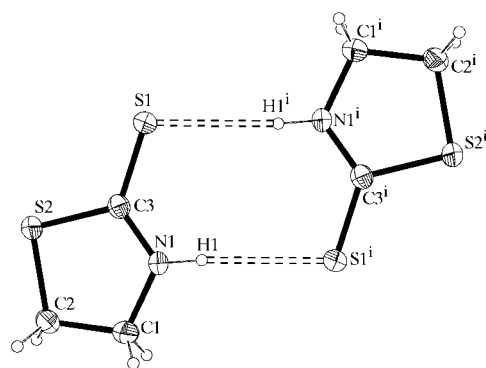
Figure 1
An *ORTEP-3* (Farrugia, 1997) view of (2), showing the atom labeling and the dimer formed by N—H⋯S hydrogen bonds (dashed lines). Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (i) $-x - 1, -y, -z + 1$.]

organic compounds

polymorphs, $P\bar{1}$ and $P2_1/n$ [denoted Raper (Raper *et al.*, 1983), Zhou (Zhou *et al.*, 1984) and Flakus (Flakus *et al.*, 2002)]. Since the asymmetric unit has two independent molecules in the monoclinic polymorph, the molecules compared with our $P\bar{1}$ polymorph were labeled as 1 and 2 in Fig. 2. The deviations between analogous atoms given by the Kabsch method are presented in Table 2. The largest deviation between analogs takes place at methylene atom C2 [the mean value is 0.25 (3) Å], except for Raper-2, for which the largest deviations occur between the N1 (0.51 Å) and S2 (0.29 Å) analogs. In other words, the main difference between the two polymorphs is in terms of their planarity. In the $P\bar{1}$ polymorph, the molecule is flat; considering the non-H atoms, the largest deviation from the least-squares plane through all atoms in the molecule is 0.008 (1) Å for atom C2. On the other hand, in the $P2_1/n$ polymorph, the molecule is non-planar. A conforma-

tional analysis of (2) in the monoclinic form shows that the ring adopts an envelope conformation, with atom C2 in the flap position. The one exception is the Raper-2 molecule, which has a more distorted conformation (Fig. 2). Raper *et al.* (1983) argue that the non-planarity is due to the presence of methylene C atoms, which showed the largest deviations (from 0.11 to 0.18 Å) from the least-squares plane through the thioamide portion (S2/C3/S1/N1) of the molecule.

Fig. 3 shows the packing of (2). The main intermolecular motif is the zero-dimensional network-forming dimer linked by N—H···S hydrogen bonds. The dimer forms parallel ribbons along the [010] direction. The dimers are also present in the monoclinic polymorph. However, in $P2_1/n$ they do not form ribbons, but are instead stacked parallel to [010]. Despite the packing differences, the hydrogen-bond geometry mediating the dimers in $P\bar{1}$ (Table 3) is very similar to that observed by Flakus *et al.* (2002).

Figure 2
An *ORTEP-3* (Farrugia, 1997) view of (2), showing the superposition of the $P\bar{1}$ (black) and $P2_1/n$ (gray) polymorphs.

Figure 3
The packing of (2), viewed along the [010] direction, showing the dimers formed by hydrogen bonds (dashed lines) and the ribbons formed by parallel dimers.

Experimental

We have been preparing soft analogs of the tripyrazolylborate ligand, $[H(pz)_3]^-$, Tp, such as hydrotris(2-mercaptothiazolyl)borate (Mt; Soares, Silva *et al.*, 2004), hydrotris(2-methimazolyl)borate (Tm; Soares, Silva *et al.*, 2004; Soares & Silva, 2002) and tetrakis(2-mercaptothiazolyl)borate (Mte; Soares, Menezes *et al.*, 2004), as well as studying their coordination chemistry. In an attempt to obtain a cobalt complex having Mte as a supporting ligand, the appropriate reagents in a 1:1 molar ratio were placed in tetrahydrofuran (not dried) at room temperature. After 12 h, a green solution and a blue solid remained. The solution was filtered and left at room temperature for three weeks, after which time colorless crystals of (2) were obtained, together with the desired complex.

Crystal data

$C_3H_5NS_2$	$Z = 2$
$M_r = 119.22$	$D_x = 1.586$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.4845$ (2) Å	Cell parameters from 5798
$b = 6.4997$ (3) Å	reflections
$c = 7.6758$ (3) Å	$\theta = 0.4$–27.5°
$\alpha = 84.121$ (2)°	$\mu = 0.90$ mm^{-1}
$\beta = 73.816$ (3)°	$T = 120$ (2) K
$\gamma = 71.792$ (3)°	Needle, colorless
$V = 249.59$ (2) Å^3	$0.08 \times 0.04 \times 0.02$ mm

Data collection

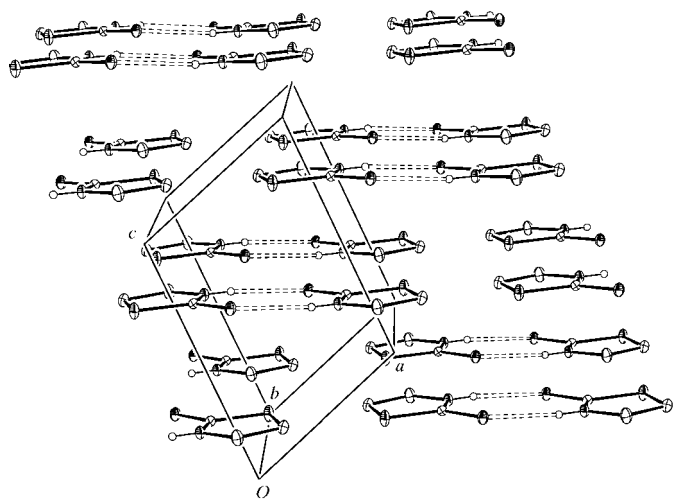|	
Nonius KappaCCD diffractometer	781 reflections with $I > 2\sigma(I)$
φ scans and ω scans with κ offsets	$R_{int} = 0.073$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(Blessing, 1995)	$h = -6 \rightarrow 6$
$T_{min} = 0.919$, $T_{max} = 0.984$	$k = -7 \rightarrow 7$
7240 measured reflections	$l = -9 \rightarrow 9$
880 independent reflections	

Table 1
Selected geometric parameters (Å, °).

S1—C3	1.671 (2)	N1—C3	1.319 (2)
S2—C3	1.745 (2)	N1—C1	1.456 (2)
S2—C2	1.812 (2)	C2—C1	1.528 (3)
C3—S2—C2	93.76 (9)	S1—C3—S2	121.28 (11)
C3—N1—C1	119.46 (17)	C1—C2—S2	107.26 (13)
N1—C3—S1	127.31 (15)	N1—C1—C2	108.11 (15)
N1—C3—S2	111.40 (14)		

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.063$

$S = 1.07$

880 reflections

59 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.1265P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.26$ e Å^{-3}

$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 2
Deviations (Å) between analogous atoms given by the Kabsch (1976) method (atom labeling as in Fig. 2).

Analogs	Raper-1	Raper-2	Zhou-1	Zhou-2	Flakus-1	Flakus-2
C1	0.0496	0.0145	0.0310	0.0650	0.0713	0.0639
C2	0.2358	0.0248	0.2084	0.2263	0.2825	0.2822
C3	0.0122	0.0210	0.0189	0.0141	0.0184	0.0180
N1	0.0588	0.5079	0.0351	0.0754	0.0812	0.0721
S1	0.0314	0.0101	0.0209	0.0385	0.0462	0.0418
S2	0.0209	0.2854	0.0187	0.0235	0.0209	0.0187

Table 3
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$S1^i	0.83 (3)	2.53 (3)	3.359 (2)	172 (2)

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

H atoms of the methylene group were positioned stereochemically and were refined with constrained displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$ and C—H = 0.99 Å]. The H atom of the amine group was located by difference Fourier synthesis and was refined isotropically.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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