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1-(Diaminomethylene)thiourea: a tautomer of 2-imino-4-thiobiuret

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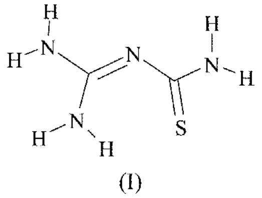
Crystals of the title compound, $C_2H_6N_4S$, are built up from nonplanar 1-(diaminomethylene)thiourea molecules. Pairs of molecules related by inversion are linked by N—H···N hydrogen bonds to form dimeric units, and weak N—H···S interactions link these dimeric units into a three-dimensional framework.

Comment

Continuing our investigations into the characterization of compounds that form multiple and different hydrogen-bonding systems in solids (Janczak & Perpétuo, 2008; Perpétuo & Janczak, 2007, 2008; Janczak & Kubiak, 2005*a*,*b*), we report here the crystal structure of the title compound, (I). The commercially available crystalline product described as 2-imino-4-thiobiuret (amidinothiourea) by Aldrich (CAS No. 2114–02-05) is in fact the tautomeric form 1-(diaminomethylene)thiourea, as shown by the present X-ray structure determination. Recrystallization from water of the product purchased from Aldrich yielded crystals of 1-(diaminomethylene)thiourea, not the imino tautomer.



(I)

Both tautomers of (I), *i.e.* 1-(diaminomethylene)thiourea and 2-imino-4-thiobiuret, are potentially interesting compounds that can be used in crystal engineering to build up extended frameworks, since they contain complementary arrays of hydrogen-bonding sites (MacDonald & Whitesides, 1994; Steiner, 2002; Desiraju, 1990, 2002). In addition, both tautomers have several potential coordination modes, since they can act as *N*,*N*- or *N*,*S*-coordinating ligands and can form several different types of complex with metal ions. The coordination of metals by these tautomers is feasible with both neutral and deprotonated (anionic) forms. A search of the Cambridge Structural Database (CSD, Version 5.29 of November 2007; Allen, 2002) for structures containing 1-(diaminomethylene)thiourea or its tautomer, 2-imino-4-thiobiuret, yielded only three structures, all of them platinum complexes (Doxiadi *et al.* 2003). In these complexes, the Pt atom is coordinated by 2-imino-4-thiobiuret or its deprotonated form. Since the crystal structures of (I) and its tautomer are not known, we therefore decided to investigate the crystal structure of 1-(diaminomethylene)thiourea, (I). In addition its X-ray geometry is compared with that in the gas phase, as predicted for isolated molecules of (I) and its tautomeric form 2-imino-4-thiobiuret using density functional theory (DFT). *Ab initio* molecular orbital calculations were performed at the B3LYP/6–31+G* level (Frisch *et al.*, 1998) and the results are illustrated in Fig. 1.

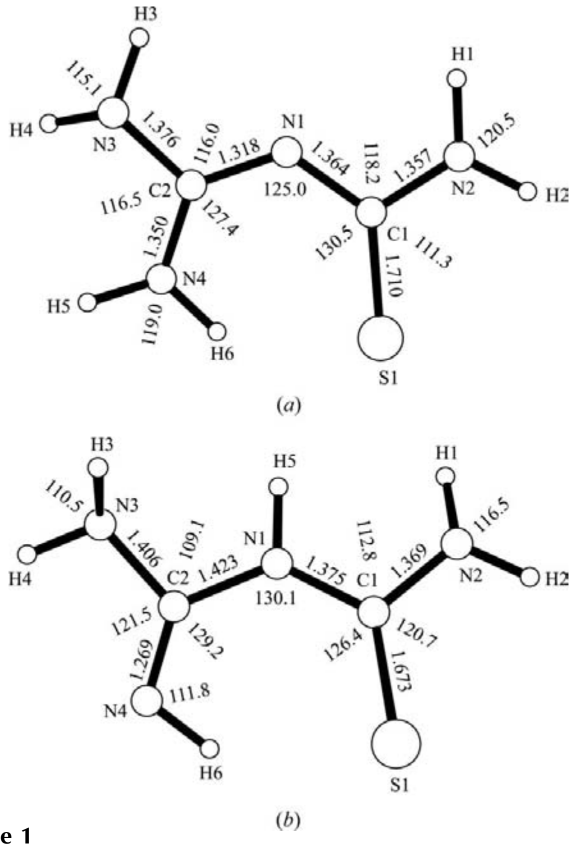


Figure 1
Results of the optimized molecular orbital calculations (at the B3LYP/6–31+G* level) for (*a*) the 1-(diaminomethylene)thiurea and (*b*) the 2-imino-4-thiobiuret tautomers of (I) (Å, °).

The asymmetric unit of (I) with the atom-labelling scheme is shown in Fig. 2. As revealed by X-ray structure analysis, the molecule of (I) is not planar. However, the two arms containing the N1/C2/N3/N4 and N1/C1/N2/S1 fragments are planar. The deviations of the non-H atoms from the weighted mean planes defined by atoms N1/C2/N3/N4 and N1/C1/N2/S1 are less than 0.017 (2) and 0.024 (2) Å, respectively. Thus, the conformation of the molecule is twisted, with the two planar fragments rotated around the C1—N1 bond by an angle of 22.2 (1)°.

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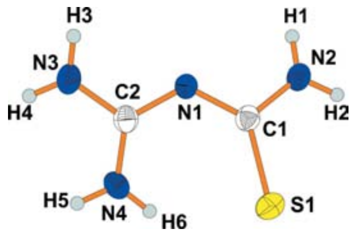

Figure 2
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

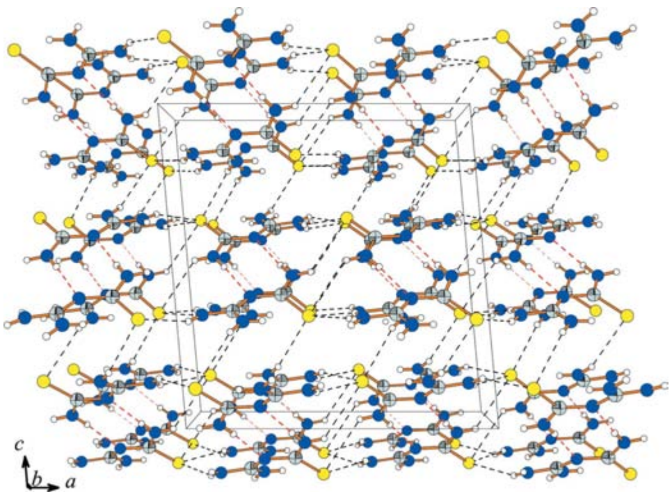

Figure 3
A view of the crystal packing in (I), showing the stacking structure. The N—H⋯N hydrogen bonds forming the dimers are represented by light dashed lines and the N—H⋯S interactions linking the dimers are represented by dark dashed lines.

The C1—S1 bond is longer by ~0.08Å than typical C=S double bonds in thiourea derivatives (mean value 1.663 Å; Allen *et al.*, 1997). In the gas phase, thioformaldehyde, CH_2=S, has a C=S bond distance of 1.6109 (8) Å (Johnson *et al.*, 1971) and this represents 100% double-bond character, while C—S bond lengths of *ca* 1.74 Å, as observed in dithiolate anions (Johnson *et al.*, 1971; Fausto *et al.*, 1989), represent 50% double-bond character.

The three C—NH_2 bond distances of (I) are in the range 1.326 (2)–1.334 (2) Å, slightly shorter than typical Csp^2—NH_2 bond lengths of 1.341–1.363 Å (Allen *et al.*, 1987). The central atom N1 links both arms of the molecule by a shorter bond to atom C2 and a longer bond to atom C1 (*i.e.* N1—C2 < N1—C1). These C—N bond lengths involving N1, the C=S bond which is slightly longer than a typical double bond, and the almost planar NH_2 groups, point to partial delocalization of the π electrons of the C2=N1 and C1=S1 double bonds over almost the whole molecule. The planarity of the NH_2 groups indicates that the lone pairs of electrons on the N atoms occupy the *p* orbitals, which are perpendicular to the planes of the amine groups. Due to symmetry of the *p* orbital at the N atoms and at the C and S atoms, partial delocalization of the electrons of the π bonds (C2=N1 and C1=S1) is possible, giving in effect an elongation of the C1=S and C2=N1 double bonds and a shortening of the other C—N single bonds. Thus, the bond order of C1$\overset{\cdots}{-}$S1 is less than 2, and the bond orders of all the C—N bonds have almost similar values, being greater than 1. The interaction of the amine group at N4 with atom S1 is stronger than the steric effect of a lone pair of electrons at the central atom N1, which is localized on the hybridized orbital sp^2 (Gillespie, 1963, 1992) and which makes the N4—C2—N1, C2—N1—C1 and N1—C1—S1 angles greater than 120°, as expected for sp^2 hybridization. Additionally, steric interaction between atoms N4 and S1 is responsible for the opposite rotation of both rigid arms of the molecule around the C—N bonds involving atom N1 (C2—N1 and C1—N1).

Comparing the X-ray diffraction results with the molecular orbital (MO) calculations for the gas phase of both tautomers of (I), it should be stated that the correlation between the calculated bond lengths and angles for 1-(diaminomethylene)thiourea give a similar pattern to that obtained by X-ray analysis. However, the small differences between the geometric parameters from the X-ray analysis and those obtained by MO calculations arise from the intermolecular interactions present in the crystal structure. The geometric parameters of the second tautomer of (I), *i.e.* 2-imino-4-thiobiuret, obtained by MO calculations and X-ray analysis show significantly greater differences, especially between the MO calculated and experimental X-ray values of the C2—N1, C2—N4, C2—N3 and C1—S1 bonds, and the C1—N1—C2, N1—C1—S1 and N1—C2—N4 angles. Moreover, the amine group containing atom N3 of 2-imino-4-thiobiuret has almost pyramidal geometry, in contrast with 1-(diaminomethylene)thiourea, in which the MO optimized geometry of all NH_2 groups is almost planar, similar to what is observed in the crystal structure. Additionally, the calculated total energy of the 1-(diaminomethylene)thiourea tautomer has a lower value than that of the 2-imino-4-thiobiuret tautomer by 58.77 kJ mol^{-1} (11.99 kcal mol^{-1}). Thus, the crystalline product of commercially available 2-imino-4-thiobiuret, as well as the crystals obtained by its recrystallization from water, are present in the other tautomeric form, *i.e.* 1-(diaminomethylene)thiourea.

In the crystal structure of (I), pairs of molecules related by an inversion interact *via* N—H⋯N hydrogen bonds to form a dimeric unit (Fig. 3). The dimers are arranged along the *b* axis forming a stacking structure. Between the dimers, weaker N—H⋯S interactions are observed. The S atom contains two lone pairs of electrons that can be involved as acceptors in N—H⋯S hydrogen bonds. A nonbonded S⋯H contact requires that the distance between the S and H atoms (d_{SH}) should be less than the sum of the van der Waals radii [r_S = 1.80 Å (Bondi, 1964) and r_H = 1.10 Å (Rowland & Taylor, 1996)]. Thus, Table 2 contains the S⋯H contacts shorter than 2.9 Å. Allen *et al.* (1997) classified the intermolecular hydrogen-bond S⋯H distances to a C=S acceptor on the basis of over 600 structures in the CSD and found that the majority of these structures (over 85%) contain S⋯H distances within the range 2.28–2.72 Å, and only about 2% have S⋯H distances of

~2.90 Å. In these structures, the overall mean S···H—N(or O) angle of 157 (1)° shows a strong tendency towards linearity in C═S···H—N(O) systems. Thus, in the present structure, the intermolecular S···H interactions, with distances in the range 2.677 (2)–2.885 (2) Å and with an average C═S···H(N) angle of 154°, are relatively weak, and they are weaker than analogous C═O···H(N) interactions since the electronegativity of S [2.44 (Allred & Rochow, 1958); 2.58 (Pauling, 1960)] is much lower than that of O (3.50 and 3.44, respectively) while being very similar to that of C (2.50 and 2.55, respectively). For this reason, hydrogen bonds with C═S acceptors exhibit an H···*A* range which is much wider than that for the C═O analogues (Allen *et al.*, 1997).

Experimental

Crystals of (I) were obtained by recrystallization of 2-imino-4-thiobiuret (Aldrich) from aqueous solution.

Crystal data

$C_2H_6N_4S$
$M_r = 118.17$
Monoclinic, $C2/c$
$a = 13.505$ (2) Å
$b = 5.380$ (1) Å
$c = 14.111$ (3) Å
$\beta = 95.05$ (2)°
$V = 1021.3$ (3) Å^3
$Z = 8$
Mo *Kα* radiation
$\mu = 0.50$ mm^{-1}
$T = 295$ (2) K
0.54 × 0.25 × 0.23 mm

Data collection

Kuma KM-4 diffractometer with CCD area-detector
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 2008)
$T_{\min} = 0.769$, $T_{\max} = 0.878$
5622 measured reflections
1261 independent reflections
1086 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.051$
$S = 1.00$
1261 reflections
88 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

H atoms were located in difference Fourier maps and were then refined, giving a range of N—H distances of 0.824 (14)–0.860 (13) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.7364 (9)	N1—C2	1.3338 (11)
C1—N2	1.3277 (12)	C2—N4	1.3263 (13)
C1—N1	1.3416 (11)	C2—N3	1.3341 (13)
N2—C1—N1	113.20 (8)	N4—C2—N1	126.53 (9)
N2—C1—S1	117.32 (7)	N4—C2—N3	117.38 (9)
N1—C1—S1	129.33 (7)	N1—C2—N3	115.99 (9)
C2—N1—C1	123.91 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···N1$^{\rm i}$	0.860 (13)	2.200 (14)	3.0584 (13)	176.5 (11)
N2—H2···S1$^{\rm ii}$	0.848 (13)	2.885 (12)	3.5406 (13)	135.6 (10)
N3—H3···S1$^{\rm iii}$	0.826 (13)	2.762 (13)	3.5180 (12)	153.0 (11)
N3—H4···S1$^{\rm iv}$	0.853 (15)	2.677 (15)	3.4868 (12)	159.0 (12)
N4—H5···S1$^{\rm v}$	0.843 (14)	2.691 (13)	3.4419 (12)	149.0 (11)
N4—H6···S1	0.824 (14)	2.385 (14)	3.0153 (11)	133.9 (12)

Symmetry codes: (i) $-x+\frac{3}{2}, -y-\frac{1}{2}, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (iv) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (v) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3190). Services for accessing these data are described at the back of the journal.

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