1-(4-Methylamino-1,2,5-thiadiazole-3-carbonyl)thiosemicarbazide

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In the title compound, $C_5H_8N_6OS_2$, the supramolecular architecture is sustained by two N—H···O and three N—H···S hydrogen bonds, and by N···S electrostatic interactions. The hydrogen-bond network generates a sheet structure, which extends in the a and b directions and is one c-cell dimension thick. These extended sheets are then linked across inversion centres in the c direction by N···S electrostatic interactions, thus forming a three-dimensional network. The principal intermolecular dimensions include N(H)···O distances of 2.8393 (17) and 3.0268 (16) Å, N(H)···S distances in the range 3.2896 (14)–3.5924 (16) Å and N···S distances of 3.0822 (16) Å.

Comment

Thiosemicarbazides and their derivatives are widely used as ligands for the sensing of metal cations (Busev, 1972). In addition, the close intermolecular N···S contacts that have been observed in a variety of compounds containing thiadiazole or thiadiazine rings (Daley *et al.*, 1984; Yamashita *et al.*, 1990; Suzuki *et al.*, 1992, 1997) are an interesting feature of the ═N—S—N═ linkage. These contacts may be due to an intermolecular electrostatic interaction between –N—S⁺═N– dipoles and/or weak intermolecular bonding involving a partial rehybridization at the S atom, with *d*-orbital participation (Gieren *et al.*, 1979).

The title compound, $C_5H_8N_6OS_2$, (I), crystallizes in space group $P\bar{1}$. Bond lengths and angles in (I) (Table 1) agree with the corresponding values in related compounds (Kivikoski & Valkonen, 1990; Yamaguchi *et al.*, 1990). In (I) (Fig. 1), the methylated amine group and the neighbouring carbonyl O atom are essentially in the plane of the thiadiazole ring, and the folded conformation of the molecule is sustained by the intramolecular N—H···O hydrogen bond [N4···O1 = 2.839 (2) Å; Table 2] that closes the six-membered ring. The

conjugated thiadiazole and hydrogen-bonded rings afford a practically planar bicyclic system, with a dihedral angle between the two rings of 2.02 (5)°.

(I)
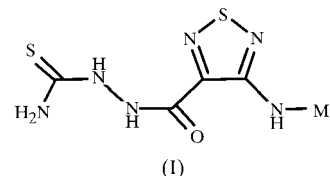
The supramolecular architecture is generated by two N—H···O and three N—H···S hydrogen bonds, and by N···S electrostatic interactions. The N—H···O hydrogen bonds are responsible for linking adjacent molecules into a centrosymmetric tetramer. Carbonyl atom O1 acts as an acceptor, *via* atoms H31 and H32, in a three-centre hydrogen bond with the amine function [N3···O1($-x + 1, -y, -z + 1$) = 2.9830 (17) Å and N3···O1($x - 1, y, z$) = 3.0268 (16) Å; Fig. 2]. The combination of these two three-centre interactions affords a cyclic $R_2^2(8)$ synthon (Etter, 1990; Bernstein *et al.*, 1995), and the propagation of this motif along the [100] direction generates chains. The robustness of the chains is also sustained by an N(H)···S interaction between the methylated N4 and thiosemicarbazide S1 atoms. Two such interactions [N4···S1($-x + 2, -y, -z + 1$) = 3.5924 (16) Å], related by the inversion centre, close the 18-membered $R_2^2(18)$ ring (Fig. 2).

These chains are then linked into sheets *via* two N—H···S hydrogen bonds (Fig. 3). The N1—N2 hydrazine bridge atoms act as hydrogen-bond donors, *via* atoms H1 and H2, to S1 atoms in two different molecules [N1···S1($-x + 1, -y + 1, -z + 1$) = 3.3446 (14) Å and N2···S1($-x + 2, -y + 1, -z + 1$) = 3.2896 (14) Å]. In this manner, a chain of edge-fused (along the S1—C8 covalent bond) $R_2^2(8)$ and $R_2^2(10)$ rings running parallel to [100] is generated by translation. The dihedral angle between the planes defined by the eight- and ten-membered rings is 97.5 (2)°. A similar closed ten-membered ring based on the thiosemicarbazide branch was found in the demethylated analogue of (I) in its cocrystal with 18-crown-6 (Fonari *et al.*, 2003). Thus, the sheets arranged parallel to the (110) plane are sustained by N—H···O and N—H···S hydrogen bonds.
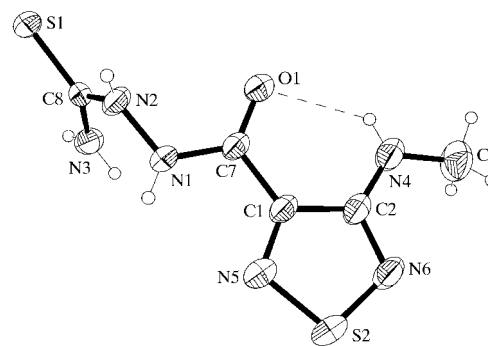

Figure 1
A view of the structure of (I), showing displacement ellipsoids at the 50% probability level. The dashed line designates the intramolecular hydrogen bond.
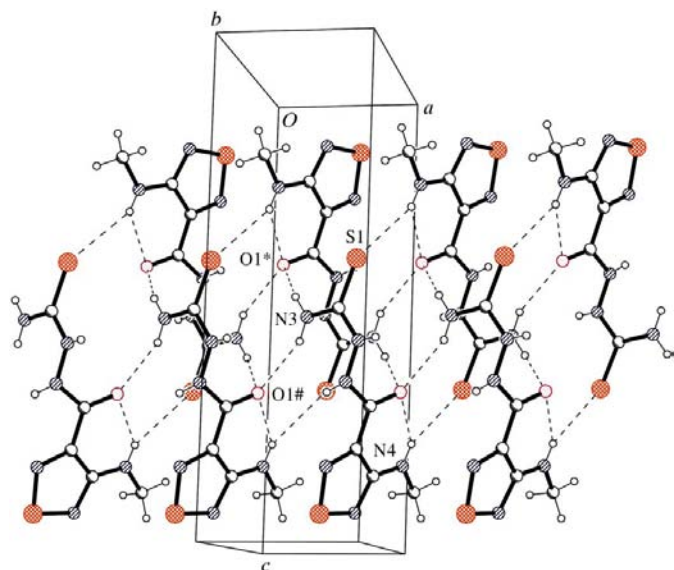
Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x + 1, -y, -z + 1)$ and $(x - 1, y, z)$, respectively.

Neighbouring sheets along the [001] direction, which are a c-cell translation thick, are connected by secondary bonding (Starbuck *et al.*, 1999) [N6···S2(1 − x, −y, 2 − z) = 3.0822 (16) Å] into a three-dimensional network (Fig. 4). This contact distance is significantly shorter than the sum of the van der Waals radii for the N and S atoms (3.35 Å) and leads to a centrosymmetric parallelogram whose sides are the S2—N6 bond [1.632 (2) Å] and the 3.0822 (16) Å intermolecular contact. A search of the Cambridge Structural Database
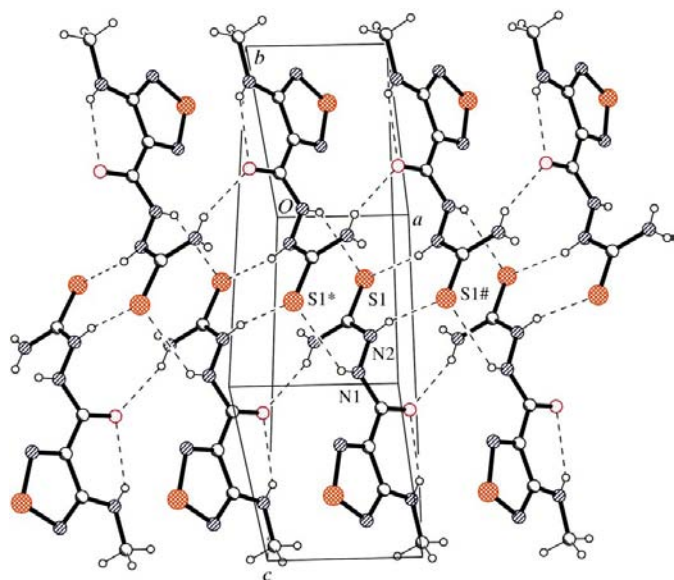

Figure 3
Part of the crystal structure of (I), showing the formation of an edge-fused chain of $R_2^2(8)$ and $R_2^2(10)$ rings along [100]. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x + 1, -y + 1, -z + 1)$ and $(-x + 2, -y + 1, -z + 1)$, respectively.

(Version of November 2002; Allen, 2002) for related molecules resulted in 17 structures that exhibit similar preferentially centrosymmetric interactions between the thiadiazole rings with contact distances in the range 3.022–3.268 Å. Molecules of (I) in neighbouring sheets are uniformly stacked along the a axis, with centroid–centroid separations of
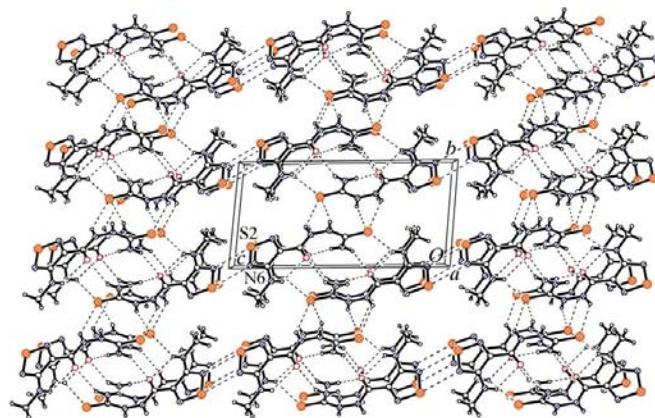

Figure 4
The three-dimensional network in (I), sustained by hydrogen bonds and secondary N···S interactions.

4.660 (1) Å (the a-axis cell length). A similar stacking arrangement of the thiadiazole rings has been found in 4,7-dimethyl-4,7-dihydro-1,2,5-thiadiazolo[3,4-*b*]pyrazine (plane–plane distance = 3.35 Å; Yamashita *et al.*, 1990), in the thiadiazole derivative of tetracyanoquinodimethane (3.48 Å; Suzuki *et al.*, 1992) and in the naphtho derivative of bis-1,2,6-thiadiazine (3.794 Å, which is equal in length to the c axis; Gieren *et al.*, 1979).

Experimental

The hydrazide of 4-methylamino-1,2,5-thiadiazole-3-carbonic acid was obtained from the ethyl ester of 4-methylamino-1,2,5-thiadiazole-3-carbonic acid as described by Ivanov *et al.* (1992). To a mixture of the hydrazide (3.18 g, 0.02 mol) and ammonium isothiocyanate (1.52 g, 0.02 mol) in water (70 ml) was added concentrated hydrochloric acid (2.0 ml). The reaction mixture was boiled for 3 h in a water bath. The precipitate that formed after the hot solution was cooled to room temperature was then recrystallized from methanol/ethyl acetate (1:1) *via* solvent evaporation to give colourless crystals of (I) after 2–3 d (m.p. 519–520 K). Analysis found: S 31.95, N 13.75%; $C_5H_8N_6OS_2$ requires: S 32.07, N 14.01%.

Crystal data

$C_5H_8N_6OS_2$	$Z = 2$
$M_r = 232.29$	$D_x = 1.548$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 4.660$ (1) Å	Cell parameters from 24
$b = 7.288$ (2) Å	reflections
$c = 14.868$ (4) Å	$\theta = 5.6–16.2°$
$\alpha = 95.28$ (1)°	$\mu = 0.51$ mm^{-1}
$\beta = 91.97$ (1)°	$T = 293$ (2) K
$\gamma = 97.21$ (1)°	Prism, pale yellow
$V = 498.3$ (2) Å^3	$0.35 \times 0.20 \times 0.15$ mm

Data collection

Kuma KM-4 diffractometer	$h = 0 \rightarrow 7$
ω–2θ scans	$k = -11 \rightarrow 11$
4300 measured reflections	$l = -23 \rightarrow 23$
4300 independent reflections	3 standard reflections
3297 reflections with $I > 2\sigma(I)$	every 100 reflections
$\theta_{max} = 34.9°$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 0.1303P]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4300 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
148 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.6996 (12)	N3—C8	1.3181 (16)
S2—N5	1.6251 (12)	N4—C2	1.340 (2)
S2—N6	1.6320 (15)	N4—C9	1.445 (2)
O1—C7	1.2268 (15)	N5—C1	1.3231 (18)
N1—C7	1.3532 (16)	N6—C2	1.3356 (17)
N1—N2	1.3830 (14)	C1—C2	1.4427 (18)
N2—C8	1.3472 (16)	C1—C7	1.4687 (16)
N5—S2—N6	99.22 (6)	N6—C2—N4	122.61 (12)
C7—N1—N2	118.46 (11)	N6—C2—C1	112.04 (13)
C8—N2—N1	121.17 (10)	N4—C2—C1	125.35 (11)
C2—N4—C9	121.90 (13)	O1—C7—N1	122.81 (11)
C1—N5—S2	107.22 (9)	O1—C7—C1	121.71 (11)
C2—N6—S2	107.59 (10)	N1—C7—C1	115.46 (11)
N5—C1—C2	113.94 (11)	N3—C8—N2	118.16 (10)
N5—C1—C7	121.91 (11)	N3—C8—S1	122.96 (9)
C2—C1—C7	124.15 (12)	N2—C8—S1	118.88 (9)

Methyl H atoms were included in calculated positions and refined as riding, with isotropic displacement parameters, while H atoms bound to N atoms were found from Fourier maps and were treated isotropically, subject to a DFIX restraint (*SHELXL*97; Sheldrick, 1997).

Data collection: *KM*-4 *Software* (Galdecki *et al.*, 1996); cell refinement: *KM*-4 *Software*; data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$S1[i]	0.854 (15)	2.723 (18)	3.3446 (14)	130.9 (16)
N2—H2$\cdots$S1[ii]	0.853 (14)	2.478 (14)	3.2896 (14)	159.1 (16)
N3—H31$\cdots$O1[iii]	0.864 (14)	2.203 (15)	2.9830 (17)	150.0 (17)
N3—H32$\cdots$O1[iv]	0.856 (14)	2.218 (15)	3.0268 (16)	157.3 (17)
N4—H4$\cdots$O1	0.844 (15)	2.264 (19)	2.8393 (16)	125.5 (18)
N4—H4$\cdots$S1[v]	0.844 (15)	2.864 (17)	3.5924 (16)	145.5 (18)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, 1 - z$; (iii) $1 - x, -y, 1 - z$; (iv) $x - 1, y, z$; (v) $2 - x, -y, 1 - z$.

molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1695). Services for accessing these data are described at the back of the journal.

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