Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Acetone-4-methylthiosemicarbazone at 220 K

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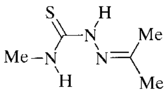
Received 23 August 1999
Accepted 9 November 1999

In the title compound, $C_5H_{11}N_3S$, the *trans* conformation is stabilized by a weak intramolecular N—H···N hydrogen bond. Unusually, one N—H bond is not involved in any hydrogen-bond interactions and instead the molecules form a one-dimensional polymer *via* N—H···S intermolecular hydrogen bonds.

Comment

Thiosemicarbazides and thiosemicarbazones are known to exhibit biological activity (Agrawal *et al.*, 1972; Nandi *et al.*, 1986; Chattopadhyay *et al.*, 1988) including antibacterial (Nandi *et al.*, 1984) and infertility (Nagarajan *et al.*, 1984) properties. These properties are thought to arise from the metal chelating ability of these ligands, and this has led to considerable interest in their coordination chemistry. In almost all cases the ligands are bidentate and bind to the metal through the S and hydrazinic N atoms, although there are examples of them acting as monodentate ligands binding only through sulfur (Valdes-Martines *et al.*, 1996). The crystal structure analysis described here is of the most simple parent compound, (I), and will provide a reference for comparison with more complex homologues.



(I)

The asymmetric unit of (I) with the atomic numbering scheme and intramolecular hydrogen bonding is shown in Fig. 1. The molecule is almost planar with the maximum deviation of 0.012 Å from the least-squares plane seen for S1. The r.m.s. deviation from the least-squares plane is 0.006 Å. As with related molecules the C—S bond length is indicative of a double bond, confirming that the molecule adopts the thione tautomeric form in agreement with spectroscopic data obtained for (I). Typically for this type of molecule the S and hydrazinic N atoms are mutually *trans* which allows for a weak intramolecular hydrogen bond between N4 and N2 [N4···N2 2.629 (3), H4···N2 2.18 (3), N4—H4 0.85 (3) Å, N4—H4···N2 113 (2)°]. Such contacts have been observed in other derivatives (Park & Ahn, 1985). The availability of the lone pair on N4 imparts some double-bond character to the N4—C1 bond and it is shorter than that seen in 4-aryl derivatives (Palenik *et al.*, 1974) but comparable to other reported 4-alkyl derivatives (Park & Ahn, 1985). In addition to the weak intramolecular interaction, H4 is involved in a stronger intermolecular contact to S1 in an adjacent molecule {N4···S1^i 3.492 (3), H4···S1^i 2.69 (2), N4—H4 0.85 (3) Å, N4—H4···S1^i 157 (2)° [symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$]}. This is shown in Fig. 1 and results in a planar one-dimensional hydrogen-bonded polymer structure. In other systems, although hydrogen bonds are prevalent, they lead to dimeric rather than polymeric structures and involve the strong hydrogen-bond donor unit N1—H1 (Chattopadhyay *et al.*, 1988; Park & Ahn, 1985). Unusually, the hydrogen-bond donor unit N1—H1 is not involved in any intra- or intermolecular interactions in this structure.

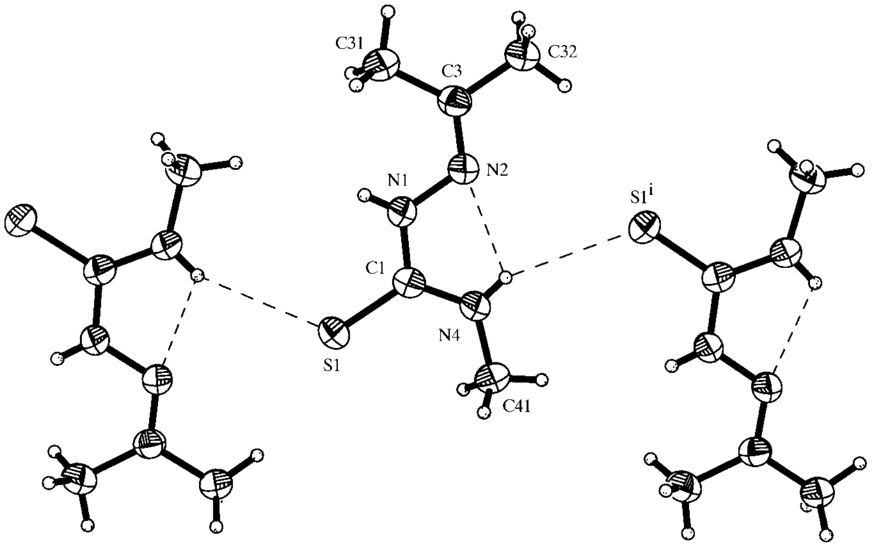


Figure 1
A view of the molecule with atom-numbering scheme and showing intra- and intermolecular hydrogen bonding. Displacement ellipsoids enclose 50% probability surfaces. [Symmetry code: (i) $x, \frac{1}{2} - y, -\frac{1}{2} + z$].

Experimental

N(4)-Methyl thiosemicarbazide and acetone were purchased from the Aldrich Chemical Co. and used as received. The compound was synthesized by the method of Scovill (1991). The ketone and carbazide were mixed in a 1:1 ratio in absolute ethanol with a catalytic amount of concentrated sulfuric acid for 12 h. Addition of aqueous sodium hydroxide to pH 8 precipitated the product which was collected by filtration. A suitable crystal was obtained by slow cooling of a hot cyclohexane solution. Because of physical constraints on the diffractometer some of the reflections could not be accessed and the data set was limited to 92% completion.

Crystal data

$C_5H_{11}N_3S$
$M_r = 145.23$
Monoclinic, $P2_1/c$
$a = 7.067$ (4) Å
$b = 9.783$ (5) Å
$c = 11.440$ (6) Å
$\beta = 103.43$ (3)°
$V = 769.3$ (7) Å^3
$Z = 4$

$D_x = 1.254$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 31 reflections
$\theta = 20$–22°
$\mu = 3.092$ mm^{-1}
$T = 220$ (2) K
Plate developed in (001), colourless
0.42 × 0.31 × 0.12 mm

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems open flow cryostat
ω–θ scans
Absorption correction: optimized numerical (*X-SHAPE*; Stoe & Cie, 1997)
$T_{\min} = 0.302$, $T_{\max} = 0.658$
2687 measured reflections
1348 independent reflections

1181 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 69.93°$
$h = -7 \rightarrow 8$
$k = -7 \rightarrow 11$
$l = -12 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.122$
$S = 1.055$
1348 reflections
94 parameters
H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 0.705P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.018$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0144 (15)

Methyl groups were treated as rotating rigid groups with $U_{\rm iso}(\rm H) = 1.5U_{\rm eq}(\rm C)$; H atoms attached to N were refined freely with isotropic displacement parameters.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1994).

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.689 (2)	N2—C3	1.281 (3)
C1—N4	1.325 (3)	C3—C32	1.492 (3)
C1—N1	1.361 (3)	C3—C31	1.497 (3)
N1—N2	1.382 (3)	N4—C41	1.451 (3)
N4—C1—N1	116.0 (2)	N2—C3—C32	116.8 (2)
N4—C1—S1	124.93 (19)	N2—C3—C31	124.6 (2)
N1—C1—S1	119.08 (18)	C32—C3—C31	118.6 (2)
C1—N1—N2	119.8 (2)	C1—N4—C41	124.0 (2)
C3—N2—N1	117.6 (2)		

We thank EPSRC for provision of a four-circle diffractometer and Zeneca Specialties plc for funding.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1372). Services for accessing these data are described at the back of the journal.

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