

1,3-Dimethyl-4-imino-5-oxoimidazolidine-2-thione

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Abstract. $C_5H_7N_3OS$, monoclinic, $P2_1/c$, $Z=4$, M.W. 157.2, $a=4.457$ (1), $b=6.929$ (3), $c=23.847$ (8) Å, $\beta=91.81$ (2)°, $D_x=1.42$, $D_m=1.41$ g cm⁻³ (by flotation). Final residual $R=0.055$.

Introduction. As has already been reported (Kinoshita, Sato & Tamura, 1971), the reaction of methylaminoacetonitrile with methyl isocyanate in methanol gives 1,3-dimethyl-4-imino-5-oxoimidazolidine-2-thione. An imino group in this sort of structure is not commonly encountered and seems to be rather labile. It was therefore desirable to obtain accurate structural information about this group on the basis of counter data, the preliminary investigation having been made by the photographic method.

The crystals were obtained as yellow needles from an ethanol solution. A set of counter data was re-collected on a Rigaku automatic diffractometer in the ω - 2θ scan mode with monochromatized Mo $K\alpha$ radiation. Three standard reflexions were measured every 51 reflexions and showed a uniformly decreasing intensity. Thus all intensity data were scaled to the initial standard intensities. 623 independent reflexions were used for the final refinement cycles.

The structure determination was begun with the photographic data. The phases for 181 reflexions with $E \geq 1.5$ were determined by the symbolic addition procedure. The E map computed with these signs gave the positions of all ten non-hydrogen atoms. The structural parameters were refined by full-matrix least-squares procedures and gave an R value of 0.14 with anisotropic temperature factors.

The atomic parameters were further refined with the counter data. After five cycles of block-diagonal least-squares refinement, a difference Fourier synthesis was computed. This gave the positions of six hydrogen

atoms around two methyl carbon atoms, although no clear assignment was possible for the imino hydrogen atom. Three least-squares refinement cycles with anisotropic temperature factors for heavy atoms and isotropic for methyl hydrogen atoms gave an R value of 0.066. However, it was still difficult to locate the hydrogen atom of the imino group in a second difference Fourier map. Consequently we assumed a position for this atom on the basis of the molecular geometry. Final refinement cycles including an isotropic hydrogen atom for the imino group gave an R of 0.055. The final positional and thermal parameters are given in Table 1. Bond lengths and angles are shown in Fig. 1.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31517 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

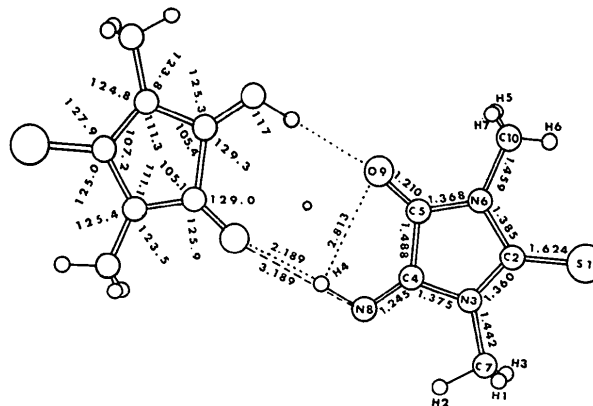


Fig. 1. Bond lengths (Å) and angles (°). (The mean values of the standard deviations are 0.008 Å for distances and 0.5° for angles.)

Table 1. Fractional coordinates and anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form:

$$\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>b</i> ₁₁	<i>b</i> ₂₂	<i>b</i> ₃₃	<i>b</i> ₁₂	<i>b</i> ₁₃	<i>b</i> ₂₃
S(1)	4350 (4)	2652 (4)	1683 (1)	539 (9)	508 (8)	25 (0)	-19 (8)	-18 (2)	45 (2)
C(2)	1966 (12)	3530 (10)	1401 (3)	338 (30)	267 (19)	20 (1)	-78 (20)	16 (5)	11 (4)
N(3)	514 (10)	5255 (8)	1416 (2)	425 (27)	273 (16)	19 (1)	-35 (18)	14 (4)	-16 (4)
C(4)	-1424 (12)	5469 (10)	960 (3)	358 (30)	230 (17)	21 (1)	-28 (20)	10 (5)	4 (4)
C(5)	-1022 (12)	3706 (9)	614 (2)	355 (30)	242 (18)	18 (1)	-67 (20)	1 (5)	9 (4)
N(6)	1071 (10)	2627 (8)	906 (2)	412 (25)	197 (13)	20 (1)	-4 (17)	5 (4)	-2 (3)
C(7)	784 (17)	6628 (13)	1869 (3)	848 (52)	413 (28)	23 (2)	-44 (32)	14 (7)	-23 (6)
N(8)	-3104 (11)	6880 (8)	872 (2)	519 (31)	256 (31)	31 (1)	61 (19)	9 (5)	10 (4)
O(9)	-2281 (9)	3254 (7)	177 (2)	621 (28)	323 (15)	23 (1)	-80 (17)	-14 (4)	-2 (3)
C(10)	2051 (16)	720 (11)	727 (3)	690 (48)	221 (20)	39 (2)	-44 (26)	27 (8)	7 (6)

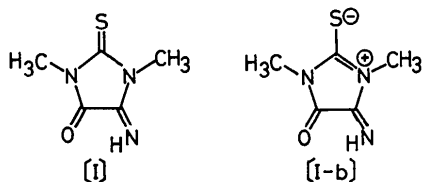
Table 1 (*cont.*)

Fractional coordinates ($\times 10^3$), isotropic temperature parameters (\AA^2) and bond distances (\AA) for the hydrogen atoms. Estimated standard deviations are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_i</i>	X-H
H(1)	277 (14)	735 (11)	182 (3)	8.9 (1.9)	1.03 (5)
H(2)	-83 (12)	759 (9)	179 (2)	5.8 (1.4)	0.99 (6)
H(3)	58 (13)	603 (9)	221 (2)	6.3 (1.6)	0.91 (6)
H(4)	-460 (11)	679 (8)	55 (2)	4.8 (1.3)	1.00 (5)
H(5)	33 (13)	-29 (9)	75 (2)	6.3 (1.6)	1.04 (6)
H(6)	379 (13)	41 (9)	94 (2)	6.5 (1.6)	0.94 (6)
H(5)	246 (11)	80 (8)	37 (2)	4.9 (1.4)	0.84 (7)

Discussion. The S(1)–C(2) bond length, 1.624 \AA , has strong double-bond character [pure S=C double-bond length: 1.608 \AA (Abrahams, 1956)], as compared with thiourea (1.720 \AA , Truter, 1967) and related compounds (*e.g.* 1.708 \AA , Wheatley, 1953; 1.673 \AA , Valle, Cojazzi Busetti & Mammi, 1970; 1.706 and 1.690 \AA , Palenik, Rendle & Carter, 1974). The influence of the other atoms bonded to sulphur in exocyclic S=C bonds has been discussed by Johnson & Paul (1970). The sums of the bond angles about the two nitrogen atoms in the ring are 359.9 and 360.0°, indicating that the atomic configurations are represented by sp^2 hybridization. Although there is no double bond in the endocyclic imidazolidine ring system, it could be said that these sp^2 -hybridized nitrogen atoms contribute to the π -electron ring current.

With respect to the symmetrical thiourea fragment, N(3)–C(2)S(1)–N(6), the C(2)–N(3) bond length is slightly shorter than C(2)–N(6), which implies that there may be some contribution from structure [I-b].



However, it is hard to judge whether this shortening arises from the conjugated form of the five-membered ring. The C(4)–C(5) bond length, 1.488 \AA , agrees with the usual C(sp^2)–C(sp^2) value. A distinctive feature is the extremely short C(4)–N(8) bond length of 1.245 \AA . Studies on the $>\text{C}=\text{NH}$ bond have been reported: creatinine (1.30 \AA , Pr e & Mendel, 1955), 2-imino-5-phenyl-4-thiazolidin-4-one (1.309 \AA , Plastas & Stewart, 1969) and 2-imino-4-thiazolidinone (1.305 \AA , Amirthalingam & Muralidharan, 1972). However, these structures contain a tautomeric form involving the exocyclic imino-amino structure:



Therefore, the C–N bond of the imino group in these cases may be longer than for a pure $>\text{C}=\text{NH}$ bond, because of increased single-bond character.

Table 2. Distances (\AA) of atoms from least-squares planes

Distances of atoms not included in the calculations are given in parentheses.

S(1)	-0.026	(-0.055)
C(2)	0.006	-0.016
N(3)	0.032	0.016
C(4)	0.001	-0.010
C(5)	0.013	0.000
N(6)	0.029	0.009
C(7)	-0.006	(-0.021)
N(8)	-0.021	(-0.026)
O(9)	-0.017	(-0.027)
C(10)	-0.011	(-0.035)

Table 3. Intermolecular contacts $< 3.7 \text{\AA}$

C(4) \cdots O(9 ⁱⁱ)	3.339	C(5) \cdots C(5 ⁱⁱ)	3.579
C(5) \cdots O(9 ⁱⁱ)	3.216	N(8) \cdots O(9 ⁱⁱⁱ)	3.189
N(8) \cdots O(9 ⁱⁱ)	3.521	O(9) \cdots O(9 ⁱⁱ)	3.288
O(9) \cdots O(9 ⁱⁱⁱ)	3.509	O(9) \cdots C(10 ⁱ)	3.501

Symmetry code

- (i) $-x, -y, -z$
- (ii) $-x, 1-y, -z$
- (iii) $-1-x, 1-y, -z$

The molecule is almost planar with an average deviation of 0.016 \AA and maximum deviation of 0.032 \AA (Table 2). A stricter planarity is shown by the five atoms of the imidazolidine ring, from which the C(2)–S(1), N(3)–C(7), C(4)–N(8), C(5)–O(9) and N(6)–C(10) bonds deviate to the same side by 1.3, 1.2, 0.6, 1.5 and 2.0° respectively. As shown in Fig. 1, the planar molecules are linked to form dimers through $=\text{NH} \cdots \text{O}=\text{bonds}^*$ across the centre of symmetry. The hydrogen-bond distance of 3.189 \AA [N(8) \cdots O(9)] is somewhat long, but this bond may play an important role in the stability of the crystal structure and of the imino group.

* As a result of an inadequate process in the computation of intermolecular atomic distances, no details of the intermolecular hydrogen bonding could be given in the preliminary report.

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