

**cis-2-Isopropyl-1,3-dioxane-5-carbothioamide**

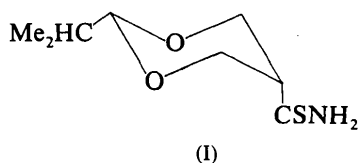
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**Abstract.**  $C_8H_{15}NO_2S$ , monoclinic,  $P2_1/c$ ,  $a = 17.401(1)$ ,  $b = 5.402(1)$ ,  $c = 11.450(1)$  Å,  $\beta = 105.36(2)^\circ$ ,  $V = 1037.9(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.21$ ,  $D_m = 1.25$  Mg m<sup>-3</sup> (floatation in  $CCl_4$ -isooctane at 298 K). The structure was solved by the heavy-atom method using 1738 diffractometer-measured, independent, observed reflections. Refinement by block-diagonal least-squares methods led to  $R = 0.053$  for observed reflections only. The amino group takes part in an intramolecular [N—H...O(1) of the ring] and an intermolecular (N—H...S) hydrogen bond.

**Introduction.** An X-ray crystal structure determination of the title compound (I) was carried out in order to define the geometry of 1,3-dioxane more accurately, and also to investigate the possible existence of intramolecular hydrogen bonding, as discussed for a 5-hydroxy derivative (Kobayashi & Iitaka, 1977), but not so far demonstrated for  $NH_2$  substituents. Probably because of the difficulty of obtaining good quality crystals, only four previous structure determinations have been made on derivatives of 1,3-dioxane, and in the first of these the e.s.d.'s were rather high (de Kok & Romers, 1970; Nader, 1975*a,b*; Eliel, Bailey, Wiberg, Connon & Nader, 1976; Kobayashi & Iitaka, 1977).



Single crystals of (I) were obtained by slow evaporation of a cyclohexane solution. These were large, well-formed, colorless and almost transparent. X-ray data were collected with Ni-filtered  $Cu K\alpha$  radiation on an Enraf-Nonius CAD-4 automated diffractometer using the  $\omega$ - $2\theta$  scanning mode. Accurate cell parameters were obtained by a least-squares fit of the angular settings for 15 high-angle reflections. The intensities of 2143 independent reflections within the range  $2\theta < 160^\circ$  were measured; 1738 reflections were considered observed on the criterion  $I > 1.5\sigma_I$ . The dimensions of the crystal used were  $0.40 \times 0.18 \times 0.10$  mm.

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Absorption corrections were applied using the bounding faces  $\pm(010)$ ,  $(101)$ ,  $(10\bar{1})$  with the program ORABS2 (Busing, 1972). The absorption corrections to the intensities were in the range 1.25–1.82 [ $\mu(Cu K\alpha) = 2.39$  mm<sup>-1</sup>].

The structure was solved by the heavy-atom method from the S-atom coordinates as determined from the Patterson map. Refinement of the positional and anisotropic thermal parameters of the 12 non-hydrogen atoms by block-diagonal least-squares methods

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for the non-hydrogen atoms

	x	y	z
S	435 (1)	3471 (1)	6795 (1)
N	772 (1)	2113 (4)	4803 (1)
O(1)	2273 (1)	-754 (3)	5176 (1)
C(2)	2929 (1)	120 (6)	6078 (2)
O(3)	2684 (1)	1820 (3)	6846 (1)
C(4)	2164 (1)	683 (6)	7465 (2)
C(5)	1434 (1)	-340 (5)	6555 (2)
C(6)	1712 (1)	-2035 (5)	5695 (3)
C(7)	888 (1)	1726 (4)	5967 (2)
C(8)	3498 (1)	1447 (6)	5487 (3)
C(9)	3751 (2)	-275 (10)	4610 (3)
C(10)	4209 (2)	2507 (10)	6428 (4)

Table 2. Fractional atomic coordinates ( $\times 10^3$ ), and isotropic thermal parameters for the hydrogen atomsThe temperature factors used were of the form  $\exp(-B \sin^2 \theta/\lambda^2)$ .

	x	y	z	B (Å <sup>2</sup> )
H(1N)	103 (1)	119 (4)	448 (2)	2.7 (5)
H(2N)	43 (1)	339 (4)	446 (2)	3.0 (5)
H(C2)	316 (1)	-130 (5)	658 (2)	3.6 (6)
H(1C4)	242 (1)	-68 (5)	793 (2)	4.2 (6)
H(2C4)	202 (1)	205 (5)	798 (2)	3.9 (6)
H(C5)	112 (1)	-138 (5)	696 (2)	4.0 (6)
H(1C6)	198 (1)	-338 (5)	616 (2)	4.5 (6)
H(2C6)	128 (1)	-257 (5)	499 (2)	3.1 (5)
H(C8)	322 (2)	291 (5)	506 (2)	4.4 (7)
H(1C9)	330 (2)	-89 (7)	398 (3)	7.6 (10)
H(2C9)	413 (2)	66 (8)	431 (3)	8.5 (10)
H(3C9)	399 (2)	-191 (6)	503 (3)	6.9 (8)
H(1C10)	442 (2)	90 (6)	686 (3)	6.3 (8)
H(2C10)	461 (3)	356 (9)	602 (4)	12.3 (15)
H(3C10)	406 (2)	400 (8)	699 (3)	9.4 (12)

(Ahmed, Hall, Pippy & Huber, 1973) resulted in  $R = 0.083$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 4I Lp/(\sigma_f^2 + 0.02I^2)$ . The 15 H atoms were then located from a difference electron density map, and 12 cycles of refinement carried out on all positional parameters, isotropic thermal parameters for the H atoms and anisotropic thermal parameters for the other atoms. In the final refinement the unobserved reflections were included with a constant weight such that the mean value of  $w|AF|^2$  for the unobserved reflections was equal to that for the observed reflections. In the final cycle  $R = 0.053$  (observed reflections only) and  $R = 0.060$ ,  $R_w = 0.053$  (all reflections).\* The average and maximum values of the shift/e.s.d. ratio were 0.19 and 0.39. The scattering factors used were taken from *International Tables for X-ray Crystallography* (1968). The final fractional atomic coordinates for the non-hydrogen atoms are given in Table 1, and the H atomic parameters in Table 2.

**Discussion.** The bond distances between the non-hydrogen atoms are shown in Fig. 1 and the bond angles in Table 3. These are uncorrected for thermal

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33913 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond angles (°)

S—C(7)—N	121.1 (2)	O(1)—C(2)—O(3)	110.8 (2)
S—C(7)—C(5)	120.1 (2)	C(2)—O(3)—C(4)	111.4 (2)
N—C(7)—C(5)	118.8 (2)	O(3)—C(4)—C(5)	109.9 (2)
C(7)—C(5)—C(4)	110.6 (2)	O(3)—C(2)—C(8)	108.1 (2)
C(7)—C(5)—C(6)	115.5 (2)	O(1)—C(2)—C(8)	109.2 (2)
C(4)—C(5)—C(6)	108.2 (2)	C(2)—C(8)—C(9)	110.1 (3)
C(5) C(6)—O(1)	110.1 (2)	C(2) C(8) C(10)	111.4 (3)
C(6)—O(1)—C(2)	111.4 (2)	C(9)—C(8)—C(10)	112.0 (3)

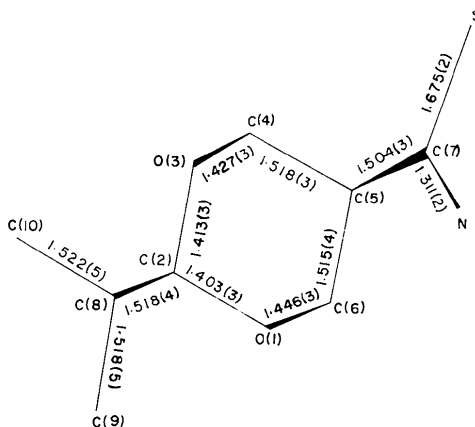


Fig. 1. Bond distances (Å) for the non-hydrogen atoms.

vibrational effects. The C—H bond distances range from 0.94–1.10 Å with an average value of 1.00 Å and e.s.d.'s of 0.02–0.05 Å. The N—H distances are 0.82 (2) and 0.92 (2) Å. The torsion angles for the *cis*-dioxane ring are shown in Fig. 2. These are all of the stable ( $\pm$ )-synclinal type and define the chair conformation. The C—O bonds of the ring average 1.422 Å, considerably shorter than the average C—C distance of 1.516 Å. This has the consequence, as found in other reported structures of 1,3-dioxane derivatives (de Kok & Romers, 1970; Nader, 1975*a,b*; Kobayashi & Itaka, 1977), that the O(1)—C(2)—O(3) side of the ring is more puckerd than the C(4)—C(5)—C(6) side. The mean of the torsion angles O(3)—C(4)—C(5)—C(6) and C(4)—C(5)—C(6)—O(1) is 53.8°. This is almost identical with the value found in a 4,6-dimethyl substituted 1,3-dioxane (Nader, 1975*b*), indicating a negligible effect of the ring conformation on substitution of the methyl groups.

An intramolecular hydrogen bond is formed between the amino group and O(1) of the ring. The distance N to O(1) is 2.968 Å, H(1N)···O(1) is 2.34 Å and the angle N—H(1N)···O(1) is 133°. This considerable bending is due to geometrical hindrance and the hydrogen bonding is facilitated by a twist of the whole

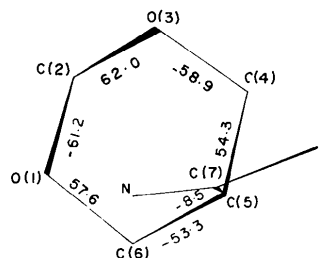


Fig. 2. Torsion angles (°) in the 1,3-dioxane ring, and for C(6)—C(5)—C(7)—N.

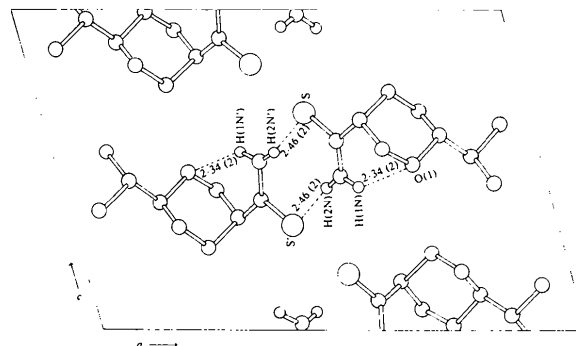


Fig. 3. Packing of molecules in the (010) projection showing intra- and intermolecular hydrogen bonding.

group bonded to C(5) about the C(5)—C(7) bond, the torsion angle N—C(7)—C(5)—C(6) being  $-8.5^\circ$ . While the C(5)—C(7) bond distance is in good agreement with that calculated for a C(sp<sup>3</sup>)—C(sp<sup>2</sup>) bond (Bastiansen & Skancke, 1961), the C(7)—N bond length of 1.311 Å indicates about 35% double-bond character (Hahn, 1957) and, as would be expected, the atoms S, C(7), N, H(1N) and H(2N) are coplanar within the possible experimental error.

An intermolecular hydrogen bond is formed between the NH<sub>2</sub> group of one molecule and the S atom of the molecule related by a center of symmetry, forming a dimer as shown in Fig. 3. The distance H(2N)⋯S' is 2.46 Å, N to S' is 3.378 Å and the angle N—H⋯S' is 170°. These values indicate stronger hydrogen bonding than do those reported by Brown (1978) who found an H⋯S distance of 2.62 Å and an angle N—H⋯S of 152°.

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## Thienyl-DL-serine Monohydrate

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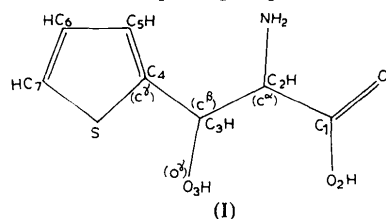
**Abstract.** C<sub>7</sub>H<sub>9</sub>NO<sub>3</sub>S·H<sub>2</sub>O, *M<sub>r</sub>* = 205.2, orthorhombic, *Pbca*, *a* = 28.038 (8), *b* = 9.817 (6), *c* = 6.536 (4) Å, *Z* = 8, *D<sub>x</sub>* = 1.516 Mg m<sup>-3</sup>, Cu *Kα* radiation ( $\lambda = 1.54178$  Å,  $\mu = 3.021$  mm<sup>-1</sup>). Final *R* = 0.078. The thienyl ring is essentially planar and is nearly perpendicular to the plane defined by C<sup>α</sup>, C<sup>β</sup> and C<sup>γ</sup>. The molecule exists as a zwitterion. The structure is stabilized by a network of strong N—H⋯O and O—H⋯O hydrogen bonds.

**Introduction.** Antimetabolites of amino acids and other biologically important molecules owe their action to a close similarity to normal metabolites and hence could easily be mistaken for normal metabolites in biological systems. In this context the structures of the hydrochlorides of *p*-nitrophenylalanine (Chacko, Swaminathan, Parthasarathy & Natarajan, 1978), an antagonist of phenylalanine and of 2-butenylglycine

(Swaminathan & Chacko, 1979), an antagonist of methionine, have already been investigated.

Thienylserine (I) is an amino acid analogue of serine (as well as of threonine) with one of the methylene H atoms at the C<sup>β</sup> position of serine (or C<sup>γ</sup> in threonine) replaced by a thienyl ring. Mathew & Nord (1951) have observed that (I) could act as an antagonist for serine in protein synthesis leading to serine deficiency. (I) also has two asymmetric C atoms and the configuration about these centres is of interest.

Needle-shaped crystals were obtained from the Sigma Chemical Company, USA. Preliminary cell dimensions and the space group were established from



\* Contribution No. 492.

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