Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonding patterns in *rac*-1-acetyl-5-methyl-2-thioxoimidazolidin-4-one

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Received 31 July 2007
Accepted 2 August 2007
Online 17 August 2007

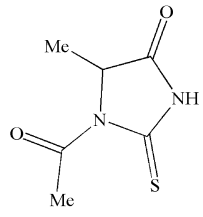
In the title compound, $C_6H_8N_2O_2S$, also known as *N*-acetyl-2-thiohydantoin–alanine, the molecules are joined by N—H···O hydrogen bonds, forming centrosymmetric $R_2^2(8)$ dimers; these dimers are linked by C—H···O interactions to form $R_2^2(10)$ rings, thus forming $C_2^2(10)$ chains that run along the [101] direction.

Comment

2-Thioxoimidazolidin-4-ones, or 2-thiohydantoins, are sulfur analogs of imidazolidine-2,4-diones, or hydantoins. These compounds are constituted by two five-membered heterocyclic systems with a very reactive nucleus, which provides four possible points of diversity. Both heterocycles represent significant building blocks for combinatorial chemistry libraries (Boeijen *et al.*, 1998; Park *et al.*, 2001; Lin & Sun, 2003; Zhang *et al.*, 2006). In recent years, there has been much interest in the search for new synthetic routes for the preparation of hydantoins and thiohydantoins, *via* solution or solid-state reactions (Kleinpeter, 1997, Muccioli *et al.*, 2003; Ganesan, 2003; Vázquez *et al.*, 2004; Alsina *et al.*, 2005; Dubey, 2006; Wang *et al.*, 2006; Reyes & Burgess, 2006).

We are interested in the *N*-carbamoyl, hydantoin and thiohydantoin derivatives of natural amino acids (Seijas *et al.*, 2006, 2007; Delgado *et al.*, 2007), and report here the structure of the title compound, (I), the *N*-acetylthiohydantoin derivative of the natural amino acid L-alanine, which is an intermediate in the preparation of 2-thiohydantoin–alanine. Compound (I) (Fig. 1) crystallizes in a centrosymmetric space group, which implies that L-alanine suffered an amino acid racemization produced by the use of acetic acid in the synthesis (Yamada *et al.*, 1983; Yoshioka, 2007).

All bond distances and angles are normal (Allen, 2002) and in agreement with the average values found in 31 entries with 36 thiohydantoin ring fragments found in a search of the



(I)

Cambridge Structural Database (CSD; Version 5.28; Allen, 2002), with atoms N1 and N3 unsubstituted and sp^3-hybridization at atom C5. The thiohydantoin ring is essentially planar, with maximum deviations of 0.020 (1) Å for atom N3 and −0.019 (2) Å for atom C4. The N1—C2—S2 angle is greater than the N3—C2—S2 angle (Table 1). This difference is also observed in the two *N*-acetylthiohydantoin compounds reported in the CSD [refcodes KOMGUO (Mackay *et al.*, 1992), with angles of 130.6 and 123.4°, and NIFHIT (Casas *et al.*, 1998), with angles of 132.0 and 121.9°]. The average values for the same angle in the 36 fragments searched above are 127.7 and 125.2°, respectively. The C2—S2 distance (Table 1) agrees with the average value of 1.646 Å found for the 36 fragments, with minimum and maximum reported values of 1.519 and 1.696 Å, respectively. The acetyl group is almost coplanar with the thiohydantoin ring, and the dihedral angle between the least-squares plane through the acetyl atoms N1, C6, O6 and C7 and the thiohydantoin ring is 13.6 (6)°. This value agrees with the equivalent in KOMGUO (12°; Mackay *et al.*, 1992) and is greater than the value of 6.7° found in NIFHIT (Casas *et al.*, 1998), indicating that the substitution at atom C5 produces a major separation of the acetyl group with regard to the thiohydantoin ring.

The molecular structure and crystal packing of (I) are stabilized by intermolecular N—H···O and C—H···O

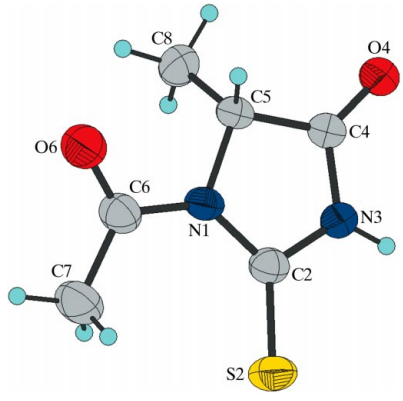


Figure 1
The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

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 DOI: 10.1107/S0108270107038012

hydrogen bonds (Table 2). The N—H···O hydrogen bond generates centrosymmetric $R_2^2(8)$ (Etter, 1990) rings (Fig. 2). This motif constitutes a typical amide–amide hydrogen bond joining pairs of molecules, and is also observed in the thiohydantoins THHYDT01 (Devillanova *et al.*, 1987) and KUWDOW (Cristiani *et al.*, 1992). These dimers are parallel linked through the C—H···O hydrogen bond to form a second centrosymmetric ring motif, of $R_2^2(10)$ type (Fig. 2). The combination of these rings produces $C_2^2(10)$ chains, which run along the [101] direction.

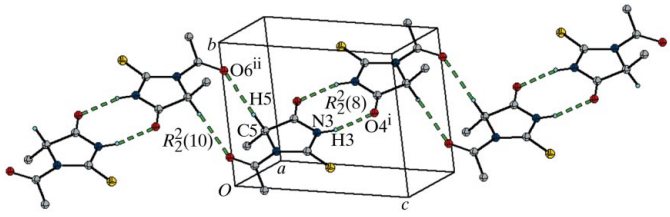

Figure 2
A partial packing view of (I). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z$.]

Experimental

L-Alanine (500 mg, 3.0 mmol) and NH_4SCN (228 mg, 3.0 mmol) were dissolved in a mixture of acetic anhydride (9 ml) and acetic acid (1 ml). This solution was warmed, with agitation, to 363 K over a period of 30 min, and then cooled in ice/water and stored in a freezer overnight. The resulting white solid was collected by filtration and washed with cold water (m.p. 430–432 K). Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in 1:1 ethanol–methanol. NMR (MSO-d_6): δ(H) 12.66 (H3, *s*), 4.68 (H5, *q*), 2.72 (H7*A* = H7*B* = H7*C*, *s*), 1.43 (H8*A* = H8*B* = H8*C*, *d*); δ(C) 182 (C2), 173.9 (C4), 169.7 (C6), 58.7 (C5), 27.3 (C7), 15.9 (C8).

Crystal data

$C_6H_8N_2O_2S$
M_r = 171.21
Triclinic, $P\overline{1}$
a = 7.001 (6) Å
b = 7.210 (6) Å
c = 8.102 (7) Å
α = 91.085 (7)°
β = 91.052 (7)°
γ = 107.764 (7)°
V = 389.3 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 295 (2) K
0.57 × 0.34 × 0.15 mm

Data collection

Stoe Stadi-4 diffractometer
Absorption correction: ψ scan (*EMPIR*; Stoe & Cie, 1992)
T_{min} = 0.860, T_{max} = 0.940
2474 measured reflections
1779 independent reflections
1322 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
3 standard reflections
every 100 reflections
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

C2—N3	1.371 (3)	C4—O4	1.211 (3)
C2—S2	1.642 (2)	O6—C6	1.205 (3)
N1—C2—S2	131.47 (16)	O4—C4—N3	126.1 (2)
N3—C2—S2	122.19 (16)	O4—C4—C5	126.77 (19)

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.105
S = 1.02
1779 reflections
102 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O4^{i}	0.86	1.99	2.824 (3)	164
C5—H5···O6^{ii}	0.98	2.38	3.271 (4)	151

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z$.

All H atoms were placed at calculated positions and treated using a riding model, with C—H distances of 0.96–0.98 Å and an N—H distance of 0.86 Å. The U_{iso}(H) parameters were fixed at 1.2U_{eq}(C,N) or 1.5U_{eq}(methyl C).

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *PLATON* (Spek, 2003).

This work was supported by CDCHT–ULA (grant Nos. C-1416-06-08-B and C-1485-07-08-F) and FONACIT (grant No. LAB-97000821).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3133). Services for accessing these data are described at the back of the journal.

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