Acta Cryst. (1999). C**55**, 1378–1380

10,10-Dimethyl-1,2,8-thiadiazecan-9-one 1,1-dioxide

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(*Received 28 April 1999; accepted 3 June 1999*)

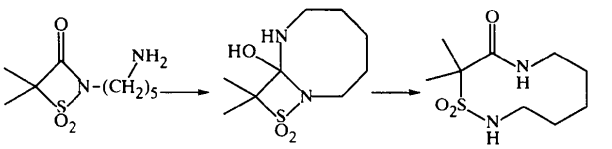
Abstract

The puckered ten-membered ring of the title compound, $C_9H_{18}N_2O_3S$, contains a sulfonamide group and an amide moiety which has the *trans* conformation. The molecules are linked into infinite two-dimensional networks by intermolecular N—H···O hydrogen bonds involving both NH groups along with the amide O atom and one of the sulfonyl O atoms from different neighbouring molecules. The title compound was prepared by a ring-enlargement reaction of the corresponding *N*-aminoalkyl 1,2-thiazetidin-3-one 1,1-dioxide.

Comment

Ring-enlargement reactions are particularly suitable for the preparation of 'medium-sized ring systems', which are often difficult to obtain by ring-closure reactions (*cf.* Hesse, 1991). Among many different reaction types, the transamidation reaction has been studied extensively for this purpose (Stach & Hesse, 1988). It has been shown that ring-enlargement proceeds easily *via* six-membered intermediates, *i.e.* with 3-aminopropyl side chains at the lactam N atom (*cf.* Jenny & Hesse, 1981; Häusermann *et al.*, 1996). However, analogous reactions involving seven-membered intermediates are more difficult to realise (Stephanou *et al.*, 1979; Begley *et al.*, 1993; Horni, 1997). For example, starting with *N*-(aminoalkyl)-substituted β-lactams, smooth ring enlargements by transamidation *via* five- or six-membered intermediates yielded the seven- and eight-membered aminolactams, respectively (Begley *et al.*, 1993). The corresponding ring enlargement involving the energetically less favourable seven-membered intermediate was successfully carried out under more drastic conditions, but all attempts to obtain products *via* eight-membered intermediates, *i.e.* with a 5-aminopentyl side chain, failed. Similar results have been reported for ring enlargements of 2-hydroxyalkyl 2-nitrocycloalkanones to give macrolides (Kostova & Hesse, 1984; Stach & Hesse, 1986; *cf.* Bhat & Cookson, 1981). In all of these reactions, a strong base was needed to deprotonate the NH_2 or OH group.

In the case of *N*-(3-aminopropyl)- and *N*-(4-aminobutyl)-substituted 1,2-thiazetidin-3-one 1,1-dioxides of type (I), ring enlargements by means of transamidation reactions gave the corresponding eight- and nine-membered heterocycles in 87 and 68% yield, respectively, at room temperature and in the absence of an additional base (Todorova *et al.*, 1999). For this reason, we expected that the *N*-(5-aminopentyl) derivative, (I), would be a suitable model for a transamidation *via* an eight-membered intermediate, (II), but the ring enlargement took place only at 353 K, leading to the ten-membered ring in the form of the title compound, (III), in 41.9% yield.



(I) (II) (III)

The low-temperature structure determination of compound (III) shows that most bond lengths and angles have values normally observed in this class of compound. An exception is the C10—S1 bond (Table 1), which at 1.8385 (13) Å is slightly longer than that usually observed for C—S bonds in a similar environment. An inspection of the April 1999 version of the Cambridge Structural Database (Allen & Kennard, 1993) indicates that the mean C—S distance for 45 error-free structures involving sulfonamides in which the S-bonded C atom is saturated is 1.77 (2) Å, with a range of 1.733–1.826 Å. The ten-membered ring has a puckered conformation, but is not bent into a bowl shape (Fig. 1). As is usual for lactams with a ring size larger then eight, the amide group (C7—N8—C9—C10) has the *trans* conformation. This is also found in the corresponding product with an eight-membered ring (Todorova *et al.*, 1999). On the other hand, the eight-membered analogue with an additional methyl group at C5 has an amide group with the *cis* conformation (Todorova *et al.*,

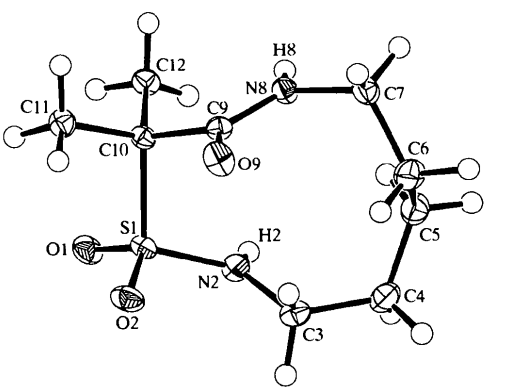


Fig. 1. View of the molecule of (III) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size.

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1999). Each NH group in the molecule of (III) acts as a donor for intermolecular hydrogen bonds (Table 2). The sulfonamide N—H group interacts with the amide O atom of a neighbouring molecule to form infinite one-dimensional chains which run parallel to the [100] direction and have a graph-set motif of $C(6)$ (Bernstein *et al.*, 1995). The amide N—H group interacts with one of the sulfonyl O atoms in a different neighbouring molecule to form infinite one-dimensional chains which run parallel to the [0$\bar{1}$0] direction and also have a graph-set motif of $C(6)$. The combination of both interactions links the molecules into a two-dimensional network which lies perpendicular to the [001] direction.

Experimental

The title compound, (III), was obtained in 41.9% yield by stirring a mixture of 5-(4,4-dimethyl-1,1-dioxido-3-oxo-1,2-thiazetidin-2-yl)pentylammonium trifluoroacetate (150 mg, 0.43 mmol) and (piperidinylmethyl)polystyrene (3.2 g, 2.6–2.8 mmol) in refluxing acetonitrile (120 ml) for 45 h. Filtration, evaporation of the solvent, and chromatography (SiO_2, dichloromethane/methanol/25% aqueous ammonium hydroxide 40:3:0.6) yielded the pure product, which was recrystallized from acetonitrile (Todorova *et al.*, 1999) to give colourless plates (m.p. 456.3–466.4 K). Diffraction quality crystals were obtained by slow evaporation from a solution of (III) in a mixture of dichloromethane, acetonitrile and hexane.

Crystal data

$C_9H_{18}N_2O_3S$
M_r = 234.31
Monoclinic
$P2_1$
a = 5.6804 (15) Å
b = 11.117 (2) Å
c = 8.7621 (8) Å
β = 94.270 (13)°
V = 551.77 (19) Å^3
Z = 2
D_x = 1.410 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 21 reflections
θ = 19.5–20.0°
μ = 0.284 mm^{-1}
T = 173 (1) K
Plate
0.48 × 0.45 × 0.13 mm
Colourless

Data collection

Rigaku AFC-5R diffractometer
ω–2θ scans
Absorption correction: none
3674 measured reflections
1682 independent reflections (plus 1529 Friedel-related reflections)
3127 reflections with $I > 2\sigma(I)$

R_{int} = 0.014
θ_{max} = 30°
$h = -7 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 12$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.072
S = 1.062
3211 reflections
146 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.0342P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (5)

Table 1. *Selected geometric parameters (Å, °)*

S1—N2	1.6067 (11)	N2—C3	1.4746 (15)
S1—C10	1.8385 (13)	N8—C9	1.3340 (15)
O9—C9	1.2371 (15)	N8—C7	1.4620 (15)
C10—S1—N2—C3	101.16 (11)	C5—C6—C7—N8	51.52 (17)
S1—N2—C3—C4	−157.77 (10)	C7—N8—C9—C10	−169.80 (11)
N2—C3—C4—C5	64.55 (16)	N8—C9—C10—S1	103.60 (11)
C3—C4—C5—C6	58.32 (16)	N2—S1—C10—C9	−48.90 (9)
C4—C5—C6—C7	−129.35 (13)	H8—N8—C9—O9	−178.0 (14)
C9—N8—C7—C6	73.91 (17)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O9^{i}	0.857 (9)	2.033 (12)	2.8540 (15)	160 (2)
N8—H8···O1^{ii}	0.872 (9)	2.203 (12)	2.9953 (15)	150.9 (16)

Symmetry codes: (i) $1 + x, y, z$; (ii) $2 - x, y - \frac{1}{2}, 1 - z$.

Although the title compound is not a chiral molecule, it crystallizes in an enantiomorphous space group. The reflection data included the intensities of the Friedel opposites of all symmetry-unique reflections. The value of the Flack (1983) parameter confirms the absolute structure. The origin was fixed according to the method of Flack & Schwarzenbach (1988). An absorption correction was not applied because ψ scans produced a flat absorption profile. The N—H group H atoms were refined, but a restraint of 0.88 (1) Å was applied to the length of each N—H bond. Methyl-group H atoms were located from a difference electron-density map, then geometrically idealized and refined as rigid groups allowed to rotate, but not to tip, and with $U_{iso}(H) = 1.5U_{eq}(C)$. The positions of all other H atoms were geometrically idealized and allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: direct methods *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

The Swiss National Science Foundation and F. Hoffmann–La Roche AG, Basel, are thanked for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1340). Services for accessing these data are described at the back of the journal.

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