

## An unusual methylene aziridine refined in $P2_1/c$ and the nonstandard setting $P2_1/n$

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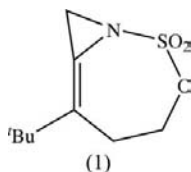
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The unusual methylene aziridine 6-*tert*-butyl-3-oxa-2-thia-1-azabicyclo[5.1.0]oct-6-ene 2,2-dioxide,  $C_9H_{15}NO_3S$ , was found to crystallize with two molecules in the asymmetric unit. The structure was solved in both the approximately orthogonal and the oblique settings of space group No. 14, *viz.*  $P2_1/n$  and  $P2_1/c$ , respectively. A comparison of these results clearly displayed an increase in the correlation between coordinates in the *ac* plane for the oblique cell. The increase in the corresponding covariances makes a significant contribution to the standard uncertainties of derived parameters, *e.g.* bond lengths. Since there is yet no CIF definition for the full variance–covariance matrix, there are clear advantages to reporting the structure in the nonstandard space-group setting.

### Comment

The title compound, 6-*tert*-butyl-3-oxa-2-thia-1-azabicyclo[5.1.0]oct-6-ene 2,2-dioxide, (1), and related methylene aziridines (Feast *et al.* 2009) were prepared during our ongoing study of nitrogen-containing 1,3-dipoles (Robertson *et al.*, 2005; White, 2007) in order to probe their potential as 2-aminoallyl cation precursors (Prié *et al.*, 2004).



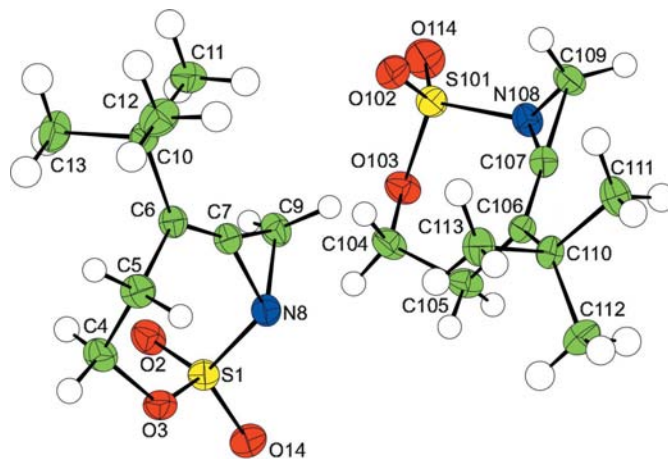
The structure of the methylene aziridine was initially determined in the monoclinic space group  $P2_1/n$ , (I), with a cell of  $a = 13.8593$  (3) Å,  $b = 10.5242$  (2) Å,  $c = 14.8044$  (4) Å

and  $\beta = 92.0014$  (7)°, and two molecules in the asymmetric unit (Fig. 1).

The unusual bond angles at C7/C107 suggested it would be advisable to carry out a comparison with the structures in the Cambridge Structural Database (CSD; Version 5.30 of November 2008, including updates 1–3; Allen, 2002) using *Mogul* (Bruno *et al.*, 2004). For comparison, *Mogul* uses a figure of merit *Z* (defined as the difference between the observed value and the median divided by the standard deviation of the *Mogul* distribution). Typically, *Z* values greater than about 2–3 indicate that a bond length or angle are sufficiently unusual to warrant further investigation. Although (I) gave a *Z* value greater than 100 for the top eight queries, each of these had only one match in the CSD and the obvious C6–C7–C9/C106–C107–C109 angle had no hits at all. Indeed, more than one-third of the queries generated by *CRYSTALS* (Betteridge *et al.*, 2003) had fewer than six hits in the CSD, suggesting the structure has little precedence in the literature. Examination of the molecular structure showed why this is the case, with the particularly unusual seven-membered ring (comprising three heteroatoms and a double bond) fused with a three-membered ring leading to an extremely strained geometry at atoms S1, C7 and N8 (and the analogous atoms S101, C107 and N108).

The two equivalent molecules have very similar conformations when overlaid (positional, bond and torsion r.m.s. deviations of 0.166 Å, 0.007 Å and 3.542°, respectively). Both symmetry equivalents (referred to by the first atom in the residue, S1 and S101) form dimers around an inversion centre. These are held together by C–H...O interactions between chemically equivalent atoms (C9/C109 and O2/O102; Table 2). The dimers form layers parallel to the [101] plane containing exclusively either S1 or S101; in turn, these layers are connected together by further C–H...O interactions (Fig. 2).

Prior to publication, the CIF was verified with the online checking facility *checkCIF*, which gave the following alert:



**Figure 1**

The title compound, (1), with displacement ellipsoids drawn at the 50% probability level.

PLAT128\_ALERT\_4\_G

Non-standard setting of Space-group  $P2_1/c \dots P2_1/n$

The hyperlink explains further: 'The reported monoclinic space-group is in a non-standard setting. Transformation to the conventional setting is indicated unless there is a good (scientific) reason not to do so.'

The unit-cell obtained from the initial indexing was then transformed using the matrix  $\mathbf{A}$ ,

$$\mathbf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & -1 \end{pmatrix}, \quad (1)$$

and reprocessed (including integration, scaling and cell final refinement) to give the data in the space group  $P2_1/c$ , with a cell of  $a = 13.8594(2) \text{ \AA}$ ,  $b = 10.5243(2) \text{ \AA}$ ,  $c = 19.9230(3) \text{ \AA}$  and  $\beta = 132.0439(7)^\circ$ , (II). The atomic coordinates from the original structure were transformed using  $(\mathbf{A}^T)^{-1}$ , given by

$$(\mathbf{A}^{-1})^T = \begin{pmatrix} 1 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad (2)$$

and the structure re-refined.

Comparison of (I) and (II) demonstrated that the bond lengths (and angles) were the same allowing for rounding error. This is as expected, since the structures are the same, merely in a different unit-cell setting. However, it has long been known that refinements in oblique cells have increased correlation between selected parameters, potentially making refinements less stable (Dunitz, 1979). Thus, a large  $\beta$  value would be expected to give increased correlation between parameters with respect to the  $a$  and  $c$  axes. In (I), the largest correlations are between the sulfur atomic displacement parameters (ADPs) and the scale factor (Table 1). However, although the correlations between the sulfur ADPs and the scale factor in (II) are of a similar magnitude, the magnitudes of the correlations between individual components of the ADPs are greater; for example, the largest correlation in (II) is 0.809 between  $U_{33}(\text{O14})$  and  $U_{13}(\text{O14})$  compared with  $-0.080$  in (I). Correlations between the positional parameters are also affected; though the changes are smaller, the effects are visible by comparing the s.u. values for derived parameters calculated with and without covariances. Since only the variances are included in the CIF, this was easily achieved using *PLATON* (Spek, 2009). Table 3 shows the bond lengths with s.u. values for (I) and (II), and it is clear that the bond lengths are very similar<sup>1</sup> in both cell settings whether determined by *PLATON* or *CRYSTALS*. The s.u. values for all the C—C and C—O bonds are also consistent for (I) and (II) calculated from the full variance-covariance matrix, and calculations using only the variances give a good estimate of the s.u. values for (I). However, the corresponding s.u. calculations for (II) are less reliable when the covariances are excluded. This effect is most

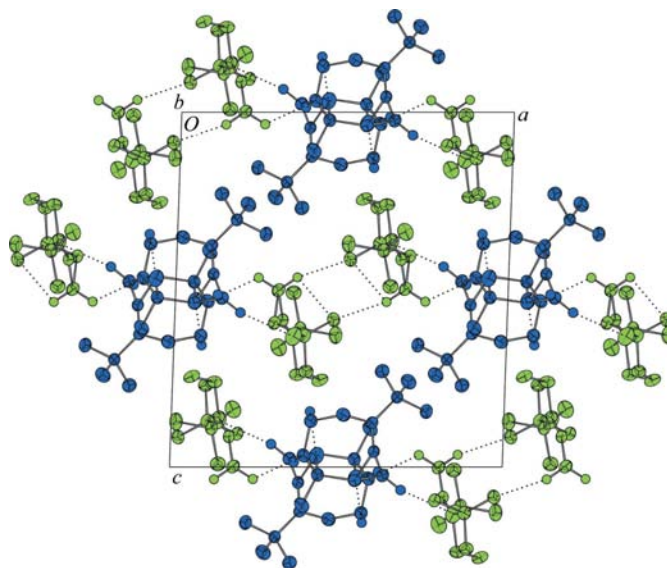


Figure 2

The crystal packing, viewed down the  $b$  axis, showing the layers. (The residues containing atoms S1 and S101 are shown in green and blue, respectively, in the electronic version of the paper.) C—H...O interactions are shown as dotted lines.

apparent where the bond is predominantly parallel to the  $a$  axis (which is unaffected by the cell transformation) where the s.u. values are nearly doubled (e.g. S101—N108, C104—C105 and C10—C13).

In conclusion, analysis of this unusual methylene aziridine has demonstrated the effect of excluding the covariances from calculations of the s.u. values and shown how this effect is enhanced for monoclinic structures in a unit-cell setting where  $\beta$  deviates significantly from  $90^\circ$ . Additionally, the increase in the correlation due to the oblique cell setting is apparent, and although there are no obvious consequences in this case, this could give rise to refinement difficulties for more complex structures.

Experimental

The title compound was crystallized by evaporation from a saturated solution in diethyl ether. NMR (100 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_C$  27.9 [ $\text{C}(\text{CH}_3)_3$ ], 28.0 ( $=\text{CCH}_2$ ), 35.3 [ $\text{C}(\text{CH}_3)_3$ ], 40.2 ( $\text{NCH}_2$ ), 75.3 ( $\text{OCH}_2$ ), 114.9 ( $\text{NC}=\text{C}$ ), 126.4 ( $\text{NC}=\text{C}$ ). In the  $^1\text{H}$  NMR at room temperature, very broad peaks are found for the C5 methylene H atoms and a broad peak contains the signals for both the C9 methylene H atoms [(400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta_H$  2.45 and 2.88 ( $2 \times 1\text{H}$ ,  $2 \times br\ s$ ,  $\text{OCH}_2\text{CH}_2$ ), 3.44 ( $2\text{H}$ ,  $br\ s$ ,  $\text{NCH}_2$ )]. Once the temperature was reduced to 228 K four distinct signals resolved, indicating that conformational change at room temperature is slow on an NMR timescale. Complete data at 228 K (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta_H$  1.11 [ $9\text{H}$ ,  $s$ , ( $\text{CH}_3$ )<sub>3</sub>], 2.39 and 2.90 ( $1\text{H}$ ,  $d$ ,  $J = 14.3$  Hz, and  $1\text{H}$ ,  $app. t.$ ,  $J = 14.3$  Hz,  $\text{OCH}_2\text{CH}_2$ ), 3.45 and 3.53 ( $2 \times 1\text{H}$ ,  $2 \times br\ s$ ,  $\text{NCH}_2$ ), 4.48–4.57 ( $2\text{H}$ ,  $m$ ,  $\text{OCH}_2$ ). IR (thin film):  $\nu_{max}$  3075 ( $m$ ), 2968 ( $s$ ), 1468 ( $m$ ), 1359 ( $s$ ), 1296 ( $w$ ), 1261 ( $w$ ), 1183 ( $s$ )  $\text{cm}^{-1}$ . High resolution mass spectrometry (ESI+): found 240.0670;  $\text{C}_9\text{H}_{15}\text{NNaO}_3\text{S}$  ( $\text{MNa}^+$ ) requires 240.0665.

<sup>1</sup> Unit-cell and atomic parameters are held to full machine precision by the refinement software (*CRYSTALS*). Some of this precision is inevitably lost when these numbers are rounded by the 'rule of 19' during the generation of the CIF.

## Determination (I)

## Crystal data

$C_9H_{15}NO_3S$	$V = 2158.02 (9) \text{ \AA}^3$
$M_r = 217.29$	$Z = 8$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.8593 (3) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$b = 10.5242 (2) \text{ \AA}$	$T = 150 \text{ K}$
$c = 14.8044 (4) \text{ \AA}$	$0.32 \times 0.26 \times 0.16 \text{ mm}$
$\beta = 92.0014 (7)^\circ$	

## Data collection

Nonius KappaCCD diffractometer	19529 measured reflections
Absorption correction: multi-scan ( <i>DENZO/SCALEPACK</i> ; Otwinowski & Minor, 1997)	4913 independent reflections 3768 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.81$ , $T_{\max} = 0.96$	$R_{\text{int}} = 0.041$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	253 parameters
$wR(F^2) = 0.123$	H-atom parameters constrained
$S = 0.94$	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
4913 reflections	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

## Determination (II)

## Crystal data

$C_9H_{15}NO_3S$	$V = 2158.07 (7) \text{ \AA}^3$
$M_r = 217.29$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.8594 (2) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$b = 10.5243 (2) \text{ \AA}$	$T = 150 \text{ K}$
$c = 19.9230 (3) \text{ \AA}$	$0.32 \times 0.26 \times 0.16 \text{ mm}$
$\beta = 132.0439 (7)^\circ$	

Table 1

Bond lengths for the methylene aziridine refined in  $P2_1/n$  [determination (I)] and  $P2_1/c$  [determination (II)] calculated with *CRYSTALS* and with *PLATON*.

	(I)	(II)	(I), excluding covariances	(II), excluding covariances
S1—O2	1.4271 (16)	1.4278 (17)	1.4272 (17)	1.428 (2)
S1—O3	1.5569 (16)	1.5573 (16)	1.5570 (16)	1.5574 (16)
S1—N8	1.6524 (18)	1.6527 (18)	1.6523 (18)	1.653 (3)
S1—O14	1.4182 (16)	1.4189 (17)	1.4182 (17)	1.4189 (19)
O3—C4	1.476 (3)	1.476 (3)	1.476 (3)	1.477 (3)
C4—C5	1.515 (3)	1.517 (3)	1.515 (3)	1.517 (4)
C5—C6	1.521 (3)	1.521 (3)	1.521 (3)	1.521 (3)
C6—C7	1.317 (3)	1.318 (3)	1.318 (3)	1.318 (3)
C6—C10	1.525 (3)	1.522 (3)	1.525 (3)	1.522 (3)
C7—N8	1.445 (3)	1.447 (3)	1.445 (3)	1.447 (3)
C7—C9	1.439 (3)	1.440 (3)	1.439 (3)	1.440 (3)
N8—C9	1.540 (3)	1.540 (3)	1.540 (3)	1.540 (3)
C10—C11	1.532 (3)	1.533 (3)	1.532 (3)	1.533 (3)
C10—C12	1.538 (3)	1.540 (3)	1.538 (3)	1.540 (4)
C10—C13	1.528 (3)	1.529 (3)	1.528 (3)	1.528 (6)
S101—O103	1.5628 (16)	1.5628 (16)	1.5628 (16)	1.5629 (19)
S101—N108	1.6577 (18)	1.6571 (19)	1.6576 (19)	1.657 (3)
S101—O114	1.4200 (18)	1.4204 (18)	1.4201 (19)	1.420 (2)
S101—O102	1.4252 (18)	1.4262 (19)	1.4252 (18)	1.4262 (19)
O103—C104	1.475 (3)	1.474 (3)	1.475 (3)	1.474 (3)
C104—C105	1.515 (3)	1.514 (3)	1.515 (3)	1.514 (5)
C105—C106	1.525 (3)	1.525 (3)	1.525 (3)	1.524 (4)
C106—C107	1.317 (3)	1.316 (3)	1.318 (3)	1.316 (3)
C106—C110	1.518 (3)	1.519 (3)	1.518 (3)	1.520 (4)
C107—N108	1.444 (3)	1.445 (3)	1.444 (3)	1.445 (3)
C107—C109	1.445 (3)	1.445 (3)	1.444 (3)	1.445 (3)
N108—C109	1.535 (3)	1.535 (3)	1.534 (3)	1.535 (4)
C110—C113	1.534 (3)	1.535 (3)	1.532 (3)	1.535 (3)
C110—C111	1.532 (3)	1.532 (3)	1.532 (3)	1.532 (4)
C110—C112	1.533 (3)	1.532 (3)	1.534 (3)	1.532 (3)

Table 2

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

The values from the refinement in  $P2_1/n$  are given first, followed by the values from the  $P2_1/c$  refinement.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H92 $\cdots$ O2 <sup>i</sup>	0.98/0.98	2.43/2.43	3.294 (3)/3.294 (3)	147/147
C9—H91 $\cdots$ O103	0.98/0.98	2.57/2.57	3.202 (3)/3.203 (3)	122/122
C109—H1092 $\cdots$ O102 <sup>ii</sup>	0.97/0.97	2.54/2.54	3.474 (3)/3.473 (3)	162/162
C109—H1091 $\cdots$ O14 <sup>iii</sup>	0.97/0.97	2.49/2.49	3.434 (3)/3.433 (3)	165/165
C104—H1042 $\cdots$ O3 <sup>iv</sup>	0.99/0.99	2.69/2.69	3.654 (3)/3.654 (3)	165/165

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x, -y, -z + 1$ ; (iii)  $-x, -y + 1, -z + 1$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .

Table 3

Largest correlations between refined parameters in determinations (I) and (II).

Parameters	Correlation in (I)	Correlation in (II)
Largest correlations in (I)		
OSF $U_{11}(S1)$	0.365	0.317
OSF $U_{22}(S1)$	0.361	0.310
OSF $U_{33}(S1)$	0.353	0.312
OSF $U_{11}(S10)$	0.357	0.307
OSF $U_{22}(S10)$	0.343	0.297
OSF $U_{33}(S10)$	0.354	0.307
Largest correlations in (II)		
$U_{11}(C13) U_{13}(C13)$	0.010	0.801
$U_{33}(C13) U_{13}(C13)$	0.023	0.805
$U_{11}(O14) U_{13}(O14)$	-0.091	0.804
$U_{33}(O14) U_{13}(O14)$	-0.080	0.809
$U_{11}(C111) U_{13}(C111)$	0.004	0.781
$U_{33}(C111) U_{13}(C111)$	0.002	0.782
$U_{11}(O102) U_{13}(O102)$	-0.042	0.795
$U_{33}(O102) U_{13}(O102)$	-0.034	0.797

Note: OSF is the overall scale factor.

## Data collection

Nonius KappaCCD diffractometer	9037 measured reflections
Absorption correction: multi-scan ( <i>DENZO/SCALEPACK</i> ; Otwinowski & Minor, 1997)	4913 independent reflections 3769 reflections with $I > 2.0\sigma(I)$
$T_{\min} = 0.81$ , $T_{\max} = 0.96$	$R_{\text{int}} = 0.026$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	253 parameters
$wR(F^2) = 0.120$	H-atom parameters constrained
$S = 0.94$	$\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
4913 reflections	$\Delta\rho_{\text{min}} = -0.45 \text{ e \AA}^{-3}$

The H atoms were all located in a difference map, but were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry ( $C-H = 0.93-0.98 \text{ \AA}$ ) and  $U_{\text{iso}}(H)$  values (in the range 1.2–1.5 times  $U_{\text{eq}}$  of the parent atom), after which the positions were refined with riding constraints. For both (I) and (II), a Chebychev polynomial weighting scheme was applied (Watkin, 1994; Prince, 1982).

For both determinations, data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) for (I); structure transformed from solution to (I) for (II). For both compounds, program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*,

2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3085). Services for accessing these data are described at the back of the journal.

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