

**(1'S,2R,3R)-3-(1'-tert-Butyldimethylsilyloxy-1'-phenylmethyl)-2-(4''-methylphenylthio)-2-nitrooxirane****William Clegg\* and Mark R. J. Elsegood†**School of Natural Sciences (Chemistry),  
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**Key indicators**

Single-crystal X-ray study

T = 160 K

Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$ 

R factor = 0.036

wR factor = 0.085

Data-to-parameter ratio = 19.5

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{22}\text{H}_{29}\text{NO}_4\text{Si}$ , displays an anomeric effect in the marked shortening of one C—O bond relative to the other in the oxirane ring, concomitantly weakening the C—S bond to the arylthio substituent. This correlates with the selective reactivity of nucleophiles at the C atom having the longer C—O bond. The absolute configuration has been determined from anomalous scattering effects.

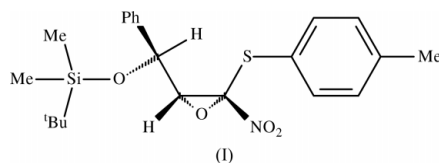
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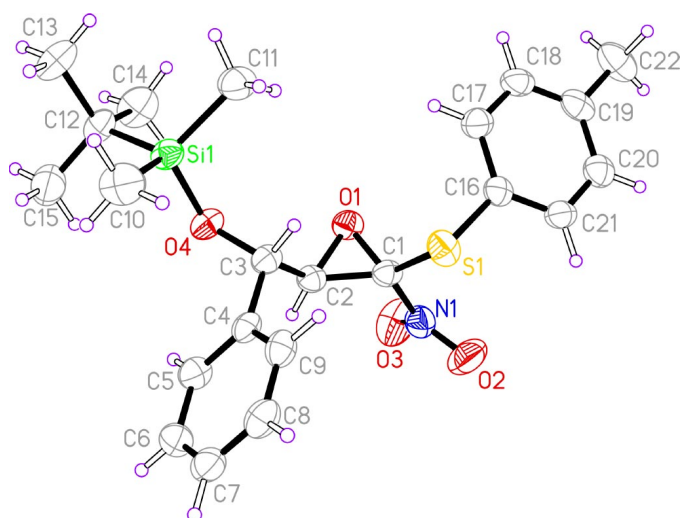
**Comment**

The title compound, (I), was prepared as one of a series of (aryltio)nitrooxiranes during the development of stereoselective syntheses of protected  $\beta$ -hydroxy- $\alpha$ -amino acids (Adams *et al.*, 1999). The original purpose of the crystal structure determination was to establish the relative stereochemistry of the epoxide ring and the adjacent C atom bearing the phenyl and protected hydroxyl groups, in order to demonstrate the stereoselectivity of the synthetic procedures. In fact, the Si and S atoms in the molecule provide sufficient anomalous scattering to enable the absolute configuration to be determined unambiguously, and it is shown in Fig. 1. It is as expected from the starting material used in the synthesis.



Further interest in the structure arises from the electronic effects of the nitro and arylthio substituents on the bond lengths of the epoxide ring. We have recently shown that a marked asymmetry in the C—O bond lengths of such rings in a number of substituted oxiranes can be ascribed to a generalized anomeric effect, in which a lone pair of electrons on the ring O atom interacts with the antibonding orbital associated with the bond to the heteroatom substituent (here the arylthio group), thus weakening this bond and strengthening the corresponding ring C—O bond (Jackson *et al.*, 2003). This effect is particularly marked with (aryltio)nitrooxiranes, and is believed to be responsible for the selective reaction of these oxiranes with nucleophiles at the C atom having the longer C—O bond.

A search of the Cambridge Structural Database (Version 5.24 plus two updates, June 2003; Allen, 2002) provides known structures for five oxiranes with a nitro substituent (Bowman *et al.*, 1991; Hartshorn *et al.*, 1983; Jackson *et al.*, 1995; Szarek *et al.*, 1988) and five oxiranes with an alkylthio or arylthio



**Figure 1**

The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

substituent (Hewkin *et al.*, 1991; Jackson *et al.*, 1995; Krishnakumar *et al.*, 2002; Valle *et al.*, 1988), two of these structures having both types of substituent. The title compound is thus the third structurally characterized example of an (arythio)-nitroxirane. In all of these structures, the C—O bond adjacent to the nitro and/or thio substituent is shortened relative to the other C—O bond, though the difference is much more marked in some cases than in others.

Of the three (arythio)nitroxiranes, the shorter C—O bond of the title compound, adjacent to the nitro and arylthio substituents, has essentially the same length as those in the other two structures [C1—O1 = 1.391 (2) Å, compared with 1.398 (7) and 1.394 (2) Å], but the longer C—O bond is somewhat shorter than the corresponding bond in the other two structures [C2—O1 = 1.448 (2) Å, compared with 1.463 (6) and 1.466 (2) Å]. This fact correlates well with the fact that the title compound is by far the least reactive towards nucleophiles; for example, it requires treatment at 353 K for 6 h with aqueous ammonia, whereas the other compounds react completely within 2 h at room temperature (Jackson, 2003). This is further evidence that the ground-state molecular geometry, resulting from the anomeric effect, influences reactivity, although the larger steric bulk of the substituents in the title compound may also contribute.

## Experimental

The synthesis and spectroscopic characterization of the title compound have been fully described by Adams *et al.* (1999).

### Crystal data

C<sub>22</sub>H<sub>29</sub>NO<sub>4</sub>SSi  
*M<sub>r</sub>* = 431.61  
 Monoclinic, *P*2<sub>1</sub>  
*a* = 10.0904 (12) Å  
*b* = 8.9428 (11) Å  
*c* = 13.1503 (16) Å  
 $\beta$  = 95.531 (3)°  
*V* = 1181.1 (2) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.214 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 5503 reflections  
 $\theta$  = 2.4–28.6°  
 $\mu$  = 0.21 mm<sup>-1</sup>  
*T* = 160 (2) K  
 Block, colourless  
 0.51 × 0.38 × 0.35 mm

### Data collection

Bruker SMART 1K CCD diffractometer  
 Thin-slice  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
*T<sub>min</sub>* = 0.90, *T<sub>max</sub>* = 0.93  
 7705 measured reflections

5239 independent reflections  
 4405 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.020  
 $\theta_{\max}$  = 28.9°  
*h* = −9 → 13  
*k* = −11 → 12  
*l* = −14 → 17

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.036  
*wR*(*F*<sup>2</sup>) = 0.085  
*S* = 0.98  
 5239 reflections  
 268 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.24 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$   
 Absolute structure: Flack (1983),  
 2251 Friedel pairs  
 Flack parameter = 0.05 (6)

**Table 1**

Selected geometric parameters (Å, °).

C1—O1	1.391 (2)	C2—C3	1.515 (3)
C2—O1	1.448 (2)	N1—O2	1.212 (2)
C1—C2	1.470 (3)	N1—O3	1.207 (2)
C1—N1	1.540 (2)	S1—C16	1.777 (2)
C1—S1	1.7656 (19)		
C1—O1—C2	62.31 (12)	O1—C2—C1	56.93 (11)
O1—C1—C2	60.76 (12)	O1—C2—C3	117.80 (15)
O1—C1—N1	111.64 (15)	C1—C2—C3	122.46 (16)
O1—C1—S1	119.93 (13)	C1—N1—O2	117.32 (18)
C2—C1—N1	114.05 (15)	C1—N1—O3	117.29 (17)
C2—C1—S1	125.27 (14)	O2—N1—O3	125.35 (19)
N1—C1—S1	114.21 (13)	C1—S1—C16	98.39 (8)

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with *U<sub>iso</sub>* constrained to be 1.2 (1.5 for methyl groups) times *U<sub>eq</sub>* of the carrier atom.

Data collection: SMART (Bruker, 2001); cell refinement: local programs; data reduction: SAINT (Bruker, 2001); program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

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