(3RS,4RS,4aSR,7SR,9aRS)-7-*tert*-Butyl-9a-methyl-5,5-dioxo-3,4-epoxy-1,2,3,4,-4a,9a-hexahydro-8-oxa-5λ⁶-thiabenzocycloheptan-9-one

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The sterochemistry of the title epoxide, $C_{14}H_{22}O_5S$, has been established by single-crystal X-ray diffraction. The compound exhibits an unusually short intermolecular C—H···O contact of 2.30 Å between the epoxide O atom and the epoxide C—H unit of a neighbouring molecule.

Comment

As detailed in an earlier series of articles (Zeller *et al.*, 2004*a*,*b*,*c*,*d*, 2006*a*,*b*,*c*; Chumachenko *et al.*, 2005), two of the current authors (NC and PS) have been exploring the potential utility of sulfone-based tethers in intramolecular Diels–Alder cycloaddition reactions. This has resulted in the preparation of a series of bicyclic β-acyloxy sulfone cyclo-adducts. Epoxidation of the alkene group of one of these products, (4a*RS*,7*SR*,9a*RS*)-7-*tert*-butyl-9a-methyl-5,5-dioxo-1,2,4a,9a-tetrahydro-8-oxa-5λ⁶-thiabenzocycloheptan-9-one, (I), with *m*-CPBA (*m*-chloroperoxybenzoic acid) in dichloromethane for 5 d at room temperature produces a 1:1 mixture of diastereomeric epoxides, (II) and (III). Both products are crystalline materials and have sufficiently different R_f values [0.65 for (III) and 0.32 for (II) in EtOAc–hexanes 2:1] to be easily separated by column chromatography. Nuclear Overhauser effect experiments did not allow for a definitive assignment of the relative stereochemistry of the epoxide rings. However, crystals of diastereomer (II) were suitable for single-crystal diffraction and the results are presented here.
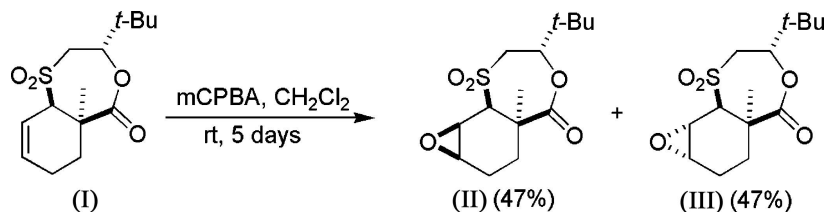
The title compound, (II), crystallizes in the monoclinic space group $P2_1/n$ as a racemic mixture of both enantiomers. The cyclohexane ring adopts a sofa-like conformation; only atom C1 is non-coplanar with the other atoms of the six-membered ring. The r.m.s. fit for the plane defined by atoms C2, C3, C4 and C4a is 0.0622 Å and the deviation of atom C1 from the least-squares plane is 0.646 (2) Å. For the atoms defining the plane, the largest deviation is 0.082 (1) Å for atom C4a. The angles at the epoxy ring C atoms are 121.93 (13)° for C4—C3—C2 and 123.39 (13)° for C4a—C4—C3 (Fig. 1). The seven-membered ring displays an irregular chair-like conformation, and the sterically demanding *tert*-butyl group at C7 is located in a pseudo-equatorial position.
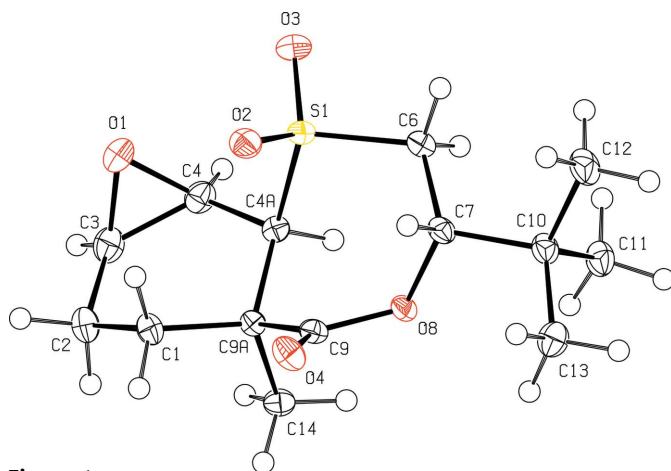
Figure 1
The molecular structure of (II), showing 50% probability displacement ellipsoids.

When compared with the alkene starting material, (I) (Zeller *et al.*, 2006*b*), the conformation and overall shape of epoxide (II) are basically unchanged. A molecular fit of the two molecules (I) and (II), excluding the epoxide O atom, yields an r.m.s. deviation of only 0.0592 Å.

In contrast, the packing arrangements for both compounds are quite different. For alkene (I), no significant inter-molecular interactions have been observed. In the case of compound (II), on the other hand, the epoxide O atom is in close contact with a C—H bond of the epoxide unit of a neighbouring molecule, thus forming an infinite chain of C—H⋯O linked molecules aligned parallel to the *b* axis. The distance between atoms H3 and O1^i (2.30 Å) is unusually short [C3⋯O1^i = 3.247 (2) Å and C3—H3⋯O1^i = 159°; symmetry code: (i) $-\frac{1}{2} - x$, $y + \frac{1}{2}$, $\frac{1}{2} - z$]. Out of 831 1,2-disubstituted epoxides listed in the Cambridge Structural Database (Version 5.27 plus one update; Allen, 2002), only 11 exhibit C—H⋯O (epoxide) distances shorter than 2.31 Å. The smallest value, found for two examples, is 2.25 Å (Park *et al.*, 2004; Immel *et al.*, 2000), which is only 0.05 Å shorter than observed for (II). Thus, the extremely short intermolecular contact observed for compound (II) seems to be at least part of the driving force favouring the observed packing pattern over other alternative arrangements.

Experimental

A solution of the starting material, (4a*RS*,7*SR*,9a*RS*)-7-*tert*-butyl-9a-methyl-5,5-dioxo-1,2,4a,9a-tetrahydro-8-oxa-5λ^6-thiabenzocyclo-heptan-9-one, (I) (0.573 g, 2.00 mmol, 1 equivalent), and *m*-CPBA (65%, 1.32 g, *ca* 5 mmol, 2.5 equivalents) in dichloromethane (20 ml) was stirred for 5 d, diluted with dichloromethane (30 ml) and treated with saturated aqueous Na$_2$SO$_3$ (7 ml). The layers were separated and the organic layer was washed with water (2 × 20 ml) and dried over MgSO$_4$, and the solvent was evaporated *in vacuo*. Epoxide (II) (0.28 g, 0.93 mmol, 47%) and the diastereomeric epoxide, (III) (0.28 g, 0.93 mmol, 47%), were separated by column chromatography [for (II), R_F (EtOAc–hexanes, 2:1) = 0.32; for (III), R_F (EtOAc–hexanes, 2:1) = 0.65] as white solids [for (II), m.p. 458 K; for (III), m.p. 471–472 K]. Detailed spectroscopic data for (II) and (III) will be

reported elsewhere. Single crystals of (II) were grown from a concentrated solution in ethyl acetate. The crystals are slightly corrugated and appear to be either colourless or milky, depending on the direction of viewing.

Crystal data

C$_{14}$H$_{22}$O$_5$S	$D_x = 1.360$ Mg m^{-3}
$M_r = 302.38$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 6709
$a = 11.9812$ (9) Å	reflections
$b = 5.6631$ (4) Å	$\theta = 2.8$–30.5°
$c = 21.7870$ (17) Å	$\mu = 0.24$ mm^{-1}
$\beta = 92.099$ (1)°	$T = 100$ (2) K
$V = 1477.27$ (19) Å^3	Block, colourless
$Z = 4$	0.52 × 0.46 × 0.41 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3659 independent reflections
ω scans	3423 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.033$
(*SADABS* in *SAINT-Plus*;	$\theta_{max} = 28.3°$
Bruker, 2003)	$h = -15 \rightarrow 15$
$T_{min} = 0.722$, $T_{max} = 0.908$	$k = -7 \rightarrow 7$
14255 measured reflections	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.8178P]$
$wR(F^2) = 0.120$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
3659 reflections	$\Delta\rho_{max} = 0.69$ e Å^{-3}
185 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters constrained	

All H atoms were positioned geometrically, with C—H distances in the range 0.98–1.0 Å. They were refined with U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(C) for all others. Methyl H atoms were allowed to rotate to best fit the experimental data. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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