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tert-Butyl (7*R*)-7-[(4*S*)-2,2-dimethyl-[1,3]dioxolan-4-yl]-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate

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The title compound, $C_{17}H_{29}NO_6$, crystallizes with two molecules in the asymmetric unit. The independent molecules differ in the conformation of the side chain attached to nitrogen. The piperidine ring adopts a chair conformation, with the 1,3-dioxolane ring occupying an axial position.

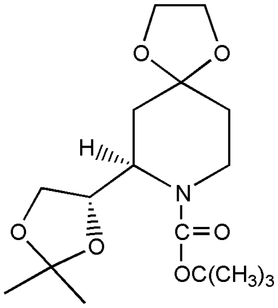
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.049
wR factor = 0.119
Data-to-parameter ratio = 7.6

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

Comment

Some time ago, we reported the asymmetric hetero-Diels–Alder reaction of (*R*)-2,3-di-*O*-benzylglyceraldehyde (*S*)-*N*-α-methylbenzylimine with Danishefsky's diene as a new approach to piperidine building blocks. When this reaction was carried out in acetonitrile and in the presence of ZnI_2, the corresponding 4-piperidinone was obtained as a single diastereoisomer (Badorrey *et al.*, 1999). The absolute configuration at the newly formed stereogenic centre was determined by conversion of the resulting product to *tert*-butyl-(7*R*)-7-[(1*S*)-1,2-dihydroxyethyl]-1,4-dioxa-8-azaspiro[4.5]-decane-8-carboxylate, which is an intermediate product in the synthesis of naturally occurring (*R*)-4-oxopipecolic acid (Badorrey *et al.*, 1997), and comparison of the measured specific rotation with the reported value.



(I)

The X-ray analysis of the title compound, (I), has been carried out in order to determine unambiguously the configuration at the asymmetric carbon formed in the above-mentioned hetero-Diels–Alder reaction. Compound (I) crystallizes with two molecules (*A* and *B*) in the asymmetric unit. X-ray analysis confirms the previously assigned stereochemistry at the asymmetric carbon of the piperidine ring. The *R* configuration is deduced from the known *S* stereochemistry of the chiral centre at C8 for conformer *A* or C25 for conformer *B*; this originates from (*R*)-2,3-di-*O*-benzylglyceraldehyde.

The two independent molecules differ substantially in the conformation of the *tert*-butoxycarbonyl group in relation to

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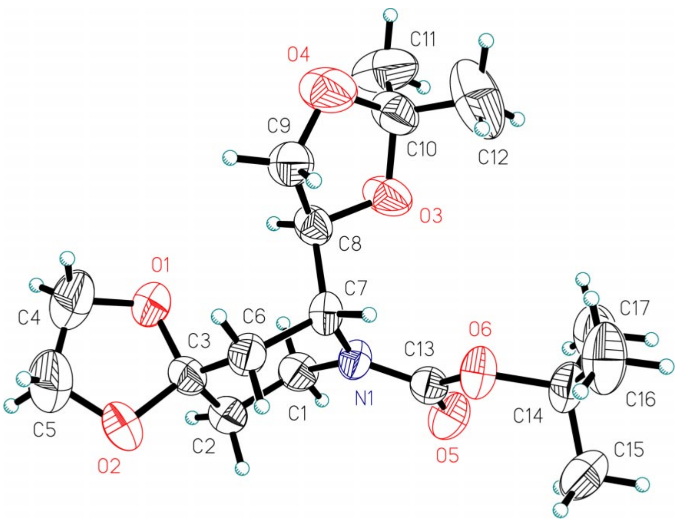

Figure 1
The molecular structure of the independent molecule *A*, showing 50% probability displacement ellipsoids.

the piperidine ring. In both comformers, the urethane linkage is found in its usual planar conformation. However, the *tert*-butoxy group in molecule *A* adopts a spatial disposition *cis* relative to the asymmetric carbon of the piperidine ring attached to the 1,3-dioxolane ring; in contrast, the same group in molecule *B* adopts a *trans* disposition. The spiro-fused 1,3-dioxolane ring in molecule *A* is found in an envelope conformation, with atom O1 deviating by 0.248 (3) Å from the plane formed by the remaining four ring atoms. The 1,3-dioxolane ring bonded to C7 adopts a half-chair conformation, twisted about the C8—C9 bond. On the other hand, both 1,3-dioxolane rings in molecule *B* adopt half-chair conformations, twisted about the bonds C20—O8 and C26—O10, respectively.

In both independent molecules, the piperidine ring adopts similar chair conformations and the substituent at position 7 is found to be in the axial conformation.

The values of bond lengths and angles lie within the expected ranges. In the crystal structure, there are some possible borderline cases of C—H···O hydrogen bonds (Table 2).

Experimental

Compound (I) was prepared according to the following procedure: to a solution of *tert*-butyl (7*R*)-7-[(1*S*)-1,2-dihydroxyethyl]-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxylate (Badorrey *et al.*, 1999) (100 mg) in acetone (10 ml) and 2,2-dimethoxypropanone (2 ml) was added *p*-toluenesulfonic acid monohydrate (5 mg), and the mixture was stirred at room temperature for 4 h. The reaction mixture was treated with 1% aqueous sodium bicarbonate and extracted with methylene chloride. The organic phase was dried over anhydrous magnesium sulfate and evaporated to dryness. The title compound was purified by column chromatography, using ethyl ether as eluent. Crystals were obtained by slow evaporation of a methanol solution.

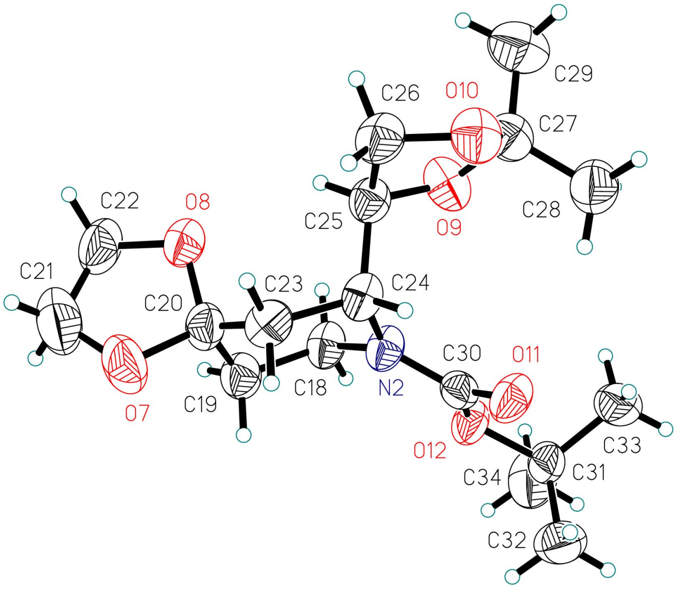

Figure 2
The molecular structure of the independent molecule *B*, showing 50% probability displacement ellipsoids.

Crystal data

$C_{17}H_{29}NO_6$
$M_r = 343.41$
Triclinic, $P\bar{1}$
$a = 9.641\ (1)$ Å
$b = 9.997\ (1)$ Å
$c = 11.042\ (1)$ Å
$\alpha = 84.77\ (1)^\circ$
$\beta = 69.72\ (1)^\circ$
$\gamma = 69.59\ (1)^\circ$
$V = 935.1\ (2)$ Å^3

$Z = 2$
$D_x = 1.220$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 7.2$–12.5°
$\mu = 0.09$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.44 × 0.32 × 0.28 mm

Data collection

Siemens *P*4 diffractometer
ω–2θ scans
Absorption correction: none
3913 measured reflections
3277 independent reflections
2068 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$

$\theta_{\rm max} = 25.0^\circ$
$h = -1 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 13$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.119$
$S = 0.97$
3277 reflections
433 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.1664P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}

Table 1
Selected torsion angles (Å).

C7—N1—C13—O6	7.0 (6)	C18—N2—C24—C25	−70.7 (5)
C1—N1—C13—O6	−177.3 (4)	C1—N1—C7—C8	−70.5 (5)
C24—N2—C30—O12	−173.4 (4)	C8—C7—C6—C3	76.0 (5)
C18—N2—C30—O12	3.8 (7)	C25—C24—C23—C20	74.5 (5)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H2$B\cdots$O9^{i}	0.97	2.45	3.409 (6)	171
C5—H5$A\cdots$O5^{ii}	0.97	2.59	3.383 (10)	139
C18—H18$B\cdots$O2^{iii}	0.97	2.72	3.643 (7)	158
C22—H22$A\cdots$O11^{ii}	0.97	2.59	3.266 (7)	127
C26—H26$A\cdots$O3	0.97	2.70	3.558 (7)	148

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

Owing to the absence of significant anomalous scatterers, the absolute configuration could not be determined [Flack (1983) parameter = 0.2 (15), 636 Friedel pairs]; accordingly, Friedel pairs were merged for the final refinement. H atoms were fixed at ideal positions and during the refinement were allowed to ride on their carrier atoms. The isotropic displacement parameters of the H atoms were coupled to the equivalent isotropic displacement parameters of their carrier atoms [$U_{\rm iso}$(H) = $1.5U_{\rm eq}$($C_{\rm methyl}$) or $1.2U_{\rm eq}$(C)]. The software used for molecular geometry calculations was *PLATON* (Spek, 1999).

Data collection: *XSCANS* (Siemens, 1993); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1989); software used to prepare material for publication: *SHELXL*97.

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