IUCrData

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(5*R*,6*R*)-*rel*-9-*tert*-Butyl-*trans*-5,6-dimethoxy-6,7-dihydro-5*H*-benzocycloheptene

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Keywords: crystal structure; relative stereochemistry; acid-catalysed ring-opening.

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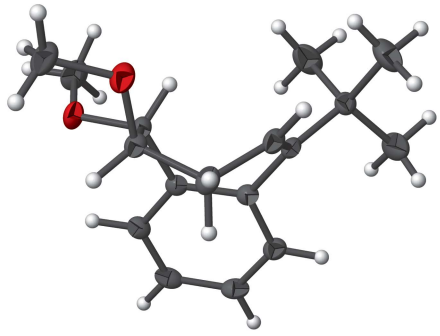
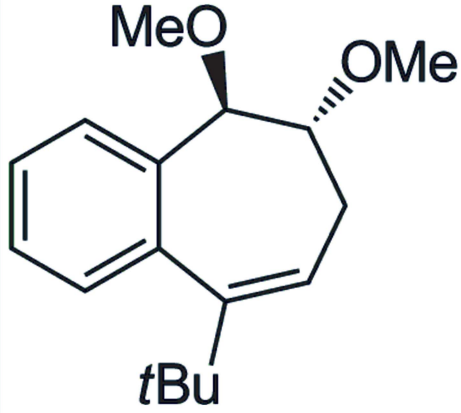
Structural data: full structural data are available from iucrdata.iucr.org

The relative stereochemistry of the title compound, $C_{17}H_{24}O_2$, has been confirmed by the X-ray analysis. The seven-membered ring is in a pseudo-boat conformation with both methoxy substituents in equatorial sites.

3D view



Chemical scheme



Structure description

In recent years, we have been investigating the acid-catalysed ring-opening reactions of cyclopropanated 7-oxabenzonorbornadienes with alcohols (Tigchelaar *et al.*, 2014). When bridgehead *tert*-butylated substrate **I** (Fig. 1) was reacted with methanol in the presence of catalytic *para*-toluenesulfonic acid, it was found that dihydro-5*H*-benzocycloheptene **II** was produced alongside methoxymethylnaphthalene **III**. The relative stereochemistry of the two methoxy groups in **II** was determined by this single-crystal X-ray analysis. Of the *cis* or *trans* isomers which were possible, the reaction was found to give solely the *trans* stereoisomer.

The molecular structure of the title compound is shown in Fig. 2. The seven-membered ring is in a psuedo-boat conformation with atom C3 at the prow and atoms C6 and C11 forming the stern. Both methoxy substituents are in equatorial sites.

Synthesis and crystallization

In a small screw-cap vial containing a stir-bar, cyclopropanated oxabenzonorbornadiene **I** (23.4 mg, 0.109 mmol, 1.0 equiv.) was dissolved in methanol (0.5 ml). The reaction was cooled to 273 K, and *p*-toluenesulfonic acid monohydrate (3.0 mg, 0.016 mmol, 0.1 equiv.) was added as a solid. The vial was sealed and heated to 313 K with continuous stirring for 48 h. The crude product was concentrated *in vacuo* and purified by column chromatography (EtOAc:hexanes=1:9), followed by static vacuum sublimation for two weeks over a 313–343 K gradient to give clear, colourless crystals of **II**.

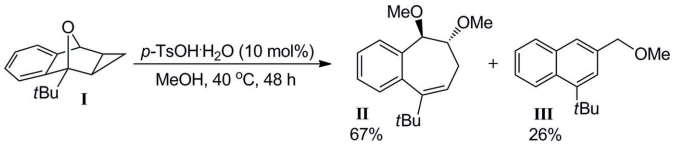


Figure 1
The reaction scheme.

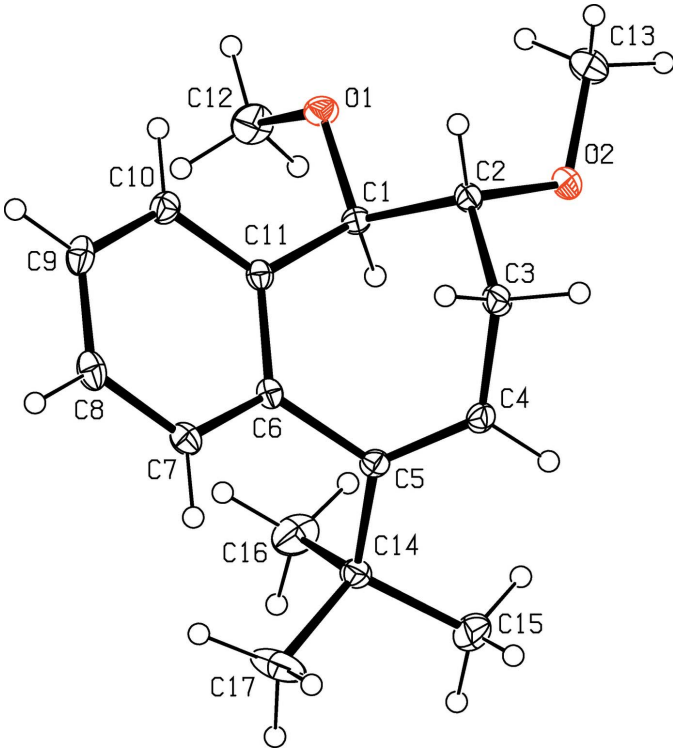


Figure 2
The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{24}O_2$
M_r	260.36
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	147
a, b, c (Å)	8.9716 (10), 9.5283 (10), 9.8080 (12)
α, β, γ (°)	80.493 (3), 73.205 (4), 69.547 (3)
V (Å^3)	750.14 (15)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.33 × 0.29 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEX DUO CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.723, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24158, 3493, 2784
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.654
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.104, 1.03
No. of reflections	3493
No. of parameters	176
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.24

Computer programs: *APEX2* (and *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Funding information

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full crystallographic data

IUCrData (2017). **2**, x171417 [https://doi.org/10.1107/S2414314617014171]

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Crystal data

$C_{17}H_{24}O_2$
$M_r = 260.36$
Triclinic, $P\overline{1}$
$a = 8.9716$ (10) Å
$b = 9.5283$ (10) Å
$c = 9.8080$ (12) Å
$\alpha = 80.493$ (3)°
$\beta = 73.205$ (4)°
$\gamma = 69.547$ (3)°
$V = 750.14$ (15) Å^3
$Z = 2$
$F(000) = 284$
$D_x = 1.153$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8137 reflections
$\theta = 2.5$–27.5°
$\mu = 0.07$ mm^{-1}
$T = 147$ K
Block, colourless
0.33 × 0.29 × 0.20 mm

Data collection

Bruker Kappa APEX DUO CCD diffractometer
Radiation source: sealed tube with Bruker Triumph monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min} = 0.723$, $T_{max} = 0.746$
24158 measured reflections
3493 independent reflections
2784 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.7°$, $\theta_{min} = 2.2°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.104$
$S = 1.03$
3493 reflections
176 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.3109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. H atoms were placed in calculated positions with C–H = 0.95–1.00 Å and included in the refinement with U_{iso}(H)=1.2U_{eq}(C) or 1.5U_{eq}(C_{methyl}).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.25107 (11)	1.06653 (9)	0.84723 (9)	0.0240 (2)
O2	0.02295 (10)	1.05373 (9)	0.68789 (10)	0.0265 (2)
C1	0.26686 (14)	0.93904 (12)	0.77944 (12)	0.0183 (2)
H1A	0.1975	0.8816	0.8461	0.022*
C2	0.19875 (14)	0.99851 (13)	0.64668 (13)	0.0196 (2)
H2A	0.2412	1.0820	0.5954	0.023*
C3	0.24839 (15)	0.87513 (13)	0.54445 (13)	0.0221 (3)
H3A	0.1786	0.9087	0.4758	0.027*
H3B	0.3639	0.8585	0.4895	0.027*
C4	0.23111 (14)	0.72916 (13)	0.62286 (13)	0.0208 (2)
H4A	0.1425	0.6991	0.6178	0.025*
C5	0.33519 (14)	0.64025 (12)	0.69922 (12)	0.0183 (2)
C6	0.47614 (14)	0.68980 (13)	0.70089 (12)	0.0182 (2)
C7	0.64007 (15)	0.60102 (14)	0.65369 (13)	0.0230 (3)
H7A	0.6641	0.5045	0.6225	0.028*
C8	0.76832 (15)	0.65192 (15)	0.65179 (14)	0.0260 (3)
H8A	0.8789	0.5897	0.6205	0.031*
C9	0.73536 (15)	0.79289 (15)	0.69531 (14)	0.0257 (3)
H9A	0.8229	0.8269	0.6959	0.031*
C10	0.57333 (15)	0.88461 (14)	0.73825 (13)	0.0219 (3)
H10A	0.5508	0.9822	0.7663	0.026*
C11	0.44351 (14)	0.83514 (13)	0.74073 (12)	0.0180 (2)
C12	0.2426 (2)	1.03586 (17)	0.99566 (14)	0.0348 (3)
H12A	0.2318	1.1271	1.0366	0.052*
H12B	0.1471	1.0027	1.0433	0.052*
H12C	0.3429	0.9566	1.0094	0.052*
C13	−0.04585 (17)	1.20808 (15)	0.71351 (17)	0.0341 (3)
H13A	−0.1653	1.2393	0.7278	0.051*
H13B	0.0006	1.2672	0.6313	0.051*
H13C	−0.0205	1.2246	0.7991	0.051*
C14	0.30606 (15)	0.50389 (13)	0.79729 (14)	0.0221 (3)
C15	0.15674 (19)	0.47157 (17)	0.78247 (18)	0.0381 (4)
H15A	0.0587	0.5590	0.8079	0.057*
H15B	0.1419	0.3842	0.8464	0.057*
H15C	0.1737	0.4507	0.6836	0.057*
C16	0.2732 (2)	0.54034 (18)	0.95218 (16)	0.0406 (4)
H16A	0.3647	0.5677	0.9628	0.061*
H16B	0.2628	0.4521	1.0166	0.061*
H16C	0.1712	0.6245	0.9760	0.061*
C17	0.45407 (19)	0.36098 (16)	0.7681 (2)	0.0488 (5)
H17A	0.5472	0.3735	0.7920	0.073*
H17B	0.4838	0.3423	0.6669	0.073*
H17C	0.4259	0.2757	0.8267	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0318 (5)	0.0196 (4)	0.0224 (4)	−0.0064 (4)	−0.0091 (4)	−0.0059 (3)
O2	0.0193 (4)	0.0208 (4)	0.0385 (5)	−0.0004 (3)	−0.0108 (4)	−0.0066 (4)
C1	0.0194 (6)	0.0168 (5)	0.0192 (6)	−0.0047 (4)	−0.0055 (4)	−0.0041 (4)
C2	0.0187 (6)	0.0182 (5)	0.0211 (6)	−0.0031 (4)	−0.0069 (5)	−0.0025 (4)
C3	0.0252 (6)	0.0207 (6)	0.0207 (6)	−0.0030 (5)	−0.0102 (5)	−0.0037 (5)
C4	0.0194 (6)	0.0207 (6)	0.0236 (6)	−0.0044 (4)	−0.0066 (5)	−0.0075 (5)
C5	0.0166 (5)	0.0173 (5)	0.0200 (6)	−0.0034 (4)	−0.0024 (4)	−0.0065 (4)
C6	0.0170 (5)	0.0194 (5)	0.0174 (5)	−0.0046 (4)	−0.0057 (4)	0.0004 (4)
C7	0.0197 (6)	0.0215 (6)	0.0242 (6)	−0.0031 (5)	−0.0047 (5)	−0.0013 (5)
C8	0.0160 (6)	0.0322 (7)	0.0254 (6)	−0.0041 (5)	−0.0047 (5)	0.0011 (5)
C9	0.0206 (6)	0.0363 (7)	0.0234 (6)	−0.0136 (5)	−0.0077 (5)	0.0029 (5)
C10	0.0235 (6)	0.0248 (6)	0.0201 (6)	−0.0103 (5)	−0.0073 (5)	0.0003 (5)
C11	0.0184 (5)	0.0200 (6)	0.0154 (5)	−0.0058 (4)	−0.0056 (4)	0.0007 (4)
C12	0.0471 (9)	0.0370 (8)	0.0219 (7)	−0.0116 (6)	−0.0093 (6)	−0.0090 (6)
C13	0.0282 (7)	0.0242 (7)	0.0445 (8)	0.0020 (5)	−0.0086 (6)	−0.0116 (6)
C14	0.0194 (6)	0.0187 (6)	0.0273 (6)	−0.0055 (4)	−0.0051 (5)	−0.0017 (5)
C15	0.0379 (8)	0.0361 (8)	0.0498 (9)	−0.0231 (6)	−0.0172 (7)	0.0074 (7)
C16	0.0574 (10)	0.0447 (9)	0.0275 (7)	−0.0300 (8)	−0.0095 (7)	0.0048 (6)
C17	0.0337 (8)	0.0187 (7)	0.0731 (12)	−0.0022 (6)	0.0057 (8)	0.0053 (7)

Geometric parameters (Å, º)

O1—C12	1.4218 (16)	C9—C10	1.3908 (18)
O1—C1	1.4248 (13)	C9—H9A	0.9500
O2—C13	1.4160 (15)	C10—C11	1.3939 (16)
O2—C2	1.4316 (14)	C10—H10A	0.9500
C1—C11	1.5218 (16)	C12—H12A	0.9800
C1—C2	1.5376 (16)	C12—H12B	0.9800
C1—H1A	1.0000	C12—H12C	0.9800
C2—C3	1.5334 (16)	C13—H13A	0.9800
C2—H2A	1.0000	C13—H13B	0.9800
C3—C4	1.5095 (17)	C13—H13C	0.9800
C3—H3A	0.9900	C14—C15	1.5252 (18)
C3—H3B	0.9900	C14—C17	1.5313 (18)
C4—C5	1.3388 (16)	C14—C16	1.5361 (19)
C4—H4A	0.9500	C15—H15A	0.9800
C5—C6	1.5014 (16)	C15—H15B	0.9800
C5—C14	1.5365 (17)	C15—H15C	0.9800
C6—C7	1.3997 (16)	C16—H16A	0.9800
C6—C11	1.4090 (16)	C16—H16B	0.9800
C7—C8	1.3907 (18)	C16—H16C	0.9800
C7—H7A	0.9500	C17—H17A	0.9800
C8—C9	1.3830 (19)	C17—H17B	0.9800
C8—H8A	0.9500	C17—H17C	0.9800

C12—O1—C1	113.00 (9)	C11—C10—H10A	119.6
C13—O2—C2	115.05 (10)	C10—C11—C6	119.80 (11)
O1—C1—C11	112.30 (9)	C10—C11—C1	120.67 (10)
O1—C1—C2	107.02 (9)	C6—C11—C1	119.47 (10)
C11—C1—C2	111.61 (9)	O1—C12—H12A	109.5
O1—C1—H1A	108.6	O1—C12—H12B	109.5
C11—C1—H1A	108.6	H12A—C12—H12B	109.5
C2—C1—H1A	108.6	O1—C12—H12C	109.5
O2—C2—C3	107.31 (9)	H12A—C12—H12C	109.5
O2—C2—C1	110.13 (10)	H12B—C12—H12C	109.5
C3—C2—C1	111.78 (9)	O2—C13—H13A	109.5
O2—C2—H2A	109.2	O2—C13—H13B	109.5
C3—C2—H2A	109.2	H13A—C13—H13B	109.5
C1—C2—H2A	109.2	O2—C13—H13C	109.5
C4—C3—C2	112.00 (10)	H13A—C13—H13C	109.5
C4—C3—H3A	109.2	H13B—C13—H13C	109.5
C2—C3—H3A	109.2	C15—C14—C17	107.98 (12)
C4—C3—H3B	109.2	C15—C14—C16	108.03 (12)
C2—C3—H3B	109.2	C17—C14—C16	108.57 (13)
H3A—C3—H3B	107.9	C15—C14—C5	111.73 (10)
C5—C4—C3	122.84 (11)	C17—C14—C5	112.59 (11)
C5—C4—H4A	118.6	C16—C14—C5	107.80 (10)
C3—C4—H4A	118.6	C14—C15—H15A	109.5
C4—C5—C6	116.82 (10)	C14—C15—H15B	109.5
C4—C5—C14	123.59 (11)	H15A—C15—H15B	109.5
C6—C5—C14	119.15 (10)	C14—C15—H15C	109.5
C7—C6—C11	118.47 (11)	H15A—C15—H15C	109.5
C7—C6—C5	122.24 (10)	H15B—C15—H15C	109.5
C11—C6—C5	119.11 (10)	C14—C16—H16A	109.5
C8—C7—C6	121.03 (11)	C14—C16—H16B	109.5
C8—C7—H7A	119.5	H16A—C16—H16B	109.5
C6—C7—H7A	119.5	C14—C16—H16C	109.5
C9—C8—C7	120.18 (11)	H16A—C16—H16C	109.5
C9—C8—H8A	119.9	H16B—C16—H16C	109.5
C7—C8—H8A	119.9	C14—C17—H17A	109.5
C8—C9—C10	119.61 (11)	C14—C17—H17B	109.5
C8—C9—H9A	120.2	H17A—C17—H17B	109.5
C10—C9—H9A	120.2	C14—C17—H17C	109.5
C9—C10—C11	120.85 (11)	H17A—C17—H17C	109.5
C9—C10—H10A	119.6	H17B—C17—H17C	109.5

C12—O1—C1—C11	−82.00 (13)	C6—C7—C8—C9	−0.77 (19)
C12—O1—C1—C2	155.18 (10)	C7—C8—C9—C10	−1.28 (19)
C13—O2—C2—C3	−147.34 (11)	C8—C9—C10—C11	1.29 (18)
C13—O2—C2—C1	90.77 (12)	C9—C10—C11—C6	0.74 (17)
O1—C1—C2—O2	−75.43 (11)	C9—C10—C11—C1	−176.41 (11)
C11—C1—C2—O2	161.33 (9)	C7—C6—C11—C10	−2.72 (17)
O1—C1—C2—C3	165.38 (9)	C5—C6—C11—C10	−177.88 (10)

C11—C1—C2—C3	42.13 (13)	C7—C6—C11—C1	174.46 (10)
O2—C2—C3—C4	−77.69 (12)	C5—C6—C11—C1	−0.69 (16)
C1—C2—C3—C4	43.16 (13)	O1—C1—C11—C10	−16.07 (15)
C2—C3—C4—C5	−73.62 (14)	C2—C1—C11—C10	104.12 (12)
C3—C4—C5—C6	−1.72 (17)	O1—C1—C11—C6	166.77 (10)
C3—C4—C5—C14	170.68 (11)	C2—C1—C11—C6	−73.04 (13)
C4—C5—C6—C7	−121.27 (13)	C4—C5—C14—C15	7.05 (17)
C14—C5—C6—C7	65.98 (15)	C6—C5—C14—C15	179.28 (11)
C4—C5—C6—C11	53.70 (15)	C4—C5—C14—C17	128.78 (14)
C14—C5—C6—C11	−119.05 (12)	C6—C5—C14—C17	−59.00 (16)
C11—C6—C7—C8	2.76 (18)	C4—C5—C14—C16	−111.50 (13)
C5—C6—C7—C8	177.75 (11)	C6—C5—C14—C16	60.73 (14)