

2,4-Dimethyl-6-phenyl-8-oxabicyclo[3.2.1]-
octan-3-oneChris Dockendorff, Mark
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The asymmetric unit of the title crystal structure, $C_{15}H_{18}O_2$, contains two independent molecules which have essentially the same conformation. Two independent one-dimensional chains are formed *via* weak C—H \cdots O hydrogen bonds. A further single weak C—H \cdots O interaction links the two types of chain, forming extended tapes running in the *a*-axis direction.

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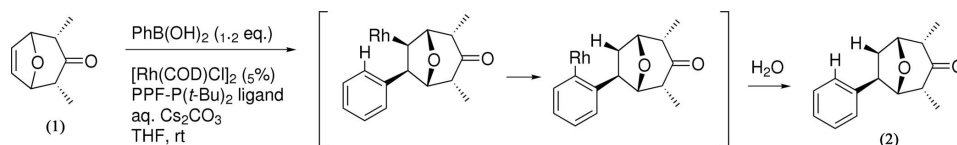
Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.049
 wR factor = 0.129
Data-to-parameter ratio = 10.4

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

Comment

The Rh^I -catalysed asymmetric ring-opening of oxabicyclic alkenes with boronic acid nucleophiles was reported several years ago (Lautens *et al.*, 2002). During efforts to expand the scope of this reaction, we discovered that, in some cases, unopened addition products are obtained, such as in the synthesis of the title compound, (2). The product is thought to occur *via* a 1,4-rhodium shift on to an adjacent aryl group, a mechanism supported by similar reactions performed in D_2O , which led to deuterium incorporation on the aryl group (Dockendorff, 2006). Oguma *et al.*, (2000) have reported a related pathway in the Rh^I -catalysed alkylation of phenylboronic acid with norbornene.



A view of the asymmetric unit of (2) is shown in Fig. 1. The two molecules in the asymmetric unit (*A* and *B*) have essentially the same conformation. Table 1 lists the pertinent torsion angles, which reflect the differences of the molecules with respect to any slight rotation of the phenyl ring about the C6—C10 bond. In the crystal structure, two independent one-dimensional $C(4)$ chains (Bernstein *et al.*, 1995) are formed *via* weak intermolecular C—H \cdots O interactions (Table 2), connecting molecules related by unit-cell translations in the *a*-axis direction. A single weak C—H \cdots O hydrogen bond links both types of chain, giving rise to fused $R_4^4(20)$ rings forming extended tapes in the *a*-axis direction (Fig. 2).

Experimental

A 5 ml flask was charged with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) (8.2 mg, 0.017 mmol), (*R*)-(*S*)-PPF-P(*t*-Bu) $_2$ [(*S*)-1-[(*R*)-2-diphenylphosphino]ferrocenyl]ethyl-di-*tert*-butylphosphine) (from Solvias Inc.; 18.2 mg, 0.033 mmol), phenylboronic acid (49 mg, 0.40 mmol) and the oxabicyclic (1) (prepared according to Lautens & Bouchain, 2002). A stirrer bar was added and the flask was sealed and

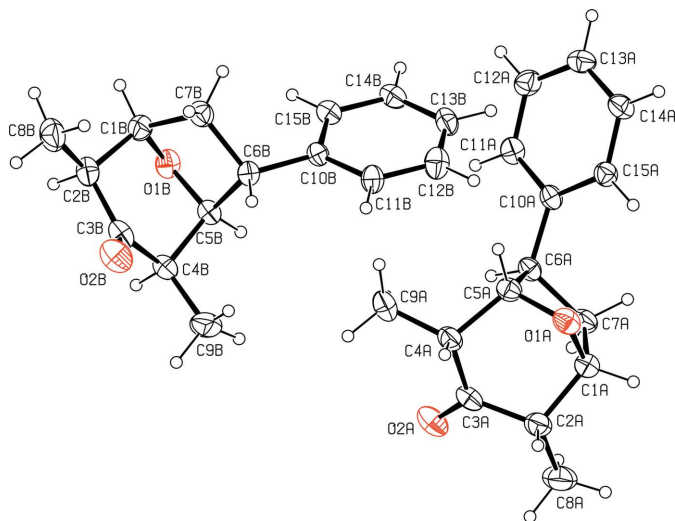


Figure 1
View of the two molecules (*A* and *B*) in the asymmetric unit of (2), showing 30% probability displacement ellipsoids (arbitrary spheres for H atoms).

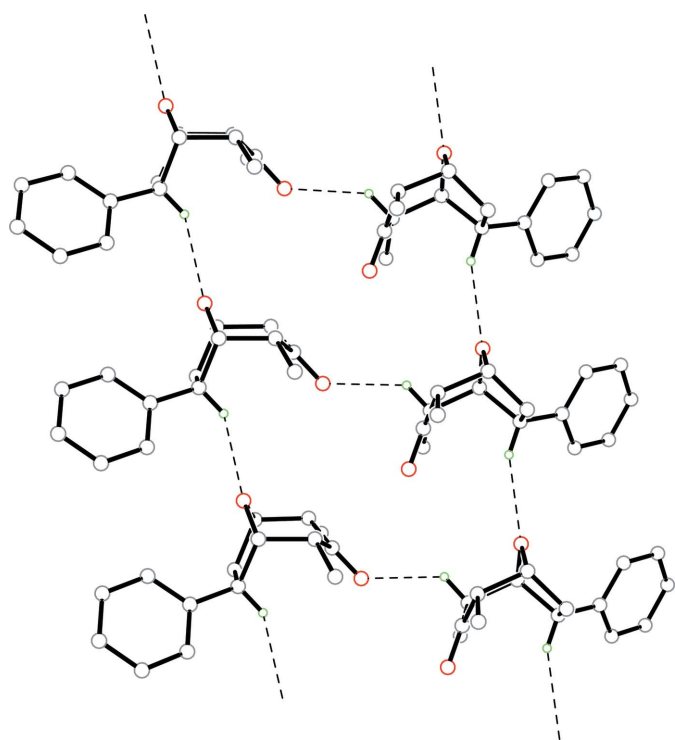


Figure 2
A partial packing plot (Spek, 2003) of (2), showing hydrogen bonds as dashed lines. The chain of molecule *A* is on the right-hand side. The hydrogen-bonded tapes propagate in the *a*-axis direction.

flushed with N₂ before distilled tetrahydrofuran (2 ml) and Cs₂CO₃ (5 M) in H₂O (34 μl, 0.17 mmol Cs₂CO₃) were added by syringe. The reaction was stirred for 20 h, after which time thin-layer chromatographic analysis (25% EtOAc/hexanes) indicated the reaction was complete. The solvent was then evaporated and the crude product was dissolved in CH₂Cl₂ and transferred on to a glass column packed with silica gel (1.3 cm × 20.3 cm) and eluted with 5–10% EtOAc–hexanes. Both opened and unopened phenyl adducts were well

separated, with the unopened product, (2), eluting first (yield 78%). X-ray quality crystals were obtained by dissolving (2) in hexanes and storing in a vial in a 258 K freezer.

Crystal data

C₁₅H₁₈O₂
M_r = 230.29
 Orthorhombic, *P*2₁2₁2₁
a = 5.5808 (3) Å
b = 14.8272 (6) Å
c = 30.3806 (17) Å
V = 2513.9 (2) Å³
Z = 8
D_x = 1.217 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 10473 reflections
 θ = 2.7–27.5°
 μ = 0.08 mm⁻¹
T = 150 (1) K
 Block, colourless
 0.27 × 0.20 × 0.17 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
 φ scans and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing 1995)
T_{min} = 0.743, *T_{max}* = 0.988
 10473 measured reflections

3223 independent reflections
 1912 reflections with *I* > 2σ(*I*)
R_{int} = 0.067
 θ_{max} = 27.5°
h = −7 → 7
k = −16 → 18
l = −39 → 39

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.129
S = 1.00
 3223 reflections
 311 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0596*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/ σ)_{max} < 0.001
 Δρ_{max} = 0.17 e Å⁻³
 Δρ_{min} = −0.19 e Å⁻³

Table 1

Selected torsion angles (°).

C7A–C6A–C10A–C15A	−53.1 (4)	C7B–C6B–C10B–C15B	−53.9 (4)
C7A–C6A–C10A–C11A	132.8 (3)	C7B–C6B–C10B–C11B	127.1 (3)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C4A–H4AA...O2B ⁱ	1.00	2.56	3.230 (4)	124
C6A–H6AA...O1A ⁱⁱ	1.00	2.55	3.452 (4)	150
C6B–H6BA...O1B ⁱⁱⁱ	1.00	2.54	3.395 (4)	144

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

H atoms were placed in calculated positions, with C–H distances ranging from 0.95 to 1.00 Å. They were included in the refinement in the riding-model approximation, with *U*_{iso}(H) = 1.2*U*_{eq}(C) or *U*_{iso}(H) = 1.5*U*_{eq}(C) for methyl H atoms. In the absence of significant anomalous dispersion effects, Friedel pairs were merged before refinement. Although we do not have direct proof of the absolute stereochemistry, it has been tentatively assigned by analogy with the [2.2.1] systems (Lautens *et al.*, 2002) and the absolute configuration of a related thiophenyl tetralin, 2-methoxy-*N*-[2-(3-thienyl)-1,2,3,4-tetrahydro-1-naphthyl]acetamide (Dockendorff *et al.*, 2006).

Data collection: COLLECT (Nonius, 2002); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL/PC

(Sheldrick, 2001); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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