

1-[(1*R**,2*R**)-1,2-Dihydroxy-1,2-dihydronaphthalen-1-yl]ethan-1-one

Alan J. Lough,^{a*} Jarvis Hill^b and William Tam^b^aDepartment of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada, and ^bDepartment of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. *Correspondence e-mail: alan.lough@utoronto.ca

Received 29 April 2019

Accepted 1 May 2019

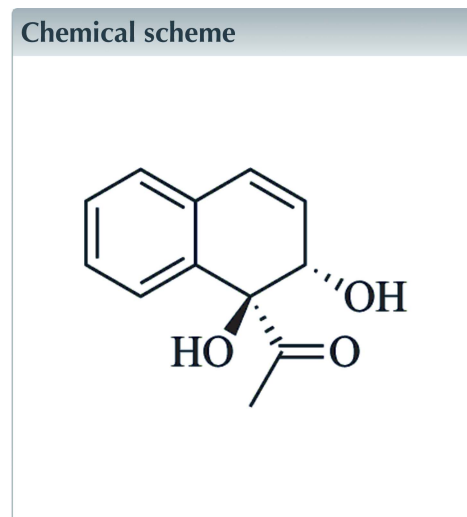
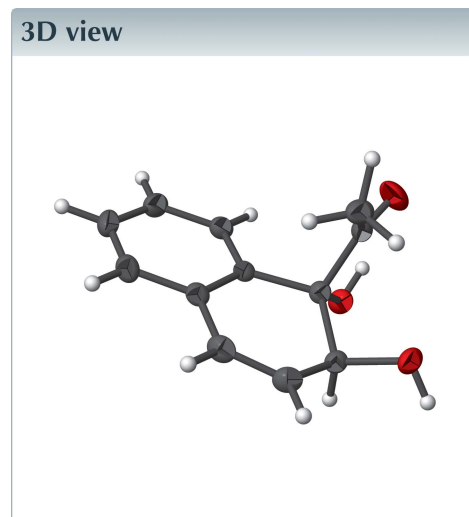
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; relative stereochemistry; hydrogen bonding; ring-opening reaction.

CCDC reference: 1913420

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

The crystal structure of the centrosymmetric title compound, C₁₂H₁₂O₃, confirms the relative stereochemistry. The 1,2-dihydrobenzene ring is in a flattened half-chair conformation. In the crystal, O—H···O hydrogen bonds link the molecules into layers lying parallel to (001).



Structure description

In past years, our research group has investigated the effects of various C₁-substituted oxabenzonorbornadienes (OBDs) on controlling the regioselectivity of ring-opening reactions (Ballantine *et al.*, 2009; Edmunds *et al.*, 2015, 2016; Raheem *et al.*, 2014). Very recently, Yang *et al.* (2019) reported the first iridium-catalysed ring-opening reaction of oxa/aza benzonorbornadienes with various alcohol nucleophiles. Based upon these findings, we set out to determine the effect of C₁ substitution on controlling the regioselectivity of this reaction on unsymmetrical OBDs. The reaction of the C₁-substituted OBD (**I**) with water in the presence of [Ir(COD)Cl]₂ and tetrabutylammonium iodide afforded exclusively the C₂ regioisomer (**II**) in an 85% yield (Fig. 1). The relative stereochemistry of the diol system was determined by single-crystal X-ray analysis: of the *cis* or *trans* isomers potentially formed, only the *trans* stereoisomer was obtained.

The molecular structure of the title compound is shown in Fig. 2. The 1,2-dihydrobenzene ring is in a flattened half-chair conformation. Atoms C3/C3'/C5/C10 are essentially planar and atoms C1 and C2 deviate from this plane by −0.248 (1) and 0.149 (1) Å, respectively. In the crystal, O—H···O hydrogen bonds link the molecules (Table 1, Fig. 3) forming a two-dimensional network lying parallel to (001).

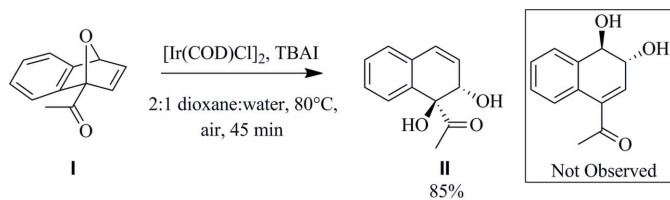


Figure 1
The reaction scheme.

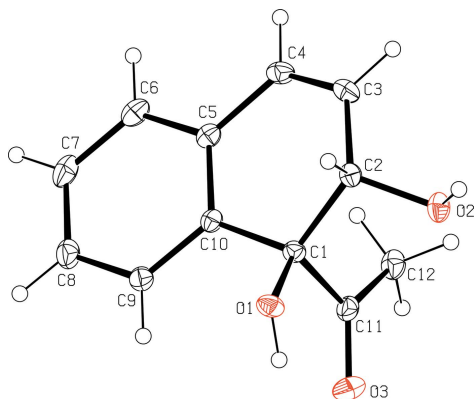


Figure 2
The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level.

Synthesis and crystallization

To a 100 ml round-bottom flask open to air was added tetrabutylammonium iodide (TBAI) (989 mg, 1 equiv), oxabenzonorbornadiene (**I**) (2.68 mmol), and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (36 mg, 2 mol%) dissolved in a 40 ml 2:1 dioxane:water mixture. This reaction was left to stir at 353 K for 45 min, after which it was cooled to room temperature and diluted in EtOAc (20 ml) and subsequently washed with EtOAc (3×15 ml). The combined organic layers were concentrated and the crude reaction mixture was purified by flash chromatography (EtOAc:hexanes 1:2) to obtain the ring-opened product **II** (462 mg,

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1}-\text{H1O} \cdots \text{O3}$	0.85 (2)	2.08 (2)	2.5970 (13)	118.2 (17)
$\text{O1}-\text{H1O} \cdots \text{O3}^{\text{i}}$	0.85 (2)	2.44 (2)	2.9568 (13)	119.8 (17)
$\text{O2}-\text{H2O} \cdots \text{O1}^{\text{ii}}$	0.87 (2)	1.92 (2)	2.7825 (12)	172.5 (16)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{12}\text{H}_{12}\text{O}_3$
M_r	204.22
Crystal system, space group	Orthorhombic, $Pbca$
Temperature (K)	150
a, b, c (\AA)	10.8313 (4), 7.6180 (3), 24.1463 (8)
V (\AA^3)	1992.38 (13)
Z	8
Radiation type	$\text{Cu } K\alpha$
μ (mm^{-1})	0.80
Crystal size (mm)	$0.21 \times 0.18 \times 0.16$
Data collection	
Diffractometer	Bruker Kappa APEX DUO CCD
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.683, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13267, 1782, 1742
R_{int}	0.022
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.599
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.088, 1.05
No. of reflections	1782
No. of parameters	145
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($\text{e } \text{\AA}^{-3}$)	0.16, -0.21

Computer programs: APEX3 and SAINT (Bruker, 2018), SHELXT2014 (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

2.26 mmol, 85%) as a white solid. The product was recrystallized from the mixed solvents of EtOAc:hexanes (2.5:7.5 v:v) to give product **II** as colourless crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

References

- Ballantine, M., Menard, M. L. & Tam, W. (2009). *J. Org. Chem.* **74**, 7570–7573.
 Bruker (2018). APEX3, and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA
 Edmunds, M., Menard, M. L. & Tam, W. (2015). *Synth. Commun.* **45**, 458–466.
 Edmunds, M., Raheem, M.-A., Boutin, R., Tait, K. & Tam, W. (2016). *Beilstein J. Org. Chem.* **12**, 239–244.
 Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

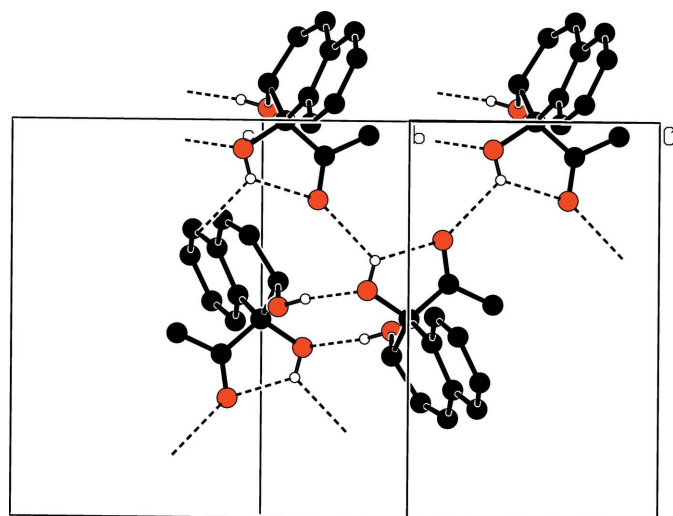


Figure 3
Part of the crystal structure of the title compound with hydrogen bonds shown as dashed lines.

- Raheem, M.-A., Edmunds, M. & Tam, W. (2014). *Can. J. Chem.* **92**, 888–895.
- Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yang, X., Yang, W., Yao, Y., Deng, Y. & Yang, D. (2019). *Org. Chem. Front.* **6**, 1151–1156.

full crystallographic data

IUCrData (2019), 4, x190609 [https://doi.org/10.1107/S2414314619006096]

1-[(1*R**,2*R**)-1,2-Dihydroxy-1,2-dihydronaphthalen-1-yl]ethan-1-one

Alan J. Lough, Jarvis Hill and William Tam

1-[(1*R**,2*R**)-1,2-Dihydroxy-1,2-dihydronaphthalen-1-yl]ethan-1-one*Crystal data*

$C_{12}H_{12}O_3$	$D_x = 1.362 \text{ Mg m}^{-3}$
$M_r = 204.22$	Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$
Orthorhombic, <i>Pbca</i>	Cell parameters from 9970 reflections
$a = 10.8313 (4) \text{ \AA}$	$\theta = 3.7\text{--}67.5^\circ$
$b = 7.6180 (3) \text{ \AA}$	$\mu = 0.80 \text{ mm}^{-1}$
$c = 24.1463 (8) \text{ \AA}$	$T = 150 \text{ K}$
$V = 1992.38 (13) \text{ \AA}^3$	Shard, colourless
$Z = 8$	$0.21 \times 0.18 \times 0.16 \text{ mm}$
$F(000) = 864$	

Data collection

Bruker Kappa APEX DUO CCD diffractometer	13267 measured reflections
Radiation source: Bruker ImuS with multi-layer optics	1782 independent reflections
φ and ω scans	1742 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.683$, $T_{\text{max}} = 0.753$	$\theta_{\text{max}} = 67.5^\circ$, $\theta_{\text{min}} = 3.7^\circ$
	$h = -12 \rightarrow 12$
	$k = -9 \rightarrow 9$
	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.034$	$w = 1/[\sigma^2(F_o^2) + (0.0445P)^2 + 0.8018P]$
$wR(F^2) = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1782 reflections	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
145 parameters	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

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 bonded to C atoms were placed in calculated positions and refined in a riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$. H atoms bonded to O atoms were refined independently with an isotropic displacement parameter.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.42766 (8)	0.51398 (11)	0.41021 (3)	0.0251 (2)
H1O	0.352 (2)	0.490 (3)	0.4061 (8)	0.061 (6)*
O2	0.52984 (8)	0.27780 (12)	0.49706 (3)	0.0271 (2)
H2O	0.5500 (15)	0.340 (2)	0.5260 (8)	0.049 (5)*
O3	0.29996 (8)	0.22665 (14)	0.40191 (4)	0.0383 (3)
C1	0.49858 (10)	0.35827 (15)	0.40262 (4)	0.0199 (3)
C2	0.59229 (10)	0.35080 (14)	0.45046 (4)	0.0210 (3)
H2A	0.614906	0.474383	0.460049	0.025*
C3	0.70942 (11)	0.25496 (15)	0.43728 (5)	0.0254 (3)
H3A	0.757906	0.211344	0.467036	0.031*
C4	0.74845 (11)	0.22829 (15)	0.38585 (5)	0.0253 (3)
H4A	0.825281	0.170966	0.380112	0.030*
C5	0.67633 (11)	0.28480 (14)	0.33766 (5)	0.0217 (3)
C6	0.72385 (11)	0.27239 (16)	0.28412 (5)	0.0283 (3)
H6A	0.802888	0.221366	0.278469	0.034*
C7	0.65723 (12)	0.33359 (18)	0.23898 (5)	0.0326 (3)
H7A	0.690314	0.323634	0.202679	0.039*
C8	0.54248 (12)	0.40913 (18)	0.24702 (5)	0.0310 (3)
H8A	0.497589	0.453920	0.216316	0.037*
C9	0.49282 (11)	0.41954 (16)	0.29999 (5)	0.0248 (3)
H9A	0.413361	0.469673	0.305235	0.030*
C10	0.55839 (10)	0.35729 (14)	0.34528 (4)	0.0194 (3)
C11	0.41033 (11)	0.19854 (17)	0.40406 (4)	0.0246 (3)
C12	0.46253 (12)	0.01786 (16)	0.40624 (5)	0.0286 (3)
H12A	0.402026	-0.065651	0.391528	0.043*
H12B	0.481906	-0.012546	0.444707	0.043*
H12C	0.538021	0.012847	0.383922	0.043*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0209 (4)	0.0274 (5)	0.0270 (4)	0.0081 (4)	-0.0010 (3)	-0.0028 (3)
O2	0.0353 (5)	0.0279 (5)	0.0180 (4)	-0.0033 (4)	0.0008 (3)	0.0007 (3)
O3	0.0209 (5)	0.0464 (6)	0.0476 (6)	-0.0060 (4)	0.0021 (4)	0.0026 (4)
C1	0.0189 (5)	0.0200 (6)	0.0208 (6)	0.0022 (4)	0.0004 (4)	-0.0005 (4)
C2	0.0230 (6)	0.0207 (5)	0.0192 (5)	0.0001 (4)	-0.0007 (4)	0.0001 (4)
C3	0.0239 (6)	0.0238 (6)	0.0287 (6)	0.0040 (5)	-0.0063 (5)	0.0010 (5)
C4	0.0197 (5)	0.0221 (6)	0.0342 (6)	0.0041 (5)	-0.0001 (5)	-0.0009 (5)
C5	0.0222 (6)	0.0171 (5)	0.0258 (6)	-0.0023 (4)	0.0026 (4)	-0.0019 (4)
C6	0.0271 (6)	0.0262 (6)	0.0316 (6)	-0.0028 (5)	0.0089 (5)	-0.0049 (5)
C7	0.0383 (7)	0.0364 (7)	0.0230 (6)	-0.0114 (6)	0.0086 (5)	-0.0031 (5)
C8	0.0348 (7)	0.0368 (7)	0.0212 (6)	-0.0089 (6)	-0.0027 (5)	0.0040 (5)
C9	0.0234 (6)	0.0270 (6)	0.0242 (6)	-0.0039 (5)	-0.0017 (4)	0.0021 (5)
C10	0.0204 (5)	0.0170 (5)	0.0207 (6)	-0.0034 (4)	0.0007 (4)	-0.0005 (4)
C11	0.0240 (6)	0.0327 (7)	0.0172 (5)	-0.0052 (5)	0.0009 (4)	0.0013 (5)

C12	0.0352 (7)	0.0260 (6)	0.0246 (6)	-0.0093 (5)	-0.0022 (5)	0.0012 (5)
-----	------------	------------	------------	-------------	-------------	------------

Geometric parameters (Å, °)

O1—C1	1.4250 (13)	C5—C6	1.3949 (17)
O1—H1O	0.85 (2)	C5—C10	1.4038 (16)
O2—C2	1.4258 (14)	C6—C7	1.3878 (19)
O2—H2O	0.87 (2)	C6—H6A	0.9500
O3—C11	1.2157 (15)	C7—C8	1.3834 (19)
C1—C10	1.5287 (14)	C7—H7A	0.9500
C1—C2	1.5387 (15)	C8—C9	1.3898 (17)
C1—C11	1.5477 (16)	C8—H8A	0.9500
C2—C3	1.4979 (16)	C9—C10	1.3875 (16)
C2—H2A	1.0000	C9—H9A	0.9500
C3—C4	1.3273 (18)	C11—C12	1.4890 (18)
C3—H3A	0.9500	C12—H12A	0.9800
C4—C5	1.4661 (17)	C12—H12B	0.9800
C4—H4A	0.9500	C12—H12C	0.9800
C1—O1—H1O	109.2 (14)	C7—C6—H6A	119.6
C2—O2—H2O	107.7 (12)	C5—C6—H6A	119.6
O1—C1—C10	110.42 (9)	C8—C7—C6	119.78 (11)
O1—C1—C2	106.85 (9)	C8—C7—H7A	120.1
C10—C1—C2	113.59 (9)	C6—C7—H7A	120.1
O1—C1—C11	108.58 (9)	C7—C8—C9	120.04 (11)
C10—C1—C11	106.15 (9)	C7—C8—H8A	120.0
C2—C1—C11	111.19 (9)	C9—C8—H8A	120.0
O2—C2—C3	112.29 (9)	C10—C9—C8	120.51 (11)
O2—C2—C1	107.09 (9)	C10—C9—H9A	119.7
C3—C2—C1	114.66 (9)	C8—C9—H9A	119.7
O2—C2—H2A	107.5	C9—C10—C5	119.81 (10)
C3—C2—H2A	107.5	C9—C10—C1	119.68 (10)
C1—C2—H2A	107.5	C5—C10—C1	120.41 (10)
C4—C3—C2	122.89 (11)	O3—C11—C12	122.53 (12)
C4—C3—H3A	118.6	O3—C11—C1	117.90 (12)
C2—C3—H3A	118.6	C12—C11—C1	119.54 (10)
C3—C4—C5	121.86 (11)	C11—C12—H12A	109.5
C3—C4—H4A	119.1	C11—C12—H12B	109.5
C5—C4—H4A	119.1	H12A—C12—H12B	109.5
C6—C5—C10	118.94 (11)	C11—C12—H12C	109.5
C6—C5—C4	121.28 (11)	H12A—C12—H12C	109.5
C10—C5—C4	119.76 (10)	H12B—C12—H12C	109.5
C7—C6—C5	120.88 (11)		
O1—C1—C2—O2	82.61 (10)	C8—C9—C10—C1	-175.77 (11)
C10—C1—C2—O2	-155.38 (9)	C6—C5—C10—C9	-1.80 (16)
C11—C1—C2—O2	-35.72 (12)	C4—C5—C10—C9	176.51 (11)
O1—C1—C2—C3	-152.09 (9)	C6—C5—C10—C1	174.58 (10)

C10—C1—C2—C3	-30.08 (13)	C4—C5—C10—C1	-7.11 (15)
C11—C1—C2—C3	89.58 (11)	O1—C1—C10—C9	-39.09 (14)
O2—C2—C3—C4	143.39 (11)	C2—C1—C10—C9	-159.09 (10)
C1—C2—C3—C4	20.86 (16)	C11—C1—C10—C9	78.42 (12)
C2—C3—C4—C5	-2.66 (18)	O1—C1—C10—C5	144.53 (10)
C3—C4—C5—C6	173.34 (11)	C2—C1—C10—C5	24.52 (14)
C3—C4—C5—C10	-4.93 (17)	C11—C1—C10—C5	-97.96 (11)
C10—C5—C6—C7	1.26 (17)	O1—C1—C11—O3	11.68 (13)
C4—C5—C6—C7	-177.03 (11)	C10—C1—C11—O3	-107.04 (12)
C5—C6—C7—C8	0.46 (19)	C2—C1—C11—O3	128.96 (11)
C6—C7—C8—C9	-1.64 (19)	O1—C1—C11—C12	-170.17 (10)
C7—C8—C9—C10	1.10 (18)	C10—C1—C11—C12	71.11 (12)
C8—C9—C10—C5	0.64 (17)	C2—C1—C11—C12	-52.88 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1O \cdots O3	0.85 (2)	2.08 (2)	2.5970 (13)	118.2 (17)
O1—H1O \cdots O3 ⁱ	0.85 (2)	2.44 (2)	2.9568 (13)	119.8 (17)
O2—H2O \cdots O1 ⁱⁱ	0.87 (2)	1.92 (2)	2.7825 (12)	172.5 (16)

Symmetry codes: (i) $-x+1/2, y+1/2, z$; (ii) $-x+1, -y+1, -z+1$.