IUCrData

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(1a*R**,2*R**,7*S**,7a*S**)-*rel*-3,6-Dimethoxy-2-methyl-1a,2,7,7a-tetrahydro-2,7-epoxy-1*H*-cyclopropa[*b*]-naphthalene

Alan J. Lough,[a]* Emily Carlson[b] and William Tam[b]

[a]Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada, and [b]Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada. *Correspondence e-mail: alough@chem.utoronto.ca

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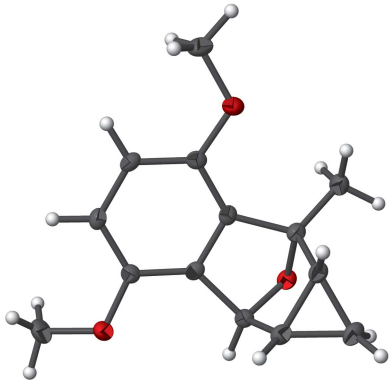
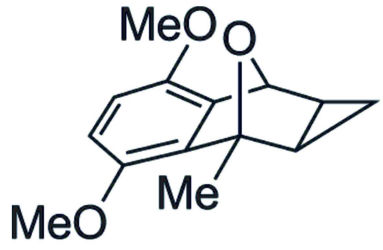
Structural data: full structural data are available from iucrdata.iucr.org

In the racemic title compound, $C_{14}H_{16}O_3$, the dihedral angle formed by the mean planes of the cyclopropane and benzene rings is 5.0 (2)°. In the crystal, a pair of weak C—H···O hydrogen bonds connect two molecules related by a twofold rotation axis, thus forming a dimer with an $R_2^2(10)$ motif.

3D view



Chemical scheme



Structure description

We have recently investigated the palladium-catalysed cyclopropanation reactions of [2.2.1] heterobicyclic compounds (Carlson *et al.*, 2016). Substituted 7-oxabenzonorbornadiene (I) reacts with diazomethane in the presence of catalytic $Pd(OAc)_2$ in THF to give the cyclopropane (II) as a single stereoisomer (see Fig. 1). The stereochemistry of (II) was determined by this single-crystal X-ray analysis. Of the *exo* or *endo* isomers which could be formed, the reaction was found to give solely the *exo* stereoisomer.

The molecular structure of the title compound is shown in Fig. 2. The dihedral angle formed by the mean planes of the cyclopropane and benzene rings C3/C4/C5 and C1/C7/C8/C9/C10/C11, respectively is 5.0 (2)°. In the crystal, a pair of weak C—H···O hydrogen bonds (Table 1 and Fig. 3) between two molecules related by a twofold rotation axis forms a dimer with an $R_2^2(10)$ motif.

Synthesis and crystallization

HAZARD ALERT! Diazomethane can be fatal if inhaled and capable of detonation if appreciably concentrated. See Carlson *et al.* (2016) for a detailed figure of the experimental apparatus. Alkene (I) (9.2 mmol), $Pd(OAc)_2$ (0.092 mmol) and THF (40 ml) were

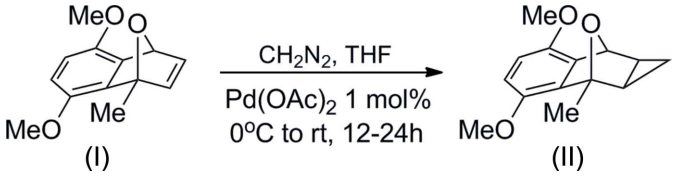


Figure 1
The reaction scheme.

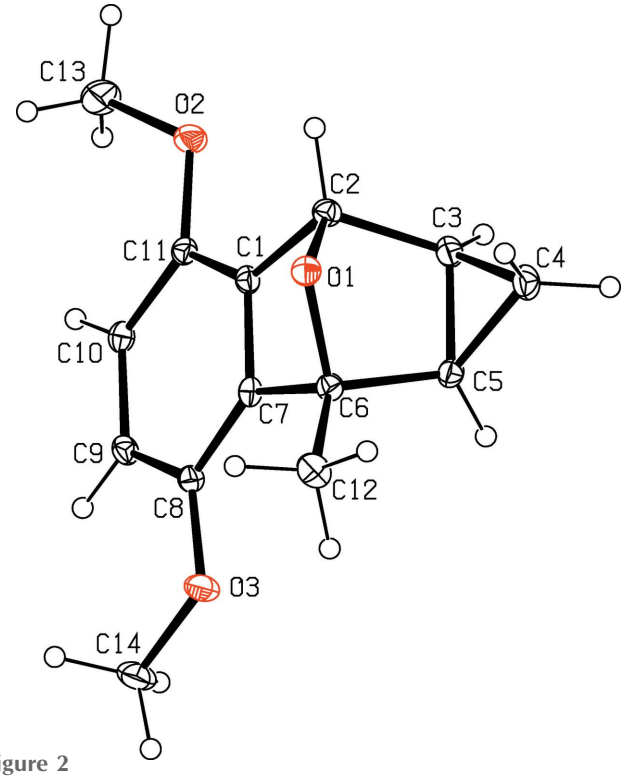


Figure 2
The molecular structure of the title compound showing 30% probability ellipsoids.

stirred in a sealed reaction flask at 273 K, connected to a 1:1 glacial acetic acid: water trap and vented to the back of the fumehood. Diazomethane was generated in a separate flask by dropwise addition (2 ml min^{-1}) of 12.5 *M* aqueous NaOH (1.3 mol) to Diazald (23.8 mmol) stirred in 95% EtOH (50 ml), and directed under a steady stream of argon to the reaction flask. Formation of the light-yellow CH_2N_2 was observed with the dissolution of Diazald. Upon completion of the reaction (monitored by TLC and dissipation of any yellow colour), the crude reaction mixture was filtered through Celite, rinsed with Et_2O (3 × 10 ml), concentrated and purified by column chromatography (EtOAc:hexanes = 1:9) followed by recrystallization from pentane solution to give the *exo* cyclopropane (II) in the form of colourless plates in 82% yield.

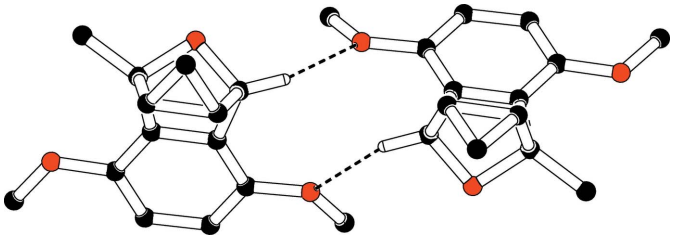


Figure 3
A pair of molecules connected by weak hydrogen bonds shown as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O2^{i}	1.00	2.44	3.2777 (17)	141

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{16}O_3$
M_r	232.27
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	147
a, *b*, *c* (Å)	16.401 (2), 6.9386 (9), 20.666 (2)
β (°)	97.089 (3)
V (Å^3)	2333.8 (5)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.33 × 0.23 × 0.06
Data collection	
Diffractometer	Bruker Kappa APEX DUO CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.703, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17093, 2681, 1972
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.041, 0.104, 1.02
No. of reflections	2681
No. of parameters	157
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.20

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

Refinement

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

References

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Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
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full crystallographic data

IUCrData (2016). **1**, x160341 [doi:10.1107/S2414314616003412]

(1a*R**,2*R**,7*S**,7a*S**)-*rel*-3,6-Dimethoxy-2-methyl-1a,2,7,7a-tetrahydro-2,7-epoxy-1*H*-cyclopropa[*b*]naphthalene

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(1a*R,2*R**,7*S**,7a*S**)-*rel*-3,6-Dimethoxy-2-methyl-1a,2,7,7a-tetrahydro-2,7-epoxy-1*H*-cyclopropa[*b*]naphthalene**

Crystal data

$C_{14}H_{16}O_3$
M_r = 232.27
Monoclinic, *C*2/*c*
a = 16.401 (2) Å
b = 6.9386 (9) Å
c = 20.666 (2) Å
β = 97.089 (3)°
V = 2333.8 (5) Å^3
Z = 8
F(000) = 992
D_x = 1.322 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 4973 reflections
θ = 2.5–27.4°
μ = 0.09 mm^{-1}
T = 147 K
Plate, colourless
0.33 × 0.23 × 0.06 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} = 0.703, T_{max} = 0.746
17093 measured reflections
2681 independent reflections
1972 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.5°, θ_{min} = 2.0°
h = −21→21
k = −8→9
l = −17→26

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.02
2681 reflections
157 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 2.2112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.02986 (6)	0.82417 (15)	0.09283 (5)	0.0194 (2)
O2	0.09941 (7)	1.03830 (15)	0.28403 (5)	0.0253 (3)
O3	0.26711 (6)	1.04938 (15)	0.06547 (5)	0.0248 (3)
C1	0.11743 (8)	0.9435 (2)	0.17734 (7)	0.0167 (3)
C2	0.04984 (9)	0.7949 (2)	0.16232 (7)	0.0190 (3)
H2A	0.0027	0.8064	0.1885	0.023*
C3	0.09260 (9)	0.5976 (2)	0.16523 (7)	0.0207 (3)
H3A	0.1212	0.5476	0.2074	0.025*
C4	0.06766 (10)	0.4617 (2)	0.10921 (8)	0.0249 (3)
H4A	0.0822	0.3239	0.1154	0.030*
H4B	0.0148	0.4864	0.0818	0.030*
C5	0.13667 (9)	0.6032 (2)	0.10507 (7)	0.0191 (3)
H5A	0.1946	0.5565	0.1073	0.023*
C6	0.11289 (9)	0.8013 (2)	0.07536 (7)	0.0185 (3)
C7	0.15865 (9)	0.9463 (2)	0.12220 (7)	0.0167 (3)
C8	0.22780 (9)	1.0607 (2)	0.12042 (7)	0.0177 (3)
C9	0.25244 (9)	1.1778 (2)	0.17404 (7)	0.0189 (3)
H9A	0.2988	1.2596	0.1735	0.023*
C10	0.20992 (9)	1.1766 (2)	0.22880 (7)	0.0187 (3)
H10A	0.2273	1.2587	0.2646	0.022*
C11	0.14249 (9)	1.0565 (2)	0.23120 (7)	0.0173 (3)
C12	0.11176 (10)	0.8263 (2)	0.00304 (7)	0.0260 (4)
H12A	0.1676	0.8113	−0.0085	0.039*
H12B	0.0911	0.9551	−0.0097	0.039*
H12C	0.0758	0.7287	−0.0198	0.039*
C13	0.10349 (12)	1.1913 (3)	0.32903 (8)	0.0383 (5)
H13A	0.0652	1.1671	0.3609	0.057*
H13B	0.0886	1.3120	0.3059	0.057*
H13C	0.1595	1.2013	0.3516	0.057*
C14	0.33542 (10)	1.1738 (3)	0.06247 (8)	0.0320 (4)
H14A	0.3577	1.1538	0.0211	0.048*
H14B	0.3779	1.1452	0.0988	0.048*
H14C	0.3177	1.3081	0.0654	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0152 (5)	0.0205 (5)	0.0219 (5)	0.0000 (4)	−0.0003 (4)	−0.0001 (4)
O2	0.0300 (6)	0.0246 (6)	0.0233 (5)	−0.0053 (5)	0.0113 (5)	−0.0050 (5)
O3	0.0249 (6)	0.0280 (6)	0.0232 (5)	−0.0074 (5)	0.0095 (4)	−0.0026 (5)
C1	0.0156 (7)	0.0139 (7)	0.0203 (7)	0.0002 (5)	0.0009 (6)	0.0015 (6)
C2	0.0181 (7)	0.0195 (8)	0.0194 (7)	−0.0016 (6)	0.0029 (6)	−0.0003 (6)
C3	0.0221 (8)	0.0168 (7)	0.0233 (7)	−0.0014 (6)	0.0026 (6)	0.0009 (6)
C4	0.0266 (8)	0.0165 (7)	0.0311 (8)	−0.0032 (6)	0.0024 (7)	−0.0021 (6)
C5	0.0177 (7)	0.0157 (7)	0.0239 (7)	0.0002 (6)	0.0030 (6)	−0.0027 (6)

C6	0.0178 (7)	0.0171 (7)	0.0206 (7)	−0.0008 (6)	0.0028 (6)	−0.0009 (6)
C7	0.0184 (7)	0.0131 (7)	0.0181 (7)	0.0015 (5)	0.0000 (6)	0.0004 (5)
C8	0.0179 (7)	0.0165 (7)	0.0189 (7)	0.0012 (6)	0.0034 (6)	0.0024 (6)
C9	0.0163 (7)	0.0159 (7)	0.0242 (7)	−0.0030 (6)	0.0010 (6)	0.0008 (6)
C10	0.0203 (7)	0.0161 (7)	0.0192 (7)	−0.0001 (6)	−0.0004 (6)	−0.0025 (6)
C11	0.0186 (7)	0.0156 (7)	0.0179 (7)	0.0023 (6)	0.0029 (6)	0.0009 (6)
C12	0.0314 (9)	0.0264 (8)	0.0198 (7)	−0.0061 (7)	0.0016 (7)	−0.0013 (6)
C13	0.0530 (12)	0.0355 (10)	0.0302 (9)	−0.0071 (9)	0.0204 (9)	−0.0129 (8)
C14	0.0301 (9)	0.0336 (9)	0.0350 (9)	−0.0122 (8)	0.0153 (7)	−0.0030 (8)

Geometric parameters (Å, º)

O1—C2	1.4474 (17)	C5—H5A	1.0000
O1—C6	1.4598 (16)	C6—C12	1.503 (2)
O2—C11	1.3776 (16)	C6—C7	1.527 (2)
O2—C13	1.4074 (19)	C7—C8	1.3886 (19)
O3—C8	1.3755 (16)	C8—C9	1.393 (2)
O3—C14	1.4218 (18)	C9—C10	1.4006 (19)
C1—C11	1.382 (2)	C9—H9A	0.9500
C1—C7	1.3951 (19)	C10—C11	1.391 (2)
C1—C2	1.5177 (19)	C10—H10A	0.9500
C2—C3	1.536 (2)	C12—H12A	0.9800
C2—H2A	1.0000	C12—H12B	0.9800
C3—C4	1.510 (2)	C12—H12C	0.9800
C3—C5	1.5137 (19)	C13—H13A	0.9800
C3—H3A	1.0000	C13—H13B	0.9800
C4—C5	1.509 (2)	C13—H13C	0.9800
C4—H4A	0.9900	C14—H14A	0.9800
C4—H4B	0.9900	C14—H14B	0.9800
C5—C6	1.536 (2)	C14—H14C	0.9800
C2—O1—C6	97.26 (10)	C7—C6—C5	104.78 (11)
C11—O2—C13	117.86 (12)	C8—C7—C1	120.60 (13)
C8—O3—C14	116.97 (12)	C8—C7—C6	134.34 (12)
C11—C1—C7	121.62 (13)	C1—C7—C6	105.01 (12)
C11—C1—C2	133.42 (12)	O3—C8—C7	117.17 (12)
C7—C1—C2	104.93 (12)	O3—C8—C9	124.78 (13)
O1—C2—C1	100.24 (10)	C7—C8—C9	118.05 (12)
O1—C2—C3	102.13 (11)	C8—C9—C10	120.98 (13)
C1—C2—C3	106.21 (11)	C8—C9—H9A	119.5
O1—C2—H2A	115.4	C10—C9—H9A	119.5
C1—C2—H2A	115.4	C11—C10—C9	120.64 (13)
C3—C2—H2A	115.4	C11—C10—H10A	119.7
C4—C3—C5	59.87 (9)	C9—C10—H10A	119.7
C4—C3—C2	116.57 (13)	O2—C11—C1	117.11 (12)
C5—C3—C2	101.93 (12)	O2—C11—C10	124.83 (13)
C4—C3—H3A	120.4	C1—C11—C10	118.04 (12)
C5—C3—H3A	120.4	C6—C12—H12A	109.5

C2—C3—H3A	120.4	C6—C12—H12B	109.5
C5—C4—C3	60.20 (9)	H12A—C12—H12B	109.5
C5—C4—H4A	117.8	C6—C12—H12C	109.5
C3—C4—H4A	117.8	H12A—C12—H12C	109.5
C5—C4—H4B	117.8	H12B—C12—H12C	109.5
C3—C4—H4B	117.8	O2—C13—H13A	109.5
H4A—C4—H4B	114.9	O2—C13—H13B	109.5
C4—C5—C3	59.93 (10)	H13A—C13—H13B	109.5
C4—C5—C6	116.73 (12)	O2—C13—H13C	109.5
C3—C5—C6	103.18 (11)	H13A—C13—H13C	109.5
C4—C5—H5A	120.1	H13B—C13—H13C	109.5
C3—C5—H5A	120.1	O3—C14—H14A	109.5
C6—C5—H5A	120.1	O3—C14—H14B	109.5
O1—C6—C12	109.65 (12)	H14A—C14—H14B	109.5
O1—C6—C7	99.92 (10)	O3—C14—H14C	109.5
C12—C6—C7	119.96 (12)	H14A—C14—H14C	109.5
O1—C6—C5	101.35 (11)	H14B—C14—H14C	109.5
C12—C6—C5	118.17 (12)		

C6—O1—C2—C1	53.68 (11)	C11—C1—C7—C6	179.16 (13)
C6—O1—C2—C3	−55.53 (11)	C2—C1—C7—C6	1.12 (14)
C11—C1—C2—O1	147.94 (15)	O1—C6—C7—C8	−150.61 (15)
C7—C1—C2—O1	−34.35 (13)	C12—C6—C7—C8	−30.9 (2)
C11—C1—C2—C3	−106.10 (17)	C5—C6—C7—C8	104.75 (17)
C7—C1—C2—C3	71.61 (14)	O1—C6—C7—C1	32.10 (13)
O1—C2—C3—C4	−27.71 (15)	C12—C6—C7—C1	151.76 (13)
C1—C2—C3—C4	−132.31 (13)	C5—C6—C7—C1	−72.55 (13)
O1—C2—C3—C5	34.38 (13)	C14—O3—C8—C7	176.96 (13)
C1—C2—C3—C5	−70.21 (13)	C14—O3—C8—C9	−3.2 (2)
C2—C3—C4—C5	88.68 (14)	C1—C7—C8—O3	177.28 (13)
C3—C4—C5—C6	−90.21 (14)	C6—C7—C8—O3	0.3 (2)
C2—C3—C5—C4	−113.95 (13)	C1—C7—C8—C9	−2.6 (2)
C4—C3—C5—C6	113.46 (13)	C6—C7—C8—C9	−179.56 (14)
C2—C3—C5—C6	−0.49 (14)	O3—C8—C9—C10	−178.34 (13)
C2—O1—C6—C12	−179.66 (12)	C7—C8—C9—C10	1.5 (2)
C2—O1—C6—C7	−52.73 (11)	C8—C9—C10—C11	0.8 (2)
C2—O1—C6—C5	54.68 (12)	C13—O2—C11—C1	−158.53 (14)
C4—C5—C6—O1	29.64 (15)	C13—O2—C11—C10	22.9 (2)
C3—C5—C6—O1	−33.09 (13)	C7—C1—C11—O2	−177.80 (13)
C4—C5—C6—C12	−90.13 (16)	C2—C1—C11—O2	−0.4 (2)
C3—C5—C6—C12	−152.87 (13)	C7—C1—C11—C10	0.9 (2)
C4—C5—C6—C7	133.21 (13)	C2—C1—C11—C10	178.31 (14)
C3—C5—C6—C7	70.48 (13)	C9—C10—C11—O2	176.62 (13)
C11—C1—C7—C8	1.4 (2)	C9—C10—C11—C1	−2.0 (2)
C2—C1—C7—C8	−176.63 (12)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O2^{i}	1.00	2.44	3.2777 (17)	141

Symmetry code: (i) −*x*, *y*, −*z*+1/2.