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The *rel-R,R*-enantiomer of 7-[7-hydroxybicyclo-[4.2.0]octa-1(6),2,4-trien-7-yl]bicyclo[4.2.0]octa-1(6),2,4-trien-7-ol

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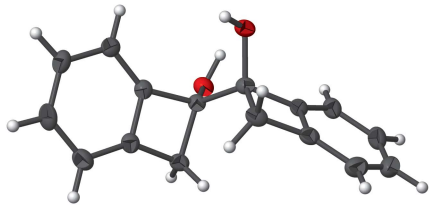
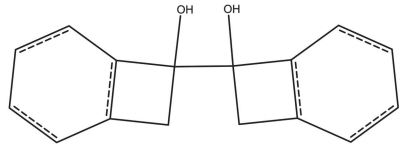
Structural data: full structural data are available from iucrdata.iucr.org

A single crystal of the *rel-R,R*-enantiomer of the title compound, $C_{16}H_{14}O_2$, was analyzed. The molecular structure is characterized by nearly planar cyclobutene rings and a torsion angle of the diol unit of 68.3 (2)°. Strands parallel to the *b* axis are built from diols connected *via* hydrogen bonds.

3D view



Chemical scheme



Structure description

A single-crystal of the isomeric mixture of the title compound (Fig. 1) was analysed, consisting of the pure *rel-R,R*-enantiomer. The bond lengths of the benzocyclobutene fragments are typical for this unit, both four-membered rings are planar, the sums of bond angles are 359.96° and 359.45° resp. The bond angles at the sp^2-carbons are 93.1 (2)° (C9—C16—C11), 93.8 (2)° (C10—C11—C16), 94.3 (2)° (C8—C3—C2), and 93.2 (2)° (C3—C8—C1).

The dihedral angle between the best planes of the cyclobutane units is 58.5 (2)° and the central torsion angle of the glycol subunit is 68.2 (3)°. In the crystal, the molecules (symmetry transformed by a a twofold screw axis) form strands along the *b*-axis direction. Hydrogen bonds (Fig. 2, Table 1) parallel to the *b*-axis [O1—H1···O2, 1.92 (4) Å, 170 (3)°] connect molecules with translational symmetry, hydrogen bonds in direction of the *c*-axis [O2—H2···O1, 1.91 (4) Å, 152.0 (4)°] connect two molecules which are symmetry-related by the screw axis.

Synthesis and crystallization

The reductive coupling of aldehydes or ketones with low-valent titanium (McMurry, 1989) is an important route to stilbenes (Meier, 1992), even to stilbenes with severe

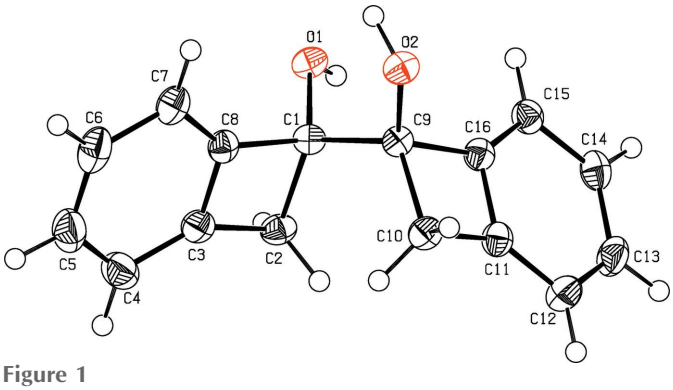


Figure 1
Perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

geometrical strain (Lenoir, 1989; Dobryakov *et al.*, 2016). The reaction proceeds *via* a pinacol intermediate, the geometry of which is decisive for the configuration of the product. The McMurry reaction of benzocyclobutenone (Schiess & Heitzmann, 1977) results in a mixture of *E*– and *Z*-di(benzocyclobutylidene) (Schneider *et al.*, 1999) together with a pinacol (40%) of unknown geometry (Oelgemöller *et al.*, 2002). H NMR spectroscopy of the crude product mixture showed a 6:4 ratio of the stilbene (*ca* 1:1 mixture of both isomers) and the diol. A single crystal from the mixture of the diols was investigated.

H NMR (400 MHz; $CDCl_3$): δ**H =** 1.53 (2 H, *br s*, OH), 3.04 (2 H, *d*, *J* = 14.4, 2-H), 3.17 (2 H, *br s*, 1-H), 3.30 (2 H, *d*, *J* = 14.4, 2-H), 7.01–7.18 (8 H, *br m*, H_{arom}); C NMR (100 MHz; $CDCl_3$) δ**C =** 42.7 (*t*, 2 × C-2), 82.9 (*d*, 2 × C-1), 121.4 (*d*, 2 × C_{arom}), 123.2 (*d*, 2 × C_{arom}), 127.1 (*d*, 2 × C_{arom}), 129.5 (*d*, 2 × C_{arom}), 142.3 (*s*, 2 × C_{arom}) and 146.8 (*s*, 2 × C_{arom}). Recrystallization from chloroform/propanol-2 (*v*/*v* = 1:3) yielded colourless crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The absolute configuration could not be determined and was arbitrarily set.

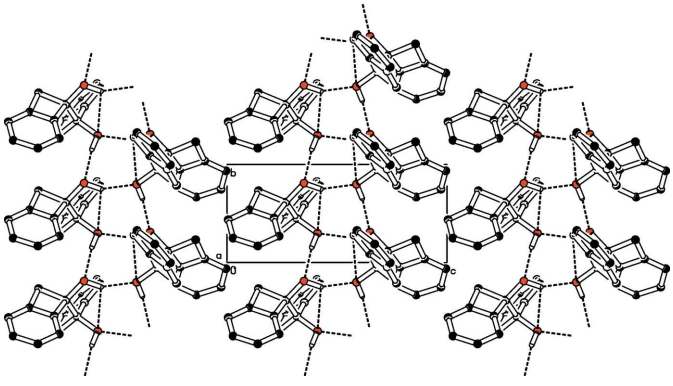


Figure 2
Partial packing diagram, view along the *a* axis. Hydrogen bonds are drawn with dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.87 (4)	1.92 (4)	2.782 (3)	170 (3)
O2—H2···O1^{ii}	0.94 (4)	1.91 (4)	2.782 (3)	152 (4)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{14}O_2$
M_r	238.27
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	193
a, *b*, *c* (Å)	10.1497 (12), 5.1276 (4), 11.6896 (16)
β (°)	99.541 (10)
V (Å^3)	599.95 (12)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.09
Crystal size (mm)	0.50 × 0.13 × 0.07
Data collection	
Diffractometer	Stoe IPDS 2T
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4954, 2964, 2371
R_{int}	0.032
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.043, 0.097, 1.05
No. of reflections	2964
No. of parameters	171
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.18
Absolute structure	Flack *x* determined using 875 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	1.6 (10)

Computer programs: *X-AREA* and *X-RED* (Stoe & Cie, 1996), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2009).

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x181550 [https://doi.org/10.1107/S241431461801550X]

The *rel-R,R*-enantiomer of 7-[7-hydroxybicyclo[4.2.0]octa-1(6),2,4-trien-7-yl]bicyclo[4.2.0]octa-1(6),2,4-trien-7-ol

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7-[7-Hydroxybicyclo[4.2.0]octa-1(6),2,4-trien-7-yl]bicyclo[4.2.0]octa-1(6),2,4-trien-7-ol

Crystal data

$C_{16}H_{14}O_2$
M_r = 238.27
Monoclinic, $P2_1$
a = 10.1497 (12) Å
b = 5.1276 (4) Å
c = 11.6896 (16) Å
β = 99.541 (10)°
V = 599.95 (12) Å^3
Z = 2
$F(000)$ = 252
D_x = 1.319 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4652 reflections
θ = 2.0–28.5°
μ = 0.09 mm^{-1}
T = 193 K
Needle, colourless
0.50 × 0.13 × 0.07 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method scans
4954 measured reflections
2964 independent reflections
2371 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 28.4°, θ_{min} = 2.0°
h = −13→13
k = −6→6
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.097
S = 1.05
2964 reflections
171 parameters
1 restraint
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.2519P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack x determined using 875 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 1.6 (10)

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. Hydroxyl hydrogen atoms were localized in difference fourier maps and freely refined.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.51056 (18)	0.2981 (4)	0.41147 (15)	0.0237 (4)
H1	0.471 (3)	0.154 (8)	0.385 (3)	0.044 (10)*
O2	0.40202 (18)	0.8096 (4)	0.35005 (17)	0.0249 (4)
H2	0.421 (4)	0.750 (8)	0.427 (4)	0.061 (12)*
C1	0.5454 (3)	0.4489 (5)	0.3182 (2)	0.0212 (5)
C2	0.6155 (3)	0.2889 (6)	0.2297 (2)	0.0253 (6)
H2A	0.627109	0.101101	0.248340	0.030*
H2B	0.576281	0.316258	0.147268	0.030*
C3	0.7381 (3)	0.4546 (5)	0.2718 (2)	0.0253 (6)
C4	0.8688 (3)	0.4972 (6)	0.2584 (3)	0.0352 (7)
H4	0.909902	0.401865	0.204145	0.042*
C5	0.9363 (3)	0.6876 (7)	0.3290 (3)	0.0387 (8)
H5	1.026509	0.725004	0.322585	0.046*
C6	0.8763 (3)	0.8265 (7)	0.4093 (3)	0.0369 (7)
H6	0.926413	0.955950	0.455706	0.044*
C7	0.7447 (3)	0.7799 (6)	0.4230 (2)	0.0289 (6)
H7	0.703271	0.872062	0.477908	0.035*
C8	0.6785 (3)	0.5907 (5)	0.3514 (2)	0.0225 (6)
C9	0.4249 (3)	0.6156 (5)	0.2679 (2)	0.0206 (5)
C10	0.4233 (3)	0.7324 (5)	0.1430 (2)	0.0247 (6)
H10A	0.394867	0.917068	0.134744	0.030*
H10B	0.506586	0.702490	0.111143	0.030*
C11	0.3129 (3)	0.5373 (5)	0.1021 (2)	0.0246 (6)
C12	0.2315 (3)	0.4363 (6)	0.0055 (3)	0.0321 (7)
H12	0.237744	0.491510	−0.070953	0.038*
C13	0.1395 (3)	0.2481 (6)	0.0277 (3)	0.0327 (7)
H13	0.081726	0.172058	−0.035734	0.039*
C14	0.1298 (3)	0.1684 (6)	0.1395 (3)	0.0289 (6)
H14	0.064511	0.042157	0.150384	0.035*
C15	0.2132 (2)	0.2686 (5)	0.2363 (2)	0.0253 (6)
H15	0.207527	0.213816	0.312948	0.030*
C16	0.3047 (3)	0.4528 (5)	0.2133 (2)	0.0227 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0308 (10)	0.0192 (9)	0.0210 (9)	−0.0022 (9)	0.0038 (7)	0.0016 (8)
O2	0.0318 (10)	0.0181 (9)	0.0245 (10)	0.0027 (9)	0.0040 (8)	−0.0024 (8)
C1	0.0246 (13)	0.0176 (12)	0.0217 (13)	−0.0008 (11)	0.0051 (10)	0.0004 (11)
C2	0.0323 (14)	0.0225 (13)	0.0213 (12)	0.0031 (13)	0.0047 (10)	−0.0012 (12)
C3	0.0280 (14)	0.0239 (13)	0.0239 (14)	0.0040 (12)	0.0039 (11)	0.0061 (12)
C4	0.0309 (15)	0.0411 (18)	0.0357 (17)	0.0050 (14)	0.0111 (13)	0.0094 (14)
C5	0.0263 (14)	0.0472 (19)	0.0417 (18)	−0.0035 (14)	0.0028 (13)	0.0137 (16)
C6	0.0313 (15)	0.0356 (16)	0.0395 (17)	−0.0075 (15)	−0.0068 (13)	0.0077 (15)
C7	0.0294 (14)	0.0255 (14)	0.0294 (14)	−0.0023 (13)	−0.0020 (11)	0.0007 (13)

C8	0.0232 (13)	0.0202 (13)	0.0236 (13)	0.0024 (11)	0.0020 (11)	0.0045 (11)
C9	0.0230 (13)	0.0171 (12)	0.0213 (13)	0.0005 (10)	0.0030 (10)	0.0001 (10)
C10	0.0280 (13)	0.0217 (14)	0.0241 (13)	0.0000 (11)	0.0035 (11)	0.0039 (11)
C11	0.0235 (13)	0.0227 (14)	0.0268 (14)	0.0024 (11)	0.0022 (11)	0.0007 (11)
C12	0.0334 (16)	0.0367 (16)	0.0246 (14)	0.0015 (14)	0.0004 (12)	0.0019 (13)
C13	0.0271 (14)	0.0370 (18)	0.0308 (15)	−0.0011 (13)	−0.0050 (12)	−0.0093 (14)
C14	0.0214 (13)	0.0277 (15)	0.0370 (17)	−0.0024 (12)	0.0027 (12)	−0.0020 (12)
C15	0.0235 (12)	0.0246 (14)	0.0277 (13)	0.0027 (12)	0.0044 (10)	0.0025 (12)
C16	0.0226 (12)	0.0208 (13)	0.0244 (13)	0.0019 (11)	0.0029 (10)	−0.0012 (11)

Geometric parameters (Å, º)

O1—C1	1.429 (3)	C7—C8	1.380 (4)
O1—H1	0.87 (4)	C7—H7	0.9500
O2—C9	1.428 (3)	C9—C16	1.527 (4)
O2—H2	0.94 (4)	C9—C10	1.576 (4)
C1—C8	1.527 (4)	C10—C11	1.519 (4)
C1—C9	1.528 (3)	C10—H10A	0.9900
C1—C2	1.579 (4)	C10—H10B	0.9900
C2—C3	1.519 (4)	C11—C12	1.384 (4)
C2—H2A	0.9900	C11—C16	1.386 (4)
C2—H2B	0.9900	C12—C13	1.397 (4)
C3—C4	1.379 (4)	C12—H12	0.9500
C3—C8	1.380 (4)	C13—C14	1.388 (4)
C4—C5	1.385 (5)	C13—H13	0.9500
C4—H4	0.9500	C14—C15	1.393 (4)
C5—C6	1.397 (5)	C14—H14	0.9500
C5—H5	0.9500	C15—C16	1.382 (4)
C6—C7	1.391 (4)	C15—H15	0.9500
C6—H6	0.9500		
C1—O1—H1	110 (2)	C7—C8—C1	144.2 (3)
C9—O2—H2	113 (2)	O2—C9—C16	117.0 (2)
O1—C1—C8	112.6 (2)	O2—C9—C1	109.9 (2)
O1—C1—C9	108.2 (2)	C16—C9—C1	112.82 (19)
C8—C1—C9	116.7 (2)	O2—C9—C10	112.4 (2)
O1—C1—C2	114.5 (2)	C16—C9—C10	86.32 (19)
C8—C1—C2	86.47 (19)	C1—C9—C10	117.0 (2)
C9—C1—C2	117.3 (2)	C11—C10—C9	86.26 (19)
C3—C2—C1	86.04 (19)	C11—C10—H10A	114.3
C3—C2—H2A	114.3	C9—C10—H10A	114.3
C1—C2—H2A	114.3	C11—C10—H10B	114.3
C3—C2—H2B	114.3	C9—C10—H10B	114.3
C1—C2—H2B	114.3	H10A—C10—H10B	111.4
H2A—C2—H2B	111.5	C12—C11—C16	121.8 (3)
C4—C3—C8	122.3 (3)	C12—C11—C10	144.3 (3)
C4—C3—C2	143.4 (3)	C16—C11—C10	93.8 (2)
C8—C3—C2	94.3 (2)	C11—C12—C13	115.7 (3)

C3—C4—C5	115.7 (3)	C11—C12—H12	122.1
C3—C4—H4	122.1	C13—C12—H12	122.1
C5—C4—H4	122.1	C14—C13—C12	122.2 (3)
C4—C5—C6	122.1 (3)	C14—C13—H13	118.9
C4—C5—H5	118.9	C12—C13—H13	118.9
C6—C5—H5	118.9	C13—C14—C15	121.8 (3)
C7—C6—C5	121.6 (3)	C13—C14—H14	119.1
C7—C6—H6	119.2	C15—C14—H14	119.1
C5—C6—H6	119.2	C16—C15—C14	115.6 (3)
C8—C7—C6	115.6 (3)	C16—C15—H15	122.2
C8—C7—H7	122.2	C14—C15—H15	122.2
C6—C7—H7	122.2	C15—C16—C11	122.9 (3)
C3—C8—C7	122.7 (3)	C15—C16—C9	143.9 (3)
C3—C8—C1	93.2 (2)	C11—C16—C9	93.1 (2)
O1—C1—C2—C3	−114.5 (2)	C2—C1—C9—C16	67.0 (3)
C8—C1—C2—C3	−1.30 (18)	O1—C1—C9—C10	−162.1 (2)
C9—C1—C2—C3	117.1 (2)	C8—C1—C9—C10	69.7 (3)
C1—C2—C3—C4	179.5 (4)	C2—C1—C9—C10	−30.8 (3)
C1—C2—C3—C8	1.4 (2)	O2—C9—C10—C11	−122.9 (2)
C8—C3—C4—C5	−0.7 (4)	C16—C9—C10—C11	−5.15 (19)
C2—C3—C4—C5	−178.4 (3)	C1—C9—C10—C11	108.6 (2)
C3—C4—C5—C6	0.4 (5)	C9—C10—C11—C12	−174.8 (4)
C4—C5—C6—C7	0.2 (5)	C9—C10—C11—C16	5.7 (2)
C5—C6—C7—C8	−0.7 (4)	C16—C11—C12—C13	1.1 (4)
C4—C3—C8—C7	0.3 (4)	C10—C11—C12—C13	−178.3 (4)
C2—C3—C8—C7	179.0 (3)	C11—C12—C13—C14	0.4 (4)
C4—C3—C8—C1	179.9 (3)	C12—C13—C14—C15	−1.2 (5)
C2—C3—C8—C1	−1.5 (2)	C13—C14—C15—C16	0.5 (4)
C6—C7—C8—C3	0.4 (4)	C14—C15—C16—C11	1.0 (4)
C6—C7—C8—C1	−178.9 (3)	C14—C15—C16—C9	−172.8 (3)
O1—C1—C8—C3	116.5 (2)	C12—C11—C16—C15	−1.8 (4)
C9—C1—C8—C3	−117.4 (2)	C10—C11—C16—C15	177.8 (3)
C2—C1—C8—C3	1.4 (2)	C12—C11—C16—C9	174.5 (3)
O1—C1—C8—C7	−64.1 (5)	C10—C11—C16—C9	−5.9 (2)
C9—C1—C8—C7	61.9 (5)	O2—C9—C16—C15	−66.3 (5)
C2—C1—C8—C7	−179.2 (4)	C1—C9—C16—C15	62.7 (5)
O1—C1—C9—O2	68.3 (2)	C10—C9—C16—C15	−179.6 (4)
C8—C1—C9—O2	−59.9 (3)	O2—C9—C16—C11	118.9 (2)
C2—C1—C9—O2	−160.4 (2)	C1—C9—C16—C11	−112.1 (2)
O1—C1—C9—C16	−64.3 (3)	C10—C9—C16—C11	5.6 (2)
C8—C1—C9—C16	167.5 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.87 (4)	1.92 (4)	2.782 (3)	170 (3)

O2—H2···O1^{ii}	0.94 (4)	1.91 (4)	2.782 (3)	152 (4)

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