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rac-(*E*,*trans*)-4-Bromo-10,10-dimethyl-9,11-dioxabicyclo[6.3.0]undec-4-ene

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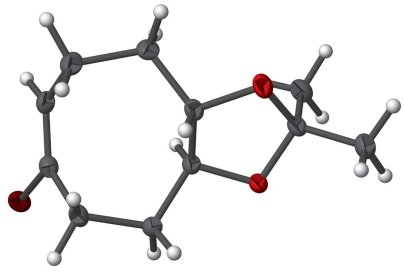
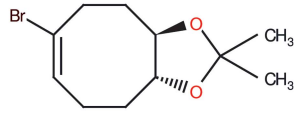
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, a cyclooctene ring in a twist-boat conformation and a dioxolane ring with a distorted envelope conformation are annulated in a *trans* configuration. Alternating strands of single enantiomers build up the crystal. Within the strands, the molecules are connected by weak C—H···O hydrogen bonds.

3D view



Chemical scheme



Structure description

The title compound (Fig. 1) crystallizes as a racemic mixture of *R*,*R*- and *S*,*S*-enantiomers forming strands of identical enantiomers along the *b*-axis direction (Fig. 2). The molecules in the strands are connected *via* weak C—H···O contacts (H7*B*···O9 2.586 Å). A center of inversion relates these molecules with their enantiomeric counterparts in the parallel strands. The eight-membered ring features a twist-boat conformation. It is annulated to a dioxolane ring in a distorted envelope conformation. Within this envelope, atoms C4, C5, O11, and C10 are essentially coplanar (r.m.s. deviation 0.017 Å) but O9 lies 0.477 (2) Å below the mean plane. The cyclooctene part has two planar moieties: one is the olefinic part (C2—C1—C8—C7), the other one [planar within 0.034 (2) Å] is composed of the four methylene groups (C3—C2—C7—C6); these planes subtend a dihedral angle of 69.3 (2)°. A *trans*-ethylene bridge (C4,C5) connects the rings; atom C4 lies 0.357 (5) Å above the central plane of the cyclooctene moiety while C5 is positioned 0.541 (5) Å below this plane.

Synthesis and crystallization

The title compound was prepared in two steps from 4-bromo-9-oxabicyclo[6.1.0]non-4-ene (Mayer & Meier, 1989) *via* hydrolysis of the epoxide to the *trans*-diol in alkaline (pH 10) water/dioxane (1/4) [^{1}H NMR: 6.02 (*t*, 1H), 3.58 (*m*, 2 H), 3.17 (*s*, 2 H, OH), 2.81 (*ddd*,

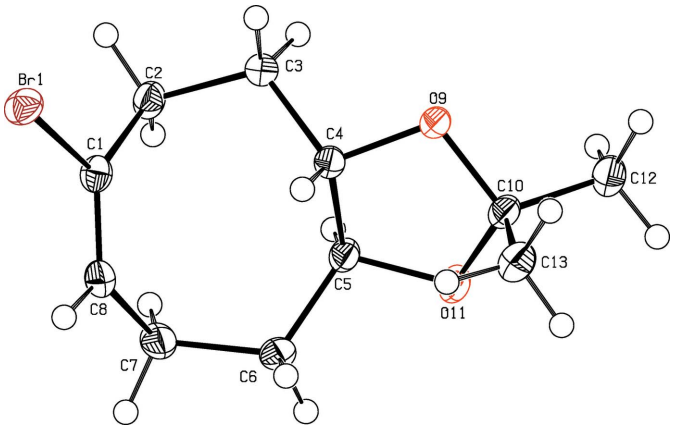


Figure 1
Perspective view of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

1 H), 2.58 (*ddd*, 1 H), 2.0–2.33 (*m*, 4 H), 1.58 (*m*, 12 H); IR: (KBr): 3320, 2918, 1635, 1450, 1430, 1040, 980) and cetalization with 2,2-dimethoxypropane. Alternatively, it may be prepared, more conveniently, from 10,10-dimethyl-9,11-dioxabicyclo[6.3.0]undec-4-ene (Golding *et al.*, 1980) *via* bromination (Takahashi *et al.*, 2000) and dehydrobromination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Procedure: DBU (6 ml) was added to 4,5-dibromo-10,10-dimethyl-9,11-dioxabicyclo[6.3.0]undec-4-ene (8.92 g, 0.026 mol) in toluene (20 ml) and the mixture was stirred for 72 h. After filtration, the organic layer was washed with water (3 × 20 ml), brine, and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and

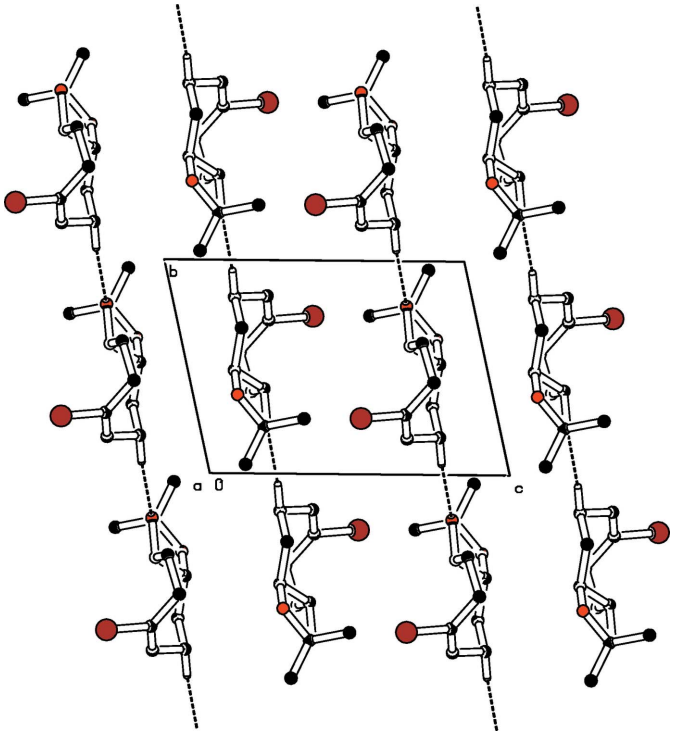


Figure 2
Partial packing diagram of the title compound, viewed along the *a* axis. H atoms not involved in C—H···O contacts are omitted.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{17}BrO_2$
M_r	261.15
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	120
a, b, c (Å)	7.5770 (6), 7.6838 (6), 10.2038 (8)
α, β, γ (°)	101.843 (6), 90.893 (6), 104.642 (6)
V (Å^3)	561.11 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.64
Crystal size (mm)	0.38 × 0.32 × 0.28
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2019)
T_{min}, T_{max}	0.195, 0.460
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4770, 2631, 2481
R_{int}	0.018
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.087, 1.15
No. of reflections	2631
No. of parameters	129
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.47

Computer programs: *X-AREA WinXpose*, *Recipe* and *Integrate* (Stoe & Cie, 2019), *SIR2004* (Burla *et al.*, 2005), *SHELXL2018/3* (Sheldrick, 2015) and *PLATON* (Spek, 2020).

the residue purified by chromatography on silica (cyclohexane/ethyl acetate 40/1) to give the title compound as a yellowish oil in 88% yield (5.98 g). Crystallization from ethanol solution yielded colorless crystals, m.p. 313 K.

Spectroscopic data: ^{1}H NMR ($CDCl_3$): 6.03 (*t*, *J* = 8.2 Hz, 1 H), 3.88 (*m*, 2 H), 2.76 (*ddd*, *J* = 15.1 Hz, *J*′ = 10.4 Hz, *J*″ = 10.2 Hz), 1 H), 2.54 (*ddd*, *J* = 14.7 Hz, *J* = 6.6 Hz, *J*″ = 3.9 Hz, 1 H), 2.30 (*m*, 1 H), 2.16 (*m*, 3H), 1.55 (*m*, 2H), 1.38 (*s*, 3H), 1.37 (*s*, 3H). ^{13}C NMR: 130.6 (CH), 124.0 (C—Br), 107.7 (O—C—O), 80.7(C—O), 79.9 (C—O), 32.2, 32.0, 29.4, 26.8 (CH_3), 24.7.

Refinement

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

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full crystallographic data

IUCrData (2020). **5**, x201302 [https://doi.org/10.1107/S2414314620013024]

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Crystal data

$C_{11}H_{17}BrO_2$
$M_r = 261.15$
Triclinic, $P\overline{1}$
$a = 7.5770$ (6) Å
$b = 7.6838$ (6) Å
$c = 10.2038$ (8) Å
$\alpha = 101.843$ (6)°
$\beta = 90.893$ (6)°
$\gamma = 104.642$ (6)°
$V = 561.11$ (8) Å^3
$Z = 2$
$F(000) = 268$
$D_x = 1.546$ Mg m^{-3}
Melting point: 313 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 10380 reflections
$\theta = 2.8$–$28.4°$
$\mu = 3.64$ mm^{-1}
$T = 120$ K
Block, colourless
0.38 × 0.32 × 0.28 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, ω scans
Absorption correction: integration (X-RED32; Stoe & Cie, 2019)
$T_{min} = 0.195$, $T_{max} = 0.460$
4770 measured reflections
2631 independent reflections
2481 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.9°$, $\theta_{min} = 2.8°$
$h = -9\rightarrow9$
$k = -9\rightarrow10$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 1.15$
2631 reflections
129 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0141P)^2 + 2.0148P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ 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. Hydrogen atoms were placed at calculated positions and were refined in the riding-model approximation with C–H ranging from 0.95 Å to 1.00 Å, and with U_{iso}(H) = 1.5 U_{eq}(C_{methyl}) or U_{iso}(H) = 1.2 U_{eq}(C) for the remaining H atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.69071 (4)	0.73859 (5)	0.45594 (3)	0.02384 (10)
C1	0.5268 (4)	0.7199 (4)	0.3056 (3)	0.0190 (6)
C2	0.5275 (4)	0.5685 (4)	0.1873 (3)	0.0213 (6)
H2A	0.653108	0.553370	0.179600	0.026*
H2B	0.491553	0.603426	0.104621	0.026*
C3	0.3971 (4)	0.3848 (4)	0.1982 (3)	0.0202 (6)
H3A	0.383050	0.297930	0.110069	0.024*
H3B	0.453460	0.332706	0.263967	0.024*
C4	0.2085 (4)	0.3970 (4)	0.2404 (3)	0.0186 (6)
H4	0.217565	0.462069	0.336747	0.022*
C5	0.0995 (4)	0.4826 (4)	0.1559 (3)	0.0191 (6)
H5	0.143866	0.470280	0.063509	0.023*
C6	0.0962 (4)	0.6811 (4)	0.2095 (3)	0.0216 (6)
H6A	0.059598	0.693629	0.302984	0.026*
H6B	0.001262	0.708981	0.155601	0.026*
C7	0.2785 (4)	0.8259 (4)	0.2082 (3)	0.0243 (7)
H7A	0.329199	0.797994	0.119793	0.029*
H7B	0.254789	0.948843	0.219350	0.029*
C8	0.4184 (4)	0.8321 (4)	0.3168 (3)	0.0219 (6)
H8	0.429359	0.921776	0.398046	0.026*
O9	0.0976 (3)	0.2121 (3)	0.2245 (2)	0.0214 (5)
C10	−0.0876 (4)	0.2202 (4)	0.2147 (3)	0.0208 (6)
O11	−0.0850 (3)	0.3686 (3)	0.1490 (3)	0.0252 (5)
C12	−0.1986 (4)	0.0422 (5)	0.1258 (4)	0.0260 (7)
H12A	−0.149514	0.026435	0.037059	0.039*
H12B	−0.326342	0.046279	0.116452	0.039*
H12C	−0.191901	−0.061399	0.166112	0.039*
C13	−0.1592 (5)	0.2577 (5)	0.3534 (4)	0.0265 (7)
H13A	−0.081067	0.372480	0.407651	0.040*
H13B	−0.158069	0.155628	0.397053	0.040*
H13C	−0.284551	0.269087	0.344726	0.040*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02067 (16)	0.02777 (17)	0.02333 (17)	0.00805 (12)	−0.00350 (11)	0.00432 (12)
C1	0.0179 (14)	0.0207 (14)	0.0172 (14)	0.0025 (11)	−0.0001 (11)	0.0049 (11)
C2	0.0169 (14)	0.0223 (15)	0.0221 (15)	0.0023 (11)	0.0036 (11)	0.0026 (12)
C3	0.0181 (14)	0.0179 (14)	0.0245 (15)	0.0050 (11)	0.0011 (11)	0.0042 (12)
C4	0.0162 (14)	0.0169 (14)	0.0228 (15)	0.0034 (11)	−0.0005 (11)	0.0056 (11)
C5	0.0146 (13)	0.0196 (14)	0.0234 (15)	0.0029 (11)	−0.0011 (11)	0.0073 (12)

C6	0.0194 (14)	0.0219 (15)	0.0249 (16)	0.0077 (12)	−0.0029 (12)	0.0055 (12)
C7	0.0242 (16)	0.0199 (15)	0.0290 (17)	0.0057 (12)	−0.0057 (13)	0.0065 (13)
C8	0.0198 (15)	0.0172 (14)	0.0253 (16)	0.0014 (11)	−0.0019 (12)	0.0019 (12)
O9	0.0145 (10)	0.0178 (10)	0.0331 (13)	0.0040 (8)	0.0007 (9)	0.0088 (9)
C10	0.0142 (13)	0.0214 (15)	0.0281 (16)	0.0042 (11)	−0.0002 (11)	0.0088 (12)
O11	0.0159 (11)	0.0232 (11)	0.0375 (14)	0.0019 (9)	−0.0047 (9)	0.0136 (10)
C12	0.0197 (15)	0.0251 (16)	0.0309 (18)	0.0017 (12)	0.0003 (13)	0.0064 (13)
C13	0.0199 (15)	0.0303 (17)	0.0288 (17)	0.0058 (13)	0.0034 (13)	0.0065 (14)

Geometric parameters (Å, º)

Br1—C1	1.917 (3)	C6—H6A	0.9900
C1—C8	1.324 (4)	C6—H6B	0.9900
C1—C2	1.496 (4)	C7—C8	1.507 (4)
C2—C3	1.532 (4)	C7—H7A	0.9900
C2—H2A	0.9900	C7—H7B	0.9900
C2—H2B	0.9900	C8—H8	0.9500
C3—C4	1.519 (4)	O9—C10	1.423 (4)
C3—H3A	0.9900	C10—O11	1.433 (4)
C3—H3B	0.9900	C10—C12	1.512 (5)
C4—O9	1.432 (4)	C10—C13	1.521 (5)
C4—C5	1.531 (4)	C12—H12A	0.9800
C4—H4	1.0000	C12—H12B	0.9800
C5—O11	1.441 (4)	C12—H12C	0.9800
C5—C6	1.518 (4)	C13—H13A	0.9800
C5—H5	1.0000	C13—H13B	0.9800
C6—C7	1.541 (4)	C13—H13C	0.9800
C8—C1—C2	125.9 (3)	C7—C6—H6B	108.5
C8—C1—Br1	118.7 (2)	H6A—C6—H6B	107.5
C2—C1—Br1	115.3 (2)	C8—C7—C6	113.1 (3)
C1—C2—C3	112.4 (3)	C8—C7—H7A	109.0
C1—C2—H2A	109.1	C6—C7—H7A	109.0
C3—C2—H2A	109.1	C8—C7—H7B	109.0
C1—C2—H2B	109.1	C6—C7—H7B	109.0
C3—C2—H2B	109.1	H7A—C7—H7B	107.8
H2A—C2—H2B	107.9	C1—C8—C7	123.8 (3)
C4—C3—C2	114.7 (3)	C1—C8—H8	118.1
C4—C3—H3A	108.6	C7—C8—H8	118.1
C2—C3—H3A	108.6	C10—O9—C4	106.7 (2)
C4—C3—H3B	108.6	O9—C10—O11	105.1 (2)
C2—C3—H3B	108.6	O9—C10—C12	108.3 (3)
H3A—C3—H3B	107.6	O11—C10—C12	108.9 (3)
O9—C4—C3	107.0 (2)	O9—C10—C13	110.8 (3)
O9—C4—C5	103.2 (2)	O11—C10—C13	110.8 (3)
C3—C4—C5	117.5 (3)	C12—C10—C13	112.7 (3)
O9—C4—H4	109.6	C10—O11—C5	109.5 (2)
C3—C4—H4	109.6	C10—C12—H12A	109.5

C5—C4—H4	109.6	C10—C12—H12B	109.5
O11—C5—C6	107.9 (2)	H12A—C12—H12B	109.5
O11—C5—C4	103.7 (2)	C10—C12—H12C	109.5
C6—C5—C4	117.6 (3)	H12A—C12—H12C	109.5
O11—C5—H5	109.1	H12B—C12—H12C	109.5
C6—C5—H5	109.1	C10—C13—H13A	109.5
C4—C5—H5	109.1	C10—C13—H13B	109.5
C5—C6—C7	115.2 (3)	H13A—C13—H13B	109.5
C5—C6—H6A	108.5	C10—C13—H13C	109.5
C7—C6—H6A	108.5	H13A—C13—H13C	109.5
C5—C6—H6B	108.5	H13B—C13—H13C	109.5

C8—C1—C2—C3	−90.1 (4)	Br1—C1—C8—C7	−177.4 (2)
Br1—C1—C2—C3	86.3 (3)	C6—C7—C8—C1	83.7 (4)
C1—C2—C3—C4	46.3 (4)	C3—C4—O9—C10	−158.8 (2)
C2—C3—C4—O9	170.9 (3)	C5—C4—O9—C10	−34.3 (3)
C2—C3—C4—C5	55.6 (4)	C4—O9—C10—O11	32.6 (3)
O9—C4—C5—O11	22.7 (3)	C4—O9—C10—C12	148.9 (3)
C3—C4—C5—O11	140.1 (3)	C4—O9—C10—C13	−87.1 (3)
O9—C4—C5—C6	141.8 (3)	O9—C10—O11—C5	−17.2 (3)
C3—C4—C5—C6	−100.8 (3)	C12—C10—O11—C5	−133.1 (3)
O11—C5—C6—C7	−173.1 (3)	C13—C10—O11—C5	102.5 (3)
C4—C5—C6—C7	70.1 (4)	C6—C5—O11—C10	−129.1 (3)
C5—C6—C7—C8	−74.8 (4)	C4—C5—O11—C10	−3.6 (3)
C2—C1—C8—C7	−1.2 (5)		