electronic reprint

IUCrData

ISSN: 2414-3146
iucrdata.iucr.org/x

(1*R**,2*R**,5*R**,6*S**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-ol

Lea Simon, Heiner Detert and Dieter Schollmeyer

IUCrData (2025). **10**, x250854

IUCrData

ISSN 2414-3146

(1*R**,2*R**,5*R**,6*S**)-6-Bromo-9-oxabicyclo[3.3.1]-nonan-2-ol

Lea Simon, Heiner Detert* and Dieter Schollmeyer

University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany. *Correspondence e-mail: detert@uni-mainz.de

Received 24 September 2025
Accepted 29 September 2025

Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

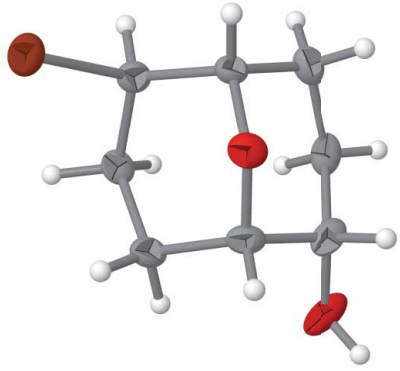
Keywords: crystal structure; heterocycle; bromine; hydrogen bridge.

CCDC reference: 2492093

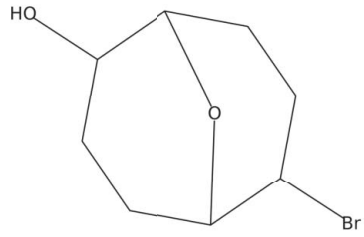
Structural data: full structural data are available from iucrdata.iucr.org

Both six-membered rings in the title bicyclo[3.3.1] system, $C_8H_{13}BrO_2$, adopt a chair conformation. Hydrogen bonds from the hydroxy group to the ether bridge connect the molecules into zigzag chains: single-enantiomer chains propagating along the *b*-axis direction form the crystal.

3D view



Chemical scheme



Structure description

The title compound, $C_8H_{13}BrO_2$ (Fig. 1), was prepared as part of a project on medium-sized rings (Detert *et al.*, 1994; Detert & Meier 1997*a*,*b*) and transannular reactions (Detert *et al.*, 1992, Kraemer *et al.*, 2009; Meier *et al.*, 2009). The oxabicyclo[3.3.1] framework is close to being perfectly C_{2v} symmetrical with both six-membered rings in a chair conformation. The centrosymmetrical crystal is composed of two counter-directional chains generated by a twofold screw axis. Both of these zigzag chains run along the *b*-axis direction (Fig. 2). Each chain is composed of a single enantiomer, the molecules are connected *via* hydrogen-bond bridges (O10—H10···O9) with an O···O distance of 1.91 (6) Å and an O—H···O 164 (3)° angle. The chains are connected by C—H···O contacts (Table 1).

Synthesis and crystallization

The synthesis of the title compound was performed by dihydroxylation of 1,5-cyclooctadiene (Yates *et al.*, 1972), acetalization, addition of bromine (Schollmeyer *et al.*, 2020) and hydrolysis of the acetal concomitant with an intramolecular nucleophilic substitution of one bromine atom by a hydroxyl group according to Takahashi *et al.* (2000). (1*R**,4*S**,5*S**,8*R**)-4,5-Dibromo-10,10-dimethyl-9,11-dioxabicyclo[6.3.0]undecane was the main isomer (*ca* 10/1) of the bromination step. 2.50 g of the crude product were purified *via* silica column chromatography using a cyclohexane–ethyl acetate (1:10) and 2% triethylamine eluent. (1*R**,4*S**,5*S**,8*R**)-4,5-Dibromo-10,10-dimethyl-9,11-dioxabicyclo[6.3.0]undecane (4b) was obtained as a colorless oil (1.03 g, 3.01 mmol, 46% of

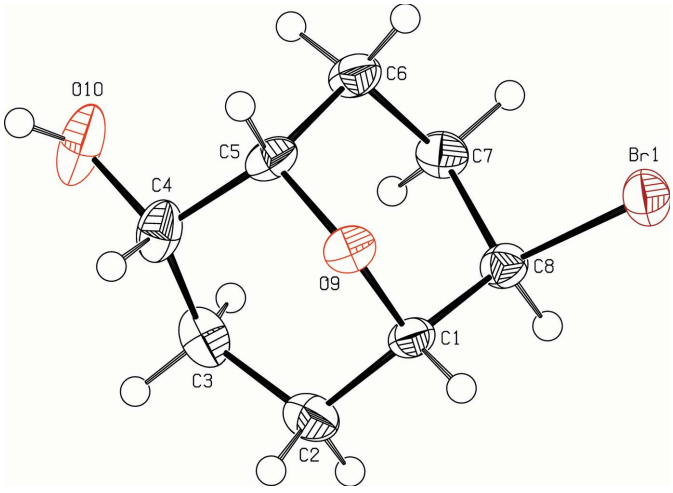


Figure 1
View (Spek, 2009) of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

theory). Then 0.90 g (2.63 mmol) of this mixture were dissolved in THF (4 ml), hydrochloric acid (1*M*, 4 ml) was added and the mixture was stirred at 323 K for 16 h while the reaction progress was monitored *via* TLC. After full conversion, the mixture was neutralized with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (4 × 25 ml). The combined organic layers were washed with brine (2 × 30 ml), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography using cyclohexane-ethyl acetate as an eluent (1:1, R_f = 0.32). (1*R**,2*R**,5*R**,6*S**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-ol was obtained as a crystalline, colorless solid (0.54 g, 2.44 mmol, 93% of theory) with m.p. = 341–344 K. Spectroscopic data: (assignment of signals follows IUPAC nomenclature): IR (ATR): ν (cm^{-1}) = 3390*mb*, 2940*s*,1733*w*, 1481*m*, 1443*m*, 1232*m*, 1084*m*, 1028*s*, 978*m*, 895*s*, 871*s*, 849*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.37–4.28 (*m*, 1H, 1-H), 4.14–3.95 (*m*, 2H, 2-H, 6-H), 3.90 (*t*, *J* = 5.92 Hz, 1H, 5-H), 2.56 (*s*, 1H, OH), 2.50–2.15 (*m*, 2H, 7-H, 8-H), 2.19–1.92 (*m*, 3H, 3-H, 4-H, 8′-H), 1.92–1.64 (*m*, 3H, 3-H, 4-H, 7′-H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 71.92 (2-C), 70.05 (5-C), 68.07 (6-C), 53.08 (1-C), 29.07 (8-C), 27.48 (4-C), 27.38 (3-C), 17.99 (7-C). LC–MS: *m*/*z* 221.000 $[M + H]^+$; (calculated for $C_8H_{14}O_2Br$ $[M + H]^+$: 221.018).

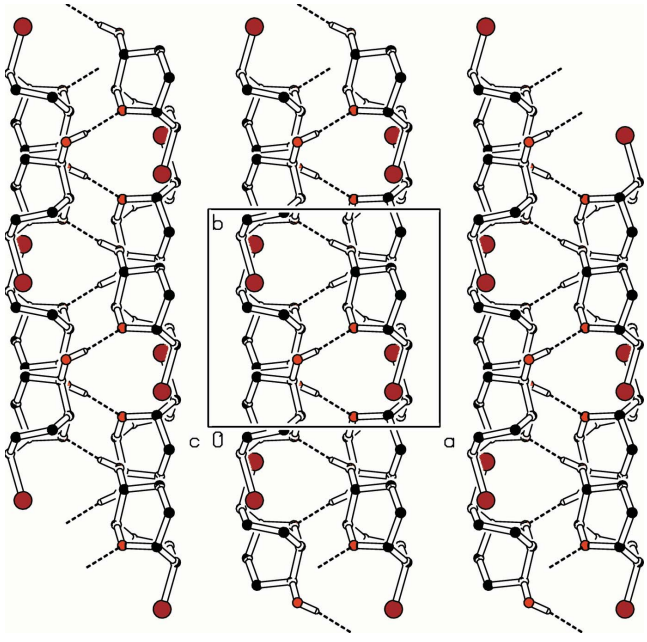


Figure 2
Part of the packing diagram. View along the *c*-axis direction (Spek, 2009). Hydrogen atoms bonded to C atoms are omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O10^{i}	0.95 (4)	2.45 (4)	3.378 (5)	164 (3)
O10—H10···O9^{ii}	0.83 (6)	1.91 (6)	2.732 (4)	166 (5)

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{13}BrO_2$
M_r	221.09
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, *b*, *c* (Å)	9.5387 (7), 8.8911 (8), 10.2453 (7)
β (°)	97.088 (6)
V (Å^3)	862.26 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.72
Crystal size (mm)	0.60 × 0.35 × 0.14
Data collection	
Diffractometer	Stoe *IPDS* 2T
Absorption correction	Integration (*X-RED32*; Stoe & Cie, 2020)
T_{min}, T_{max}	0.196, 0.519
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4579, 2057, 1808
R_{int}	0.023
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.659
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.042, 0.089, 1.27
No. of reflections	2057
No. of parameters	146
H-atom treatment	Only H-atom coordinates refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.54

Computer programs: *X-AREA WinXpose*, *Recipe* and *Integrate* (Stoe & Cie, 2020), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*) and *PLATON* (Spek, 2009).

Refinement

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

References

Detert, H., Antony–Mayer, C. & Meier, H. (1992). *Angew. Chem.* **104**, 755–757.
Detert, H. & Meier, H. (1997*a*). *Liebigs Ann. Recl* pp. 1557–1563.

Detert, H. & Meier, H., (1997*b*). *Liebigs Ann. Recl*, pp. 1565—1570.
Detert, H., Rose, B., Mayer, W. & Meier, H. (1994). *Chem. Ber.* **127**, 1529–1532.
Krämer, G., Detert, H. & Meier, H. (2009). *Tetrahedron Lett.* **50**, 4810–4812.
Meier, H., Krämer, G. & Detert, H. (2009). *Heterocycles* **78**, 2201–2208.
Schollmeyer, D., Heidrich, M. & Detert, H. (2020). *IUCrData* **5**, x201302.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stoe & Cie (2020). *X-RED* and *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Takahashi, A., Aso, M., Tanaka, M. & Suemune, H. (2000). *Tetrahedron* **56**, 1999–2006.
Yates, P., Lewars, E. G. & McCabe, P. H. (1972). *Can. J. Chem.* **50**, 1548–1556.

full crystallographic data

IUCrData (2025). **10**, x250854 [https://doi.org/10.1107/S2414314625008545]

(1*R**,2*R**,5*R**,6*S**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-ol

Lea Simon, Heiner Detert and Dieter Schollmeyer

(1*R**,2*R**,5*R**,6*S**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-ol

Crystal data

$C_8H_{13}BrO_2$
M_r = 221.09
Monoclinic, $P2_1/c$
a = 9.5387 (7) Å
b = 8.8911 (8) Å
c = 10.2453 (7) Å
β = 97.088 (6)°
V = 862.26 (12) Å^3
Z = 4
$F(000)$ = 448
D_x = 1.703 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8646 reflections
θ = 2.8–28.4°
μ = 4.72 mm^{-1}
T = 120 K
Block, colorless
0.60 × 0.35 × 0.14 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, 2020)
T_{min} = 0.196, T_{max} = 0.519
4579 measured reflections
2057 independent reflections
1808 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.9°, θ_{min} = 3.0°
h = −11→12
k = −11→10
l = −13→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.089
S = 1.27
2057 reflections
146 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 1.9676P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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 freely refined, except H1 and H5 which were refined with U(H)=1.2U_{eq}(C). The H atoms of each CH_2 group were given a common displacement parameter.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.19929 (4)	0.83866 (4)	0.25179 (4)	0.03210 (13)
C1	0.2223 (4)	0.5517 (4)	0.1306 (3)	0.0235 (7)
H1	0.220 (4)	0.620 (4)	0.059 (4)	0.028*
C2	0.1690 (4)	0.3953 (5)	0.0871 (4)	0.0306 (8)
H2A	0.065 (4)	0.393 (5)	0.065 (4)	0.029 (7)*
H2B	0.213 (4)	0.371 (5)	0.011 (4)	0.029 (7)*
C3	0.2108 (4)	0.2714 (4)	0.1884 (4)	0.0334 (8)
H3A	0.149 (5)	0.269 (5)	0.260 (4)	0.041 (9)*
H3B	0.196 (5)	0.176 (5)	0.148 (5)	0.041 (9)*
C4	0.3622 (4)	0.2883 (4)	0.2501 (4)	0.0316 (8)
H4	0.431 (4)	0.266 (5)	0.185 (4)	0.032 (11)*
C5	0.3972 (4)	0.4502 (4)	0.2913 (3)	0.0255 (7)
H5	0.492 (4)	0.458 (5)	0.314 (4)	0.031*
C6	0.3264 (4)	0.5148 (5)	0.4058 (3)	0.0277 (7)
H6A	0.343 (5)	0.436 (5)	0.472 (5)	0.045 (9)*
H6B	0.382 (5)	0.608 (6)	0.434 (4)	0.045 (9)*
C7	0.1695 (4)	0.5486 (4)	0.3687 (3)	0.0262 (7)
H7A	0.113 (4)	0.454 (5)	0.366 (4)	0.032 (8)*
H7B	0.138 (4)	0.616 (5)	0.439 (4)	0.032 (8)*
C8	0.1421 (4)	0.6236 (4)	0.2342 (3)	0.0247 (7)
H8	0.044 (4)	0.631 (4)	0.201 (4)	0.020 (9)*
O9	0.3704 (2)	0.5456 (3)	0.1771 (2)	0.0250 (5)
O10	0.3857 (4)	0.1913 (4)	0.3610 (3)	0.0464 (8)
H10	0.466 (6)	0.153 (6)	0.362 (5)	0.057 (16)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0394 (2)	0.02595 (18)	0.03210 (19)	0.00348 (17)	0.00881 (14)	0.00081 (15)
C1	0.0223 (16)	0.0300 (18)	0.0177 (15)	0.0044 (14)	0.0005 (12)	0.0003 (13)
C2	0.0251 (18)	0.038 (2)	0.0291 (18)	−0.0019 (16)	0.0043 (15)	−0.0090 (15)
C3	0.033 (2)	0.0276 (18)	0.041 (2)	−0.0023 (16)	0.0112 (17)	−0.0056 (16)
C4	0.031 (2)	0.0299 (18)	0.0356 (19)	0.0081 (15)	0.0133 (16)	0.0093 (15)
C5	0.0185 (16)	0.0355 (19)	0.0219 (16)	0.0024 (14)	0.0006 (13)	0.0047 (14)
C6	0.0258 (18)	0.037 (2)	0.0197 (15)	0.0042 (16)	0.0017 (14)	0.0017 (14)
C7	0.0272 (18)	0.0313 (18)	0.0210 (16)	−0.0015 (15)	0.0072 (14)	0.0000 (13)
C8	0.0210 (16)	0.0287 (18)	0.0241 (16)	0.0013 (14)	0.0016 (13)	−0.0004 (13)
O9	0.0230 (12)	0.0299 (13)	0.0228 (11)	−0.0029 (10)	0.0051 (9)	0.0041 (10)
O10	0.0464 (19)	0.0454 (18)	0.0523 (18)	0.0253 (15)	0.0260 (15)	0.0253 (14)

Geometric parameters (Å, º)

Br1—C8	1.991 (4)	C4—H4	1.01 (4)
C1—O9	1.435 (4)	C5—O9	1.443 (4)
C1—C8	1.523 (5)	C5—C6	1.535 (5)

C1—C2	1.529 (5)	C5—H5	0.91 (4)
C1—H1	0.95 (4)	C6—C7	1.528 (5)
C2—C3	1.533 (6)	C6—H6A	0.97 (5)
C2—H2A	0.99 (4)	C6—H6B	1.01 (5)
C2—H2B	0.95 (4)	C7—C8	1.524 (5)
C3—C4	1.511 (6)	C7—H7A	1.00 (4)
C3—H3A	1.00 (5)	C7—H7B	1.01 (4)
C3—H3B	0.95 (5)	C8—H8	0.96 (4)
C4—O10	1.422 (4)	O10—H10	0.83 (6)
C4—C5	1.526 (6)		

O9—C1—C8	110.1 (3)	O9—C5—C6	110.5 (3)
O9—C1—C2	109.9 (3)	C4—C5—C6	117.6 (3)
C8—C1—C2	114.1 (3)	O9—C5—H5	104 (3)
O9—C1—H1	102 (3)	C4—C5—H5	108 (3)
C8—C1—H1	108 (2)	C6—C5—H5	107 (3)
C2—C1—H1	112 (2)	C7—C6—C5	113.1 (3)
C1—C2—C3	114.0 (3)	C7—C6—H6A	113 (3)
C1—C2—H2A	112 (2)	C5—C6—H6A	102 (3)
C3—C2—H2A	108 (2)	C7—C6—H6B	112 (3)
C1—C2—H2B	106 (2)	C5—C6—H6B	105 (3)
C3—C2—H2B	106 (2)	H6A—C6—H6B	111 (4)
H2A—C2—H2B	110 (3)	C8—C7—C6	111.4 (3)
C4—C3—C2	111.6 (3)	C8—C7—H7A	108 (2)
C4—C3—H3A	109 (3)	C6—C7—H7A	111 (2)
C2—C3—H3A	112 (3)	C8—C7—H7B	111 (2)
C4—C3—H3B	111 (3)	C6—C7—H7B	108 (2)
C2—C3—H3B	110 (3)	H7A—C7—H7B	108 (3)
H3A—C3—H3B	104 (4)	C1—C8—C7	113.6 (3)
O10—C4—C3	108.8 (3)	C1—C8—Br1	108.1 (2)
O10—C4—C5	110.1 (3)	C7—C8—Br1	108.9 (2)
C3—C4—C5	112.0 (3)	C1—C8—H8	110 (2)
O10—C4—H4	111 (2)	C7—C8—H8	114 (2)
C3—C4—H4	112 (2)	Br1—C8—H8	102 (2)
C5—C4—H4	104 (2)	C1—O9—C5	111.1 (2)
O9—C5—C4	108.6 (3)	C4—O10—H10	108 (4)

O9—C1—C2—C3	49.8 (4)	C5—C6—C7—C8	−42.9 (4)
C8—C1—C2—C3	−74.3 (4)	O9—C1—C8—C7	−53.9 (4)
C1—C2—C3—C4	−42.3 (4)	C2—C1—C8—C7	70.1 (4)
C2—C3—C4—O10	168.0 (3)	O9—C1—C8—Br1	67.1 (3)
C2—C3—C4—C5	46.0 (4)	C2—C1—C8—Br1	−168.9 (2)
O10—C4—C5—O9	−179.2 (3)	C6—C7—C8—C1	43.8 (4)
C3—C4—C5—O9	−58.1 (4)	C6—C7—C8—Br1	−76.8 (3)
O10—C4—C5—C6	−52.9 (4)	C8—C1—O9—C5	63.7 (3)
C3—C4—C5—C6	68.3 (4)	C2—C1—O9—C5	−62.8 (3)
O9—C5—C6—C7	52.5 (4)	C4—C5—O9—C1	67.1 (3)
C4—C5—C6—C7	−72.9 (4)	C6—C5—O9—C1	−63.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*B*···O10^{i}	0.95 (4)	2.45 (4)	3.378 (5)	164 (3)
O10—H10···O9^{ii}	0.83 (6)	1.91 (6)	2.732 (4)	166 (5)

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