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rac-4,5-*trans*-Dibromo-9,9-dichloro-*cis*-bicyclo-[6.1.0]nonane

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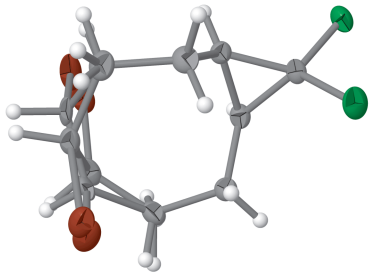
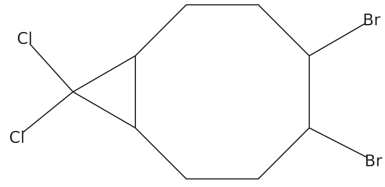
Structural data: full structural data are available from iucrdata.iucr.org

The crystal structure of the title tetrahalogenated bicyclononane, $C_9H_{12}Br_2Cl_2$, is reported. The molecule adopts a distorted twist-chair conformation. The cyclopropane ring is almost parallel to the plane formed by the four methylene carbon atoms.

3D view



Chemical scheme



Structure description

The title compound, $C_9H_{12}Br_2Cl_2$ (Fig. 1), was prepared as part of a project focusing on medium-sized bicyclic cycloalkynes (Meier *et al.*, 1987; Detert & Meier, 1997). Both enantiomers [*(S,S)* and *(R,R-)*] occupy the same positions in the crystal, resulting in disorder on C1 and C2, but the ratio is 0.638 (9)/0.362 (9). The eight-membered ring adopts a distorted twist-chair conformation and the annulated cyclopropane group is in an *exo*-position. The four methylene carbons (C3, C4, C7, C8) lie in a common plane. This plane is nearly parallel to the cyclopropane ring, their normals enclose a small angle of only 0.5 (3)°. The bond lengths of the bromine-bound carbon atoms are significantly different: C1—C8: 1.487 (7) Å; C2—C3: 1.567 (7) Å. Furthermore, the C—C—C bond angles are opened to 120.5 (5)° (C2—C8—C1) and even 121.8 (5)° (C1—C2—C3). The same holds for the minor occupied sites. The packing is shown in Fig. 2.

Synthesis and crystallization

The title compound, first mentioned by Fray (1963), was prepared by careful addition of bromine to 9.9-dichlorobicyclo[6.1.0]non-4-ene. Crystals were grown by slow evaporation of a solution in chloroform and propanol-2 to yield colorless crystals with a m.p. of 336–340 K. The annotation of the NMR signals follows IUPAC nomenclature. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.1 (*bs*, 1 H, OH), 2.75 (*t*, 2 H, J = 6.1 Hz), 2.37 (*t*, 2 H, J = 6 Hz), 2.20-1.95 (*m*, 6 H, 3,4,7-H), 1.80 (*m*, 4 H, 8,9-H); ^{13}C-NMR (100 MHz, $CDCl_3$): 160.3 (C═N), 84.9, 83.4 (C-5, C-6), 26.1, 24.3, 23.9 (C-3,8,9), 19.6, 18.3 (C-4, 7).

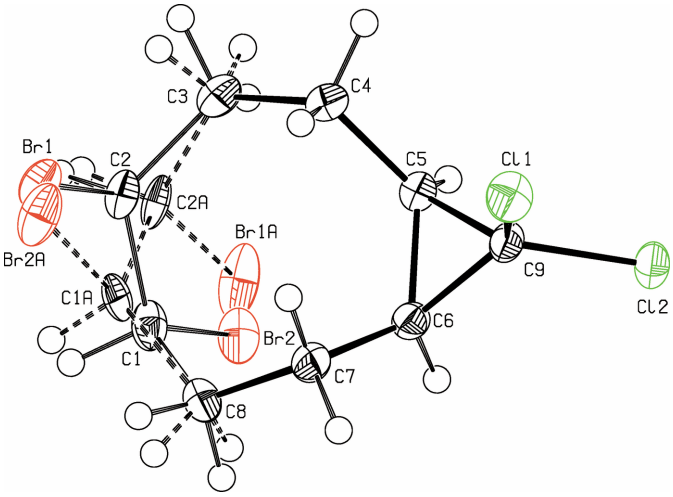


Figure 1
View (Spek, 2009) of the title compound. Displacement ellipsoids are drawn at the 50% probability level. The minor occupied component is drawn with dashed lines.

Refinement

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

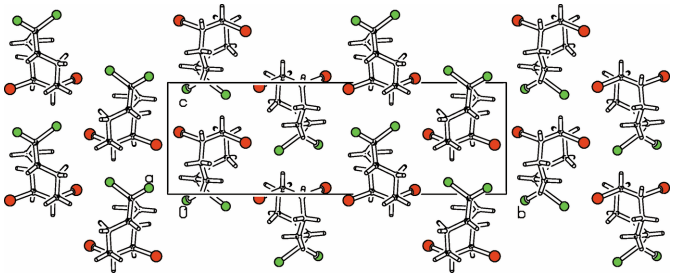


Figure 2
Partial packing diagram (Spek, 2009), viewed along the *a*-axis direction. The minor occupied component is omitted.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}Br_2Cl_2$
M_r	350.91
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	7.2027 (3), 22.1157 (10), 7.5534 (3)
β (°)	105.517 (3)
V (Å^3)	1159.35 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.41
Crystal size (mm)	0.50 × 0.46 × 0.13
Data collection	
Diffractometer	Stoe *IPDS* 2T
Absorption correction	Integration [*X-RED32* (Stoe & Cie, 2020) absorption correction by Gaussian integration]
T_{min}, T_{max}	0.069, 0.358
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6364, 2766, 2469
R_{int}	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.659
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.100, 1.19
No. of reflections	2766
No. of parameters	155
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.40

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

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full crystallographic data

IUCrData (2025). **10**, x250573 [https://doi.org/10.1107/S2414314625005735]

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Crystal data

$C_9H_{12}Br_2Cl_2$
M_r = 350.91
Monoclinic, $P2_1/c$
a = 7.2027 (3) Å
b = 22.1157 (10) Å
c = 7.5534 (3) Å
β = 105.517 (3)°
V = 1159.35 (9) Å^3
Z = 4
$F(000)$ = 680
D_x = 2.010 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9471 reflections
θ = 2.8–28.4°
μ = 7.41 mm^{-1}
T = 120 K
Plate, colorless
0.50 × 0.46 × 0.13 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12x0.4mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
rotation method, ω scans
Absorption correction: integration [X-Red32 (Stoe & Cie, 2020) absorption correction by Gaussian integration]
T_{min} = 0.069, T_{max} = 0.358
6364 measured reflections
2766 independent reflections
2469 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 27.9°, θ_{min} = 2.9°
h = −9→9
k = −29→29
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
S = 1.19
2766 reflections
155 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 2.8083P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 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 attached to carbons were placed at calculated positions and were refined in the riding-model approximation with $C_{methylene}$–H = 0.99 Å or $C_{tertiary}$–H = 1.00 Å, and with U_{iso}(H) = 1.2 U_{eq}(C).

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.67566 (14)	0.67134 (4)	0.60825 (12)	0.0288 (2)	
Cl2	0.83981 (13)	0.55561 (4)	0.55570 (12)	0.02610 (19)	
Br1	0.0626 (5)	0.72992 (15)	0.0378 (5)	0.0261 (4)	0.638 (9)
Br2	0.2483 (2)	0.53409 (6)	−0.0565 (4)	0.0289 (4)	0.638 (9)
C1	0.1135 (9)	0.6031 (4)	0.0199 (9)	0.0243 (14)	0.638 (9)
H1	−0.023418	0.599338	−0.054723	0.029*	0.638 (9)
C2	0.1880 (9)	0.6610 (3)	−0.0491 (8)	0.0232 (13)	0.638 (9)
H2	0.130604	0.660373	−0.185198	0.028*	0.638 (9)
Br1A	0.2998 (9)	0.5459 (2)	−0.1082 (6)	0.0393 (12)	0.362 (9)
Br2A	0.0345 (11)	0.7209 (3)	0.0592 (9)	0.0336 (10)	0.362 (9)
C1A	0.0875 (14)	0.6337 (7)	0.0252 (13)	0.021 (2)	0.362 (9)
H1A	−0.033261	0.617909	−0.061182	0.026*	0.362 (9)
C2A	0.2366 (16)	0.6317 (6)	−0.0823 (13)	0.024 (2)	0.362 (9)
H2A	0.167411	0.645242	−0.209057	0.028*	0.362 (9)
C3	0.4082 (6)	0.67226 (18)	−0.0243 (5)	0.0287 (8)	
H3A	0.457248	0.639468	−0.088844	0.034*	0.638 (9)
H3B	0.422031	0.710584	−0.087348	0.034*	0.638 (9)
H3C	0.360886	0.713840	−0.057962	0.034*	0.362 (9)
H3D	0.492984	0.662025	−0.103791	0.034*	0.362 (9)
C4	0.5379 (5)	0.67580 (16)	0.1709 (5)	0.0242 (7)	
H4A	0.657883	0.697353	0.169044	0.029*	
H4B	0.472136	0.699838	0.246652	0.029*	
C5	0.5899 (5)	0.61482 (15)	0.2597 (5)	0.0192 (6)	
H5	0.653803	0.586721	0.190526	0.023*	
C6	0.4614 (5)	0.58393 (15)	0.3632 (5)	0.0206 (7)	
H6	0.454627	0.538915	0.350552	0.025*	
C7	0.2773 (5)	0.61350 (17)	0.3764 (5)	0.0237 (7)	
H7A	0.295303	0.657907	0.382082	0.028*	
H7B	0.248641	0.600487	0.491711	0.028*	
C8	0.1061 (5)	0.59791 (18)	0.2141 (5)	0.0266 (7)	
H8A	0.070570	0.555553	0.232062	0.032*	0.638 (9)
H8B	−0.002787	0.623390	0.226302	0.032*	0.638 (9)
H8C	−0.013285	0.604977	0.252293	0.032*	0.362 (9)
H8D	0.112053	0.554131	0.188845	0.032*	0.362 (9)
C9	0.6542 (5)	0.60790 (15)	0.4640 (5)	0.0201 (6)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0330 (5)	0.0250 (4)	0.0246 (4)	−0.0022 (3)	0.0013 (3)	−0.0062 (3)
Cl2	0.0220 (4)	0.0268 (4)	0.0258 (4)	0.0037 (3)	0.0001 (3)	0.0047 (3)
Br1	0.0348 (8)	0.0208 (6)	0.0219 (8)	0.0074 (5)	0.0063 (5)	0.0023 (5)
Br2	0.0291 (5)	0.0228 (4)	0.0295 (7)	0.0041 (3)	−0.0016 (4)	−0.0071 (4)
C1	0.022 (3)	0.019 (3)	0.027 (3)	0.004 (2)	−0.002 (2)	−0.004 (3)
C2	0.025 (3)	0.025 (3)	0.017 (3)	0.007 (2)	0.001 (2)	0.002 (2)

Br1A	0.0497 (17)	0.0319 (11)	0.0262 (10)	0.0215 (11)	−0.0075 (11)	−0.0111 (9)
Br2A	0.044 (2)	0.032 (2)	0.0244 (13)	0.0204 (15)	0.0094 (10)	0.0019 (12)
C1A	0.013 (4)	0.030 (7)	0.016 (4)	−0.001 (5)	−0.005 (3)	−0.005 (5)
C2A	0.029 (5)	0.027 (6)	0.009 (4)	0.010 (4)	−0.004 (4)	0.002 (4)
C3	0.032 (2)	0.0309 (19)	0.0226 (17)	−0.0001 (15)	0.0064 (15)	0.0088 (15)
C4	0.0259 (18)	0.0212 (16)	0.0256 (17)	−0.0017 (13)	0.0071 (14)	0.0047 (13)
C5	0.0205 (16)	0.0189 (15)	0.0178 (15)	0.0017 (12)	0.0046 (12)	0.0003 (12)
C6	0.0218 (17)	0.0196 (15)	0.0187 (15)	−0.0025 (13)	0.0025 (13)	0.0018 (12)
C7	0.0220 (17)	0.0286 (17)	0.0208 (16)	0.0011 (14)	0.0062 (13)	0.0060 (14)
C8	0.0181 (16)	0.0328 (19)	0.0270 (17)	−0.0009 (14)	0.0027 (14)	0.0034 (15)
C9	0.0210 (16)	0.0191 (15)	0.0183 (15)	0.0019 (12)	0.0017 (13)	0.0029 (12)

Geometric parameters (Å, º)

Cl1—C9	1.758 (3)	C3—H3C	0.9900
Cl2—C9	1.763 (3)	C3—H3D	0.9900
Br1—C2	1.972 (9)	C4—C5	1.508 (5)
Br2—C1	1.975 (9)	C4—H4A	0.9900
C1—C8	1.487 (7)	C4—H4B	0.9900
C1—C2	1.533 (10)	C5—C9	1.495 (5)
C1—H1	1.0000	C5—C6	1.524 (5)
C2—C3	1.567 (7)	C5—H5	1.0000
C2—H2	1.0000	C6—C9	1.491 (5)
Br1A—C2A	1.973 (14)	C6—C7	1.505 (5)
Br2A—C1A	1.997 (18)	C6—H6	1.0000
C1A—C2A	1.510 (17)	C7—C8	1.528 (5)
C1A—C8	1.606 (12)	C7—H7A	0.9900
C1A—H1A	1.0000	C7—H7B	0.9900
C2A—C3	1.495 (12)	C8—H8A	0.9900
C2A—H2A	1.0000	C8—H8B	0.9900
C3—C4	1.522 (5)	C8—H8C	0.9900
C3—H3A	0.9900	C8—H8D	0.9900
C3—H3B	0.9900		
C8—C1—C2	120.5 (6)	C5—C4—H4B	108.8
C8—C1—Br2	112.3 (4)	C3—C4—H4B	108.8
C2—C1—Br2	107.6 (5)	H4A—C4—H4B	107.7
C8—C1—H1	105.0	C9—C5—C4	121.5 (3)
C2—C1—H1	105.0	C9—C5—C6	59.2 (2)
Br2—C1—H1	105.0	C4—C5—C6	121.1 (3)
C1—C2—C3	121.8 (5)	C9—C5—H5	114.7
C1—C2—Br1	107.4 (5)	C4—C5—H5	114.7
C3—C2—Br1	112.1 (4)	C6—C5—H5	114.7
C1—C2—H2	104.6	C9—C6—C7	121.9 (3)
C3—C2—H2	104.6	C9—C6—C5	59.4 (2)
Br1—C2—H2	104.6	C7—C6—C5	120.4 (3)
C2A—C1A—C8	124.1 (10)	C9—C6—H6	114.7
C2A—C1A—Br2A	106.6 (10)	C7—C6—H6	114.7

C8—C1A—Br2A	109.6 (6)	C5—C6—H6	114.7
C2A—C1A—H1A	105.0	C6—C7—C8	112.6 (3)
C8—C1A—H1A	105.0	C6—C7—H7A	109.1
Br2A—C1A—H1A	105.0	C8—C7—H7A	109.1
C3—C2A—C1A	118.5 (10)	C6—C7—H7B	109.1
C3—C2A—Br1A	114.3 (7)	C8—C7—H7B	109.1
C1A—C2A—Br1A	107.3 (10)	H7A—C7—H7B	107.8
C3—C2A—H2A	105.2	C1—C8—C7	122.7 (4)
C1A—C2A—H2A	105.2	C7—C8—C1A	117.4 (5)
Br1A—C2A—H2A	105.2	C1—C8—H8A	106.7
C2A—C3—C4	124.0 (4)	C7—C8—H8A	106.7
C4—C3—C2	117.6 (3)	C1—C8—H8B	106.7
C4—C3—H3A	107.9	C7—C8—H8B	106.7
C2—C3—H3A	107.9	H8A—C8—H8B	106.6
C4—C3—H3B	107.9	C7—C8—H8C	108.0
C2—C3—H3B	107.9	C1A—C8—H8C	108.0
H3A—C3—H3B	107.2	C7—C8—H8D	108.0
C2A—C3—H3C	106.3	C1A—C8—H8D	108.0
C4—C3—H3C	106.3	H8C—C8—H8D	107.2
C2A—C3—H3D	106.3	C6—C9—C5	61.4 (2)
C4—C3—H3D	106.3	C6—C9—Cl1	121.0 (3)
H3C—C3—H3D	106.4	C5—C9—Cl1	120.6 (2)
C5—C4—C3	113.6 (3)	C6—C9—Cl2	118.2 (2)
C5—C4—H4A	108.8	C5—C9—Cl2	117.7 (2)
C3—C4—H4A	108.8	Cl1—C9—Cl2	110.36 (19)

C8—C1—C2—C3	84.4 (8)	C9—C6—C7—C8	158.3 (3)
Br2—C1—C2—C3	−46.0 (7)	C5—C6—C7—C8	87.5 (4)
C8—C1—C2—Br1	−46.9 (7)	C2—C1—C8—C7	−49.5 (8)
Br2—C1—C2—Br1	−177.3 (3)	Br2—C1—C8—C7	78.9 (5)
C8—C1A—C2A—C3	−82.3 (15)	C6—C7—C8—C1	−49.5 (6)
Br2A—C1A—C2A—C3	46.3 (10)	C6—C7—C8—C1A	−79.0 (7)
C8—C1A—C2A—Br1A	48.9 (11)	C2A—C1A—C8—C7	60.9 (13)
Br2A—C1A—C2A—Br1A	177.6 (5)	Br2A—C1A—C8—C7	−66.4 (7)
C1A—C2A—C3—C4	52.0 (13)	C7—C6—C9—C5	−108.9 (3)
Br1A—C2A—C3—C4	−76.0 (7)	C7—C6—C9—Cl1	1.5 (4)
C1—C2—C3—C4	−62.2 (7)	C5—C6—C9—Cl1	110.4 (3)
Br1—C2—C3—C4	67.1 (5)	C7—C6—C9—Cl2	143.1 (3)
C2A—C3—C4—C5	44.4 (8)	C5—C6—C9—Cl2	−108.0 (3)
C2—C3—C4—C5	79.2 (5)	C4—C5—C9—C6	109.9 (4)
C3—C4—C5—C9	−158.2 (3)	C4—C5—C9—Cl1	−1.2 (5)
C3—C4—C5—C6	−87.6 (4)	C6—C5—C9—Cl1	−111.1 (3)
C4—C5—C6—C9	−110.5 (4)	C4—C5—C9—Cl2	−141.4 (3)
C9—C5—C6—C7	111.4 (4)	C6—C5—C9—Cl2	108.7 (3)
C4—C5—C6—C7	0.9 (5)		