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(1*S*,3*R*,8*R*,11*S*)-11-Bromo-10-bromomethyl-2,2-dichloro-3,7,7-trimethyltricyclo[6.4.0.0^{1,3}]dodec-9-ene

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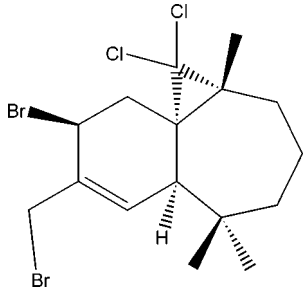
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.038; wR factor = 0.102; data-to-parameter ratio = 19.9.

The title compound, $C_{16}H_{22}Br_2Cl_2$, was synthesized from β-himachalene (3,5,5,9-tetramethyl-2,4a,5,6,7,8-hexahydro-1*H*-benzocycloheptene), which was isolated from the essential oil of the Atlas cedar (*Cedrus Atlantica*). The molecule is built up from fused six- and seven-membered rings and an appended three-membered ring. The six-membered ring has a half-chair conformation, whereas the seven-membered ring displays a chair conformation. The dihedral angle between the two best plane through each ring is 59.5 (2)°. No specific intermolecular interactions were discerned in the crystal packing.

Related literature

For the reactivity and biological properties of β-himachalene, see: El Haib *et al.* (2011); El Jamili *et al.* (2002); Daoubi *et al.* (2004). For related structures, see: Oukhrib *et al.* (2013); Ourhriss *et al.* (2013); Benharref *et al.*(2013). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{16}H_{22}Br_2Cl_2$
M_r = 445.06
Orthorhombic, $P2_12_12_1$
a = 8.2594 (7) Å
b = 13.0352 (11) Å
c = 16.6241 (13) Å
V = 1789.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.82 mm^{-1}
T = 293 K
0.20 × 0.15 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SHELXS97*; Sheldrick,2008)
T_{min} = 0.423, T_{max} = 0.617
10693 measured reflections
3654 independent reflections
3183 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.102
S = 1.05
3654 reflections
184 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Absolute structure: Flack & Bernardinelli (2000), 614 Friedel pairs
Absolute structure parameter: 0.022 (13)

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5241).

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supporting information

Acta Cryst. (2013). E**69**, o1283 [doi:10.1107/S1600536813019697]

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S1. Comment

The bicyclic sesquiterpene *β*-himachalene is the main constituent (50%) of the essential oil of the Atlas cedar (*Cedrus atlantica*) (El Haib *et al.*, 2011). The reactivity of this sesquiterpene and its derivatives has been studied extensively by our team in order to prepare new products having biological proprieties (El Jamili *et al.*, 2002; Daoubi *et al.*, 2004; Ourhriss *et al.*, 2013; Oukhrib *et al.*, 2013; Benharref *et al.*, 2013). In this work, we present the crystal structure of the title compound, (1*S*,3*R*,8*R*,11*S*)- 10- bromomethyl-11-bromo-2,2-dichloro-3,7,7-trimethyltricyclo [6.4.0.0$_{1,3}$] dodec-9-ene. The molecule contains fused six-and seven-membered rings, which is fused to a three-membered ring as shown in Fig. 1. The six-membered ring has a half-chair conformation, as indicated by the total puckering amplitude QT = 0.466 (4) Å and spherical polar angle θ = 129.9 (7)° with φ = 152.5 (7)°, whereas the seven-membered ring displays a chair conformation with QT = 0.8129 (51) Å, θ = 32.71 (40)°, φ2 = -46.29 (5)° and φ3 = -77.86 (39)° (Cremer & Pople, 1975). Owing to the presence of Br atoms, the absolute configuration could be fully confirmed, by refining the Flack parameter (Flack & Bernardinelli, 2000) as C1(*S*), C3(*R*), C8(*R*) and C11(*S*).

S2. Experimental

In a reactor equipped with a stirrer, a condenser, a dropping funnel and a thermometer containing (1*S*,3*R*,8*R*)-2,2-dichloro-3,7,7,10-tetramethyltricyclo [6.4.0.01,3] dodec-9-ene (2 g, 7 mmol) (El Jamili *et al.*, 2002) and carbon tetrachloride (60 ml) was added slowly over an 1.5 h by heating and stirring a solution of bromine (1.6 g, 10 mmol) in carbon tetrachloride (5 ml). Heating and stirring were maintained for 1 h after the addition of bromine. Thereafter the reaction mixture was cooled and concentrated to evaporate the carbon tetrachloride. the residue obtained was chromatographed on silica eluting with hexane, which allowed the isolation of pure (1*S*,3*R*,8*R*,11*S*)-10-bromomethyl-11-bromo-2,2-dichloro-3,7,7-trimethyltricyclo [6.4.0.01,3] dodec-9-ene in a yield of 20% (623 mg, 1.4 mmol). The title compound was recrystallized from its hexane solution.

S3. Refinement

All H atoms were fixed geometrically and treated as riding with C—H = 0.96 Å (methyl), 0.97 Å (methylene), 0.98 Å (methine) with U_{iso}(H) = 1.2U_{eq}(methylene, methine) or U_{iso}(H) = 1.5U_{eq}(methyl).

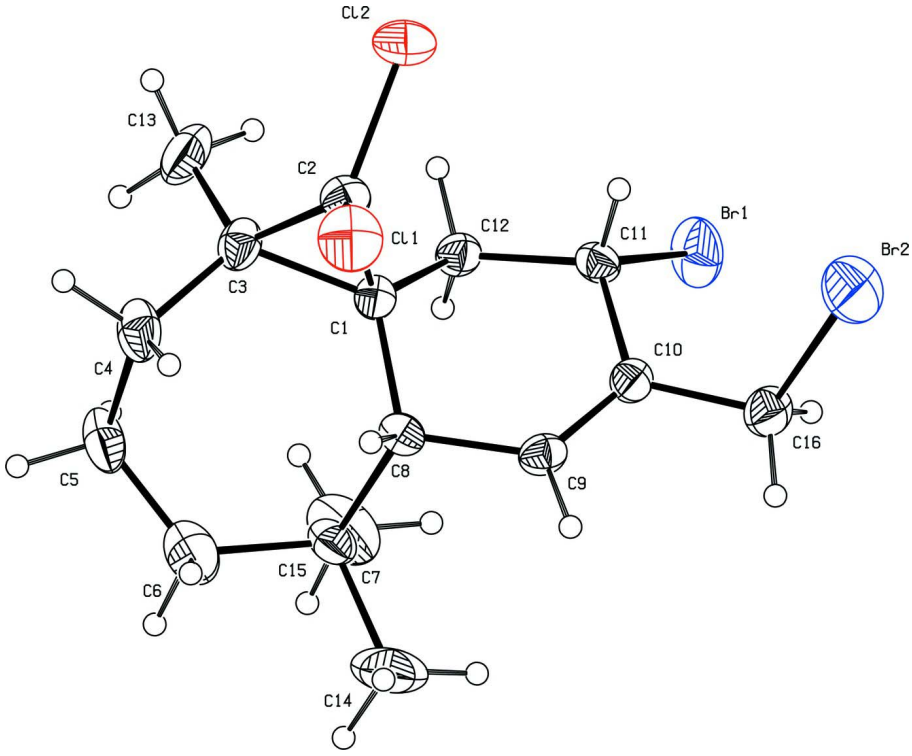

Figure 1

Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability. level. H atoms are represented as small spheres of arbitrary radii.

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c = 16.6241 (13) Å
V = 1789.8 (3) Å^3
Z = 4

$F(000)$ = 888
D_x = 1.652 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3653 reflections
θ = 2.8–26.4°
μ = 4.82 mm^{-1}
T = 293 K
Block, colourless
0.20 × 0.15 × 0.12 mm

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Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan *SHELXS97* (Sheldrick,2008)
T_{min} = 0.423, T_{max} = 0.617

10693 measured reflections
3654 independent reflections
3183 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 26.4°, θ_{min} = 2.5°
h = −10→10
k = −13→16
l = −11→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.102$
$S = 1.05$
3654 reflections
184 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 1.2463P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}
Absolute structure: Flack & Bernardinelli (2000), 614 Friedel pairs
Absolute structure parameter: 0.022 (13)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3469 (4)	0.4202 (3)	0.7271 (2)	0.0346 (8)
C2	0.1795 (4)	0.3776 (4)	0.7462 (3)	0.0440 (9)
C3	0.2012 (4)	0.4409 (4)	0.6715 (2)	0.0446 (9)
C4	0.1967 (6)	0.3884 (4)	0.5903 (3)	0.0570 (12)
H4A	0.0915	0.3999	0.5659	0.068*
H4B	0.2095	0.3151	0.5979	0.068*
C5	0.3291 (6)	0.4270 (5)	0.5327 (3)	0.0598 (13)
H5A	0.2927	0.4188	0.4775	0.072*
H5B	0.3480	0.4994	0.5421	0.072*
C6	0.4858 (7)	0.3684 (5)	0.5444 (3)	0.0721 (15)
H6A	0.5565	0.3853	0.4998	0.086*
H6B	0.4610	0.2959	0.5401	0.086*
C7	0.5838 (5)	0.3841 (3)	0.6231 (2)	0.0446 (9)
C8	0.4798 (5)	0.3470 (3)	0.6986 (2)	0.0354 (8)
H8	0.4247	0.2840	0.6817	0.043*
C9	0.5846 (5)	0.3179 (3)	0.7684 (2)	0.0384 (8)
H9	0.6527	0.2619	0.7611	0.046*
C10	0.5903 (4)	0.3636 (3)	0.8394 (2)	0.0373 (8)
C11	0.4874 (5)	0.4553 (3)	0.8571 (2)	0.0370 (8)
H11	0.4009	0.4346	0.8940	0.044*
C12	0.4109 (5)	0.5026 (3)	0.7827 (2)	0.0391 (8)
H12A	0.3228	0.5475	0.7987	0.047*
H12B	0.4908	0.5436	0.7545	0.047*

C13	0.1283 (6)	0.5488 (4)	0.6685 (3)	0.0684 (14)
H13A	0.1301	0.5784	0.7214	0.103*
H13B	0.0185	0.5448	0.6498	0.103*
H13C	0.1904	0.5907	0.6325	0.103*
C14	0.7278 (9)	0.3099 (6)	0.6141 (4)	0.093 (2)
H14A	0.8067	0.3242	0.6550	0.139*
H14B	0.7761	0.3188	0.5620	0.139*
H14C	0.6904	0.2406	0.6196	0.139*
C15	0.6474 (9)	0.4891 (5)	0.6292 (4)	0.0845 (19)
H15A	0.5591	0.5365	0.6345	0.127*
H15B	0.7083	0.5052	0.5816	0.127*
H15C	0.7165	0.4943	0.6754	0.127*
C16	0.6964 (5)	0.3222 (4)	0.9042 (3)	0.0507 (10)
H16A	0.7645	0.3769	0.9247	0.061*
H16B	0.7665	0.2698	0.8817	0.061*
Cl3	0.14150 (16)	0.24471 (10)	0.74083 (8)	0.0694 (3)
Cl4	0.06998 (15)	0.42878 (14)	0.82812 (8)	0.0734 (4)
Br1	0.61787 (8)	0.56321 (4)	0.90951 (3)	0.07068 (18)
Br2	0.57150 (8)	0.26329 (6)	0.99305 (4)	0.0885 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0338 (17)	0.035 (2)	0.0352 (18)	−0.0032 (15)	−0.0007 (13)	0.0027 (15)
C2	0.0327 (18)	0.053 (3)	0.046 (2)	−0.0103 (17)	0.0056 (15)	0.0024 (19)
C3	0.0342 (18)	0.051 (2)	0.048 (2)	−0.0075 (18)	−0.0073 (15)	0.010 (2)
C4	0.051 (2)	0.076 (3)	0.045 (2)	−0.021 (2)	−0.0154 (19)	0.004 (2)
C5	0.066 (3)	0.080 (3)	0.033 (2)	−0.020 (3)	−0.0090 (18)	0.011 (2)
C6	0.075 (3)	0.091 (4)	0.051 (3)	−0.017 (3)	0.001 (2)	−0.001 (3)
C7	0.045 (2)	0.055 (2)	0.0338 (19)	−0.007 (2)	0.0081 (16)	−0.0015 (17)
C8	0.0395 (19)	0.033 (2)	0.0341 (19)	−0.0040 (15)	0.0043 (14)	−0.0020 (15)
C9	0.0385 (19)	0.0315 (19)	0.045 (2)	0.0062 (15)	0.0033 (16)	0.0031 (16)
C10	0.0346 (18)	0.040 (2)	0.0373 (19)	−0.0006 (16)	0.0011 (15)	0.0059 (16)
C11	0.0401 (19)	0.037 (2)	0.0336 (19)	0.0006 (15)	0.0026 (14)	−0.0077 (16)
C12	0.040 (2)	0.036 (2)	0.041 (2)	0.0055 (16)	−0.0017 (16)	−0.0041 (16)
C13	0.052 (3)	0.075 (4)	0.079 (3)	0.019 (3)	−0.015 (2)	0.016 (3)
C14	0.085 (4)	0.112 (5)	0.082 (4)	0.024 (4)	0.046 (4)	0.006 (4)
C15	0.097 (5)	0.082 (4)	0.074 (4)	−0.046 (4)	0.021 (3)	−0.004 (3)
C16	0.046 (2)	0.057 (3)	0.049 (2)	0.0047 (18)	0.0030 (19)	0.017 (2)
Cl3	0.0657 (7)	0.0632 (8)	0.0793 (8)	−0.0286 (6)	0.0057 (6)	0.0147 (6)
Cl4	0.0472 (6)	0.1082 (11)	0.0649 (7)	0.0060 (7)	0.0215 (5)	0.0002 (8)
Br1	0.0901 (4)	0.0583 (3)	0.0637 (3)	−0.0039 (3)	−0.0277 (3)	−0.0181 (2)
Br2	0.0869 (4)	0.1127 (5)	0.0659 (4)	−0.0004 (4)	0.0151 (3)	0.0420 (3)

Geometric parameters (Å, º)

C1—C12	1.513 (5)	C8—H8	0.9800
C1—C2	1.524 (5)	C9—C10	1.323 (6)

C1—C8	1.529 (5)	C9—H9	0.9300
C1—C3	1.541 (5)	C10—C16	1.489 (6)
C2—C3	1.502 (6)	C10—C11	1.495 (5)
C2—Cl3	1.763 (5)	C11—C12	1.520 (5)
C2—Cl4	1.765 (4)	C11—Br1	1.975 (4)
C3—C4	1.514 (7)	C11—H11	0.9800
C3—C13	1.531 (7)	C12—H12A	0.9700
C4—C5	1.538 (6)	C12—H12B	0.9700
C4—H4A	0.9700	C13—H13A	0.9600
C4—H4B	0.9700	C13—H13B	0.9600
C5—C6	1.515 (8)	C13—H13C	0.9600
C5—H5A	0.9700	C14—H14A	0.9600
C5—H5B	0.9700	C14—H14B	0.9600
C6—C7	1.552 (7)	C14—H14C	0.9600
C6—H6A	0.9700	C15—H15A	0.9600
C6—H6B	0.9700	C15—H15B	0.9600
C7—C15	1.470 (7)	C15—H15C	0.9600
C7—C14	1.540 (8)	C16—Br2	1.959 (4)
C7—C8	1.596 (5)	C16—H16A	0.9700
C8—C9	1.497 (5)	C16—H16B	0.9700

C12—C1—C2	116.6 (3)	C9—C8—H8	106.2
C12—C1—C8	112.4 (3)	C1—C8—H8	106.2
C2—C1—C8	119.2 (3)	C7—C8—H8	106.2
C12—C1—C3	121.0 (3)	C10—C9—C8	126.8 (3)
C2—C1—C3	58.7 (3)	C10—C9—H9	116.6
C8—C1—C3	118.9 (3)	C8—C9—H9	116.6
C3—C2—C1	61.2 (2)	C9—C10—C16	120.2 (4)
C3—C2—Cl3	121.2 (3)	C9—C10—C11	121.0 (3)
C1—C2—Cl3	120.6 (3)	C16—C10—C11	118.8 (3)
C3—C2—Cl4	119.5 (3)	C10—C11—C12	113.6 (3)
C1—C2—Cl4	119.2 (3)	C10—C11—Br1	110.2 (3)
Cl3—C2—Cl4	108.6 (2)	C12—C11—Br1	107.3 (3)
C2—C3—C4	119.1 (4)	C10—C11—H11	108.5
C2—C3—C13	118.9 (4)	C12—C11—H11	108.5
C4—C3—C13	112.1 (4)	Br1—C11—H11	108.5
C2—C3—C1	60.1 (2)	C1—C12—C11	110.7 (3)
C4—C3—C1	118.4 (4)	C1—C12—H12A	109.5
C13—C3—C1	119.2 (4)	C11—C12—H12A	109.5
C3—C4—C5	112.9 (4)	C1—C12—H12B	109.5
C3—C4—H4A	109.0	C11—C12—H12B	109.5
C5—C4—H4A	109.0	H12A—C12—H12B	108.1
C3—C4—H4B	109.0	C3—C13—H13A	109.5
C5—C4—H4B	109.0	C3—C13—H13B	109.5
H4A—C4—H4B	107.8	H13A—C13—H13B	109.5
C6—C5—C4	111.3 (4)	C3—C13—H13C	109.5
C6—C5—H5A	109.4	H13A—C13—H13C	109.5
C4—C5—H5A	109.4	H13B—C13—H13C	109.5

C6—C5—H5B	109.4	C7—C14—H14A	109.5
C4—C5—H5B	109.4	C7—C14—H14B	109.5
H5A—C5—H5B	108.0	H14A—C14—H14B	109.5
C5—C6—C7	119.2 (5)	C7—C14—H14C	109.5
C5—C6—H6A	107.5	H14A—C14—H14C	109.5
C7—C6—H6A	107.5	H14B—C14—H14C	109.5
C5—C6—H6B	107.5	C7—C15—H15A	109.5
C7—C6—H6B	107.5	C7—C15—H15B	109.5
H6A—C6—H6B	107.0	H15A—C15—H15B	109.5
C15—C7—C14	108.4 (5)	C7—C15—H15C	109.5
C15—C7—C6	111.6 (5)	H15A—C15—H15C	109.5
C14—C7—C6	103.8 (4)	H15B—C15—H15C	109.5
C15—C7—C8	114.9 (4)	C10—C16—Br2	112.2 (3)
C14—C7—C8	107.6 (4)	C10—C16—H16A	109.2
C6—C7—C8	110.0 (4)	Br2—C16—H16A	109.2
C9—C8—C1	109.4 (3)	C10—C16—H16B	109.2
C9—C8—C7	112.0 (3)	Br2—C16—H16B	109.2
C1—C8—C7	116.2 (3)	H16A—C16—H16B	107.9