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(1*S*,3*R*,8*R*)-2,2-Dichloro-3,7,7,10-tetramethyl-11-methylenetricyclo[6.4.0.0^{1,3}]dodec-9-ene

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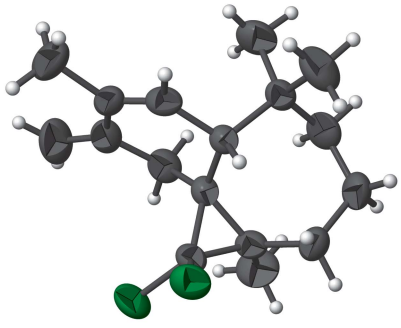
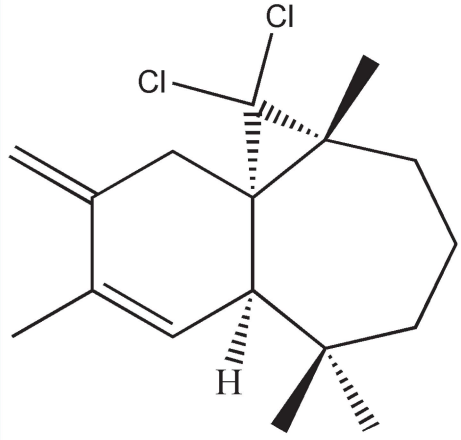
The title compound, $C_{17}H_{24}Cl_2$, was synthesized in four steps from β-himachalene (3,5,5,9-tetramethyl-2,4a,5,6,7,8-hexahydro-1*H*-benzocycloheptene), which was isolated from an essential oil of the Atlas cedar (*Cedrus atlantica*). The molecule is built from fused six- and seven-membered rings, and an additional three-membered ring. The dihedral angle between the mean planes of the cyclohexene and cycloheptane rings is 58.37 (19)°. There is an intramolecular C—H···Cl hydrogen bond present involving a Cl atom and the H atom of the unique methine C atom, forming an *S*(5) ring motif. There are no significant intermolecular interactions present.

3D view



Chemical scheme



Structure description

The essential oil of Atlas cedar(*Cedrus atlantica*) consists mainly (50%) of a hydrocarbon sesquiterpene called β-himachalene (El Haib *et al.*, 2011). The reactivity of these sesquiterpenes and their derivatives have been studied extensively by our team in order to prepare new products having biological properties (El Haib *et al.*, 2011; Benharref *et al.*, 2015, 2016; Ait Elhad *et al.*, 2017). These compounds have been tested, using the food poisoning technique, for their potential antifungal activity against the phytopathogen *Botrytis cinerea* (Daoubi *et al.*, 2004). Herein, we report on the crystal structure of the title compound.

The molecular structure is illustrated in Fig. 1. The molecule is built up from a seven-membered ring, which is fused to a six-membered ring and a three-membered ring. The six-membered ring shows a half-chair conformation, as indicated by the total puckering amplitude Q_T of 0.457 (3) Å and spherical polar angle θ = 127.5 (5)° and φ2 = 165.3 (7)°,

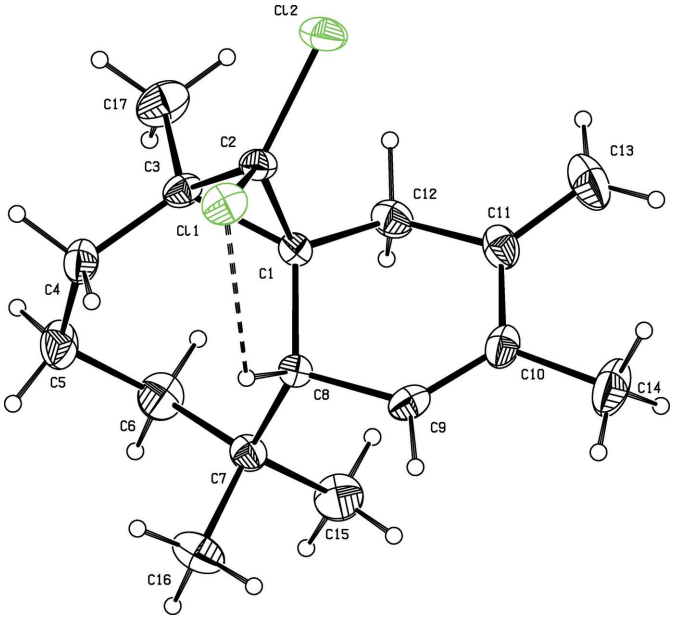


Figure 1
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular C—H···O hydrogen bond is shown as a dashed line (see Table 1).

whereas the seven-membered ring displays a boat conformation with Q_T = 1.121 (4) Å and spherical polar angle θ = 87.59 (26)°, $\varphi 2$ = 311.0 (2)° and $\varphi 3$ = 247 (5)°. The mean planes of the six- and seven-membered rings are inclined to one another by 58.37 (19)°. The three-membered ring (C1–C3) is nearly perpendicular to the six-membered ring (C1/C8–C12) mean plane, making a dihedral angle of 86.1 (3)°. There is an intramolecular C—H···Cl hydrogen bond present involving a chlorine Cl atom, Cl1 and the H atom of atom C8 common to both rings, forming an *S*(5) ring motif (Table 1 and Fig. 1). There are no significant intermolecular interactions present.

Synthesis and crystallization

In a 250 ml reactor equipped with a condenser, dropping funnel and a magnetic stirrer, was introduced 20 ml of anhydrous ether and 1 g of magnesium, and then *via* the dropping funnel, 2 ml of methyl iodide dissolved in 20 ml of ether were added dropwise. Thereafter, 6 g (20 mmol) of (1*S*,3*R*,8*R*)-2,2-dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}] dodecan-11-one (Ourhriss *et al.*, 2013) solubilized in 60 ml of ether were added dropwise. At the end of the addition, the mixture was stirred for 4 h at ambient temperature. After addition of 50 ml water, the reaction mixture was extracted three times with 20 ml of dichloromethane. The organic phases were combined, dried over sodium sulfate and then concentrated *in vacuo*. The residue obtained was chromatographed on silica eluting with hexane, which allowed the isolation of the title compound (yield 1.5 g, 25%). It was recrystallized from petroleum ether, yielding colourless prismatic crystals on slow evaporation of the solvent.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···Cl1	0.98	2.60	3.174 (3)	117

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{17}H_{24}Cl_2$
M_r	299.26
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, *b*, *c* (Å)	6.5995 (3), 13.4865 (4), 18.2435 (7)
V (Å^3)	1623.75 (11)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	0.39
Crystal size (mm)	0.24 × 0.2 × 0.15
Data collection	
Diffractometer	Bruker X8 *APEX*
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.661, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22208, 3322, 2402
R_{int}	0.061
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.044, 0.102, 1.02
No. of reflections	3322
No. of parameters	176
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.18
Absolute structure	Flack *x* determined using 811 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.02 (4)

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Owing to the presence of Cl atoms, the absolute configuration could be fully confirmed from anomalous dispersion effects [Flack parameter = −0.02 (4)], as C1(*S*), C3(*R*) and C8(*R*).

Acknowledgements

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References

Ait Elhad, M., Benharref, A., El Ammari, L., Saadi, M., Oukhrib, A. & Berraho, M. (2017). *IUCrData*, **2**, x170255.
Benharref, A., Elkarroumi, J., El Ammari, L., Saadi, M. & Berraho, M. (2015). *Acta Cryst.* E**71**, o659–o660.
Benharref, A., Oukhrib, A., Ait Elhad, M., El Ammari, L., Saadi, M. & Berraho, M. (2016). *IUCrData*, **1**, x160703.

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Daoubi, M., Durán-Patrón, R., Hmamouchi, M., Hernández-Galán, R., Benharref, A. & Collado, I. G. (2004). *Pest Manag. Sci.* **60**, 927–932.
El Haib, A., Benharref, A., Parrès-Maynadié, S., Manoury, E., Urrutigoïty, M. & Gouygou, M. (2011). *Tetrahedron Asymmetry*, **22**, 101–108.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Ourhriss, N., Benharref, A., Oukhrib, A., Daran, J.-C. & Berraho, M. (2013). *Acta Cryst.* E**69**, o830.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2017). **2**, x170421 [https://doi.org/10.1107/S2414314617004217]

(1*S*,3*R*,8*R*)-2,2-Dichloro-3,7,7,10-tetramethyl-11-methylenetricyclo-[6.4.0.0^{1,3}]dodec-9-ene

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Crystal data

$C_{17}H_{24}Cl_2$
M_r = 299.26
Orthorhombic, $P2_12_12_1$
a = 6.5995 (3) Å
b = 13.4865 (4) Å
c = 18.2435 (7) Å
V = 1623.75 (11) Å^3
Z = 4
$F(000)$ = 640
D_x = 1.224 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3322 reflections
θ = 2.7–26.4°
μ = 0.39 mm^{-1}
T = 296 K
Prismatic, colourless
0.24 × 0.2 × 0.15 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.661, T_{max} = 0.746
22208 measured reflections
3322 independent reflections
2402 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 26.4°, θ_{min} = 2.7°
h = −8→8
k = −14→16
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.102
S = 1.02
3322 reflections
176 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
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.3683P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}
Absolute structure: Flack x determined using 811 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.02 (4)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.74059 (16)	0.48733 (7)	0.22743 (5)	0.0593 (3)
Cl2	0.31946 (19)	0.46806 (9)	0.19407 (6)	0.0729 (4)
C8	0.6086 (5)	0.4877 (2)	0.39470 (17)	0.0373 (8)
H8	0.7361	0.5033	0.3697	0.045*
C1	0.4414 (5)	0.5081 (2)	0.34001 (19)	0.0393 (8)
C10	0.4643 (8)	0.3142 (3)	0.3983 (2)	0.0558 (12)
C7	0.6048 (6)	0.5533 (3)	0.4665 (2)	0.0472 (9)
C9	0.6143 (7)	0.3785 (3)	0.4108 (2)	0.0504 (10)
H9	0.7326	0.3534	0.4314	0.060*
C3	0.4449 (6)	0.6081 (3)	0.2991 (2)	0.0469 (9)
C2	0.4937 (6)	0.5133 (3)	0.25931 (19)	0.0448 (9)
C12	0.2456 (6)	0.4582 (3)	0.3607 (2)	0.0566 (10)
H12A	0.1445	0.4717	0.3234	0.068*
H12B	0.1971	0.4855	0.4067	0.068*
C11	0.2719 (7)	0.3478 (3)	0.3686 (2)	0.0574 (11)
C4	0.6192 (7)	0.6770 (3)	0.3179 (2)	0.0587 (12)
H4A	0.6261	0.7295	0.2816	0.070*
H4B	0.7454	0.6401	0.3158	0.070*
C6	0.5094 (9)	0.6556 (3)	0.4524 (2)	0.0707 (14)
H6A	0.3678	0.6449	0.4405	0.085*
H6B	0.5128	0.6918	0.4983	0.085*
C5	0.5962 (9)	0.7228 (3)	0.3940 (2)	0.0722 (15)
H5A	0.7284	0.7454	0.4102	0.087*
H5B	0.5099	0.7808	0.3899	0.087*
C15	0.4846 (8)	0.5050 (4)	0.5288 (2)	0.0763 (14)
H15A	0.4894	0.5469	0.5714	0.115*
H15B	0.5428	0.4417	0.5404	0.115*
H15C	0.3463	0.4963	0.5139	0.115*
C16	0.8238 (8)	0.5643 (4)	0.4931 (3)	0.0816 (16)
H16A	0.8256	0.6009	0.5382	0.122*
H16B	0.9016	0.5991	0.4568	0.122*
H16C	0.8815	0.4998	0.5009	0.122*
C17	0.2504 (8)	0.6630 (3)	0.2818 (3)	0.0804 (15)
H17A	0.2037	0.6968	0.3250	0.121*
H17B	0.1493	0.6165	0.2660	0.121*
H17C	0.2750	0.7104	0.2436	0.121*
C14	0.4937 (10)	0.2054 (3)	0.4160 (3)	0.095 (2)
H14A	0.6291	0.1949	0.4336	0.142*
H14B	0.4721	0.1666	0.3726	0.142*

H14C	0.3984	0.1858	0.4530	0.142*
C13	0.1223 (9)	0.2868 (4)	0.3491 (3)	0.0899 (17)
H13A	0.1381	0.2186	0.3542	0.108*
H13B	0.0021	0.3124	0.3304	0.108*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0631 (6)	0.0683 (6)	0.0464 (5)	0.0108 (6)	0.0118 (5)	−0.0042 (5)
Cl2	0.0833 (9)	0.0790 (8)	0.0562 (6)	−0.0033 (6)	−0.0283 (6)	−0.0072 (6)
C8	0.0356 (19)	0.0390 (19)	0.0374 (18)	0.0032 (16)	0.0009 (15)	−0.0028 (15)
C1	0.0363 (19)	0.0397 (19)	0.0418 (19)	0.0008 (16)	−0.0006 (15)	−0.0043 (16)
C10	0.088 (4)	0.040 (2)	0.040 (2)	−0.004 (2)	0.013 (2)	−0.0014 (17)
C7	0.049 (2)	0.051 (2)	0.041 (2)	−0.0043 (18)	0.0038 (18)	−0.0052 (17)
C9	0.059 (3)	0.052 (2)	0.040 (2)	0.016 (2)	0.000 (2)	0.0029 (17)
C3	0.054 (3)	0.045 (2)	0.042 (2)	0.0128 (19)	−0.0034 (19)	0.0017 (17)
C2	0.049 (2)	0.048 (2)	0.038 (2)	0.0028 (19)	−0.0072 (15)	−0.0032 (17)
C12	0.045 (2)	0.068 (3)	0.057 (2)	−0.003 (2)	−0.002 (2)	−0.0041 (19)
C11	0.060 (3)	0.062 (3)	0.050 (2)	−0.019 (2)	0.015 (2)	−0.0069 (18)
C4	0.078 (3)	0.042 (2)	0.056 (3)	−0.006 (2)	0.009 (2)	0.0001 (18)
C6	0.096 (4)	0.060 (3)	0.056 (3)	0.010 (3)	0.012 (3)	−0.019 (2)
C5	0.109 (4)	0.043 (2)	0.064 (3)	−0.008 (2)	0.007 (3)	−0.011 (2)
C15	0.092 (3)	0.089 (3)	0.048 (3)	−0.003 (3)	0.017 (2)	−0.008 (3)
C16	0.074 (3)	0.100 (4)	0.071 (3)	−0.010 (3)	−0.015 (3)	−0.024 (3)
C17	0.081 (4)	0.074 (3)	0.087 (4)	0.038 (3)	−0.003 (3)	0.006 (2)
C14	0.160 (6)	0.043 (2)	0.080 (4)	−0.005 (3)	0.017 (4)	0.008 (2)
C13	0.083 (4)	0.090 (4)	0.097 (4)	−0.041 (3)	0.015 (3)	−0.018 (3)

Geometric parameters (Å, º)

Cl1—C2	1.765 (4)	C4—C5	1.528 (5)
Cl2—C2	1.764 (4)	C4—H4A	0.9700
C8—C9	1.503 (5)	C4—H4B	0.9700
C8—C1	1.513 (5)	C6—C5	1.511 (6)
C8—C7	1.580 (5)	C6—H6A	0.9700
C8—H8	0.9800	C6—H6B	0.9700
C1—C12	1.505 (5)	C5—H5A	0.9700
C1—C2	1.514 (5)	C5—H5B	0.9700
C1—C3	1.542 (5)	C15—H15A	0.9600
C10—C9	1.335 (6)	C15—H15B	0.9600
C10—C11	1.453 (6)	C15—H15C	0.9600
C10—C14	1.515 (6)	C16—H16A	0.9600
C7—C15	1.532 (5)	C16—H16B	0.9600
C7—C16	1.532 (6)	C16—H16C	0.9600
C7—C6	1.539 (6)	C17—H17A	0.9600
C9—H9	0.9300	C17—H17B	0.9600
C3—C2	1.506 (5)	C17—H17C	0.9600
C3—C17	1.514 (5)	C14—H14A	0.9600

C3—C4	1.518 (6)	C14—H14B	0.9600
C12—C11	1.507 (5)	C14—H14C	0.9600
C12—H12A	0.9700	C13—H13A	0.9300
C12—H12B	0.9700	C13—H13B	0.9300
C11—C13	1.333 (6)		

C9—C8—C1	109.0 (3)	C3—C4—C5	112.2 (4)
C9—C8—C7	112.8 (3)	C3—C4—H4A	109.2
C1—C8—C7	115.6 (3)	C5—C4—H4A	109.2
C9—C8—H8	106.3	C3—C4—H4B	109.2
C1—C8—H8	106.3	C5—C4—H4B	109.2
C7—C8—H8	106.3	H4A—C4—H4B	107.9
C12—C1—C8	112.3 (3)	C5—C6—C7	120.0 (4)
C12—C1—C2	117.4 (3)	C5—C6—H6A	107.3
C8—C1—C2	118.9 (3)	C7—C6—H6A	107.3
C12—C1—C3	121.7 (3)	C5—C6—H6B	107.3
C8—C1—C3	117.8 (3)	C7—C6—H6B	107.3
C2—C1—C3	59.0 (2)	H6A—C6—H6B	106.9
C9—C10—C11	120.6 (4)	C6—C5—C4	115.8 (3)
C9—C10—C14	119.8 (5)	C6—C5—H5A	108.3
C11—C10—C14	119.5 (4)	C4—C5—H5A	108.3
C15—C7—C16	107.1 (4)	C6—C5—H5B	108.3
C15—C7—C6	107.1 (4)	C4—C5—H5B	108.3
C16—C7—C6	110.6 (4)	H5A—C5—H5B	107.4
C15—C7—C8	112.7 (3)	C7—C15—H15A	109.5
C16—C7—C8	107.6 (3)	C7—C15—H15B	109.5
C6—C7—C8	111.7 (3)	H15A—C15—H15B	109.5
C10—C9—C8	125.8 (4)	C7—C15—H15C	109.5
C10—C9—H9	117.1	H15A—C15—H15C	109.5
C8—C9—H9	117.1	H15B—C15—H15C	109.5
C2—C3—C17	119.7 (3)	C7—C16—H16A	109.5
C2—C3—C4	117.8 (3)	C7—C16—H16B	109.5
C17—C3—C4	113.0 (3)	H16A—C16—H16B	109.5
C2—C3—C1	59.6 (2)	C7—C16—H16C	109.5
C17—C3—C1	121.0 (3)	H16A—C16—H16C	109.5
C4—C3—C1	116.0 (3)	H16B—C16—H16C	109.5
C3—C2—C1	61.4 (2)	C3—C17—H17A	109.5
C3—C2—Cl2	118.7 (3)	C3—C17—H17B	109.5
C1—C2—Cl2	119.4 (3)	H17A—C17—H17B	109.5
C3—C2—Cl1	121.7 (3)	C3—C17—H17C	109.5
C1—C2—Cl1	121.5 (3)	H17A—C17—H17C	109.5
Cl2—C2—Cl1	108.11 (19)	H17B—C17—H17C	109.5
C1—C12—C11	111.5 (3)	C10—C14—H14A	109.5
C1—C12—H12A	109.3	C10—C14—H14B	109.5
C11—C12—H12A	109.3	H14A—C14—H14B	109.5
C1—C12—H12B	109.3	C10—C14—H14C	109.5
C11—C12—H12B	109.3	H14A—C14—H14C	109.5
H12A—C12—H12B	108.0	H14B—C14—H14C	109.5

C13—C11—C10	123.7 (4)	C11—C13—H13A	120.0
C13—C11—C12	120.0 (5)	C11—C13—H13B	120.0
C10—C11—C12	116.4 (4)	H13A—C13—H13B	120.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···Cl1	0.98	2.60	3.174 (3)	117