

(1*S*,2*S*,4*R*)-3,3-Dichloro-4,8,12,12-tetramethyltricyclo[5.5.0.0^{2,4}]dodeca-6,8-dieneAhmed Benharref,^{a*} Lahcen El Ammari,^b Moha Berraho^a and Esaadia Lassaba^a

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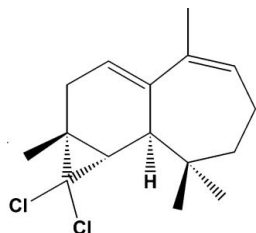
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.032; wR factor = 0.096; data-to-parameter ratio = 21.1.

The title compound, $\text{C}_{16}\text{H}_{22}\text{Cl}_2$, a derivative of β -himachalene, was semi-synthesized from natural essential oils of *Cedrus atlantica*. The molecule is built up from two fused six- and seven-membered rings. The six-membered ring has a perfect chair conformation, whereas the seven-membered ring displays a screw boat conformation; the dihedral angle between the rings is 46.48 (9°).

Related literature

For background to himachalene derivatives, see: Plattier & Teiseire (1974); Sbai *et al.* (2002). For ring puckering analysis, see: Cremer & Pople (1975). For the synthesis of the title compound, see: Lassaba *et al.* (1997). For the reactivity of this sesquiterpene, see: El Jamili *et al.* (2002); Sbai *et al.* (2002). For the olfactive properties of β -himachalene, see: Benharref *et al.* (1991); Bisarya & Dev (1968); Chekroun *et al.* (2000).

**Experimental***Crystal data*

$\text{C}_{16}\text{H}_{22}\text{Cl}_2$	$V = 1490.1$ (6) Å ³
$M_r = 285.24$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.4356$ (17) Å	$\mu = 0.42$ mm ⁻¹
$b = 8.3124$ (18) Å	$T = 298$ K
$c = 24.108$ (6) Å	$0.27 \times 0.18 \times 0.12$ mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer	3691 independent reflections
10992 measured reflections	3282 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{\text{max}} = 0.34$ e Å ⁻³
$wR(F^2) = 0.096$	$\Delta\rho_{\text{min}} = -0.29$ e Å ⁻³
$S = 1.11$	Absolute structure: Flack (1985),
3691 reflections	1535 Friedel pairs
175 parameters	Flack parameter: -0.06 (6)
H atoms treated by a mixture of independent and constrained refinement	

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT-Plus (Bruker, 2009); data reduction: SAINT-Plus; 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, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2079).

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supplementary materials

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(1*S*,2*S*,4*R*)-3,3-Dichloro-4,8,12,12-tetramethyltricyclo[5.5.0.0^{2,4}]dodeca-6,8-diene

A. Benharref, L. El Ammari, M. Berraho and E. Lassaba

Comment

Our work lies within the framework of the valorization of the most abundant essential oils in Morocco, such as *Cedrus atlantica*. This oil is made up mainly (75%) of bicyclic sesquiterpenes hydrocarbons, among which is found the compound, β -himachalene (Bisarya & Dev, 1968; Plattier & Teiseire, 1974). The reactivity of this sesquiterpene has been studied extensively by our team (El Jamili *et al.*, 2002; Sbai *et al.*, 2002) in order to prepare new products having olfactive proprieties suitable for the perfume or cosmetics industry. Thus, the action of one equivalent of *meta*-chloroperbenzoic acide (*m*-CPBA) on, β - himachalène gives in quantitative yields the monoepoxyde (Benharref *et al.*, 1991; Chekroun *et al.*, 2000). The treatment of this monoepoxyde with dichlorocarbene, generated *in situ* from chloroform and in the presence of sodium hydroxide as base and *n*-benzyltriethylammonium chloride as catalyst, give a mixture of two diastereoisomers: (1*S*,2*R*,7*S*,8*S*,10*R*) -9,9-dichloro-1,2- epoxy-2,6,6,10-tetramethyl-tricyclo[5,5,0,8,10]dodecane and (1*S*,2*R*,7*S*,8*R*,10*S*) -9,9-dichloro-1,2-epoxy-2,6,6,10-tetramethyl- tricyclo[5,5,0,0^{8,10}] dodecane (Lassaba *et al.*, 1997). Also in order to prepare products with high added value, we have treated the isomer (1*S*,2*R*,7*S*,8*S*,10*R*) -9,9-dichloro-1,2- epoxy-2,6,6,10-tetramethyl-tricyclo[5,5,0,0^{8,10}] dodecane (I) by hydrochloric acid gas and we got one sesquiterpene dichloro-hydrocarbure (II) in yield 75%. The molecule is built up from two fused six-and seven-membered rings (Fig.1). The six-membered ring has a perfect chair conformation, with as indicated by the total puckering amplitude $QT = 0.2385$ (2) Å and spherical polar angle $\theta = 99.60$ (2)° with $\varphi = -117.07$ (2)°, whereas the seven-membered ring display a screw boat conformation with $QT = 0.9566$ (2) Å, $\theta = 68.84$ (2)°, $\varphi_2 = -112.42$ (1)° and $\varphi_3 = 142.26$ (3)° (Cremer & Pople, 1975). Owing to the presence of the Cl atoms, the absolute configuration could be fully confirmed to be C7(*S*), C8(*S*) and C10(*R*) (Flack & Bernardinelli, 2000).

Experimental

100 mg (0,33 mm l) of the isomer, (1*S*,2*R*,7*S*,8*S*,10*R*)-9,9-dichloro- 1,2-epoxy-2,6,6,10- tetramethyl-tricyclo[5,5,0,8,10]dodecane, dissolved in 20 ml of dichloromethane and then treated with a stream of gaseous hydrochloric acid at 0° for 5 minutes. After concentration of solvent, the residue obtained was chromatgraphed on silica gel impregnated with silver nitrate (10%) with hexane as eluent.

Refinement

Except H3 and H12, 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 $U_{iso}(H) = 1.2U_{eq}(\text{methylene, methine})$ or $U_{iso}(H) = 1.5U_{eq}(\text{methyl})$.

Figures

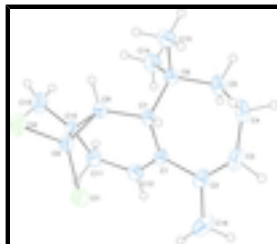


Fig. 1. : Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

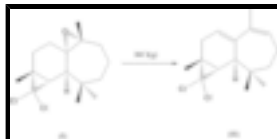


Fig. 2. The formation of the title compound.

(1*S*,2*S*,4*R*)-3,3-Dichloro-4,8,12,12-tetramethyltricyclo[5.5.0.0^{2,4}]dodeca-6,8-diene

Crystal data

$C_{16}H_{22}Cl_2$

$M_r = 285.24$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 7.4356$ (17) Å

$b = 8.3124$ (18) Å

$c = 24.108$ (6) Å

$V = 1490.1$ (6) Å³

$Z = 4$

$F(000) = 608$

$D_x = 1.271$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10992 reflections

$\theta = 1.7$ – 28.4°

$\mu = 0.42$ mm⁻¹

$T = 298$ K

Prism, colourless

$0.27 \times 0.18 \times 0.12$ mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

10992 measured reflections

3691 independent reflections

3282 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 28.4^\circ$, $\theta_{min} = 1.7^\circ$

$h = -7 \rightarrow 9$

$k = -8 \rightarrow 11$

$l = -32 \rightarrow 28$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.096$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2]$

$S = 1.11$

3691 reflections

175 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

Absolute structure: Flack (1985), 1535 Friedel pairs

Flack parameter: $-0.06 (6)$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6213 (2)	0.33418 (19)	0.89982 (6)	0.0375 (3)
C2	0.4484 (2)	0.3173 (2)	0.92944 (6)	0.0476 (4)
C3	0.3427 (3)	0.4400 (3)	0.94246 (7)	0.0551 (5)
C4	0.3834 (3)	0.6154 (3)	0.93795 (8)	0.0588 (5)
H4A	0.3146	0.6730	0.9658	0.071*
H4B	0.3451	0.6535	0.9018	0.071*
C5	0.5809 (2)	0.6534 (2)	0.94551 (7)	0.0514 (4)
H5A	0.6290	0.5834	0.9741	0.062*
H5B	0.5919	0.7633	0.9587	0.062*
C6	0.6957 (2)	0.63474 (18)	0.89326 (6)	0.0405 (3)
C7	0.6413 (2)	0.47755 (17)	0.86197 (6)	0.0341 (3)
H7	0.5234	0.4970	0.8451	0.041*
C8	0.7727 (2)	0.44941 (18)	0.81513 (6)	0.0384 (3)
H8	0.8138	0.5487	0.7973	0.046*
C9	0.7663 (2)	0.30866 (19)	0.77693 (7)	0.0427 (3)
C10	0.9167 (2)	0.3203 (2)	0.81854 (7)	0.0438 (3)
C11	0.9108 (2)	0.2114 (2)	0.86840 (8)	0.0497 (4)
H11A	0.9257	0.1014	0.8558	0.060*
H11B	1.0127	0.2368	0.8920	0.060*
C12	0.7456 (3)	0.2200 (2)	0.90240 (7)	0.0457 (4)
C13	1.1028 (3)	0.3568 (3)	0.79848 (9)	0.0628 (5)
H13A	1.1600	0.2590	0.7867	0.094*
H13B	1.1712	0.4044	0.8280	0.094*
H13C	1.0966	0.4304	0.7679	0.094*
C14	0.8912 (3)	0.6291 (2)	0.91128 (8)	0.0546 (4)
H14A	0.9119	0.5336	0.9328	0.082*
H14B	0.9181	0.7221	0.9334	0.082*
H14C	0.9673	0.6280	0.8791	0.082*
C15	0.6651 (3)	0.7795 (2)	0.85566 (8)	0.0573 (5)
H15A	0.7378	0.7690	0.8229	0.086*

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H15B	0.6978	0.8761	0.8750	0.086*
H15C	0.5406	0.7847	0.8453	0.086*
C16	0.3883 (3)	0.1489 (3)	0.94230 (11)	0.0727 (6)
H16A	0.4725	0.0996	0.9673	0.109*
H16B	0.3825	0.0876	0.9086	0.109*
H16C	0.2716	0.1518	0.9593	0.109*
C11	0.59995 (6)	0.16140 (5)	0.781164 (18)	0.05350 (13)
C12	0.81596 (8)	0.34714 (7)	0.706600 (17)	0.06577 (16)
H3	0.223 (3)	0.414 (3)	0.9587 (9)	0.074 (6)*
H12	0.732 (3)	0.127 (3)	0.9270 (9)	0.064 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0388 (7)	0.0457 (7)	0.0281 (6)	-0.0004 (7)	0.0008 (5)	-0.0004 (6)
C2	0.0430 (9)	0.0676 (11)	0.0323 (7)	-0.0041 (8)	0.0017 (6)	0.0061 (7)
C3	0.0393 (9)	0.0868 (13)	0.0391 (9)	-0.0009 (9)	0.0065 (7)	-0.0031 (9)
C4	0.0457 (10)	0.0781 (12)	0.0526 (10)	0.0142 (9)	0.0084 (8)	-0.0187 (9)
C5	0.0500 (9)	0.0632 (10)	0.0411 (8)	0.0055 (9)	-0.0002 (7)	-0.0196 (8)
C6	0.0404 (8)	0.0440 (8)	0.0370 (7)	0.0023 (7)	-0.0012 (6)	-0.0080 (6)
C7	0.0324 (7)	0.0403 (7)	0.0297 (6)	0.0027 (6)	-0.0007 (5)	-0.0020 (5)
C8	0.0422 (8)	0.0404 (7)	0.0326 (7)	-0.0017 (6)	0.0054 (6)	-0.0022 (6)
C9	0.0434 (8)	0.0512 (8)	0.0334 (7)	-0.0048 (6)	0.0071 (6)	-0.0074 (6)
C10	0.0374 (8)	0.0520 (8)	0.0420 (8)	0.0002 (7)	0.0066 (6)	-0.0116 (7)
C11	0.0441 (9)	0.0517 (9)	0.0532 (10)	0.0111 (7)	-0.0005 (8)	-0.0033 (7)
C12	0.0526 (10)	0.0458 (8)	0.0388 (8)	0.0016 (7)	-0.0013 (7)	0.0033 (7)
C13	0.0432 (9)	0.0831 (13)	0.0621 (11)	-0.0044 (10)	0.0113 (8)	-0.0171 (11)
C14	0.0431 (9)	0.0663 (11)	0.0545 (10)	-0.0054 (9)	-0.0050 (8)	-0.0144 (8)
C15	0.0744 (14)	0.0392 (8)	0.0583 (11)	0.0027 (9)	-0.0033 (10)	-0.0024 (8)
C16	0.0590 (12)	0.0815 (13)	0.0776 (14)	-0.0113 (12)	0.0084 (11)	0.0310 (12)
C11	0.0529 (2)	0.0574 (2)	0.0502 (2)	-0.0120 (2)	-0.00032 (18)	-0.00975 (19)
C12	0.0750 (3)	0.0874 (3)	0.0349 (2)	-0.0115 (3)	0.0142 (2)	-0.0107 (2)

Geometric parameters (\AA , $^\circ$)

C1—C12	1.326 (2)	C9—C10	1.505 (2)
C1—C2	1.477 (2)	C9—C11	1.7433 (16)
C1—C7	1.508 (2)	C9—C12	1.7645 (17)
C2—C3	1.326 (3)	C10—C13	1.497 (2)
C2—C16	1.502 (3)	C10—C11	1.505 (3)
C3—C4	1.493 (3)	C11—C12	1.479 (3)
C3—H3	1.00 (3)	C11—H11A	0.9700
C4—C5	1.513 (3)	C11—H11B	0.9700
C4—H4A	0.9700	C12—H12	0.98 (2)
C4—H4B	0.9700	C13—H13A	0.9600
C5—C6	1.530 (2)	C13—H13B	0.9600
C5—H5A	0.9700	C13—H13C	0.9600
C5—H5B	0.9700	C14—H14A	0.9600
C6—C14	1.519 (2)	C14—H14B	0.9600

C6—C15	1.524 (2)	C14—H14C	0.9600
C6—C7	1.562 (2)	C15—H15A	0.9600
C7—C8	1.511 (2)	C15—H15B	0.9600
C7—H7	0.9800	C15—H15C	0.9600
C8—C9	1.490 (2)	C16—H16A	0.9600
C8—C10	1.518 (2)	C16—H16B	0.9600
C8—H8	0.9800	C16—H16C	0.9600
C12—C1—C2	121.04 (16)	C8—C9—C12	116.42 (12)
C12—C1—C7	121.66 (14)	C10—C9—C12	118.25 (11)
C2—C1—C7	116.97 (14)	C11—C9—C12	109.39 (9)
C3—C2—C1	123.86 (17)	C13—C10—C11	114.00 (16)
C3—C2—C16	119.48 (18)	C13—C10—C9	118.97 (15)
C1—C2—C16	116.59 (17)	C11—C10—C9	118.17 (15)
C2—C3—C4	127.88 (17)	C13—C10—C8	119.41 (16)
C2—C3—H3	117.2 (14)	C11—C10—C8	116.60 (13)
C4—C3—H3	114.8 (13)	C9—C10—C8	59.03 (10)
C3—C4—C5	113.09 (17)	C12—C11—C10	115.96 (15)
C3—C4—H4A	109.0	C12—C11—H11A	108.3
C5—C4—H4A	109.0	C10—C11—H11A	108.3
C3—C4—H4B	109.0	C12—C11—H11B	108.3
C5—C4—H4B	109.0	C10—C11—H11B	108.3
H4A—C4—H4B	107.8	H11A—C11—H11B	107.4
C4—C5—C6	114.91 (14)	C1—C12—C11	126.00 (17)
C4—C5—H5A	108.5	C1—C12—H12	121.5 (13)
C6—C5—H5A	108.5	C11—C12—H12	112.4 (13)
C4—C5—H5B	108.5	C10—C13—H13A	109.5
C6—C5—H5B	108.5	C10—C13—H13B	109.5
H5A—C5—H5B	107.5	H13A—C13—H13B	109.5
C14—C6—C15	109.72 (16)	C10—C13—H13C	109.5
C14—C6—C5	107.57 (14)	H13A—C13—H13C	109.5
C15—C6—C5	109.07 (14)	H13B—C13—H13C	109.5
C14—C6—C7	111.10 (13)	C6—C14—H14A	109.5
C15—C6—C7	109.56 (13)	C6—C14—H14B	109.5
C5—C6—C7	109.78 (13)	H14A—C14—H14B	109.5
C1—C7—C8	113.17 (12)	C6—C14—H14C	109.5
C1—C7—C6	113.22 (12)	H14A—C14—H14C	109.5
C8—C7—C6	108.85 (12)	H14B—C14—H14C	109.5
C1—C7—H7	107.1	C6—C15—H15A	109.5
C8—C7—H7	107.1	C6—C15—H15B	109.5
C6—C7—H7	107.1	H15A—C15—H15B	109.5
C9—C8—C7	124.25 (13)	C6—C15—H15C	109.5
C9—C8—C10	60.05 (10)	H15A—C15—H15C	109.5
C7—C8—C10	121.66 (13)	H15B—C15—H15C	109.5
C9—C8—H8	113.6	C2—C16—H16A	109.5
C7—C8—H8	113.6	C2—C16—H16B	109.5
C10—C8—H8	113.6	H16A—C16—H16B	109.5
C8—C9—C10	60.92 (11)	C2—C16—H16C	109.5
C8—C9—C11	122.54 (11)	H16A—C16—H16C	109.5
C10—C9—C11	122.22 (12)	H16B—C16—H16C	109.5

Fig. 1

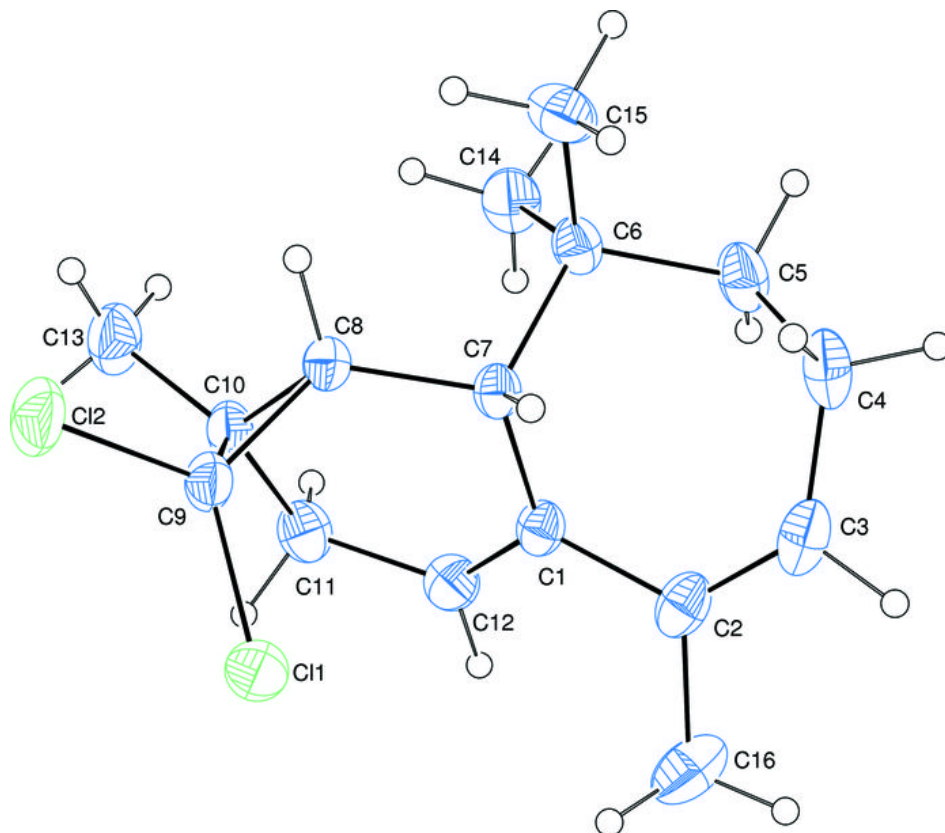


Fig. 2

