

(1*S*,2*R*,8*R*)-2,2-Dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodec-10-en-9-oneAhmed Benharref,^{a*} Lahcen El Ammari^b and Moha Berraho^a

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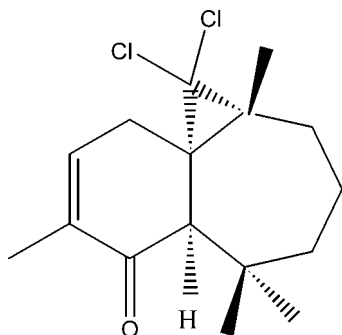
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.039; wR factor = 0.094; data-to-parameter ratio = 16.6.

The title compound, $\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{O}$, was synthesized from β -himachalene, which was isolated from essential oil of the Atlas cedar (*cedrus atlantica*). The asymmetric unit contains two independent molecules, in each of which the six-membered ring shows a half-chair conformation, whereas the seven-membered ring displays a boat conformation. The dihedral angle between the two rings is slightly different in the two molecules [63.22 (13) and 61.81 (14)°].

Related literature

For the isolation of β -himachalene, see: Joseph & Dev (1968); Plattier & Teiseire (1974). For the reactivity of this sesquiterpene, see: Lassaba *et al.* (1998); Chekroun *et al.* (2000); El Jamili *et al.* (2002); Sbai *et al.* (2002); Dakir *et al.* (2004). For its biological activity, see: Daoubi *et al.* (2004).

**Experimental***Crystal data*

$\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{O}$	$V = 1598.7(3) \text{ \AA}^3$
$M_r = 301.24$	$Z = 4$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 6.6680(7) \text{ \AA}$	$\mu = 0.40 \text{ mm}^{-1}$
$b = 18.7760(16) \text{ \AA}$	$T = 298 \text{ K}$
$c = 12.7696(12) \text{ \AA}$	$0.27 \times 0.18 \times 0.12 \text{ mm}$
$\beta = 90.430(3)^\circ$	

Data collection

Bruker X8 APEXII CCD area-detector diffractometer	5817 independent reflections
11524 measured reflections	4348 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
$wR(F^2) = 0.094$	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
$S = 1.00$	Absolute structure: Flack & Bernardinelli (2000), 1791 Friedel pairs
5817 reflections	Flack parameter: 0.01 (5)
351 parameters	
1 restraint	
H-atom parameters constrained	

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, 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: IM2235).

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supplementary materials

Acta Cryst. (2010). E66, o2911 [doi:10.1107/S1600536810040213]

(1*S*,2*R*,8*R*)-2,2-Dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodec-10-en-9-one

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

Comment

The essential oil of the Atlas cedar (*cedrus atlantica*) consists mainly (50%) of a bicyclic hydrocarbon sesquiterpene called β -himachalene (Joseph & Dev 1968; Plattier & Teiseire 1974). The reactivity of this sesquiterpene has been studied extensively by our team in order to prepare new products having biological proprieties (Lassaba *et al.*, 1998; Chekroun *et al.*, 2000; El Jamili *et al.*, 2002; Sbai *et al.*, 2002; Dakir *et al.*, 2004). Indeed, these compounds were tested, using the food poisoning technique, for their potential antifungal activity against phytopathogen *Botrytis cinerea* (Daoubi *et al.*, 2004). Thus the action of one equivalent of dichlorocarbene, generated *in situ* from chloroform and in the presence of sodium hydroxide as base and *n*-benzyltriethylammonium chloride as catalyst, followed by epoxydation with *m*-chloroperbenzoic acid (*m*-CPBA) gives a mixture of two diastereoisomers: (1*S*,3*R*,8*S*,9*S*,10*R*)-2,2-dichloro-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodecane (*X*, 70%) and (1*S*,3*R*,8*S*,9*R*,10*S*)-2,2-dichloro-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodecane (*Y*, 30%) (Sbai *et al.*, 2002). By treatment of the majority isomer (*X*) with hydrochloric acid (see experimental) we obtained the title compound in 70% yield. The structure of (*I*) was established by ¹H and ¹³C NMR and confirmed by its single crystal X-ray structure. The asymmetric unit contains two crystallographically independent molecules (Fig.1). Each molecule is built up from two fused six and seven-membered rings with the dichlorocyclopropyl ring at positions 1 and 2 in α -configuration. The six-membered ring shows a half chair conformation, whereas the seven-membered ring displays a boat conformation. In the first molecule (C1 to C16), the dihedral angle between the rings is 63.22 (13)°. The corresponding value in the second molecule (C17 to C31) is 61.81 (14)°. Owing to the presence of the Cl atoms, the absolute configuration could be fully confirmed to be (1*S*,2*R*,8*R*) for both molecules (Flack & Bernardinelli, 2000).

Experimental

A solution is prepared by bubbling gaseous hydrochloric acid into 40 ml of chloroform for 1 minute. Then 1 g (3.30 mmol) of (1*S*,3*R*,8*S*,9*S*,10*R*)-2,2-dichloro-9,10-epoxy-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodecane (*X*) dissolved in 20 ml of chloroform, is added to this solution and the resulting mixture is stirred for 1 h. After evaporation of the solvent and chromatography of the residue obtained on a column of silica gel, using as eluent hexane-ethyl acetate (95/ 5), the corresponding enol is isolated (yield: 0.6 g, 1.98 mmol, 60%). A solution of the enol (0.5 g, 1.65 mmol) in dichloromethane (20 ml) was added to a suspension of the complex (CrO₃: pyridine) (10 mmol) in another 45 ml of dichloromethane. The reaction mixture was stirred at room temperature for 1 h, then filtered through an alumina column. After evaporation of the solvent, the title compound, (1*S*,2*R*,8*R*)-2,2-Dichloro-3,7,7,10-tetramethyl-tricyclo[6.4.0.0^{1,3}]dodec-10-en-9-one, is obtained (0.35 g, 70%). Crystals suitable for X-ray analysis were produced by recrystallization from *n*-pentane.

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

Figures

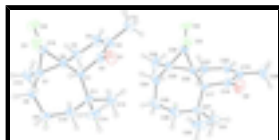


Fig. 1. Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

(1S,2R,8R)-2,2-Dichloro-3,7,7,10-tetramethyltricyclo[6.4.0.0^{1,3}]dodec-10-en-9-one

Crystal data

$\text{C}_{16}\text{H}_{22}\text{Cl}_2\text{O}$

$M_r = 301.24$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 6.6680$ (7) Å

$b = 18.7760$ (16) Å

$c = 12.7696$ (12) Å

$\beta = 90.430$ (3)°

$V = 1598.7$ (3) Å³

$Z = 4$

$F(000) = 640$

$D_x = 1.252$ Mg m⁻³

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

Cell parameters from 11524 reflections

$\theta = 2.3$ – 28.2 °

$\mu = 0.40$ 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

11524 measured reflections

5817 independent reflections

4348 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\text{max}} = 28.2$ °, $\theta_{\text{min}} = 2.7$ °

$h = -8 \rightarrow 8$

$k = -16 \rightarrow 24$

$l = -14 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.094$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$

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

$S = 1.00$	$(\Delta/\sigma)_{\max} < 0.001$
5817 reflections	$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$
351 parameters	$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
1 restraint	Absolute structure: Flack & Bernardinelli (2000), 1791 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.01 (5)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C4	0.2648 (4)	0.51700 (18)	0.1518 (2)	0.0665 (8)
H4	0.3713	0.5344	0.1916	0.080*
C5	0.3032 (4)	0.50170 (17)	0.0397 (2)	0.0566 (7)
H5A	0.3645	0.4551	0.0335	0.068*
H5B	0.3967	0.5366	0.0125	0.068*
C6	0.1141 (4)	0.50357 (13)	-0.02434 (19)	0.0428 (5)
C7	0.1190 (4)	0.50653 (15)	-0.1455 (2)	0.0555 (7)
C13	0.3194 (5)	0.5040 (2)	-0.2006 (3)	0.0842 (11)
H13A	0.3063	0.5251	-0.2688	0.126*
H13B	0.3615	0.4553	-0.2077	0.126*
H13C	0.4173	0.5298	-0.1603	0.126*
C29	0.7542 (5)	0.3406 (2)	0.3751 (3)	0.0802 (10)
H29A	0.7532	0.3825	0.3320	0.120*
H29B	0.7934	0.3003	0.3338	0.120*
H29C	0.8478	0.3469	0.4318	0.120*
C30	0.1340 (6)	0.1455 (2)	0.4271 (3)	0.1001 (13)
H30A	0.0623	0.1353	0.4903	0.150*
H30B	0.1376	0.1036	0.3841	0.150*
H30C	0.0677	0.1832	0.3898	0.150*
C32	0.4841 (4)	0.36421 (13)	0.51889 (19)	0.0483 (6)
Cl2	0.23340 (15)	0.64403 (4)	-0.07935 (7)	0.0867 (3)
Cl3	0.24108 (11)	0.40022 (3)	0.53257 (6)	0.0636 (2)
Cl4	0.65593 (14)	0.42095 (4)	0.58207 (7)	0.0779 (2)
C1	-0.0602 (3)	0.46308 (12)	0.02462 (19)	0.0401 (5)
H1	-0.1815	0.4787	-0.0126	0.048*
C2	-0.0857 (4)	0.48562 (13)	0.1377 (2)	0.0478 (6)
C3	0.0909 (4)	0.50787 (16)	0.1996 (2)	0.0577 (7)
C8	-0.0460 (5)	0.46708 (15)	-0.2027 (2)	0.0635 (8)
H8A	-0.0446	0.4806	-0.2760	0.076*
H8B	-0.1744	0.4812	-0.1742	0.076*

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C9	-0.0246 (6)	0.38591 (16)	-0.1941 (2)	0.0753 (9)
H9A	-0.1549	0.3645	-0.2070	0.090*
H9B	0.0644	0.3698	-0.2490	0.090*
C10	0.0552 (5)	0.35865 (15)	-0.0899 (2)	0.0681 (8)
H10A	0.1938	0.3738	-0.0837	0.082*
H10B	0.0560	0.3070	-0.0933	0.082*
C11	-0.0502 (4)	0.37973 (13)	0.0114 (2)	0.0476 (6)
C12	0.0569 (6)	0.52838 (19)	0.3121 (2)	0.0791 (10)
H12A	0.1817	0.5263	0.3499	0.119*
H12B	-0.0371	0.4960	0.3430	0.119*
H12C	0.0043	0.5759	0.3151	0.119*
C14	-0.2671 (5)	0.35177 (17)	0.0103 (3)	0.0793 (10)
H14A	-0.2660	0.3008	0.0045	0.119*
H14B	-0.3383	0.3718	-0.0483	0.119*
H14C	-0.3322	0.3653	0.0741	0.119*
C15	0.0620 (5)	0.34352 (16)	0.1020 (3)	0.0709 (9)
H15A	0.0584	0.2928	0.0925	0.106*
H15B	-0.0008	0.3557	0.1670	0.106*
H15C	0.1989	0.3594	0.1032	0.106*
C16	0.0640 (4)	0.57190 (14)	-0.0831 (2)	0.0545 (7)
C17	0.3373 (3)	0.23635 (12)	0.52663 (18)	0.0416 (5)
H17	0.2229	0.2643	0.5009	0.050*
C18	0.2929 (4)	0.21847 (13)	0.6403 (2)	0.0491 (6)
C19	0.4595 (4)	0.21347 (15)	0.7164 (2)	0.0566 (7)
C20	0.6448 (4)	0.23164 (15)	0.6869 (2)	0.0541 (7)
H20	0.7473	0.2279	0.7364	0.065*
C21	0.6985 (4)	0.25743 (14)	0.5803 (2)	0.0504 (6)
H21A	0.7596	0.2188	0.5415	0.060*
H21B	0.7965	0.2954	0.5867	0.060*
C22	0.5185 (4)	0.28455 (12)	0.51998 (19)	0.0394 (5)
C23	0.5449 (4)	0.32811 (15)	0.41890 (19)	0.0503 (6)
C24	0.3892 (5)	0.31700 (17)	0.3332 (2)	0.0620 (8)
H24A	0.4055	0.3534	0.2801	0.074*
H24B	0.2564	0.3223	0.3627	0.074*
C25	0.4058 (6)	0.2439 (2)	0.2822 (2)	0.0831 (10)
H25A	0.5018	0.2470	0.2256	0.100*
H25B	0.2768	0.2320	0.2513	0.100*
C26	0.4694 (5)	0.18318 (19)	0.3547 (3)	0.0788 (10)
H26A	0.6073	0.1919	0.3757	0.095*
H26B	0.4690	0.1398	0.3135	0.095*
C27	0.3494 (4)	0.16840 (15)	0.4547 (2)	0.0612 (8)
C28	0.4103 (5)	0.1891 (2)	0.8254 (3)	0.0821 (10)
H28A	0.5294	0.1903	0.8681	0.123*
H28B	0.3590	0.1414	0.8230	0.123*
H28C	0.3112	0.2201	0.8549	0.123*
C31	0.4526 (6)	0.10533 (17)	0.5119 (3)	0.0908 (11)
H31A	0.5875	0.1184	0.5304	0.136*
H31B	0.4548	0.0646	0.4665	0.136*
H31C	0.3795	0.0940	0.5742	0.136*

O1	-0.2520 (3)	0.48319 (13)	0.17818 (16)	0.0732 (6)
O2	0.1224 (3)	0.20740 (13)	0.66801 (17)	0.0771 (6)
Cl1	-0.18216 (13)	0.60662 (4)	-0.08502 (7)	0.0734 (2)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C4	0.0487 (17)	0.085 (2)	0.065 (2)	-0.0084 (15)	-0.0153 (14)	-0.0067 (17)
C5	0.0387 (14)	0.0655 (18)	0.0656 (18)	-0.0037 (12)	-0.0004 (12)	-0.0059 (14)
C6	0.0402 (13)	0.0434 (13)	0.0447 (14)	-0.0043 (10)	-0.0006 (11)	-0.0034 (11)
C7	0.0677 (18)	0.0501 (15)	0.0489 (16)	-0.0119 (13)	0.0092 (13)	-0.0005 (12)
C13	0.092 (3)	0.089 (3)	0.072 (2)	-0.019 (2)	0.0332 (19)	-0.0136 (19)
C29	0.072 (2)	0.100 (3)	0.070 (2)	-0.0123 (19)	0.0127 (17)	0.0220 (19)
C30	0.077 (2)	0.087 (3)	0.137 (3)	-0.019 (2)	-0.014 (2)	-0.052 (3)
C32	0.0542 (15)	0.0398 (13)	0.0506 (16)	0.0004 (11)	-0.0125 (12)	0.0009 (11)
Cl2	0.1082 (7)	0.0573 (5)	0.0947 (6)	-0.0378 (5)	0.0078 (5)	-0.0006 (4)
Cl3	0.0704 (5)	0.0544 (4)	0.0658 (4)	0.0229 (3)	-0.0103 (3)	-0.0051 (3)
Cl4	0.0927 (6)	0.0486 (4)	0.0918 (6)	-0.0169 (4)	-0.0318 (4)	-0.0002 (4)
C1	0.0353 (13)	0.0399 (13)	0.0449 (14)	0.0020 (10)	-0.0076 (10)	0.0039 (11)
C2	0.0454 (15)	0.0471 (14)	0.0511 (16)	0.0094 (11)	0.0035 (12)	0.0059 (12)
C3	0.0539 (18)	0.0667 (18)	0.0522 (16)	0.0042 (14)	-0.0065 (13)	-0.0101 (14)
C8	0.089 (2)	0.0588 (17)	0.0430 (15)	-0.0148 (15)	-0.0073 (14)	-0.0008 (13)
C9	0.118 (3)	0.0553 (18)	0.0527 (17)	-0.0167 (18)	-0.0016 (17)	-0.0117 (14)
C10	0.091 (2)	0.0446 (16)	0.069 (2)	0.0051 (15)	-0.0035 (16)	-0.0075 (14)
C11	0.0488 (15)	0.0406 (13)	0.0532 (15)	-0.0014 (11)	-0.0020 (12)	0.0025 (11)
C12	0.105 (3)	0.080 (2)	0.0529 (18)	-0.003 (2)	-0.0018 (17)	-0.0074 (16)
C14	0.075 (2)	0.0495 (17)	0.114 (3)	-0.0145 (15)	-0.0048 (19)	0.0074 (17)
C15	0.081 (2)	0.0552 (17)	0.076 (2)	0.0137 (15)	-0.0104 (17)	0.0120 (15)
C16	0.0626 (18)	0.0459 (14)	0.0549 (17)	-0.0149 (13)	-0.0024 (13)	-0.0026 (13)
C17	0.0348 (13)	0.0408 (13)	0.0490 (15)	0.0067 (10)	-0.0050 (10)	-0.0034 (11)
C18	0.0430 (15)	0.0421 (14)	0.0624 (17)	0.0073 (11)	0.0050 (12)	0.0054 (12)
C19	0.0551 (17)	0.0587 (17)	0.0559 (17)	0.0108 (13)	-0.0002 (13)	0.0135 (13)
C20	0.0510 (16)	0.0544 (15)	0.0566 (17)	0.0087 (12)	-0.0141 (13)	0.0066 (13)
C21	0.0460 (15)	0.0466 (14)	0.0584 (17)	0.0029 (11)	-0.0054 (12)	0.0061 (12)
C22	0.0378 (13)	0.0395 (12)	0.0410 (13)	0.0040 (10)	-0.0019 (10)	-0.0007 (10)
C23	0.0494 (16)	0.0582 (16)	0.0433 (14)	0.0008 (12)	-0.0001 (12)	0.0077 (13)
C24	0.070 (2)	0.0738 (19)	0.0416 (15)	0.0087 (15)	-0.0054 (13)	0.0035 (15)
C25	0.102 (3)	0.098 (3)	0.0487 (18)	0.011 (2)	-0.0075 (17)	-0.0172 (18)
C26	0.088 (2)	0.073 (2)	0.076 (2)	0.0114 (18)	0.0056 (18)	-0.0394 (18)
C27	0.0563 (17)	0.0455 (15)	0.082 (2)	-0.0012 (12)	-0.0020 (15)	-0.0182 (15)
C28	0.090 (2)	0.090 (3)	0.066 (2)	0.015 (2)	0.0108 (18)	0.0236 (19)
C31	0.097 (3)	0.0443 (17)	0.131 (3)	0.0114 (18)	0.003 (2)	-0.010 (2)
O1	0.0502 (12)	0.1049 (17)	0.0647 (13)	0.0081 (11)	0.0127 (10)	0.0001 (12)
O2	0.0439 (12)	0.0959 (17)	0.0917 (16)	0.0044 (11)	0.0137 (10)	0.0280 (13)
Cl1	0.0823 (6)	0.0530 (4)	0.0846 (5)	0.0118 (4)	-0.0146 (4)	0.0132 (4)

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

C4—C3	1.326 (4)	C11—C15	1.532 (4)
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supplementary materials

C4—C5	1.484 (4)	C11—C14	1.538 (4)
C4—H4	0.9300	C12—H12A	0.9600
C5—C6	1.498 (4)	C12—H12B	0.9600
C5—H5A	0.9700	C12—H12C	0.9600
C5—H5B	0.9700	C14—H14A	0.9600
C6—C16	1.522 (4)	C14—H14B	0.9600
C6—C1	1.527 (3)	C14—H14C	0.9600
C6—C7	1.549 (4)	C15—H15A	0.9600
C7—C16	1.510 (4)	C15—H15B	0.9600
C7—C8	1.510 (4)	C15—H15C	0.9600
C7—C13	1.516 (4)	C16—C11	1.766 (3)
C13—H13A	0.9600	C17—C22	1.513 (3)
C13—H13B	0.9600	C17—C18	1.521 (4)
C13—H13C	0.9600	C17—C27	1.574 (3)
C29—C23	1.526 (4)	C17—H17	0.9800
C29—H29A	0.9600	C18—O2	1.211 (3)
C29—H29B	0.9600	C18—C19	1.473 (4)
C29—H29C	0.9600	C19—C20	1.339 (4)
C30—C27	1.537 (4)	C19—C28	1.505 (4)
C30—H30A	0.9600	C20—C21	1.491 (4)
C30—H30B	0.9600	C20—H20	0.9300
C30—H30C	0.9600	C21—C22	1.509 (3)
C32—C23	1.504 (4)	C21—H21A	0.9700
C32—C22	1.513 (3)	C21—H21B	0.9700
C32—C14	1.756 (3)	C22—C23	1.539 (3)
C32—C13	1.766 (3)	C23—C24	1.517 (4)
C12—C16	1.764 (3)	C24—C25	1.523 (5)
C1—C2	1.515 (4)	C24—H24A	0.9700
C1—C11	1.576 (3)	C24—H24B	0.9700
C1—H1	0.9800	C25—C26	1.527 (5)
C2—O1	1.228 (3)	C25—H25A	0.9700
C2—C3	1.474 (4)	C25—H25B	0.9700
C3—C12	1.506 (4)	C26—C27	1.537 (5)
C8—C9	1.535 (4)	C26—H26A	0.9700
C8—H8A	0.9700	C26—H26B	0.9700
C8—H8B	0.9700	C27—C31	1.549 (5)
C9—C10	1.519 (4)	C28—H28A	0.9600
C9—H9A	0.9700	C28—H28B	0.9600
C9—H9B	0.9700	C28—H28C	0.9600
C10—C11	1.529 (4)	C31—H31A	0.9600
C10—H10A	0.9700	C31—H31B	0.9600
C10—H10B	0.9700	C31—H31C	0.9600
C3—C4—C5	125.3 (3)	C11—C14—H14A	109.5
C3—C4—H4	117.4	C11—C14—H14B	109.5
C5—C4—H4	117.4	H14A—C14—H14B	109.5
C4—C5—C6	111.8 (2)	C11—C14—H14C	109.5
C4—C5—H5A	109.3	H14A—C14—H14C	109.5
C6—C5—H5A	109.3	H14B—C14—H14C	109.5
C4—C5—H5B	109.3	C11—C15—H15A	109.5

C6—C5—H5B	109.3	C11—C15—H15B	109.5
H5A—C5—H5B	107.9	H15A—C15—H15B	109.5
C5—C6—C16	118.0 (2)	C11—C15—H15C	109.5
C5—C6—C1	113.9 (2)	H15A—C15—H15C	109.5
C16—C6—C1	117.1 (2)	H15B—C15—H15C	109.5
C5—C6—C7	121.5 (2)	C7—C16—C6	61.42 (18)
C16—C6—C7	58.90 (17)	C7—C16—C12	118.7 (2)
C1—C6—C7	116.6 (2)	C6—C16—C12	119.7 (2)
C16—C7—C8	118.4 (3)	C7—C16—C11	121.5 (2)
C16—C7—C13	119.3 (3)	C6—C16—C11	121.25 (19)
C8—C7—C13	113.7 (3)	C12—C16—C11	108.17 (15)
C16—C7—C6	59.67 (17)	C22—C17—C18	110.30 (19)
C8—C7—C6	116.4 (2)	C22—C17—C27	114.06 (19)
C13—C7—C6	119.2 (3)	C18—C17—C27	112.9 (2)
C7—C13—H13A	109.5	C22—C17—H17	106.3
C7—C13—H13B	109.5	C18—C17—H17	106.3
H13A—C13—H13B	109.5	C27—C17—H17	106.3
C7—C13—H13C	109.5	O2—C18—C19	120.1 (2)
H13A—C13—H13C	109.5	O2—C18—C17	120.4 (2)
H13B—C13—H13C	109.5	C19—C18—C17	119.5 (2)
C23—C29—H29A	109.5	C20—C19—C18	119.4 (2)
C23—C29—H29B	109.5	C20—C19—C28	123.1 (3)
H29A—C29—H29B	109.5	C18—C19—C28	117.5 (3)
C23—C29—H29C	109.5	C19—C20—C21	124.6 (2)
H29A—C29—H29C	109.5	C19—C20—H20	117.7
H29B—C29—H29C	109.5	C21—C20—H20	117.7
C27—C30—H30A	109.5	C20—C21—C22	112.3 (2)
C27—C30—H30B	109.5	C20—C21—H21A	109.1
H30A—C30—H30B	109.5	C22—C21—H21A	109.1
C27—C30—H30C	109.5	C20—C21—H21B	109.1
H30A—C30—H30C	109.5	C22—C21—H21B	109.1
H30B—C30—H30C	109.5	H21A—C21—H21B	107.9
C23—C32—C22	61.35 (17)	C21—C22—C17	113.7 (2)
C23—C32—C14	118.95 (19)	C21—C22—C32	117.3 (2)
C22—C32—C14	119.78 (18)	C17—C22—C32	118.1 (2)
C23—C32—C13	120.68 (18)	C21—C22—C23	120.8 (2)
C22—C32—C13	121.13 (18)	C17—C22—C23	117.5 (2)
C14—C32—C13	108.56 (14)	C32—C22—C23	59.02 (17)
C2—C1—C6	110.0 (2)	C32—C23—C24	119.1 (2)
C2—C1—C11	112.6 (2)	C32—C23—C29	119.7 (3)
C6—C1—C11	114.7 (2)	C24—C23—C29	112.3 (2)
C2—C1—H1	106.3	C32—C23—C22	59.62 (15)
C6—C1—H1	106.3	C24—C23—C22	116.7 (2)
C11—C1—H1	106.3	C29—C23—C22	120.0 (2)
O1—C2—C3	120.3 (2)	C23—C24—C25	112.4 (3)
O1—C2—C1	119.9 (2)	C23—C24—H24A	109.1
C3—C2—C1	119.7 (2)	C25—C24—H24A	109.1
C4—C3—C2	119.2 (3)	C23—C24—H24B	109.1
C4—C3—C12	123.0 (3)	C25—C24—H24B	109.1

supplementary materials

C2—C3—C12	117.3 (2)	H24A—C24—H24B	107.9
C7—C8—C9	112.7 (3)	C24—C25—C26	115.7 (3)
C7—C8—H8A	109.1	C24—C25—H25A	108.3
C9—C8—H8A	109.1	C26—C25—H25A	108.3
C7—C8—H8B	109.1	C24—C25—H25B	108.3
C9—C8—H8B	109.1	C26—C25—H25B	108.3
H8A—C8—H8B	107.8	H25A—C25—H25B	107.4
C10—C9—C8	115.4 (2)	C25—C26—C27	119.7 (3)
C10—C9—H9A	108.4	C25—C26—H26A	107.4
C8—C9—H9A	108.4	C27—C26—H26A	107.4
C10—C9—H9B	108.4	C25—C26—H26B	107.4
C8—C9—H9B	108.4	C27—C26—H26B	107.4
H9A—C9—H9B	107.5	H26A—C26—H26B	106.9
C9—C10—C11	119.6 (3)	C30—C27—C26	110.6 (3)
C9—C10—H10A	107.4	C30—C27—C31	107.7 (3)
C11—C10—H10A	107.4	C26—C27—C31	107.3 (3)
C9—C10—H10B	107.4	C30—C27—C17	108.0 (2)
C11—C10—H10B	107.4	C26—C27—C17	111.6 (2)
H10A—C10—H10B	106.9	C31—C27—C17	111.7 (3)
C10—C11—C15	107.4 (2)	C19—C28—H28A	109.5
C10—C11—C14	110.0 (2)	C19—C28—H28B	109.5
C15—C11—C14	108.0 (2)	H28A—C28—H28B	109.5
C10—C11—C1	111.6 (2)	C19—C28—H28C	109.5
C15—C11—C1	112.4 (2)	H28A—C28—H28C	109.5
C14—C11—C1	107.4 (2)	H28B—C28—H28C	109.5
C3—C12—H12A	109.5	C27—C31—H31A	109.5
C3—C12—H12B	109.5	C27—C31—H31B	109.5
H12A—C12—H12B	109.5	H31A—C31—H31B	109.5
C3—C12—H12C	109.5	C27—C31—H31C	109.5
H12A—C12—H12C	109.5	H31A—C31—H31C	109.5
H12B—C12—H12C	109.5	H31B—C31—H31C	109.5

Fig. 1

