organic compounds

(1S,3R,8R)-2,2-Dibromo-3,7,7,10-tetra-methyltricyclo[6.4.0.0^{1,3}]dodec-9-ene

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The title compound, C$_{16}$H$_{24}$Br$_2$, was synthesized from β-himachalene (3,5,5,9-tetramethyl-2,4a,5,6,7,8-hexahydro-1H-benzocycloheptene), which was isolated from the essential oil of the Atlas cedar (*Cedrus Atlantica*). The molecule is built up from two fused six- and seven-membered rings and an additional three-membered ring from the reaction of β-himachalene with dibromocarbene. The six-membered ring shows a screw-boat conformation, whereas the seven-membered ring displays a boat conformation; the dihedral angle between the mean planes through the rings is 57.9 (4)°. The absolute structure was established unambiguously from anomalous dispersion effects.

Related literature

For the isolation of β-himachalene, see: Joseph & Dev (1968); Plattier & Teiseire (1974). For the reactivity of this sesqui-terpene, see: Lassaba *et al.* (1997); 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). For conformational analysis, see: Cremer & Pople (1975).
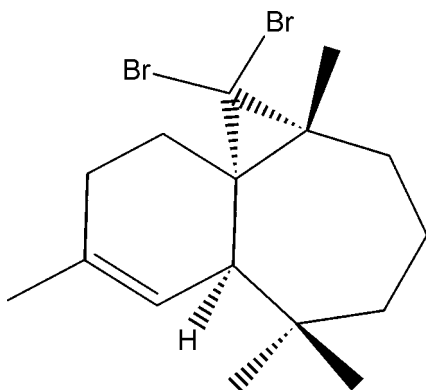
Experimental

Crystal data

C$_{16}$H$_{24}$Br$_2$	V = 1604.6 (4) Å^3
M_r = 376.17	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 9.7464 (14) Å	μ = 5.04 mm^{-1}
b = 12.1633 (16) Å	T = 298 K
c = 13.5352 (18) Å	0.78 × 0.66 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer	17190 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	3254 independent reflections
T_{min} = 0.259, T_{max} = 0.746	2281 reflections with $I > 2\sigma(I)$
	R_{int} = 0.086

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049	$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$wR(F^2)$ = 0.132	$\Delta\rho_{min}$ = −1.05 e Å^{-3}
S = 1.06	Absolute structure: Flack (1983), 1380 Friedel pairs
3254 reflections	Flack parameter: 0.07 (2)
167 parameters	
H-atom parameters constrained	

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).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2394).

References

Bruker (2009). *APEX2* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chekroun, A., Jarid, A., Benharref, A. & Boutalib, A. (2000). *J. Org. Chem.* **65**, 4431–4434.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Dakir, M., Auhmani, A., Ait Itto, M. Y., Mazoir, N., Akssira, M., Pierrot, M. & Benharref, A. (2004). *Synth. Commun.* **34**, 2001–2008.

Daoubi, M., Duran -Patron, R., Hmamouchi, M., Hernandez-Galan, R., Benharref, A. & Isidro, G. C. (2004). *Pest Manag. Sci.* **60**, 927–932.

El Jamili, H., Auhmani, A., Dakir, M., Lassaba, E., Benharref, A., Pierrot, M., Chiaroni, A. & Riche, C. (2002). *Tetrahedron Lett.* **43**, 6645–6648.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Joseph, T. C. & Dev, S. (1968). *Tetrahedron*, **24**, 3841–3859.

Lassaba, E., Chekroun, A., Benharref, A., Chiaroni, A., Riche, C. & Lavergne, J.-P. (1997). *Bull. Soc. Chim. Belg.* **106**, 281–288.

Plattier, M. & Teiseire, P. (1974). *Recherche*, **19**, 131–144.

Sbai, F., Dakir, M., Auhmani, A., El Jamili, H., Akssira, M., Benharref, A., Kenz, A. & Pierrot, M. (2002). *Acta Cryst.* C**58**, o518–o520.

Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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

Ahmed Benharref, Lahcen El Ammari, Essêdiya Lassaba, Najia Ourhriss and Moha Berraho

Comment

The bicyclic sesquiterpene *β*-himachalene is the main constituent of the essential oil of the Atlas cedar (Cedrus atlantica) (Plattier & Teiseire, 1974); Joseph & Dev, 1968). The reactivity of this sesquiterpene and its derivatives has been studied extensively by our team in order to prepare new products having biological proprieties. Lassaba et al., 1997; 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 dibromocarbene, generated in situ from bromoform in the presence of sodium hydroxide as base and n-benzyltriethylammonium chloride as catalyst, on *β*-himachalene produces the title compound (I) with a yield of 22%. The structure of this new product was determined by its single-crystal X-ray structure analysis. The molecule is built up from two fused six-and seven- membered rings and an additional three-membered ring from the reaction with the carbene (Fig.1). The six-membered ring has a screw boat conformation, as indicated by the total puckering amplitude QT = 0.485 (19) Å and spherical polar angle θ = 128.1 (11)° with φ = 155.7 (14)°, whereas the seven-membered ring displays a boat conformation with QT = 1.1497 (1) Å, θ = 88.51 (5)°, $\varphi2$ = 311.8 (5)° and $\varphi3$ = 238.26 (19)° (Cremer & Pople, 1975). Owing to the presence of Br atoms, the absolute configuration could be fully confirmed, by refining the Flack parameter (Flack, 1983) as C1(S), C3(R) and C8(R).

Experimental

A solution containing 5 g (24 mmol) of *β*-himachalene and 3 ml (37 mmol) of CHBr$_3$ in 30 ml of dichloromethane was added in dropwise fashion at 0°C over 30 min to 1,5 g (37 mmol) of pulverized sodium hydroxide and 50 mg of N–benzyltriethylammonium chloride placed in a 100 ml three – necked flask. After stirring at room temperature for 2 h, the mixture was filtered on celite and concentrated in vacuum. The residue obtained was chromatographed on silica gel using hexane as eluting agent to give 2 g (5,3 mmol) of (1*S*,3*R*,8*R*)-2,2-Dibromo-3,7,7,10-tetramethyl-tricyclo [6.4.0.0^{1,3}]dodec-9-ene with a yield of 22%. The title compound was recrystallized from 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) and with U_{iso}(H) = 1.2 U_{eq}(C) for methylene and methine hydrogen atoms or U_{iso}(H) = 1.5 U_{eq}(C) for methyl groups.

Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus* (Bruker, 2009); 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).
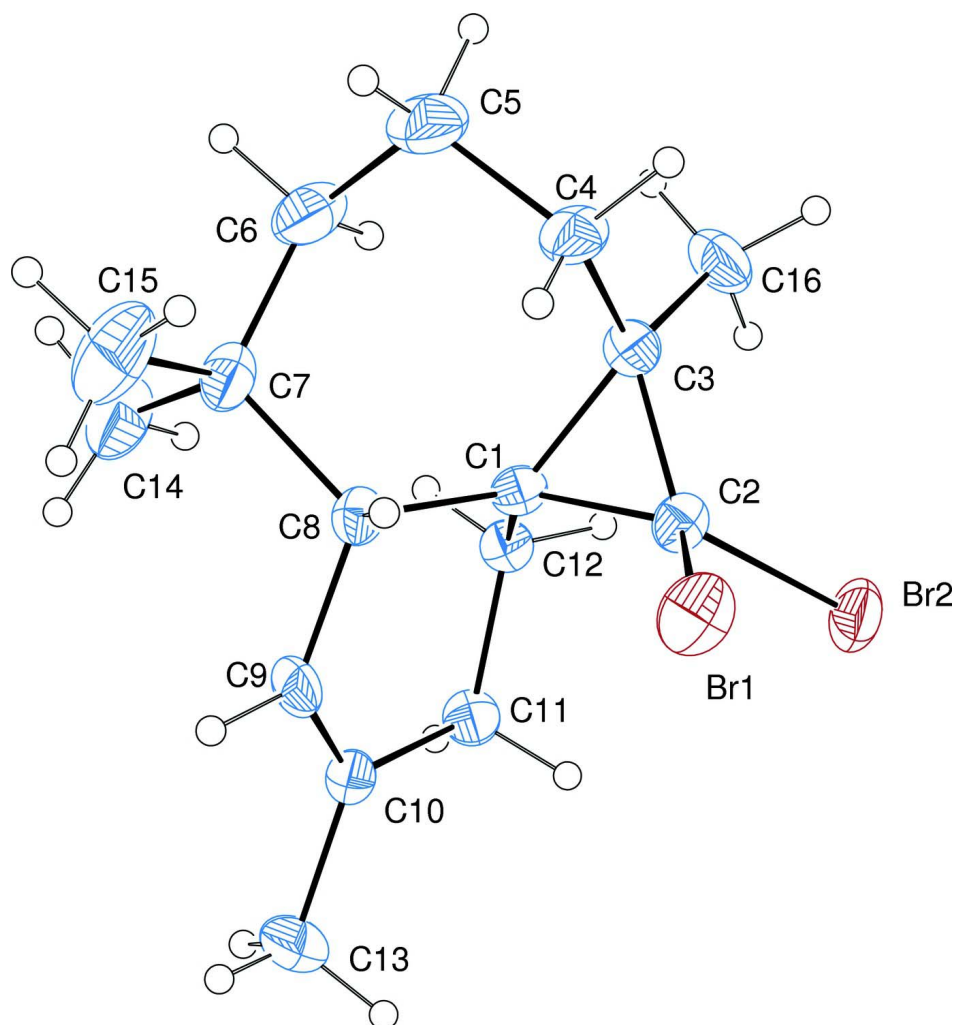
Figure 1

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

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

Crystal data

$C_{16}H_{24}Br_2$	$F(000) = 760$
$M_r = 376.17$	$D_x = 1.557$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 17190 reflections
$a = 9.7464$ (14) Å	$\theta = 2.6–26.4°$
$b = 12.1633$ (16) Å	$\mu = 5.04$ mm^{-1}
$c = 13.5352$ (18) Å	$T = 298$ K
$V = 1604.6$ (4) Å^3	Prism, colourless
$Z = 4$	$0.78 \times 0.66 \times 0.24$ mm

Data collection

Bruker APEXII CCD diffractometer	17190 measured reflections
Radiation source: fine-focus sealed tube	3254 independent reflections
Graphite monochromator	2281 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.086$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	$\theta_{max} = 26.4°$, $\theta_{min} = 2.6°$
	$h = -12 \rightarrow 12$
$T_{min} = 0.259$, $T_{max} = 0.746$	$k = -15 \rightarrow 15$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0682P)^2 + 0.6114P]$
$wR(F^2) = 0.132$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
3254 reflections	$\Delta\rho_{max} = 0.85$ e Å^{-3}
167 parameters	$\Delta\rho_{min} = -1.05$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 1380 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.07 (2)
Secondary atom site location: difference Fourier map	

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.3347 (7)	0.6855 (4)	0.2295 (4)	0.0321 (13)
C2	0.4162 (7)	0.7675 (5)	0.1685 (5)	0.0368 (15)
C3	0.3869 (8)	0.6562 (5)	0.1251 (5)	0.0413 (15)
C4	0.2801 (8)	0.6488 (6)	0.0455 (5)	0.0486 (19)
H4A	0.3251	0.6479	−0.0185	0.058*
H4B	0.2221	0.7135	0.0482	0.058*
C5	0.1901 (11)	0.5455 (7)	0.0554 (6)	0.067 (2)
H5A	0.2369	0.4842	0.0243	0.080*
H5B	0.1049	0.5575	0.0199	0.080*
C6	0.1559 (10)	0.5140 (6)	0.1633 (6)	0.062 (2)
H6A	0.2404	0.4906	0.1948	0.074*
H6B	0.0953	0.4507	0.1616	0.074*
C7	0.0886 (7)	0.6022 (6)	0.2302 (5)	0.0480 (17)
C8	0.1814 (6)	0.7070 (5)	0.2427 (4)	0.0340 (13)
H8	0.1550	0.7576	0.1897	0.041*

C9	0.1592 (8)	0.7681 (5)	0.3381 (5)	0.0457 (17)
H9	0.0743	0.8016	0.3471	0.055*
C10	0.2497 (7)	0.7784 (5)	0.4100 (5)	0.0424 (17)
C11	0.3862 (7)	0.7238 (5)	0.4053 (4)	0.0399 (16)
H11A	0.4029	0.6870	0.4678	0.048*
H11B	0.4561	0.7798	0.3974	0.048*
C12	0.4011 (8)	0.6409 (4)	0.3229 (4)	0.0349 (14)
H12A	0.3576	0.5723	0.3417	0.042*
H12B	0.4976	0.6265	0.3109	0.042*
C13	0.2240 (10)	0.8474 (8)	0.4997 (7)	0.075 (3)
H13A	0.1371	0.8839	0.4932	0.113*
H13B	0.2955	0.9013	0.5060	0.113*
H13C	0.2229	0.8014	0.5573	0.113*
C14	0.0598 (10)	0.5426 (7)	0.3284 (7)	0.072 (3)
H14A	0.0060	0.4779	0.3159	0.108*
H14B	0.0103	0.5907	0.3718	0.108*
H14C	0.1451	0.5219	0.3586	0.108*
C15	−0.0479 (10)	0.6373 (8)	0.1882 (9)	0.092 (3)
H15A	−0.0345	0.6672	0.1232	0.138*
H15B	−0.0880	0.6923	0.2301	0.138*
H15C	−0.1079	0.5749	0.1844	0.138*
C16	0.5021 (8)	0.5748 (6)	0.1134 (6)	0.058 (2)
H16A	0.5482	0.5876	0.0518	0.088*
H16B	0.4656	0.5015	0.1142	0.088*
H16C	0.5660	0.5834	0.1668	0.088*
Br1	0.33615 (9)	0.89924 (6)	0.11733 (6)	0.0589 (3)
Br2	0.60263 (7)	0.80174 (6)	0.20570 (6)	0.0556 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.037 (3)	0.027 (3)	0.033 (3)	0.000 (3)	−0.005 (3)	0.001 (2)
C2	0.039 (4)	0.036 (3)	0.035 (3)	−0.004 (3)	−0.003 (3)	0.006 (2)
C3	0.045 (4)	0.043 (3)	0.036 (3)	−0.005 (3)	0.003 (4)	−0.002 (3)
C4	0.060 (6)	0.056 (4)	0.030 (3)	−0.016 (4)	−0.007 (4)	−0.002 (3)
C5	0.081 (7)	0.074 (5)	0.046 (4)	−0.020 (5)	−0.010 (5)	−0.015 (4)
C6	0.071 (6)	0.056 (4)	0.058 (4)	−0.021 (4)	−0.011 (5)	−0.006 (4)
C7	0.038 (4)	0.058 (4)	0.048 (4)	−0.012 (4)	−0.003 (4)	0.004 (3)
C8	0.028 (4)	0.040 (3)	0.034 (3)	0.000 (3)	−0.004 (3)	0.003 (2)
C9	0.031 (4)	0.041 (3)	0.065 (4)	0.007 (3)	0.017 (4)	−0.008 (3)
C10	0.039 (4)	0.048 (4)	0.040 (4)	−0.012 (3)	0.007 (3)	−0.007 (3)
C11	0.038 (4)	0.052 (4)	0.030 (3)	−0.001 (3)	−0.007 (3)	−0.002 (2)
C12	0.036 (4)	0.033 (3)	0.036 (3)	0.002 (3)	−0.001 (3)	0.002 (2)
C13	0.067 (6)	0.089 (6)	0.070 (6)	−0.011 (5)	0.019 (5)	−0.045 (5)
C14	0.063 (6)	0.076 (5)	0.077 (6)	−0.025 (4)	−0.004 (5)	0.013 (4)
C15	0.051 (6)	0.099 (7)	0.127 (9)	−0.014 (5)	−0.034 (7)	0.009 (6)
C16	0.059 (5)	0.057 (4)	0.060 (5)	0.009 (4)	0.023 (4)	−0.012 (4)
Br1	0.0687 (6)	0.0419 (3)	0.0662 (5)	−0.0017 (4)	−0.0037 (4)	0.0198 (3)
Br2	0.0369 (4)	0.0639 (4)	0.0661 (5)	−0.0149 (3)	0.0047 (4)	0.0019 (4)

Geometric parameters (Å, º)

C1—C2	1.519 (8)	C8—H8	0.9800
C1—C12	1.520 (8)	C9—C10	1.319 (10)
C1—C8	1.527 (9)	C9—H9	0.9300
C1—C3	1.545 (9)	C10—C11	1.488 (10)
C2—C3	1.503 (8)	C10—C13	1.497 (9)
C2—Br1	1.913 (6)	C11—C12	1.510 (8)
C2—Br2	1.931 (7)	C11—H11A	0.9700
C3—C4	1.501 (10)	C11—H11B	0.9700
C3—C16	1.505 (10)	C12—H12A	0.9700
C4—C5	1.539 (11)	C12—H12B	0.9700
C4—H4A	0.9700	C13—H13A	0.9600
C4—H4B	0.9700	C13—H13B	0.9600
C5—C6	1.546 (12)	C13—H13C	0.9600
C5—H5A	0.9700	C14—H14A	0.9600
C5—H5B	0.9700	C14—H14B	0.9600
C6—C7	1.550 (11)	C14—H14C	0.9600
C6—H6A	0.9700	C15—H15A	0.9600
C6—H6B	0.9700	C15—H15B	0.9600
C7—C15	1.508 (12)	C15—H15C	0.9600
C7—C14	1.539 (11)	C16—H16A	0.9600
C7—C8	1.573 (9)	C16—H16B	0.9600
C8—C9	1.506 (9)	C16—H16C	0.9600
C2—C1—C12	117.6 (6)	C9—C8—H8	106.2
C2—C1—C8	117.5 (5)	C1—C8—H8	106.2
C12—C1—C8	112.4 (5)	C7—C8—H8	106.2
C2—C1—C3	58.8 (4)	C10—C9—C8	125.7 (6)
C12—C1—C3	122.6 (5)	C10—C9—H9	117.2
C8—C1—C3	118.0 (5)	C8—C9—H9	117.2
C3—C2—C1	61.5 (4)	C9—C10—C11	121.6 (6)
C3—C2—Br1	122.4 (5)	C9—C10—C13	122.6 (7)
C1—C2—Br1	122.2 (5)	C11—C10—C13	115.7 (7)
C3—C2—Br2	118.4 (5)	C10—C11—C12	114.6 (6)
C1—C2—Br2	119.5 (4)	C10—C11—H11A	108.6
Br1—C2—Br2	107.3 (3)	C12—C11—H11A	108.6
C4—C3—C2	117.8 (6)	C10—C11—H11B	108.6
C4—C3—C16	113.8 (6)	C12—C11—H11B	108.6
C2—C3—C16	119.4 (7)	H11A—C11—H11B	107.6
C4—C3—C1	116.3 (6)	C11—C12—C1	109.6 (5)
C2—C3—C1	59.8 (4)	C11—C12—H12A	109.8
C16—C3—C1	119.6 (6)	C1—C12—H12A	109.8
C3—C4—C5	112.4 (6)	C11—C12—H12B	109.8
C3—C4—H4A	109.1	C1—C12—H12B	109.8
C5—C4—H4A	109.1	H12A—C12—H12B	108.2
C3—C4—H4B	109.1	C10—C13—H13A	109.5
C5—C4—H4B	109.1	C10—C13—H13B	109.5
H4A—C4—H4B	107.8	H13A—C13—H13B	109.5
C4—C5—C6	114.1 (6)	C10—C13—H13C	109.5

C4—C5—H5A	108.7	H13A—C13—H13C	109.5
C6—C5—H5A	108.7	H13B—C13—H13C	109.5
C4—C5—H5B	108.7	C7—C14—H14A	109.5
C6—C5—H5B	108.7	C7—C14—H14B	109.5
H5A—C5—H5B	107.6	H14A—C14—H14B	109.5
C5—C6—C7	118.2 (7)	C7—C14—H14C	109.5
C5—C6—H6A	107.8	H14A—C14—H14C	109.5
C7—C6—H6A	107.8	H14B—C14—H14C	109.5
C5—C6—H6B	107.8	C7—C15—H15A	109.5
C7—C6—H6B	107.8	C7—C15—H15B	109.5
H6A—C6—H6B	107.1	H15A—C15—H15B	109.5
C15—C7—C14	107.4 (8)	C7—C15—H15C	109.5
C15—C7—C6	110.4 (7)	H15A—C15—H15C	109.5
C14—C7—C6	104.8 (6)	H15B—C15—H15C	109.5
C15—C7—C8	108.6 (6)	C3—C16—H16A	109.5
C14—C7—C8	113.2 (6)	C3—C16—H16B	109.5
C6—C7—C8	112.3 (6)	H16A—C16—H16B	109.5
C9—C8—C1	109.0 (5)	C3—C16—H16C	109.5
C9—C8—C7	114.2 (5)	H16A—C16—H16C	109.5
C1—C8—C7	114.3 (5)	H16B—C16—H16C	109.5