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6-Bromo-2-(1,4-dibromo-4-methylcyclohexyl)-6-methylheptan-4-one

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Keywords: crystal structure; α-atlantone and γ-atlantone; Atlas cedar (*Cedrus Atlantica*); C—H···O hydrogen bonding.

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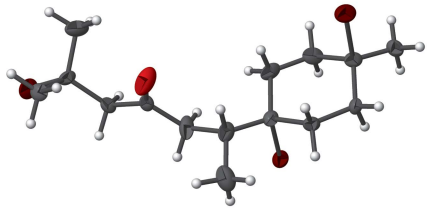
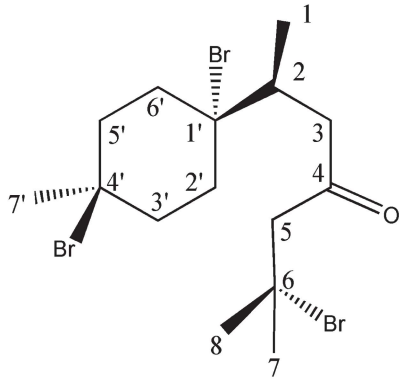
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{15}H_{25}Br_3O$, was synthesized in one step from a mixture of α-atlantone [2-methyl-6-(4-methylcyclohex-3-en-1-yl)hepta-2,5-dien-4-one] and γ-atlantone [2-methyl-6-(4-methylcyclohex-3-en-1-ylidene)hept-2-en-4-one], which were isolated from an essential oil of the Atlas cedar (*Cedrus Atlantica*). The molecule is built up from the bromo ethyl cyclohexane ring, which has a substituent bromomethylhexanone group. The cyclohexane ring adopts a chair conformation. In the crystal, molecules are linked by C—H···O hydrogen bonds, forming zigzag chains parallel to [100].

3D view



Chemical scheme



Structure description

α-Atlantone and γ-atlantone are constituents (5–6%) of the essential oil of the Atlas cedar (*Cedrus Atlantica*) (Plattier & Teisseire,1974; Mazoir *et al.*, 2016). The reactivity of these sesquiterpenes and their derivatives has been studied by our team (Loughzail *et al.*, 2009; Mazoir *et al.*, 2009, 2016) in order to prepare new products with biological properties. Indeed, these compounds have been tested for their potential antifungal activity against the phytopathogen *Botrytis cinerea* (Daoubi *et al.*,2004).

Herein, we report on the synthesis and crystal structure of the title compound, 6-bromo-2-(1,4-dibromo-4-methylcyclohexyl)-6-methylheptan-4-one. The bromo ethyl cyclohexane ring has a bromomethylhexanone group as a substituent (Fig. 1). The cyclohexane ring has a chair conformation as indicated by the total puckering amplitude Q_T = 0.486 (10) Å and spherical polar angle θ = 1.6 (12)° with φ = 105 (27)°.

In the crystal, the molecules are linked by C—H···O hydrogen bonds, forming zigzag chains parallel to [100] (Table 1, Fig. 2).

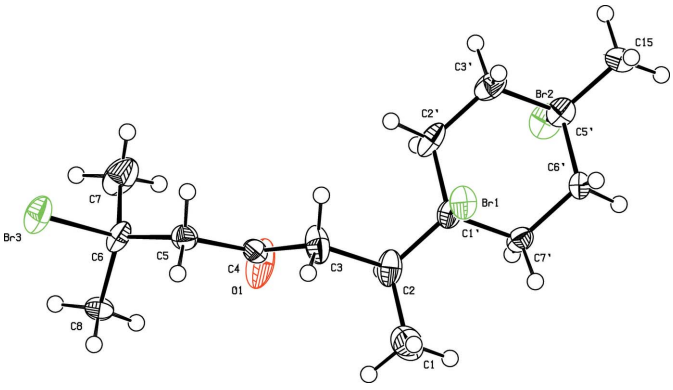


Figure 1
A view of the molecular structure of the molecule of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

Synthesis and crystallization

In a 100 ml reactor equipped with a magnetic stirrer, dichloromethane (40 ml) was added to 2 g (9 mmol) of a mixture of α- and γ-atlantone. 15 ml of 33% bromohydric acid in acetic acid were then added dropwise with stirring. The reaction mixture was stirred for 1 h, then the solvent was removed and the residue obtained was chromatographed on silica, eluting with petroleum ether, which allowed the isolation of the title compound (yield 1.5 g, 73%). The title compound was recrystallized from pentane at room temperature.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. With the Flack parameter (Flack & Bernardinelli, 2000) close to 0.5, we can not determine the absolute structure. The synthesis leads to a racemic compound. Most likely, we have an inversion twin, with two enantiomers present in the crystal.

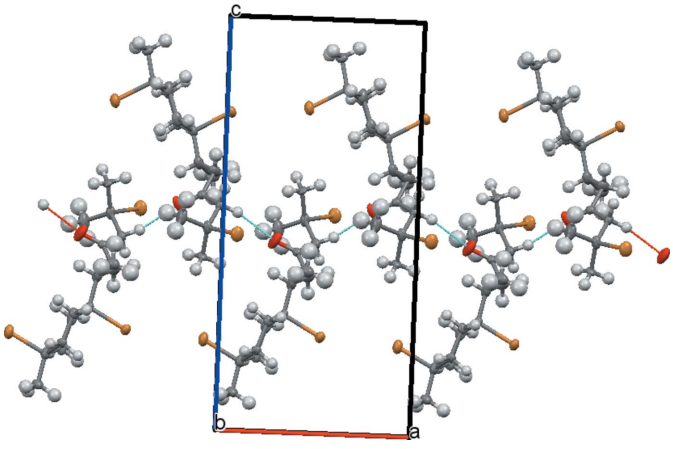


Figure 2
A partial view down [010] of the crystal packing of the title compound, showing the C—H···O hydrogen bonds as blue lines (see Table 1).

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5A···O1^{i}	0.97	2.43 (1)	3.377 (12)	167

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{25}Br_3O$
M_r	461.08
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	173
a, b, c (Å)	9.2060 (11), 9.6974 (12), 19.605 (3)
V (Å^3)	1750.2 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.91
Crystal size (mm)	0.37 × 0.25 × 0.07
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2008)
T_{min}, T_{max}	0.245, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8603, 2872, 2532
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.581
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.090, 1.08
No. of reflections	2872
No. of parameters	177
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.15, −0.55
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.52 (3)

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

Acknowledgements

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full crystallographic data

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6-Bromo-2-(1,4-dibromo-4-methylcyclohexyl)-6-methylheptan-4-one

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Crystal data

$C_{15}H_{25}Br_3O$
M_r = 461.08
Orthorhombic, $P2_12_12_1$
a = 9.2060 (11) Å
b = 9.6974 (12) Å
c = 19.605 (3) Å
V = 1750.2 (4) Å^3
Z = 4
F(000) = 912
D_x = 1.750 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4050 reflections
θ = 2.3–24.3°
μ = 6.91 mm^{-1}
T = 173 K
Fragment, colourless
0.37 × 0.25 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2008)
T_{min} = 0.245, T_{max} = 0.745
8603 measured reflections
2872 independent reflections
2532 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 24.4°, θ_{min} = 2.4°
h = −10→10
k = −11→11
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.090
S = 1.08
2872 reflections
177 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 1.8613P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.52 (3)

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.
Refinement. Refined as a 2-component inversion twin

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0606 (13)	−0.0653 (10)	0.3905 (6)	0.046 (3)
H1A	−0.0342	−0.0762	0.3707	0.069*
H1B	0.0515	−0.0516	0.4388	0.069*
H1C	0.1172	−0.1466	0.3819	0.069*
C2	0.1345 (10)	0.0577 (9)	0.3591 (5)	0.032 (2)
H2	0.2285	0.0654	0.3822	0.038*
C3	0.0507 (12)	0.1918 (9)	0.3770 (5)	0.037 (3)
H3A	0.0492	0.2508	0.3370	0.045*
H3B	−0.0490	0.1679	0.3876	0.045*
C4	0.1123 (10)	0.2716 (9)	0.4353 (5)	0.024 (2)
C5	0.0179 (10)	0.3905 (8)	0.4577 (5)	0.025 (2)
H5A	−0.0736	0.3531	0.4739	0.030*
H5B	−0.0035	0.4463	0.4179	0.030*
C6	0.0783 (9)	0.4849 (7)	0.5129 (5)	0.027 (2)
C7	0.2130 (11)	0.5610 (10)	0.4895 (7)	0.047 (3)
H7A	0.2900	0.4962	0.4817	0.071*
H7B	0.2421	0.6256	0.5240	0.071*
H7C	0.1922	0.6096	0.4479	0.071*
C8	0.0986 (10)	0.4182 (9)	0.5837 (5)	0.024 (2)
H8A	0.0081	0.3793	0.5986	0.036*
H8B	0.1297	0.4870	0.6158	0.036*
H8C	0.1706	0.3468	0.5809	0.036*
C1′	0.1698 (9)	0.0440 (8)	0.2835 (5)	0.024 (2)
C7′	0.2495 (9)	−0.0911 (8)	0.2673 (6)	0.025 (2)
H7′1	0.3321	−0.0992	0.2978	0.030*
H7′2	0.1846	−0.1674	0.2770	0.030*
C6′	0.3031 (10)	−0.1052 (8)	0.1948 (5)	0.023 (2)
H6′1	0.2200	−0.1216	0.1655	0.028*
H6′2	0.3650	−0.1859	0.1922	0.028*
C5′	0.3866 (9)	0.0173 (9)	0.1670 (5)	0.028 (2)
C3′	0.3048 (11)	0.1524 (9)	0.1821 (6)	0.033 (3)
H3′1	0.3676	0.2296	0.1710	0.040*
H3′2	0.2204	0.1577	0.1525	0.040*
C2′	0.2560 (10)	0.1661 (8)	0.2548 (6)	0.032 (3)
H2′1	0.1966	0.2483	0.2586	0.039*
H2′2	0.3412	0.1798	0.2831	0.039*
C15	0.4196 (11)	0.0017 (9)	0.0926 (5)	0.030 (2)
H15A	0.4814	−0.0769	0.0859	0.045*
H15B	0.4679	0.0831	0.0763	0.045*
H15C	0.3307	−0.0111	0.0678	0.045*
O1	0.2291 (8)	0.2476 (7)	0.4609 (5)	0.050 (2)
Br1	−0.02173 (9)	0.03945 (9)	0.23253 (5)	0.0297 (2)
Br2	0.57752 (10)	0.02694 (9)	0.21677 (6)	0.0367 (3)
Br3	−0.07495 (12)	0.62940 (9)	0.52607 (6)	0.0417 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.052 (7)	0.051 (6)	0.036 (7)	0.014 (5)	0.007 (6)	0.002 (5)
C2	0.025 (5)	0.032 (5)	0.039 (7)	0.009 (4)	−0.005 (4)	−0.011 (5)
C3	0.038 (7)	0.042 (5)	0.031 (7)	0.016 (5)	−0.004 (5)	−0.012 (5)
C4	0.026 (6)	0.025 (4)	0.019 (6)	0.001 (4)	0.003 (4)	0.001 (4)
C5	0.022 (5)	0.026 (4)	0.026 (6)	0.003 (4)	0.004 (4)	0.002 (4)
C6	0.021 (4)	0.016 (4)	0.043 (7)	0.000 (4)	−0.001 (4)	−0.006 (4)
C7	0.031 (6)	0.033 (5)	0.078 (10)	−0.007 (4)	0.008 (6)	−0.004 (6)
C8	0.027 (5)	0.028 (4)	0.018 (6)	0.003 (4)	−0.006 (4)	0.007 (4)
C1′	0.021 (4)	0.023 (4)	0.028 (6)	0.002 (4)	−0.003 (4)	−0.004 (5)
C7′	0.023 (5)	0.020 (4)	0.032 (7)	−0.002 (3)	0.002 (5)	0.001 (4)
C6′	0.026 (6)	0.021 (4)	0.022 (6)	0.001 (4)	0.001 (4)	−0.005 (4)
C5′	0.020 (5)	0.028 (5)	0.035 (7)	−0.001 (4)	−0.002 (4)	0.000 (4)
C3′	0.026 (6)	0.023 (5)	0.050 (8)	0.006 (4)	0.001 (5)	0.007 (5)
C2′	0.027 (5)	0.016 (4)	0.053 (9)	0.004 (4)	−0.007 (5)	−0.004 (4)
C15	0.034 (5)	0.032 (5)	0.024 (6)	−0.002 (4)	0.005 (5)	0.005 (4)
O1	0.041 (5)	0.043 (4)	0.065 (7)	0.023 (4)	−0.027 (4)	−0.022 (4)
Br1	0.0244 (5)	0.0343 (4)	0.0305 (6)	0.0016 (4)	−0.0050 (4)	−0.0067 (5)
Br2	0.0239 (5)	0.0375 (5)	0.0488 (8)	−0.0001 (4)	−0.0044 (5)	−0.0034 (5)
Br3	0.0411 (6)	0.0266 (4)	0.0575 (8)	0.0071 (4)	0.0018 (6)	−0.0087 (5)

Geometric parameters (Å, º)

C1—C2	1.505 (14)	C8—H8B	0.9600
C1—H1A	0.9600	C8—H8C	0.9600
C1—H1B	0.9600	C1′—C2′	1.532 (12)
C1—H1C	0.9600	C1′—C7′	1.535 (11)
C2—C1′	1.523 (14)	C1′—Br1	2.027 (9)
C2—C3	1.552 (12)	C7′—C6′	1.511 (14)
C2—H2	0.9800	C7′—H7′1	0.9700
C3—C4	1.492 (13)	C7′—H7′2	0.9700
C3—H3A	0.9700	C6′—C5′	1.517 (12)
C3—H3B	0.9700	C6′—H6′1	0.9700
C4—O1	1.209 (11)	C6′—H6′2	0.9700
C4—C5	1.509 (12)	C5′—C15	1.498 (14)
C5—C6	1.522 (12)	C5′—C3′	1.540 (12)
C5—H5A	0.9700	C5′—Br2	2.012 (9)
C5—H5B	0.9700	C3′—C2′	1.501 (15)
C6—C7	1.515 (13)	C3′—H3′1	0.9700
C6—C8	1.544 (13)	C3′—H3′2	0.9700
C6—Br3	2.005 (8)	C2′—H2′1	0.9700
C7—H7A	0.9600	C2′—H2′2	0.9700
C7—H7B	0.9600	C15—H15A	0.9600
C7—H7C	0.9600	C15—H15B	0.9600
C8—H8A	0.9600	C15—H15C	0.9600

C2—C1—H1A	109.5	H8B—C8—H8C	109.5
C2—C1—H1B	109.5	C2—C1′—C2′	113.6 (8)
H1A—C1—H1B	109.5	C2—C1′—C7′	112.2 (8)
C2—C1—H1C	109.5	C2′—C1′—C7′	109.6 (7)
H1A—C1—H1C	109.5	C2—C1′—Br1	107.2 (6)
H1B—C1—H1C	109.5	C2′—C1′—Br1	106.7 (6)
C1—C2—C1′	115.2 (8)	C7′—C1′—Br1	107.2 (6)
C1—C2—C3	110.3 (8)	C6′—C7′—C1′	115.3 (8)
C1′—C2—C3	113.6 (8)	C6′—C7′—H7′1	108.5
C1—C2—H2	105.7	C1′—C7′—H7′1	108.5
C1′—C2—H2	105.7	C6′—C7′—H7′2	108.5
C3—C2—H2	105.7	C1′—C7′—H7′2	108.5
C4—C3—C2	114.8 (8)	H7′1—C7′—H7′2	107.5
C4—C3—H3A	108.6	C7′—C6′—C5′	115.7 (7)
C2—C3—H3A	108.6	C7′—C6′—H6′1	108.4
C4—C3—H3B	108.6	C5′—C6′—H6′1	108.4
C2—C3—H3B	108.6	C7′—C6′—H6′2	108.4
H3A—C3—H3B	107.5	C5′—C6′—H6′2	108.4
O1—C4—C3	123.8 (8)	H6′1—C6′—H6′2	107.4
O1—C4—C5	122.6 (9)	C15—C5′—C6′	112.0 (8)
C3—C4—C5	113.6 (8)	C15—C5′—C3′	111.8 (8)
C4—C5—C6	117.1 (8)	C6′—C5′—C3′	110.5 (7)
C4—C5—H5A	108.0	C15—C5′—Br2	107.5 (6)
C6—C5—H5A	108.0	C6′—C5′—Br2	107.8 (6)
C4—C5—H5B	108.0	C3′—C5′—Br2	107.1 (6)
C6—C5—H5B	108.0	C2′—C3′—C5′	113.8 (8)
H5A—C5—H5B	107.3	C2′—C3′—H3′1	108.8
C7—C6—C5	112.2 (9)	C5′—C3′—H3′1	108.8
C7—C6—C8	112.2 (8)	C2′—C3′—H3′2	108.8
C5—C6—C8	115.6 (7)	C5′—C3′—H3′2	108.8
C7—C6—Br3	105.9 (5)	H3′1—C3′—H3′2	107.7
C5—C6—Br3	104.8 (6)	C3′—C2′—C1′	115.8 (8)
C8—C6—Br3	105.2 (6)	C3′—C2′—H2′1	108.3
C6—C7—H7A	109.5	C1′—C2′—H2′1	108.3
C6—C7—H7B	109.5	C3′—C2′—H2′2	108.3
H7A—C7—H7B	109.5	C1′—C2′—H2′2	108.3
C6—C7—H7C	109.5	H2′1—C2′—H2′2	107.4
H7A—C7—H7C	109.5	C5′—C15—H15A	109.5
H7B—C7—H7C	109.5	C5′—C15—H15B	109.5
C6—C8—H8A	109.5	H15A—C15—H15B	109.5
C6—C8—H8B	109.5	C5′—C15—H15C	109.5
H8A—C8—H8B	109.5	H15A—C15—H15C	109.5
C6—C8—H8C	109.5	H15B—C15—H15C	109.5
H8A—C8—H8C	109.5		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*A*···O1^{i}	0.97	2.43 (1)	3.377 (12)	167

Symmetry code: (i) $x-1/2, -y+1/2, -z+1$.