

## Two natural products from the algae *Laurencia scoparia*

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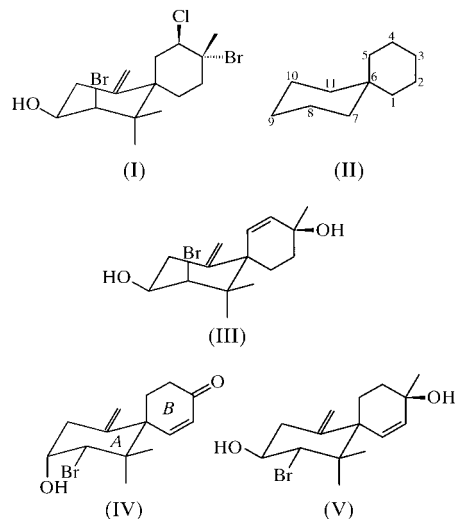
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The structures and absolute stereochemistries of two chamigrene-type metabolites (spiro[5.5]undecane derivatives) isolated from the red algae *Laurencia scoparia* are described. One, a non-sesquiterpene named maílione (8-bromo-9-hydroxy-7,7-dimethyl-11-methylenespiro[5.5]undec-1-en-3-one), C<sub>14</sub>H<sub>19</sub>BrO<sub>2</sub>, was detected previously in *Laurencia cartilaginea*, while the other, the sesquiterpene isorigidol (8-bromo-3,7,7-trimethyl-11-methylenespiro[5.5]undec-1-ene-3,9-diol), C<sub>15</sub>H<sub>23</sub>BrO<sub>2</sub>, is a new isomer of rigidol, first isolated from *Laurencia rigida*. The A rings of these spirocyclic compounds show the same carbon skeleton. However, the relative stereochemistry of the 8-Br and 9-OH substituents is different. While maílione displays the usual *syn* (or *cis*) relative stereochemistry of the bromohydroxy vicinal group, isorigidol shows an *anti* (or *trans*) arrangement. The 8-Br and 9-OH groups are both in equatorial positions in isorigidol, while the 9-OH group is axial in maílione, as in most chamigrenes. The absolute configurations of the chiral centers were determined as 6*S*, 8*S* and 9*R* in maílione, and 3*R*, 6*S*, 8*S* and 9*S* in isorigidol.

### Comment

Chamigrenes are natural sesquiterpenes isolated from the red algae of the genus *Laurencia* and from sea hares (opisthobranch mollusks of the genus *Aplysia*) which feed on it. They comprise a large group of bicyclic compounds with a spiro[5.5]undecane derivative carbon skeleton. The structures of two representative chamigrenes, isobtusol, (I), and cartilagineol, (II) (González *et al.*, 1979; Francisco *et al.*, 1998), as well as the structure of obtusol acetate (Perales *et al.*, 1979), have been reported. The structures of other chamigrenes, such as rigidol, (III) (König & Wright, 1997), have been determined by spectroscopic measurement, but have not been established by X-ray diffraction. The structures of maílione, (IV), and

isorigidol, (V), described in this manuscript, are compared with the proposed stereochemistry of rigidol (König & Wright, 1997).



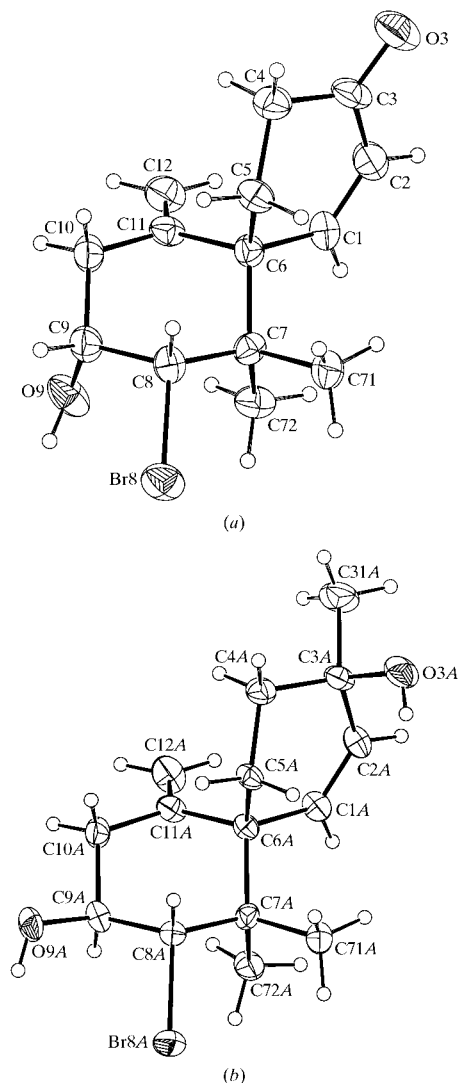
In accord with the literature, the six-membered rings of the spirocyclic system are labelled *A* and *B*, as shown in the Scheme. Ring *A* (C6–C11) shows the same hydrocarbon skeleton and substitution pattern (8-bromo-3-hydroxy) in compounds (I)–(V). The second ring, *B* (C1–C6), has different substituents and can include a double bond. The most significant difference is the presence of a methyl group substituent at C3 in (I)–(III) and (V) (sesquiterpenes). This group is replaced by a carbonyl group in maílione (non-sesquiterpene). Compound (V) crystallizes with two molecules per asymmetric unit which are labelled (VA) and (VB). Molecular dimensions in (IV) and both molecules of (V) are as expected.

The results reported here establish unequivocally the absolute configurations of (IV) and (V), and especially the stereochemistry of the 8-bromo-9-hydroxy vicinal groups. While compounds (I)–(IV) display the usual *syn* (or *cis*) configuration (typical stereochemistry observed in chamigrenes), isorigidol, (V), shows an *anti* (or *trans*) arrangement. Only two other chamigrenes have been reported previously as having the hydroxy and bromine substituents in an *anti* configuration, namely (–)-10 $\alpha$ -bromo-9 $\beta$ -hydroxy- $\alpha$ -chamigrene (König & Wright, 1997) and (1*Z*,8*R*\*,9*R*\*)-8-bromo-chamigra-1,11(12)-diene-9-ol (Wright & Coll, 1990). In maílione, (IV), the 8-bromo group is equatorial and the 9-hydroxy group is axial (8*S*, 9*R* configuration), and in isorigidol, (V), both substituents are equatorial (8*S*, 9*S* configuration). The expected configuration for this vicinal group in rigidol, (III) (König & Wright, 1997) (see Scheme), is 8*R*, 9*R*. While the absolute configuration of C6 is reversed in isorigidol and maílione from that in rigidol [*S* in (IV) and (V), and *R* in (III)], C3 adopts the same *R* configuration in rigidol and isorigidol, as expected.

Ring *A* in maílione and in both independent molecules of isorigidol (VA and VB) adopts a chair conformation, as can be seen in Figs. 1(a) and 1(b), and deduced from the Cremer & Pople parameters *Q*,  $\theta$  and  $\varphi$  with values of 0.568 (7) Å, 7.8 (7)° and 41 (5)° in (IV), 0.584 (5) Å, 7.5 (5)° and 61 (4)° in

(VA), and 0.571 (5) Å, 8.6 (5)° and 81 (4)° in (VB) ( $Q = 0.6$  Å and  $\theta = 0$  or 180° for the ideal cyclohexane chair). Ring B adopts an approximate half-chair puckering conformation.  $Q$ ,  $\theta$  and  $\varphi$  are 0.475 (7) Å, 127.0 (8)° and 48.2 (11)° in (IV), 0.511 (5) Å, 128.3 (6)° and 43.1 (7)° in (VA), and 0.511 (5) Å, 126.9 (6)° and 42.4 (7)° in (VB), while the expected  $\theta$  and  $\varphi$  values for the exact half-chair conformation are 129.2 and 30°, respectively (Cremer & Pople, 1975). The conformations of both rings in the three independent molecules described here are for the most part very similar. Table 1 shows torsion angles where there are major differences between (IV) and (V). These differences arise because of the different relative stereochemistry of the bromohydroxy vicinal groups in ring A, as well as the different hybridization at C3 ( $sp^2$  in mailione and  $sp^3$  in isorigidol).

The packing in both structures is determined by O—H...O hydrogen bonds; details are given in Tables 1 and 1. In mailione, the 9-OH group is hydrogen bonded to the oxo group (O3) of a molecule related by the twofold screw axis



**Figure 1**  
The molecular structures of (a) mailione and (b) one molecule of isorigidol, with displacement ellipsoids at the 30% probability level in each case. H atoms are represented by spheres of arbitrary radii.

parallel to the  $b$ -axis direction and thereby forms an infinite spiral (see Table 2). In isorigidol, the formation of an  $R_4^4(8)$  ring between four alternate (VA) and (VB) molecules is observed (Table 3). The ring corresponds to O9A—H9A...O9B—H9B...O3A<sup>iii</sup>—H3A<sup>iii</sup>...O3B<sup>iv</sup>—H3B<sup>iv</sup>...O9A [symmetry codes: (iii)  $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$ ; (iv)  $\frac{3}{2} - x, -y, \frac{1}{2} + z$ ]. Each of the molecules participates in two of these rings, thus forming a three-dimensional network.

## Experimental

The air-dried algae were extracted three times with dichloromethane over a period of 1 d each time. Solvent was removed by evaporation at reduced pressure. The residue was fractionated on a silica-gel 60 flash chromatography column, with polarity-increasing mixtures of  $n$ -hexane—EtOAc—MeOH as eluent. Some fractions were further purified using a Sephadex LH-20 column with  $n$ -hexane—CHCl<sub>3</sub>—MeOH (1:1:1). The crude compounds were purified by medium-pressure liquid chromatography on silica gel 100 with  $n$ -hexane—EtOAc mixtures to obtain pure compounds. Compounds (IV) and (V) were spectroscopically characterized before recrystallization. Single crystals of mailione were obtained by slow evaporation of a mixture of  $n$ -hexane—CH<sub>2</sub>Cl<sub>2</sub> at room temperature, while single crystals of isorigidol were obtained by slow evaporation of  $n$ -hexane at 268 (2) K.

## Compound (IV)

### Crystal data

C<sub>14</sub>H<sub>19</sub>BrO<sub>2</sub>  
 $M_r = 299.20$   
Orthorhombic,  $P2_12_12_1$   
 $a = 9.9411$  (16) Å  
 $b = 18.0364$  (14) Å  
 $c = 7.3758$  (18) Å  
 $V = 1322.5$  (4) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.503$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 24 reflections  
 $\theta = 10.16$ – $22.09^\circ$   
 $\mu = 3.097$  mm<sup>-1</sup>  
 $T = 273$  (2) K  
Prism, colourless  
 $0.22 \times 0.15 \times 0.12$  mm

### Data collection

Rigaku AFC-7S diffractometer  
 $\theta/2\theta$  scans  
Absorption correction:  $\psi$  scan  
(North *et al.*, 1968; Molecular Structure Corporation, 1993)  
 $T_{\min} = 0.549$ ,  $T_{\max} = 0.708$   
2172 measured reflections  
2005 independent reflections  
1106 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$   
 $\theta_{\text{max}} = 27.49^\circ$   
 $h = -4 \rightarrow 12$   
 $k = -17 \rightarrow 23$   
 $l = -7 \rightarrow 9$   
3 standard reflections  
every 150 reflections  
intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.128$   
 $S = 0.936$   
2005 reflections  
158 parameters  
H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0766P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.70$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.74$  e Å<sup>-3</sup>  
Extinction correction: SHELXL97  
Extinction coefficient: 0.0053 (14)  
Absolute structure: Flack (1983)  
Flack parameter =  $-0.03$  (2)

**Table 1**  
Hydrogen-bonding geometry (Å, °) for (IV).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9...O3 <sup>i</sup>	0.82	2.11	2.902 (7)	164

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

**Table 2**

Selected torsion angles ( $^{\circ}$ ) for molecules (IV), (VA) and (VB).

Molecule (IV) is mailleone, and molecules (VA) and (VB) are isorigidol.

	(IV)	(VA)	(VB)
Br8—C8—C9—O9	-62.2 (6)	61.9 (5)	61.7 (5)
C7—C8—C9—O9	65.6 (7)	-173.2 (4)	-174.1 (4)
O9—C9—C10—C11	-75.4 (8)	171.6 (4)	170.2 (4)
C1—C2—C3—O3	176.3 (6)	115.8 (6)	114.9 (5)
O3—C3—C4—C5	-146.7 (6)	-82.9 (5)	-82.0 (5)

**Compound (V)**

*Crystal data*

$C_{15}H_{23}BrO_2$  Mo  $K\alpha$  radiation  
 $M_r = 315.25$  Cell parameters from 25 reflections  
 Orthorhombic,  $P2_12_12_1$   $\theta = 7.53$ – $11.40^{\circ}$   
 $a = 11.872$  (5) Å  $\mu = 2.691$  mm $^{-1}$   
 $b = 11.897$  (4) Å  $T = 273$  (2) K  
 $c = 21.575$  (4) Å Parallelepiped, colourless  
 $V = 3047.2$  (17) Å $^3$   $0.23 \times 0.17 \times 0.13$  mm  
 $Z = 8$   
 $D_x = 1.374$  Mg m $^{-3}$

*Data collection*

Rigaku AFC-7S diffractometer  $R_{int} = 0.029$   
 $\theta/2\theta$  scans  $\theta_{max} = 27.50^{\circ}$   
 Absorption correction:  $\psi$  scan  $h = -1 \rightarrow 15$   
 (North *et al.*, 1968; Molecular  $k = -1 \rightarrow 15$   
 Structure Corporation, 1993)  $l = 0 \rightarrow 28$   
 $T_{min} = 0.577$ ,  $T_{max} = 0.721$  3 standard reflections  
 4662 measured reflections every 150 reflections  
 4525 independent reflections intensity decay: none  
 2442 reflections with  $I > 2\sigma(I)$

*Refinement*

Refinement on  $F^2$   $(\Delta/\sigma)_{max} = 0.001$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   $\Delta\rho_{max} = 0.42$  e Å $^{-3}$   
 $wR(F^2) = 0.094$   $\Delta\rho_{min} = -0.60$  e Å $^{-3}$   
 $S = 0.941$  Extinction correction: *SHELXL97*  
 4525 reflections Extinction coefficient: 0.0032 (3)  
 336 parameters Absolute structure: Flack (1983)  
 H-atom parameters constrained Flack parameter = -0.011 (11)  
 $w = 1/[\sigma^2(F_o^2) + (0.0373P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

**Table 3**

Hydrogen-bonding geometry (Å,  $^{\circ}$ ) for (V).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3A—H3A $\cdots$ O3B $^i$	0.82	1.99	2.779 (6)	160
O3B—H3B $\cdots$ O9A $^{ii}$	0.82	2.08	2.855 (5)	158
O9A—H9A $\cdots$ O9B	0.82	2.00	2.790 (5)	162
O9B—H9B $\cdots$ O3A $^{iii}$	0.82	2.04	2.765 (5)	147

Symmetry codes: (i)  $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ ; (ii)  $\frac{3}{2} + x, -\frac{1}{2} - y, -z$ ; (iii)  $-x, \frac{3}{2} + y, \frac{3}{2} - z$ .

In both compounds, all H atoms were clearly visible in difference maps and these were then allowed for as riding atoms in the final refinement cycles, with O—H = 0.82 Å and C—H in the range 0.93–0.98 Å. In the refinement of (IV), there were 1765 unique reflections and 240 Friedel pairs; the corresponding numbers in the refinement of (V) were 3919 and 606, respectively. The values of the Flack parameters (see tabular material) establish unequivocally the absolute configurations of (IV) and (V).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON98* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1116). Services for accessing these data are described at the back of the journal.

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## supporting information

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### Computing details

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON98* (Spek, 1990).

### (IV)

#### Crystal data

$C_{14}H_{19}BrO_2$

$M_r = 299.20$

Orthorhombic,  $P2_12_12_1$

$a = 9.9411$  (16) Å

$b = 18.0364$  (14) Å

$c = 7.3758$  (18) Å

$V = 1322.5$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 616$

$D_x = 1.503$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å

Cell parameters from 24 reflections

$\theta = 10.2$ – $22.1^\circ$

$\mu = 3.10$  mm<sup>-1</sup>

$T = 273$  K

Prism, colourless

$0.22 \times 0.15 \times 0.12$  mm

#### Data collection

Rigaku AFC-7S  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\theta/2\theta$  scans

Absorption correction: y scan

(North et al., 1968; Molecular Structure Corporation, 1993)

$T_{\min} = 0.549$ ,  $T_{\max} = 0.708$

2172 measured reflections

2005 independent reflections

1106 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -4 \rightarrow 12$

$k = -17 \rightarrow 23$

$l = -7 \rightarrow 9$

3 standard reflections every 150 reflections

intensity decay: none

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.128$

$S = 0.94$

2005 reflections

158 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

$$w = 1/[\sigma^2(F_o^2) + (0.0766P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.74 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97*,

$$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0053 (14)

Absolute structure: Flack (1983)

Absolute structure parameter: -0.03 (2)

*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.

**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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br8	0.05566 (9)	0.34591 (4)	0.13905 (10)	0.0713 (3)
O3	-0.0630 (6)	-0.0922 (3)	-0.1194 (7)	0.0851 (16)
O9	0.0501 (7)	0.2535 (2)	0.5094 (6)	0.0733 (16)
H9	0.0600	0.2984	0.5194	0.110*
C1	0.1285 (7)	0.0459 (3)	0.1051 (8)	0.0520 (17)
H1	0.2181	0.0528	0.1374	0.062*
C2	0.0967 (9)	-0.0168 (4)	0.0189 (9)	0.063 (2)
H2	0.1655	-0.0498	-0.0092	0.076*
C3	-0.0372 (9)	-0.0358 (4)	-0.0322 (8)	0.061 (2)
C4	-0.1442 (8)	0.0159 (4)	0.0287 (10)	0.0599 (19)
H4A	-0.1733	0.0022	0.1497	0.072*
H4B	-0.2210	0.0120	-0.0518	0.072*
C5	-0.0934 (7)	0.0960 (3)	0.0300 (9)	0.0540 (18)
H5A	-0.1649	0.1284	0.0715	0.065*
H5B	-0.0701	0.1106	-0.0927	0.065*
C6	0.0305 (6)	0.1060 (3)	0.1536 (8)	0.0438 (15)
C7	0.0991 (6)	0.1854 (3)	0.1231 (8)	0.0442 (15)
C71	0.1309 (9)	0.1966 (4)	-0.0788 (9)	0.065 (2)
H71A	0.1913	0.2378	-0.0926	0.098*
H71B	0.0491	0.2065	-0.1437	0.098*
H71C	0.1721	0.1526	-0.1264	0.098*
C72	0.2312 (8)	0.1901 (4)	0.2275 (11)	0.062 (2)
H72A	0.2656	0.2397	0.2212	0.093*
H72B	0.2953	0.1565	0.1752	0.093*
H72C	0.2160	0.1769	0.3520	0.093*
C8	-0.0046 (7)	0.2432 (4)	0.1848 (7)	0.0489 (18)
H8	-0.0846	0.2356	0.1096	0.059*
C9	-0.0516 (8)	0.2386 (3)	0.3813 (8)	0.0559 (17)
H9A	-0.1253	0.2739	0.3994	0.067*

C10	-0.1037 (8)	0.1606 (3)	0.4162 (9)	0.0600 (18)
H10A	-0.1188	0.1547	0.5453	0.072*
H10B	-0.1897	0.1549	0.3558	0.072*
C11	-0.0116 (7)	0.1003 (3)	0.3532 (9)	0.0473 (16)
C12	0.0263 (8)	0.0448 (4)	0.4605 (9)	0.065 (2)
H12A	-0.0046	0.0425	0.5794	0.078*
H12B	0.0837	0.0082	0.4166	0.078*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br8	0.1013 (6)	0.0493 (4)	0.0632 (4)	-0.0078 (4)	-0.0029 (5)	0.0114 (4)
O3	0.124 (5)	0.063 (3)	0.069 (3)	-0.017 (3)	-0.012 (4)	-0.014 (3)
O9	0.124 (5)	0.048 (2)	0.047 (2)	0.004 (4)	-0.016 (3)	-0.001 (2)
C1	0.053 (4)	0.057 (4)	0.046 (4)	0.011 (4)	0.003 (4)	-0.005 (3)
C2	0.074 (6)	0.057 (4)	0.059 (4)	0.003 (4)	0.003 (4)	-0.007 (4)
C3	0.093 (6)	0.048 (4)	0.042 (3)	-0.024 (5)	-0.011 (4)	-0.005 (3)
C4	0.057 (5)	0.062 (4)	0.061 (4)	-0.012 (4)	-0.005 (4)	-0.006 (4)
C5	0.057 (5)	0.050 (3)	0.055 (4)	-0.002 (3)	-0.010 (4)	-0.006 (3)
C6	0.049 (4)	0.045 (3)	0.038 (3)	0.001 (3)	0.002 (4)	-0.002 (3)
C7	0.044 (4)	0.054 (3)	0.035 (3)	-0.005 (3)	-0.002 (3)	0.005 (3)
C71	0.084 (6)	0.069 (4)	0.043 (3)	-0.008 (5)	0.015 (4)	-0.005 (3)
C72	0.062 (5)	0.057 (4)	0.066 (4)	-0.013 (4)	-0.009 (4)	-0.002 (4)
C8	0.055 (4)	0.055 (4)	0.037 (3)	0.007 (3)	-0.004 (3)	0.001 (3)
C9	0.073 (5)	0.042 (3)	0.053 (4)	0.006 (4)	0.012 (5)	0.004 (3)
C10	0.074 (5)	0.053 (4)	0.053 (3)	0.003 (4)	0.021 (4)	-0.003 (3)
C11	0.061 (4)	0.043 (3)	0.037 (3)	-0.010 (3)	-0.009 (4)	0.002 (3)
C12	0.090 (6)	0.056 (4)	0.051 (4)	-0.010 (4)	-0.005 (4)	0.005 (3)

*Geometric parameters (Å, °)*

Br8—C8	1.975 (7)	C7—C8	1.535 (9)
O3—C3	1.231 (7)	C7—C71	1.536 (9)
O9—C9	1.409 (8)	C71—H71A	0.96
O9—H9	0.82	C71—H71B	0.96
C1—C2	1.335 (9)	C71—H71C	0.96
C1—C6	1.501 (9)	C72—H72A	0.96
C1—H1	0.93	C72—H72B	0.96
C2—C3	1.426 (11)	C72—H72C	0.96
C2—H2	0.93	C8—C9	1.525 (8)
C3—C4	1.484 (10)	C8—H8	0.98
C4—C5	1.531 (9)	C9—C10	1.522 (9)
C4—H4A	0.97	C9—H9A	0.98
C4—H4B	0.97	C10—C11	1.495 (9)
C5—C6	1.543 (9)	C10—H10A	0.97
C5—H5A	0.97	C10—H10B	0.97
C5—H5B	0.97	C11—C12	1.332 (9)
C6—C11	1.534 (9)	C12—H12A	0.93

C6—C7	1.602 (9)	C12—H12B	0.93
C7—C72	1.525 (10)		
C9—O9—H9	109.5	C7—C71—H71B	109.5
C2—C1—C6	124.9 (7)	H71A—C71—H71B	109.5
C2—C1—H1	117.6	C7—C71—H71C	109.5
C6—C1—H1	117.6	H71A—C71—H71C	109.5
C1—C2—C3	123.4 (8)	H71B—C71—H71C	109.5
C1—C2—H2	118.3	C7—C72—H72A	109.5
C3—C2—H2	118.3	C7—C72—H72B	109.5
O3—C3—C2	122.1 (8)	H72A—C72—H72B	109.5
O3—C3—C4	121.9 (8)	C7—C72—H72C	109.5
C2—C3—C4	115.9 (5)	H72A—C72—H72C	109.5
C3—C4—C5	111.0 (6)	H72B—C72—H72C	109.5
C3—C4—H4A	109.4	C9—C8—C7	116.7 (5)
C5—C4—H4A	109.4	C9—C8—Br8	107.8 (4)
C3—C4—H4B	109.4	C7—C8—Br8	112.5 (4)
C5—C4—H4B	109.4	C9—C8—H8	106.4
H4A—C4—H4B	108.0	C7—C8—H8	106.4
C4—C5—C6	112.2 (6)	Br8—C8—H8	106.4
C4—C5—H5A	109.2	O9—C9—C10	107.8 (5)
C6—C5—H5A	109.2	O9—C9—C8	114.0 (6)
C4—C5—H5B	109.2	C10—C9—C8	108.4 (5)
C6—C5—H5B	109.2	O9—C9—H9A	108.8
H5A—C5—H5B	107.9	C10—C9—H9A	108.8
C1—C6—C11	111.0 (5)	C8—C9—H9A	108.8
C1—C6—C5	107.0 (5)	C11—C10—C9	114.3 (6)
C11—C6—C5	109.9 (5)	C11—C10—H10A	108.7
C1—C6—C7	109.7 (5)	C9—C10—H10A	108.7
C11—C6—C7	108.1 (5)	C11—C10—H10B	108.7
C5—C6—C7	111.2 (5)	C9—C10—H10B	108.7
C72—C7—C8	113.0 (5)	H10A—C10—H10B	107.6
C72—C7—C71	107.8 (6)	C12—C11—C10	122.4 (6)
C8—C7—C71	109.6 (5)	C12—C11—C6	122.9 (6)
C72—C7—C6	110.2 (5)	C10—C11—C6	114.6 (5)
C8—C7—C6	106.3 (5)	C11—C12—H12A	120.0
C71—C7—C6	110.0 (5)	C11—C12—H12B	120.0
C7—C71—H71A	109.5	H12A—C12—H12B	120.0
C6—C1—C2—C3	-2.5 (10)	C72—C7—C8—C9	-61.7 (8)
C1—C2—C3—O3	176.3 (6)	C71—C7—C8—C9	178.0 (6)
C1—C2—C3—C4	-4.6 (10)	C6—C7—C8—C9	59.2 (7)
O3—C3—C4—C5	-146.7 (6)	C72—C7—C8—Br8	63.7 (6)
C2—C3—C4—C5	34.2 (8)	C71—C7—C8—Br8	-56.5 (6)
C3—C4—C5—C6	-58.2 (7)	C6—C7—C8—Br8	-175.3 (4)
C2—C1—C6—C11	99.9 (7)	C7—C8—C9—O9	65.6 (7)
C2—C1—C6—C5	-20.1 (9)	Br8—C8—C9—O9	-62.2 (6)
C2—C1—C6—C7	-140.8 (6)	C7—C8—C9—C10	-54.5 (8)

C4—C5—C6—C1	49.1 (7)	Br8—C8—C9—C10	177.7 (5)
C4—C5—C6—C11	-71.5 (7)	O9—C9—C10—C11	-75.4 (7)
C4—C5—C6—C7	168.8 (6)	C8—C9—C10—C11	48.5 (8)
C1—C6—C7—C72	-54.4 (7)	C9—C10—C11—C12	128.6 (7)
C11—C6—C7—C72	66.7 (7)	C9—C10—C11—C6	-53.9 (8)
C5—C6—C7—C72	-172.5 (5)	C1—C6—C11—C12	-5.6 (9)
C1—C6—C7—C8	-177.2 (5)	C5—C6—C11—C12	112.7 (7)
C11—C6—C7—C8	-56.1 (6)	C7—C6—C11—C12	-125.8 (6)
C5—C6—C7—C8	64.7 (6)	C1—C6—C11—C10	176.9 (6)
C1—C6—C7—C71	64.3 (7)	C5—C6—C11—C10	-64.9 (7)
C11—C6—C7—C71	-174.7 (5)	C7—C6—C11—C10	56.6 (7)
C5—C6—C7—C71	-53.9 (7)		

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O9—H9 $\cdots$ O3 <sup>i</sup>	0.82	2.11	2.902 (7)	164

Symmetry code: (i)  $x+1/2, -y+1/2, -z$ .**(V)***Crystal data*C<sub>15</sub>H<sub>23</sub>BrO<sub>2</sub> $M_r = 315.25$ Orthorhombic,  $P2_12_12_1$  $a = 11.872$  (5)  $\text{\AA}$  $b = 11.897$  (4)  $\text{\AA}$  $c = 21.575$  (4)  $\text{\AA}$  $V = 3047.2$  (17)  $\text{\AA}^3$  $Z = 8$  $F(000) = 1312$  $D_x = 1.374$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71069$   $\text{\AA}$ 

Cell parameters from 25 reflections

 $\theta = 7.5$ – $11.4^\circ$  $\mu = 2.69$  mm<sup>-1</sup> $T = 273$  K

Parallelepiped, colourless

 $0.23 \times 0.17 \times 0.13$  mm*Data collection*

Rigaku AFC-7S

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\theta/2\theta$  scansAbsorption correction:  $\psi$  scan

(North et al., 1968; Molecular Structure Corporation, 1993)

 $T_{\min} = 0.577$ ,  $T_{\max} = 0.721$ 

4662 measured reflections

4525 independent reflections

2442 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.029$  $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.4^\circ$  $h = -1 \rightarrow 15$  $k = -1 \rightarrow 15$  $l = 0 \rightarrow 28$ 

3 standard reflections every 150 reflections

intensity decay: none

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.034$  $wR(F^2) = 0.094$  $S = 0.94$ 

4525 reflections

336 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



$$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL97*,  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0032 (3)  
 Absolute structure: Flack (1983)  
 Absolute structure parameter: -0.011 (11)

*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.

**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  $F^2 > \sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br8A	0.58034 (5)	0.47646 (5)	0.53216 (3)	0.05415 (18)
O3A	0.4047 (3)	1.0610 (3)	0.62965 (18)	0.0606 (11)
H3A	0.3891	0.9966	0.6403	0.091*
O9A	0.6136 (3)	0.6019 (3)	0.40352 (15)	0.0513 (10)
H9A	0.6338	0.5360	0.4037	0.077*
C1A	0.6465 (4)	0.9110 (4)	0.6057 (2)	0.0428 (13)
H1A	0.7082	0.8875	0.6289	0.051*
C2A	0.5969 (4)	1.0066 (4)	0.6217 (2)	0.0446 (14)
H2A	0.6250	1.0439	0.6564	0.053*
C3A	0.5005 (4)	1.0589 (4)	0.5890 (2)	0.0425 (13)
C31A	0.5238 (6)	1.1842 (4)	0.5752 (3)	0.0680 (18)
H31A	0.4624	1.2148	0.5517	0.102*
H31B	0.5922	1.1909	0.5518	0.102*
H31C	0.5312	1.2246	0.6135	0.102*
C4A	0.4739 (4)	0.9967 (4)	0.5284 (2)	0.0439 (13)
H4A	0.3975	1.0138	0.5156	0.053*
H4B	0.5247	1.0221	0.4961	0.053*
C5A	0.4866 (4)	0.8702 (4)	0.5372 (2)	0.0359 (11)
H5A	0.4628	0.8320	0.4997	0.043*
H5B	0.4381	0.8457	0.5707	0.043*
C6A	0.6094 (4)	0.8373 (4)	0.5520 (2)	0.0323 (11)
C7A	0.6196 (4)	0.7094 (4)	0.57085 (19)	0.0362 (12)
C71A	0.5430 (5)	0.6826 (5)	0.6264 (2)	0.0523 (15)
H71A	0.5602	0.6088	0.6418	0.078*
H71B	0.4656	0.6852	0.6135	0.078*
H71C	0.5553	0.7369	0.6586	0.078*
C72A	0.7412 (4)	0.6803 (5)	0.5899 (2)	0.0508 (15)
H72A	0.7558	0.7091	0.6307	0.076*
H72B	0.7929	0.7135	0.5610	0.076*
H72C	0.7507	0.6002	0.5899	0.076*

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C8A	0.5832 (5)	0.6394 (4)	0.51380 (19)	0.0387 (12)
H8A	0.5065	0.6621	0.5028	0.046*
C9A	0.6568 (4)	0.6577 (4)	0.4577 (2)	0.0396 (12)
H9C	0.7338	0.6324	0.4662	0.047*
C10A	0.6567 (5)	0.7810 (4)	0.4408 (2)	0.0487 (14)
H10A	0.5832	0.8008	0.4245	0.058*
H10B	0.7117	0.7937	0.4083	0.058*
C11A	0.6835 (4)	0.8573 (4)	0.4952 (2)	0.0417 (13)
C12A	0.7624 (5)	0.9339 (5)	0.4917 (3)	0.0620 (17)
H12A	0.8034	0.9425	0.4552	0.074*
H12B	0.7774	0.9798	0.5256	0.074*
Br8B	0.79350 (5)	0.20618 (6)	0.28625 (3)	0.0665 (2)
O9B	0.6791 (3)	0.3822 (3)	0.3761 (2)	0.0606 (11)
H9B	0.7452	0.3751	0.3659	0.091*
O3B	0.1961 (3)	0.1328 (4)	0.17553 (13)	0.0518 (10)
H3B	0.2581	0.1164	0.1615	0.078*
C1B	0.3628 (4)	0.0498 (4)	0.2968 (2)	0.0405 (13)
H1B	0.3908	-0.0166	0.3135	0.049*
C2B	0.2651 (4)	0.0448 (4)	0.2689 (2)	0.0414 (13)
H2B	0.2315	-0.0254	0.2649	0.050*
C3B	0.2037 (4)	0.1436 (5)	0.2432 (2)	0.0449 (13)
C31B	0.0816 (4)	0.1442 (6)	0.2649 (2)	0.0638 (17)
H31D	0.0459	0.2126	0.2517	0.096*
H31E	0.0793	0.1393	0.3093	0.096*
H31F	0.0426	0.0811	0.2473	0.096*
C4B	0.2624 (4)	0.2528 (5)	0.2597 (2)	0.0449 (14)
H4C	0.2414	0.2749	0.3014	0.054*
H4D	0.2382	0.3115	0.2316	0.054*
C5B	0.3908 (4)	0.2400 (4)	0.2559 (2)	0.0384 (12)
H5C	0.4261	0.3123	0.2634	0.046*
H5D	0.4117	0.2155	0.2146	0.046*
C6B	0.4339 (4)	0.1537 (4)	0.30408 (19)	0.0322 (11)
C7B	0.5630 (4)	0.1234 (4)	0.2932 (2)	0.0365 (11)
C71B	0.5808 (5)	0.0801 (4)	0.2262 (2)	0.0471 (13)
H71D	0.6536	0.0452	0.2230	0.071*
H71E	0.5766	0.1420	0.1977	0.071*
H71F	0.5235	0.0261	0.2162	0.071*
C72B	0.5992 (4)	0.0296 (4)	0.3382 (2)	0.0484 (13)
H72D	0.6799	0.0260	0.3398	0.073*
H72E	0.5700	-0.0411	0.3240	0.073*
H72F	0.5703	0.0454	0.3788	0.073*
C8B	0.6325 (4)	0.2310 (4)	0.3044 (2)	0.0405 (12)
H8B	0.6048	0.2889	0.2759	0.049*
C9B	0.6225 (4)	0.2765 (5)	0.3699 (2)	0.0443 (13)
H9D	0.6524	0.2222	0.3998	0.053*
C10B	0.4989 (4)	0.3010 (5)	0.3835 (2)	0.0464 (14)
H10C	0.4912	0.3200	0.4271	0.056*
H10D	0.4757	0.3660	0.3596	0.056*

C11B	0.4211 (4)	0.2042 (4)	0.36888 (19)	0.0373 (11)
C12B	0.3443 (4)	0.1731 (5)	0.4090 (2)	0.0545 (16)
H12C	0.3377	0.2107	0.4467	0.065*
H12D	0.2965	0.1135	0.3999	0.065*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br8A	0.0738 (4)	0.0342 (3)	0.0544 (3)	0.0041 (3)	-0.0034 (3)	0.0022 (3)
O3A	0.056 (3)	0.055 (2)	0.071 (3)	0.018 (2)	0.017 (2)	-0.003 (2)
O9A	0.066 (3)	0.051 (2)	0.0367 (18)	-0.003 (2)	-0.0029 (19)	-0.0173 (18)
C1A	0.035 (3)	0.046 (3)	0.047 (3)	0.003 (3)	-0.006 (3)	-0.008 (3)
C2A	0.042 (3)	0.045 (3)	0.047 (3)	-0.002 (3)	0.001 (3)	-0.014 (2)
C3A	0.044 (3)	0.029 (3)	0.054 (3)	0.006 (3)	0.010 (3)	0.000 (3)
C31A	0.086 (5)	0.034 (3)	0.084 (4)	-0.006 (4)	-0.005 (4)	-0.002 (3)
C4A	0.042 (3)	0.043 (3)	0.047 (3)	0.010 (3)	-0.005 (3)	0.000 (3)
C5A	0.037 (3)	0.030 (3)	0.041 (3)	0.001 (2)	-0.006 (2)	-0.009 (3)
C6A	0.031 (3)	0.031 (3)	0.036 (2)	-0.003 (2)	-0.002 (2)	-0.005 (2)
C7A	0.038 (3)	0.044 (3)	0.027 (2)	0.008 (3)	-0.004 (2)	0.002 (2)
C71A	0.070 (4)	0.049 (3)	0.038 (3)	0.000 (3)	0.006 (3)	-0.003 (3)
C72A	0.051 (3)	0.056 (4)	0.046 (3)	0.022 (3)	-0.015 (3)	-0.007 (3)
C8A	0.047 (3)	0.032 (3)	0.037 (3)	0.002 (3)	0.002 (2)	0.001 (2)
C9A	0.037 (3)	0.044 (3)	0.038 (3)	0.000 (3)	0.004 (2)	-0.012 (2)
C10A	0.071 (4)	0.041 (3)	0.034 (2)	-0.007 (3)	0.014 (3)	-0.002 (2)
C11A	0.039 (3)	0.034 (3)	0.051 (3)	0.001 (3)	0.007 (2)	-0.002 (3)
C12A	0.059 (4)	0.056 (4)	0.071 (4)	-0.012 (4)	0.018 (3)	-0.011 (3)
Br8B	0.0401 (3)	0.0769 (5)	0.0825 (4)	-0.0080 (4)	0.0145 (3)	-0.0286 (4)
O9B	0.047 (2)	0.052 (2)	0.083 (3)	-0.022 (2)	0.018 (2)	-0.031 (2)
O3B	0.045 (2)	0.077 (3)	0.0330 (17)	-0.002 (2)	-0.0003 (17)	-0.0043 (19)
C1B	0.048 (3)	0.033 (3)	0.041 (3)	-0.010 (3)	-0.006 (3)	0.009 (2)
C2B	0.047 (3)	0.039 (3)	0.038 (3)	-0.012 (3)	-0.001 (2)	-0.003 (2)
C3B	0.038 (3)	0.063 (4)	0.033 (3)	-0.002 (3)	0.000 (2)	-0.008 (3)
C31B	0.041 (3)	0.100 (5)	0.051 (3)	0.000 (4)	0.009 (3)	-0.007 (3)
C4B	0.044 (3)	0.045 (3)	0.046 (3)	0.007 (3)	-0.006 (2)	0.003 (3)
C5B	0.042 (3)	0.034 (3)	0.039 (2)	0.000 (3)	-0.007 (2)	0.005 (2)
C6B	0.036 (3)	0.026 (2)	0.035 (2)	-0.009 (2)	-0.001 (2)	0.006 (2)
C7B	0.042 (3)	0.028 (2)	0.040 (3)	-0.002 (2)	0.000 (2)	-0.004 (2)
C71B	0.056 (3)	0.042 (3)	0.043 (3)	0.003 (3)	0.007 (3)	-0.009 (2)
C72B	0.052 (3)	0.037 (3)	0.057 (3)	0.007 (3)	-0.013 (3)	0.004 (3)
C8B	0.037 (3)	0.038 (3)	0.047 (3)	-0.005 (3)	0.007 (2)	-0.008 (2)
C9B	0.038 (3)	0.047 (3)	0.049 (3)	-0.004 (3)	-0.001 (2)	-0.013 (3)
C10B	0.047 (3)	0.054 (4)	0.038 (3)	-0.018 (3)	0.012 (2)	-0.016 (3)
C11B	0.037 (3)	0.037 (3)	0.037 (2)	-0.004 (3)	0.002 (2)	0.002 (2)
C12B	0.056 (3)	0.067 (4)	0.041 (3)	-0.023 (3)	0.008 (3)	-0.001 (3)

*Geometric parameters (Å, °)*

Br8A—C8A	1.978 (5)	Br8B—C8B	1.973 (5)
O3A—C3A	1.437 (6)	O9B—C9B	1.432 (6)
O3A—H3A	0.82	O9B—H9B	0.82
O9A—C9A	1.438 (5)	O3B—C3B	1.468 (5)
O9A—H9A	0.82	O3B—H3B	0.82
C1A—C2A	1.327 (7)	C1B—C2B	1.308 (7)
C1A—C6A	1.517 (6)	C1B—C6B	1.505 (6)
C1A—H1A	0.93	C1B—H1B	0.93
C2A—C3A	1.482 (7)	C2B—C3B	1.490 (7)
C2A—H2A	0.93	C2B—H2B	0.93
C3A—C4A	1.535 (7)	C3B—C4B	1.517 (7)
C3A—C31A	1.544 (7)	C3B—C31B	1.524 (7)
C31A—H31A	0.96	C31B—H31D	0.96
C31A—H31B	0.96	C31B—H31E	0.96
C31A—H31C	0.96	C31B—H31F	0.96
C4A—C5A	1.525 (6)	C4B—C5B	1.534 (7)
C4A—H4A	0.97	C4B—H4C	0.97
C4A—H4B	0.97	C4B—H4D	0.97
C5A—C6A	1.543 (6)	C5B—C6B	1.547 (6)
C5A—H5A	0.97	C5B—H5C	0.97
C5A—H5B	0.97	C5B—H5D	0.97
C6A—C11A	1.527 (6)	C6B—C11B	1.529 (6)
C6A—C7A	1.580 (7)	C6B—C7B	1.593 (7)
C7A—C71A	1.538 (6)	C7B—C72B	1.540 (6)
C7A—C72A	1.541 (7)	C7B—C8B	1.542 (6)
C7A—C8A	1.548 (6)	C7B—C71B	1.549 (6)
C71A—H71A	0.96	C71B—H71D	0.96
C71A—H71B	0.96	C71B—H71E	0.96
C71A—H71C	0.96	C71B—H71F	0.96
C72A—H72A	0.96	C72B—H72D	0.96
C72A—H72B	0.96	C72B—H72E	0.96
C72A—H72C	0.96	C72B—H72F	0.96
C8A—C9A	1.509 (6)	C8B—C9B	1.518 (6)
C8A—H8A	0.98	C8B—H8B	0.98
C9A—C10A	1.512 (7)	C9B—C10B	1.524 (7)
C9A—H9C	0.98	C9B—H9D	0.98
C10A—C11A	1.518 (7)	C10B—C11B	1.509 (7)
C10A—H10A	0.97	C10B—H10C	0.97
C10A—H10B	0.97	C10B—H10D	0.97
C11A—C12A	1.309 (7)	C11B—C12B	1.311 (6)
C12A—H12A	0.93	C12B—H12C	0.93
C12A—H12B	0.93	C12B—H12D	0.93
C3A—O3A—H3A	109.5	C9B—O9B—H9B	109.5
C9A—O9A—H9A	109.5	C3B—O3B—H3B	109.5
C2A—C1A—C6A	124.4 (5)	C2B—C1B—C6B	125.6 (5)

C2A—C1A—H1A	117.8	C2B—C1B—H1B	117.2
C6A—C1A—H1A	117.8	C6B—C1B—H1B	117.2
C1A—C2A—C3A	125.3 (5)	C1B—C2B—C3B	124.7 (5)
C1A—C2A—H2A	117.3	C1B—C2B—H2B	117.6
C3A—C2A—H2A	117.3	C3B—C2B—H2B	117.6
O3A—C3A—C2A	109.2 (4)	O3B—C3B—C2B	109.4 (4)
O3A—C3A—C4A	111.4 (4)	O3B—C3B—C4B	109.7 (5)
C2A—C3A—C4A	111.2 (4)	C2B—C3B—C4B	111.3 (4)
O3A—C3A—C31A	104.1 (4)	O3B—C3B—C31B	104.3 (4)
C2A—C3A—C31A	111.1 (5)	C2B—C3B—C31B	110.8 (5)
C4A—C3A—C31A	109.7 (4)	C4B—C3B—C31B	111.1 (5)
C3A—C31A—H31A	109.5	C3B—C31B—H31D	109.5
C3A—C31A—H31B	109.5	C3B—C31B—H31E	109.5
H31A—C31A—H31B	109.5	H31D—C31B—H31E	109.5
C3A—C31A—H31C	109.5	C3B—C31B—H31F	109.5
H31A—C31A—H31C	109.5	H31D—C31B—H31F	109.5
H31B—C31A—H31C	109.5	H31E—C31B—H31F	109.5
C5A—C4A—C3A	110.5 (4)	C3B—C4B—C5B	111.0 (4)
C5A—C4A—H4A	109.5	C3B—C4B—H4C	109.4
C3A—C4A—H4A	109.5	C5B—C4B—H4C	109.4
C5A—C4A—H4B	109.5	C3B—C4B—H4D	109.4
C3A—C4A—H4B	109.5	C5B—C4B—H4D	109.4
H4A—C4A—H4B	108.1	H4C—C4B—H4D	108.0
C4A—C5A—C6A	111.7 (4)	C4B—C5B—C6B	111.0 (4)
C4A—C5A—H5A	109.3	C4B—C5B—H5C	109.4
C6A—C5A—H5A	109.3	C6B—C5B—H5C	109.4
C4A—C5A—H5B	109.3	C4B—C5B—H5D	109.4
C6A—C5A—H5B	109.3	C6B—C5B—H5D	109.4
H5A—C5A—H5B	107.9	H5C—C5B—H5D	108.0
C1A—C6A—C11A	110.8 (4)	C1B—C6B—C11B	111.3 (4)
C1A—C6A—C5A	106.7 (4)	C1B—C6B—C5B	106.9 (4)
C11A—C6A—C5A	109.8 (4)	C11B—C6B—C5B	108.7 (4)
C1A—C6A—C7A	109.8 (4)	C1B—C6B—C7B	109.7 (4)
C11A—C6A—C7A	108.2 (4)	C11B—C6B—C7B	108.6 (4)
C5A—C6A—C7A	111.7 (4)	C5B—C6B—C7B	111.7 (4)
C71A—C7A—C72A	107.4 (4)	C72B—C7B—C8B	110.7 (4)
C71A—C7A—C8A	110.1 (4)	C72B—C7B—C71B	108.0 (4)
C72A—C7A—C8A	110.6 (4)	C8B—C7B—C71B	110.5 (4)
C71A—C7A—C6A	110.8 (4)	C72B—C7B—C6B	109.9 (4)
C72A—C7A—C6A	110.9 (4)	C8B—C7B—C6B	107.7 (4)
C8A—C7A—C6A	107.0 (3)	C71B—C7B—C6B	110.2 (4)
C7A—C71A—H71A	109.5	C7B—C71B—H71D	109.5
C7A—C71A—H71B	109.5	C7B—C71B—H71E	109.5
H71A—C71A—H71B	109.5	H71D—C71B—H71E	109.5
C7A—C71A—H71C	109.5	C7B—C71B—H71F	109.5
H71A—C71A—H71C	109.5	H71D—C71B—H71F	109.5
H71B—C71A—H71C	109.5	H71E—C71B—H71F	109.5
C7A—C72A—H72A	109.5	C7B—C72B—H72D	109.5

C7A—C72A—H72B	109.5	C7B—C72B—H72E	109.5
H72A—C72A—H72B	109.5	H72D—C72B—H72E	109.5
C7A—C72A—H72C	109.5	C7B—C72B—H72F	109.5
H72A—C72A—H72C	109.5	H72D—C72B—H72F	109.5
H72B—C72A—H72C	109.5	H72E—C72B—H72F	109.5
C9A—C8A—C7A	113.5 (4)	C9B—C8B—C7B	113.6 (4)
C9A—C8A—Br8A	108.2 (3)	C9B—C8B—Br8B	108.3 (3)
C7A—C8A—Br8A	111.9 (3)	C7B—C8B—Br8B	111.3 (3)
C9A—C8A—H8A	107.7	C9B—C8B—H8B	107.8
C7A—C8A—H8A	107.7	C7B—C8B—H8B	107.8
Br8A—C8A—H8A	107.7	Br8B—C8B—H8B	107.8
O9A—C9A—C8A	112.3 (4)	O9B—C9B—C8B	111.4 (4)
O9A—C9A—C10A	104.6 (4)	O9B—C9B—C10B	105.4 (4)
C8A—C9A—C10A	109.4 (4)	C8B—C9B—C10B	108.9 (4)
O9A—C9A—H9C	110.1	O9B—C9B—H9D	110.4
C8A—C9A—H9C	110.1	C8B—C9B—H9D	110.4
C10A—C9A—H9C	110.1	C10B—C9B—H9D	110.4
C9A—C10A—C11A	113.2 (4)	C11B—C10B—C9B	113.8 (4)
C9A—C10A—H10A	108.9	C11B—C10B—H10C	108.8
C11A—C10A—H10A	108.9	C9B—C10B—H10C	108.8
C9A—C10A—H10B	108.9	C11B—C10B—H10D	108.8
C11A—C10A—H10B	108.9	C9B—C10B—H10D	108.8
H10A—C10A—H10B	107.7	H10C—C10B—H10D	107.7
C12A—C11A—C10A	121.4 (5)	C12B—C11B—C10B	120.2 (4)
C12A—C11A—C6A	124.6 (5)	C12B—C11B—C6B	124.2 (5)
C10A—C11A—C6A	114.0 (4)	C10B—C11B—C6B	115.5 (4)
C11A—C12A—H12A	120.0	C11B—C12B—H12C	120.0
C11A—C12A—H12B	120.0	C11B—C12B—H12D	120.0
H12A—C12A—H12B	120.0	H12C—C12B—H12D	120.0
C6A—C1A—C2A—C3A	-2.2 (8)	C6B—C1B—C2B—C3B	-4.3 (8)
C1A—C2A—C3A—O3A	115.8 (6)	C1B—C2B—C3B—O3B	114.9 (5)
C1A—C2A—C3A—C4A	-7.5 (7)	C1B—C2B—C3B—C4B	-6.5 (7)
C1A—C2A—C3A—C31A	-130.0 (6)	C1B—C2B—C3B—C31B	-130.7 (5)
O3A—C3A—C4A—C5A	-82.9 (5)	O3B—C3B—C4B—C5B	-82.0 (5)
C2A—C3A—C4A—C5A	39.2 (6)	C2B—C3B—C4B—C5B	39.2 (6)
C31A—C3A—C4A—C5A	162.4 (5)	C31B—C3B—C4B—C5B	163.1 (4)
C3A—C4A—C5A—C6A	-64.2 (6)	C3B—C4B—C5B—C6B	-63.7 (5)
C2A—C1A—C6A—C11A	99.8 (6)	C2B—C1B—C6B—C11B	100.6 (5)
C2A—C1A—C6A—C5A	-19.7 (7)	C2B—C1B—C6B—C5B	-18.0 (6)
C2A—C1A—C6A—C7A	-140.8 (5)	C2B—C1B—C6B—C7B	-139.2 (5)
C4A—C5A—C6A—C1A	51.6 (5)	C4B—C5B—C6B—C1B	50.1 (5)
C4A—C5A—C6A—C11A	-68.5 (5)	C4B—C5B—C6B—C11B	-70.1 (5)
C4A—C5A—C6A—C7A	171.5 (4)	C4B—C5B—C6B—C7B	170.1 (4)
C1A—C6A—C7A—C71A	61.3 (5)	C1B—C6B—C7B—C72B	-56.5 (5)
C11A—C6A—C7A—C71A	-177.7 (4)	C11B—C6B—C7B—C72B	65.3 (5)
C5A—C6A—C7A—C71A	-56.8 (5)	C5B—C6B—C7B—C72B	-174.9 (4)
C1A—C6A—C7A—C72A	-57.9 (5)	C1B—C6B—C7B—C8B	-177.2 (4)

C11A—C6A—C7A—C72A	63.1 (5)	C11B—C6B—C7B—C8B	-55.3 (5)
C5A—C6A—C7A—C72A	-176.0 (4)	C5B—C6B—C7B—C8B	64.5 (5)
C1A—C6A—C7A—C8A	-178.7 (4)	C1B—C6B—C7B—C71B	62.3 (5)
C11A—C6A—C7A—C8A	-57.7 (5)	C11B—C6B—C7B—C71B	-175.8 (4)
C5A—C6A—C7A—C8A	63.2 (5)	C5B—C6B—C7B—C71B	-56.0 (5)
C71A—C7A—C8A—C9A	-178.0 (4)	C72B—C7B—C8B—C9B	-58.5 (6)
C72A—C7A—C8A—C9A	-59.4 (6)	C71B—C7B—C8B—C9B	-178.1 (4)
C6A—C7A—C8A—C9A	61.5 (5)	C6B—C7B—C8B—C9B	61.6 (5)
C71A—C7A—C8A—Br8A	-55.2 (5)	C72B—C7B—C8B—Br8B	64.0 (5)
C72A—C7A—C8A—Br8A	63.4 (5)	C71B—C7B—C8B—Br8B	-55.5 (5)
C6A—C7A—C8A—Br8A	-175.7 (3)	C6B—C7B—C8B—Br8B	-175.9 (3)
C7A—C8A—C9A—O9A	-173.2 (4)	C7B—C8B—C9B—O9B	-174.1 (4)
Br8A—C8A—C9A—O9A	61.9 (5)	Br8B—C8B—C9B—O9B	61.7 (5)
C7A—C8A—C9A—C10A	-57.5 (6)	C7B—C8B—C9B—C10B	-58.3 (6)
Br8A—C8A—C9A—C10A	177.6 (4)	Br8B—C8B—C9B—C10B	177.5 (4)
O9A—C9A—C10A—C11A	171.6 (4)	O9B—C9B—C10B—C11B	170.2 (4)
C8A—C9A—C10A—C11A	51.1 (6)	C8B—C9B—C10B—C11B	50.6 (6)
C9A—C10A—C11A—C12A	128.1 (6)	C9B—C10B—C11B—C12B	133.1 (5)
C9A—C10A—C11A—C6A	-53.1 (6)	C9B—C10B—C11B—C6B	-51.0 (6)
C1A—C6A—C11A—C12A	-5.1 (7)	C1B—C6B—C11B—C12B	-11.0 (7)
C5A—C6A—C11A—C12A	112.4 (6)	C5B—C6B—C11B—C12B	106.4 (6)
C7A—C6A—C11A—C12A	-125.5 (5)	C7B—C6B—C11B—C12B	-131.9 (5)
C1A—C6A—C11A—C10A	176.1 (4)	C1B—C6B—C11B—C10B	173.2 (4)
C5A—C6A—C11A—C10A	-66.3 (5)	C5B—C6B—C11B—C10B	-69.4 (5)
C7A—C6A—C11A—C10A	55.8 (5)	C7B—C6B—C11B—C10B	52.3 (5)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3A—H3A...O3B <sup>i</sup>	0.82	1.99	2.779 (6)	160
O3B—H3B...O9A <sup>ii</sup>	0.82	2.08	2.855 (5)	158
O9A—H9A...O9B	0.82	2.00	2.790 (5)	162
O9B—H9B...O3A <sup>iii</sup>	0.82	2.04	2.765 (5)	147
O9B—H9B...Br8B	0.82	2.70	3.160 (4)	117

Symmetry codes: (i)  $-x+1/2, -y+1, z+1/2$ ; (ii)  $x+3/2, -y-1/2, -z$ ; (iii)  $-x, y+3/2, -z+3/2$ .