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## Structure Reports

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## Methyl 3,5-dibromo-4-methylbenzoate

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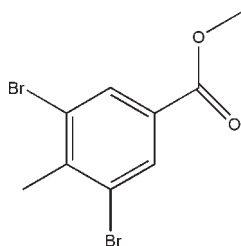
Received 18 March 2010; accepted 24 March 2010

Key indicators: single-crystal X-ray study;  $T = 89$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.033;  $wR$  factor = 0.065; data-to-parameter ratio = 28.9.

In the title compound,  $\text{C}_9\text{H}_8\text{Br}_2\text{O}_2$ , the molecule is essentially planar with an r.m.s. deviation of 0.0652 Å from the mean plane through all non-H atoms and a dihedral angle of 7.1 (2)° between the benzene ring plane and the carboxylate substituent. In the crystal structure, weak C—H···Br hydrogen bonds and weak intermolecular O···Br contacts [3.095 (2) Å], link adjacent molecules into layers parallel to (102). Additional weak intermolecular C—H···O hydrogen bond interactions stack the layers above and below the molecular plane and down the  $a$  axis.

## Related literature

For use of the title compound in the synthesis of natural products, see: Gray & Whalley (1971); Saeed & Rama (1994); Harris & Mantle (2001); Simpson (1978). For related structures, see: Moorthy *et al.* (2002); Fan *et al.* (2005). For intermolecular O···Br contacts, see: Choi *et al.* (2010*a,b*); Politzer *et al.* (2007). For bond-length data, see: Allen *et al.* (1987).



## Experimental

## Crystal data

 $\text{C}_9\text{H}_8\text{Br}_2\text{O}_2$  $M_r = 307.97$ Orthorhombic,  $P2_12_12_1$  $a = 3.9716$  (2) Å $b = 14.2359$  (7) Å $c = 17.2893$  (8) Å $V = 977.52$  (8) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 8.26$  mm<sup>-1</sup> $T = 89$  K

0.64 × 0.14 × 0.08 mm

## Data collection

Bruker APEXII CCD  
diffractometerAbsorption correction: multi-scan  
(SADABS; Bruker, 2006) $T_{\min} = 0.295$ ,  $T_{\max} = 1.000$ 

17658 measured reflections

3471 independent reflections

2922 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.061$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.033$  $wR(F^2) = 0.065$  $S = 1.09$ 

3471 reflections

120 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 1.15$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -1.09$  e Å<sup>-3</sup>

Absolute structure: Flack (1983),

1659 Friedel pairs

Flack parameter: 0.039 (14)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C8}-\text{H8C}\cdots\text{O2}^i$	0.98	2.70	3.546 (5)	145
$\text{C6}-\text{H6}\cdots\text{Br2}^{ii}$	0.95	2.93	3.838 (3)	159
$\text{C8}-\text{H8A}\cdots\text{O1}^{iii}$	0.98	2.69	3.647 (4)	167

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

Data collection: APEX2 (Bruker, 2006); cell refinement: APEX2 and SAINT (Bruker, 2006); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008) and TITAN2000 (Hunter & Simpson, 1999); molecular graphics: SHELXTL (Sheldrick, 2008) and Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97, enCIFer (Allen *et al.*, 2004), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JJ2027).

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## supporting information

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## Methyl 3,5-dibromo-4-methylbenzoate

Aamer Saeed, Hummera Rafique, Jim Simpson and Zaman Ashraf

### S1. Comment

The title ester, (I), Fig. 1, is an important intermediate towards synthesis of 3,5-dimethoxyphenylacetic acid, a key intermediate in the synthesis of a variety of natural products. These include the sclerotiorin group of fungal metabolites (Gray & Whalley, 1971), isochromans related to sclerotiorin pigments (Saeed & Rama, 1994) and isocoumarins like 7-methylmellein (Harris & Mantle, 2001) and stellatin (Simpson, 1978).  $C_9H_8O_2Br_2$ , (I), was prepared by bromination of methyl 4-methylbenzoate in presence of anhydrous aluminum chloride using an excess of catalyst and no solvent.

The molecule is essentially flat with an rms deviation of 0.0652 Å from the mean plane through all non-hydrogen atoms. The dihedral angle between the C1...C6 ring plane and that of the C7/O1/O2/C8 carboxylate unit is 7.1 (2)°. Bond distances in the molecule are normal (Allen *et al.*, 1987) and comparable to those in related structures (Moorthy *et al.*, 2002; Fan *et al.*, 2005).

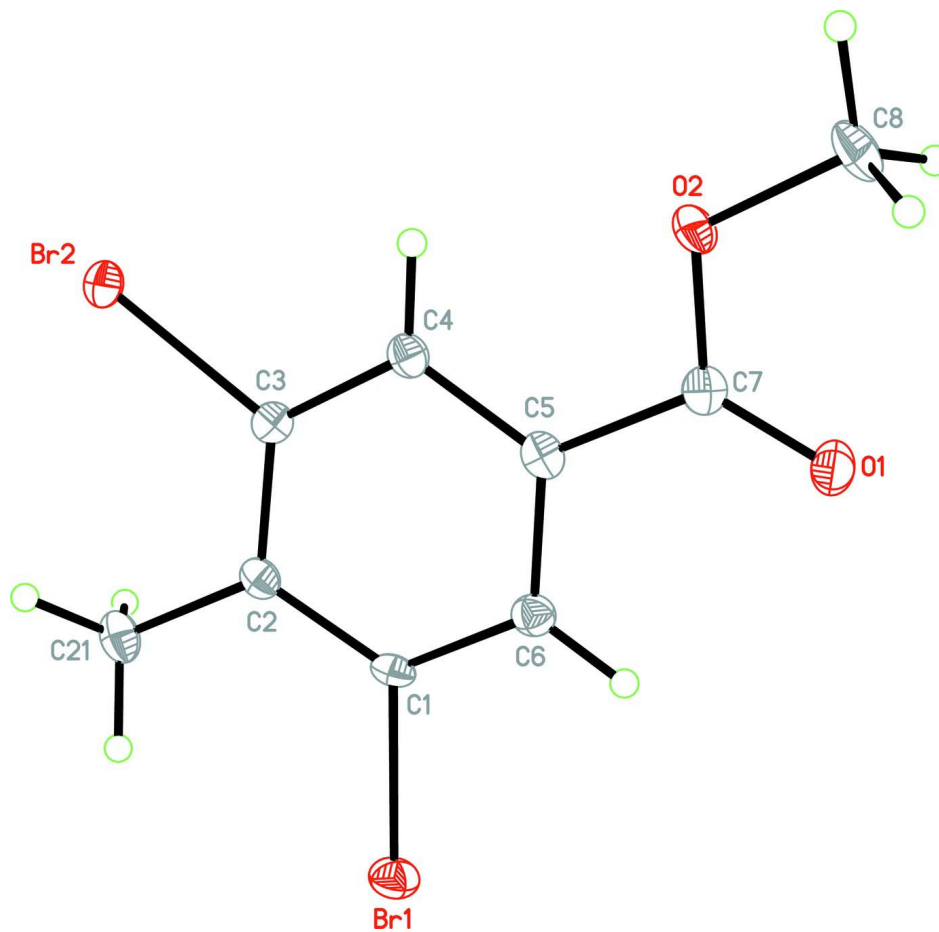
In the crystal structure weak intermolecular C6—H6...Br2 hydrogen bonds and weak O1...Br2 contacts at 3.095 (2) Å (Choi *et al.*, 2010a,b; Politzer *et al.*, 2007) link adjacent molecules into layers parallel to the (102) plane. Additional weak intermolecular C8—H8A...O1 and C8—H8C...O2 hydrogen bond interactions involving the carboxylate methyl group stack these layers above and below the molecular plane and down the *a* axis, Table 1, Fig. 2.

### S2. Experimental

Anhydrous aluminum chloride (1.60 mmol) was added portionwise to stirred methyl 4-methylbenzoate (0.6 mmol) at 0°C under a nitrogen atmosphere. Bromine was added over 45 min. and the mixture was further stirred for 30 min at room temperature and at 80 °C for 1 h. The mixture was cooled to room temperature, treated with cold methanol (100 ml) and then stirred overnight. The crude product was filtered and washed with methanol at 30°C then recrystallized from methanol at 10°C to afford the title compound (86%) as colourless crystals: Anal. calcd. for  $C_9H_8Br_2O_2$ : C, 35.10; H, 2.62; found: C, 35.23; H, 2.67 %

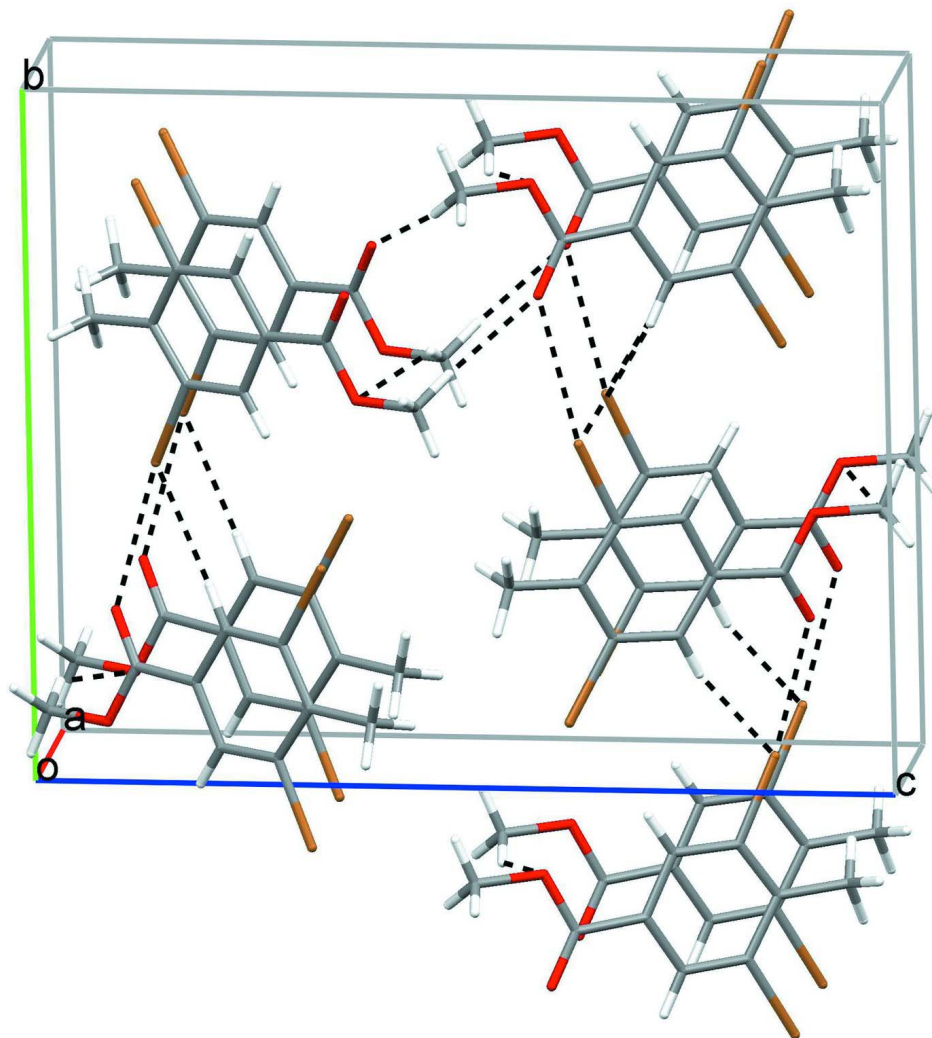
### S3. Refinement

H-atoms were positioned geometrically and refined using a riding model with  $d(C-H) = 0.95$  Å,  $U_{iso} = 1.2U_{eq}(C)$  for aromatic and  $d(C-H) = 0.98$  Å,  $U_{iso} = 1.5U_{eq}(C)$  for methyl C atoms.



**Figure 1**

The structure of (I) with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level.

**Figure 2**

Crystal packing for (I) viewed down the  $a$  axis with weak hydrogen bonds and weak  $O\cdots Br$  contacts drawn as dashed lines.

### Methyl 3,5-dibromo-4-methylbenzoate

#### Crystal data

$C_9H_8Br_2O_2$

$M_r = 307.97$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 3.9716$  (2) Å

$b = 14.2359$  (7) Å

$c = 17.2893$  (8) Å

$V = 977.52$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 592$

$D_x = 2.093$  Mg m<sup>-3</sup>

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

Cell parameters from 4848 reflections

$\theta = 2.8\text{--}30.4^\circ$

$\mu = 8.26$  mm<sup>-1</sup>

$T = 89$  K

Rectangular plate, colourless

$0.64 \times 0.14 \times 0.08$  mm

*Data collection*

Bruker APEXII CCD diffractometer	17658 measured reflections
Radiation source: fine-focus sealed tube	3471 independent reflections
Graphite monochromator	2922 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.061$
Absorption correction: multi-scan (SADABS; Bruker, 2006)	$\theta_{\text{max}} = 33.3^\circ$ , $\theta_{\text{min}} = 3.7^\circ$
$T_{\text{min}} = 0.295$ , $T_{\text{max}} = 1.000$	$h = -6 \rightarrow 4$
	$k = -21 \rightarrow 21$
	$l = -25 \rightarrow 25$

*Refinement*

Refinement on $F^2$	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + 0.5972P]$
$wR(F^2) = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3471 reflections	$\Delta\rho_{\text{max}} = 1.15 \text{ e } \text{\AA}^{-3}$
120 parameters	$\Delta\rho_{\text{min}} = -1.09 \text{ e } \text{\AA}^{-3}$
0 restraints	Absolute structure: Flack (1983), 1659 Friedel pairs
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.039 (14)
Secondary atom site location: difference Fourier map	

*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.** 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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.86943 (10)	0.87630 (2)	0.134557 (17)	0.01774 (7)
C1	0.7685 (7)	0.7603 (2)	0.18453 (18)	0.0116 (6)
C2	0.8609 (8)	0.67455 (19)	0.15060 (16)	0.0119 (5)
C21	1.0349 (8)	0.6680 (2)	0.07366 (19)	0.0172 (7)
H21A	1.2073	0.6188	0.0757	0.026*
H21B	1.1411	0.7283	0.0615	0.026*
H21C	0.8697	0.6525	0.0335	0.026*
C3	0.7704 (8)	0.5947 (2)	0.19236 (18)	0.0120 (6)
Br2	0.86513 (9)	0.47350 (2)	0.151431 (17)	0.01548 (7)
C4	0.6050 (9)	0.59686 (19)	0.26311 (17)	0.0128 (5)
H4	0.5508	0.5404	0.2897	0.015*
C5	0.5202 (7)	0.6844 (2)	0.29418 (19)	0.0122 (6)
C6	0.6011 (9)	0.7667 (2)	0.25473 (17)	0.0138 (6)
H6	0.5426	0.8262	0.2756	0.017*
C7	0.3351 (8)	0.69264 (19)	0.36902 (17)	0.0133 (5)

O1	0.2258 (6)	0.76517 (15)	0.39530 (14)	0.0181 (5)
O2	0.3030 (6)	0.60888 (15)	0.40440 (12)	0.0163 (5)
C8	0.1345 (11)	0.6119 (2)	0.47902 (17)	0.0214 (6)
H8A	0.2618	0.6524	0.5144	0.032*
H8B	0.1215	0.5483	0.5005	0.032*
H8C	-0.0933	0.6371	0.4725	0.032*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02028 (15)	0.01578 (13)	0.01716 (15)	-0.00211 (15)	0.00154 (16)	0.00416 (11)
C1	0.0112 (13)	0.0118 (13)	0.0118 (14)	-0.0026 (10)	-0.0006 (11)	0.0039 (11)
C2	0.0084 (10)	0.0148 (11)	0.0126 (13)	-0.0006 (13)	-0.0016 (14)	0.0007 (10)
C21	0.0153 (14)	0.0231 (16)	0.0131 (16)	0.0021 (13)	0.0022 (12)	0.0006 (12)
C3	0.0122 (14)	0.0129 (13)	0.0109 (14)	-0.0004 (11)	-0.0019 (11)	-0.0009 (10)
Br2	0.01713 (14)	0.01478 (12)	0.01454 (14)	0.00131 (14)	0.00229 (15)	-0.00278 (10)
C4	0.0103 (13)	0.0151 (12)	0.0131 (13)	-0.0003 (13)	-0.0004 (13)	-0.0003 (10)
C5	0.0090 (12)	0.0176 (14)	0.0099 (14)	-0.0004 (11)	-0.0032 (11)	-0.0003 (12)
C6	0.0122 (14)	0.0139 (13)	0.0152 (13)	-0.0009 (13)	-0.0006 (13)	0.0002 (10)
C7	0.0139 (14)	0.0161 (13)	0.0099 (12)	-0.0001 (11)	-0.0028 (12)	-0.0013 (10)
O1	0.0206 (12)	0.0177 (11)	0.0160 (11)	0.0043 (9)	0.0027 (9)	-0.0009 (9)
O2	0.0208 (13)	0.0181 (10)	0.0098 (10)	-0.0014 (9)	0.0048 (9)	0.0003 (8)
C8	0.0235 (16)	0.0295 (16)	0.0113 (14)	-0.0020 (18)	0.0063 (16)	0.0020 (12)

*Geometric parameters (Å, °)*

Br1—C1	1.907 (3)	C4—H4	0.9500
C1—C6	1.387 (4)	C5—C6	1.393 (4)
C1—C2	1.403 (4)	C5—C7	1.493 (4)
C2—C3	1.394 (4)	C6—H6	0.9500
C2—C21	1.502 (4)	C7—O1	1.209 (3)
C21—H21A	0.9800	C7—O2	1.346 (3)
C21—H21B	0.9800	O1—Br2 <sup>i</sup>	3.095 (2)
C21—H21C	0.9800	O2—C8	1.454 (4)
C3—C4	1.389 (4)	C8—H8A	0.9800
C3—Br2	1.902 (3)	C8—H8B	0.9800
C4—C5	1.398 (4)	C8—H8C	0.9800
C6—C1—C2	123.3 (3)	C6—C5—C4	120.4 (3)
C6—C1—Br1	116.1 (2)	C6—C5—C7	118.2 (3)
C2—C1—Br1	120.6 (2)	C4—C5—C7	121.4 (3)
C3—C2—C1	115.2 (3)	C1—C6—C5	119.0 (3)
C3—C2—C21	121.8 (3)	C1—C6—H6	120.5
C1—C2—C21	123.0 (3)	C5—C6—H6	120.5
C2—C21—H21A	109.5	O1—C7—O2	123.5 (3)
C2—C21—H21B	109.5	O1—C7—C5	124.7 (3)
H21A—C21—H21B	109.5	O2—C7—C5	111.8 (2)
C2—C21—H21C	109.5	C7—O1—Br2 <sup>i</sup>	139.7 (2)

H21A—C21—H21C	109.5	C7—O2—C8	114.9 (2)
H21B—C21—H21C	109.5	O2—C8—H8A	109.5
C4—C3—C2	124.0 (3)	O2—C8—H8B	109.5
C4—C3—Br2	116.2 (2)	H8A—C8—H8B	109.5
C2—C3—Br2	119.7 (2)	O2—C8—H8C	109.5
C3—C4—C5	118.2 (3)	H8A—C8—H8C	109.5
C3—C4—H4	120.9	H8B—C8—H8C	109.5
C5—C4—H4	120.9		
C6—C1—C2—C3	0.4 (4)	C2—C1—C6—C5	0.2 (5)
Br1—C1—C2—C3	-179.4 (2)	Br1—C1—C6—C5	-180.0 (2)
C6—C1—C2—C21	178.5 (3)	C4—C5—C6—C1	-0.4 (4)
Br1—C1—C2—C21	-1.3 (4)	C7—C5—C6—C1	-179.0 (3)
C1—C2—C3—C4	-0.9 (5)	C6—C5—C7—O1	6.2 (5)
C21—C2—C3—C4	-179.0 (3)	C4—C5—C7—O1	-172.5 (3)
C1—C2—C3—Br2	177.7 (2)	C6—C5—C7—O2	-173.9 (3)
C21—C2—C3—Br2	-0.4 (4)	C4—C5—C7—O2	7.5 (4)
C2—C3—C4—C5	0.7 (5)	O2—C7—O1—Br2 <sup>i</sup>	-172.96 (18)
Br2—C3—C4—C5	-177.9 (2)	C5—C7—O1—Br2 <sup>i</sup>	7.0 (5)
C3—C4—C5—C6	-0.1 (4)	O1—C7—O2—C8	-2.0 (4)
C3—C4—C5—C7	178.6 (3)	C5—C7—O2—C8	178.1 (3)

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C8—H8C...O2 <sup>ii</sup>	0.98	2.70	3.546 (5)	145
C6—H6...Br2 <sup>i</sup>	0.95	2.93	3.838 (3)	159
C8—H8A...O1 <sup>iii</sup>	0.98	2.69	3.647 (4)	167

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