

Crystal structure of 2-bromobenzoic acid at 120 K: a redetermination

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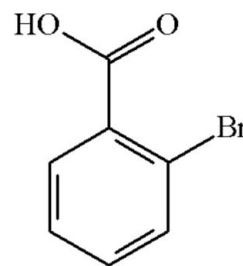
The crystal structure of the title compound, $C_7H_5BrO_2$, was originally studied using photographic data at room temperature with Cu $K\alpha$ radiation [Ferguson & Sim (1962). *Acta Cryst.* **15**, 346–350]. The present study was undertaken at 120 K with a CCD diffractometer using Cu $K\alpha$ radiation, and resulted in improved geometrical parameters. In the molecule, the carboxy group is inclined to the benzene ring by $18.7(2)^\circ$ and there is a close intramolecular $Br \cdots O$ contact of $3.009(3) \text{ \AA}$. In the crystal, molecules are linked by pairs of $O-H \cdots O$ hydrogen bonds, forming inversion dimers with the classical $R_2^2(8)$ ring motif for carboxylic acids. Neighbouring dimers are linked by weak $C-H \cdots O$ hydrogen bonds, forming tapes propagating in $[1\bar{1}0]$. Adjacent tapes interact by slipped parallel $\pi-\pi$ interactions [inter-centroid distance = $3.991(2)$, interplanar distance = $3.509(2) \text{ \AA}$, slippage = 1.900 \AA] to form columns approximately along the b -axis direction. Neighbouring columns interact dispersively, forming a three-dimensional framework structure.

Keywords: crystal structure; 2-bromobenzoic acid; redetermination; hydrogen bonds; $\pi-\pi$ interactions.

CCDC reference: 1024798

1. Related literature

For the original report of the unit-cell dimensions, space group and structure of the title compound, see: Ferguson & Sim (1962). For uses of the title compound in organic synthesis, see: Evano *et al.* (2008); Wolf *et al.* (2006), and for its physicochemical properties, see: Govindarajan *et al.* (2011); Sabbah & Aguilar (1996); Swaminathan *et al.* (2009). For related structures involving the title compound, see: Das *et al.* (2012); Wales *et al.* (2012). For reports on $Br \cdots O$ interactions, see: Jones & Lozano (2004); Saeed *et al.* (2013); Singh *et al.* (2009).



2. Experimental

2.1. Crystal data

$C_7H_5BrO_2$	$V = 1343.69(8) \text{ \AA}^3$
$M_r = 201.01$	$Z = 8$
Monoclinic, $C2/c$	Cu $K\alpha$ radiation
$a = 14.7955(4) \text{ \AA}$	$\mu = 7.76 \text{ mm}^{-1}$
$b = 3.99062(15) \text{ \AA}$	$T = 120 \text{ K}$
$c = 22.9240(8) \text{ \AA}$	$0.55 \times 0.35 \times 0.28 \text{ mm}$
$\beta = 96.906(3)^\circ$	

2.2. Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer	10883 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)	1201 independent reflections
$T_{\min} = 0.722$, $T_{\max} = 0.991$	1172 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.067$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.091$	
$S = 1.18$	$\Delta\rho_{\max} = 0.82 \text{ e \AA}^{-3}$
1201 reflections	$\Delta\rho_{\min} = -0.52 \text{ e \AA}^{-3}$
95 parameters	
1 restraint	

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O9-H9 \cdots O8^i$	0.81(3)	1.84(3)	2.643(3)	177(5)
$C5-H5 \cdots O8^{ii}$	0.93	2.65	3.514(3)	153
$C6-H6 \cdots O9^{iii}$	0.93	2.64	3.417(3)	141

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP II* (Burnett & Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2783).

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supporting information

Acta Cryst. (2014). E70, o1139–o1140 [doi:10.1107/S160053681402087X]

Crystal structure of 2-bromobenzoic acid at 120 K: a redetermination

Kornelia Kowalska, Damian Trzybiński and Artur Sikorski

S1. Comment

2-Bromobenzoic acid is a reagent widely used in organic synthesis, for example in cross-coupling reactions (Evano *et al.*, 2008; Wolf *et al.*, 2006). The physicochemical properties of title compound, such as thermodynamic (Sabbah & Aguilar, 1996) and spectroscopic (Govindarajan *et al.*, 2011; Swaminathan *et al.*, 2009) properties, were studied in literature. In 1962, Ferguson and Sim (Ferguson & Sim, 1962) determined the crystal structure of the title compound ($a = 14.82$ Å, $b = 4.10$ Å, $c = 25.90$ Å, $\beta = 118.26^\circ$, $V = 1386.2$ Å³, $R = 13.20$ %), using photographic data at room temperature.

Redetermination of the crystal structure of 2-bromobenzoic acid at 120 K shows, that the unit cell dimensions (see: *Experimental section*) differs from those reported previously.

The bond lengths and angles characterizing the geometry of molecule of the title compound (Fig. 1) are similar to those found in other structures containing 2-bromobenzoic acid (Das *et al.*, 2012; Wales *et al.*, 2012). The benzene ring makes an angle of $18.7(2)^\circ$ with the mean plane of the carboxy group. There is also a close intramolecular Br10 \cdots O8 contact [3.009(3) Å; as shown in Fig. 1].

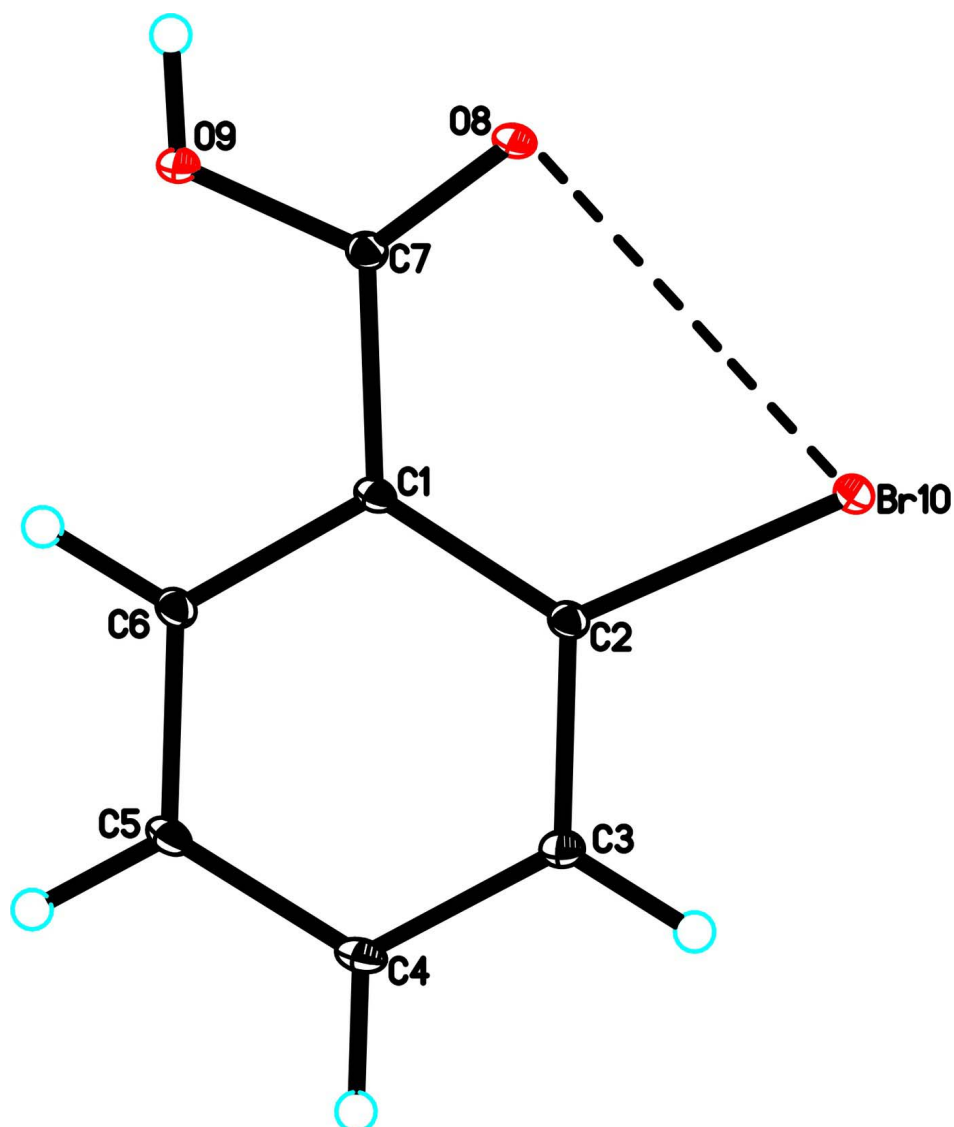
In the crystal, molecules are linked into inversion $R_2^2(8)$ dimers by pairs of O9–H9 \cdots O8ⁱ hydrogen bonds (Table 1 and Fig. 2). Neighbouring dimers are linked by C5–H5 \cdots O8ⁱⁱ and C6–H6 \cdots O9ⁱⁱⁱ interactions to produce tapes along [1 -1 0] (Table 1 and Fig. 2). Adjacent tapes interact by weak π – π interactions [$Cg\cdots Cg^{iv} = 3.991(2)$ Å; Cg is the centroid of the benzene ring C1–C6; interplanar distances = 3.509(2) Å; slippage 1.900 Å; symmetry code: (iv) $x, y-1, z$] to form stacked columns approximately along the b -axis (Fig. 3). The neighbouring columns interact dispersively to form a three-dimensional framework structure (Fig. 3).

S2. Experimental

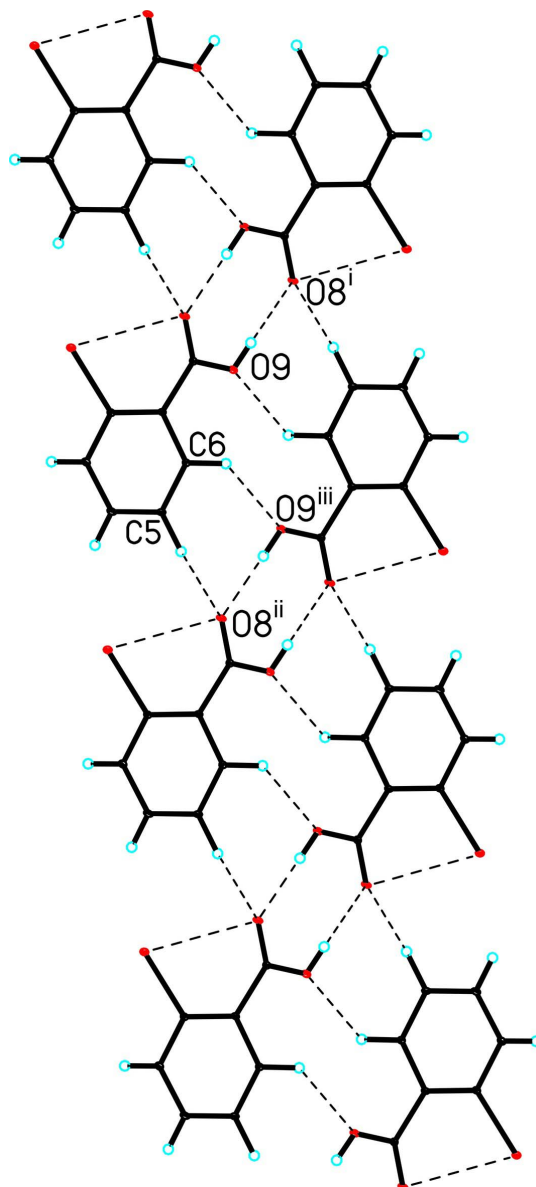
The 2-bromobenzoic acid was purchased from Sigma Aldrich and used without further purification. The single crystals suitable for X-ray investigations were grown by means of slow evaporation of a mixture of ethanol and water (1:1; v:v) solution (m.p. 422.6).

S3. Refinement

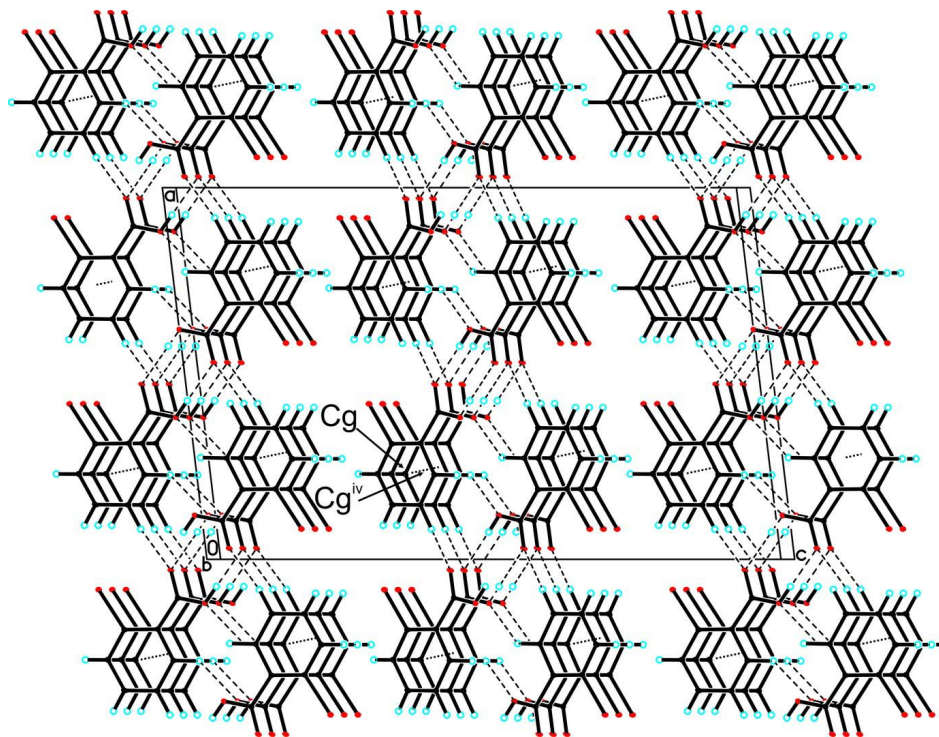
The OH H-atom was located in a difference Fourier map and refined with a distance restraint: O–H = 0.82(2) Å. The C-bound H atoms were positioned geometrically and constrained to ride on their parent atoms: C–H = 0.93 Å with $U_{iso}(H) = 1.2U_{eq}(C)$.

**Figure 1**

The molecular structure of the title molecule, with atom labeling. Displacement ellipsoids are drawn at the 25% probability level. The short intramolecular Br \cdots O contact [3.009 (3) Å] is shown as a dashed line.

**Figure 2**

A partial view perpendicular to the *ac* plane of the crystal packing of the title compound. The O–H···O and C–H···O hydrogen bonds are represented by dashed lines [see Table 1 for details; symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1/2, y+1/2, z$; (iii) $-x+1/2, -y+3/2, -z+1$].

**Figure 3**

A view along the b axis of the crystal packing of the title compound. The π - π interactions are represented by dashed lines [symmetry code: (iv) $x, y+1, z$].

2-Bromobenzoic acid

Crystal data

$C_7H_5BrO_2$

$M_r = 201.01$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 14.7955\ (4)\ \text{\AA}$

$b = 3.99062\ (15)\ \text{\AA}$

$c = 22.9240\ (8)\ \text{\AA}$

$\beta = 96.906\ (3)^\circ$

$V = 1343.69\ (8)\ \text{\AA}^3$

$Z = 8$

$F(000) = 784$

$D_x = 1.987\ \text{Mg m}^{-3}$

Melting point: 422.6 K

Cu $K\alpha$ radiation, $\lambda = 1.54184\ \text{\AA}$

Cell parameters from 10883 reflections

$\theta = 3.9\text{--}67.3^\circ$

$\mu = 7.76\ \text{mm}^{-1}$

$T = 120\ \text{K}$

Block, white

$0.55 \times 0.35 \times 0.28\ \text{mm}$

Data collection

Oxford Diffraction Gemini R Ultra Ruby CCD diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $10.4002\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.722$, $T_{\max} = 0.991$

10883 measured reflections

1201 independent reflections

1172 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.067$

$\theta_{\max} = 67.3^\circ$, $\theta_{\min} = 3.9^\circ$

$h = -17 \rightarrow 17$

$k = -4 \rightarrow 4$

$l = -27 \rightarrow 27$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.035$ $wR(F^2) = 0.091$ $S = 1.18$

1201 reflections

95 parameters

1 restraint

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 4.6943P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.82 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$ *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. 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3119 (2)	0.3168 (9)	0.40413 (14)	0.0222 (7)
C2	0.3109 (2)	0.1534 (9)	0.34999 (14)	0.0230 (7)
C3	0.2293 (2)	0.0629 (9)	0.31713 (16)	0.0268 (8)
H3	0.2296	−0.0469	0.2814	0.032*
C4	0.1473 (2)	0.1375 (10)	0.33802 (16)	0.0297 (8)
H4	0.0927	0.0740	0.3164	0.036*
C5	0.1463 (2)	0.3045 (10)	0.39040 (15)	0.0277 (8)
H5	0.0912	0.3580	0.4038	0.033*
C6	0.2278 (2)	0.3931 (10)	0.42318 (15)	0.0265 (8)
H6	0.2266	0.5057	0.4586	0.032*
C7	0.3963 (2)	0.4020 (9)	0.44374 (15)	0.0243 (7)
O8	0.47061 (15)	0.2776 (8)	0.44031 (11)	0.0337 (6)
O9	0.38191 (16)	0.6217 (8)	0.48460 (11)	0.0315 (6)
H9	0.427 (2)	0.659 (12)	0.5071 (15)	0.033 (11)*
Br10	0.41826 (2)	0.04521 (11)	0.315985 (15)	0.03005 (19)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0158 (15)	0.0262 (18)	0.0240 (16)	0.0011 (13)	−0.0009 (12)	0.0025 (14)
C2	0.0188 (15)	0.0263 (18)	0.0232 (16)	0.0026 (13)	−0.0001 (12)	0.0022 (14)
C3	0.0231 (18)	0.031 (2)	0.0248 (17)	0.0008 (14)	−0.0028 (14)	−0.0001 (14)
C4	0.0181 (16)	0.036 (2)	0.0326 (18)	−0.0030 (15)	−0.0053 (13)	0.0049 (16)
C5	0.0154 (15)	0.036 (2)	0.0308 (17)	0.0016 (14)	0.0007 (13)	0.0050 (16)

C6	0.0192 (17)	0.037 (2)	0.0225 (16)	0.0034 (15)	0.0012 (13)	0.0033 (15)
C7	0.0209 (17)	0.0309 (19)	0.0207 (16)	−0.0011 (14)	0.0009 (13)	0.0034 (14)
O8	0.0147 (12)	0.0520 (18)	0.0326 (13)	0.0064 (11)	−0.0052 (9)	−0.0121 (12)
O9	0.0183 (12)	0.0472 (17)	0.0277 (13)	0.0030 (12)	−0.0035 (10)	−0.0109 (12)
Br10	0.0190 (2)	0.0420 (3)	0.0286 (3)	0.00389 (14)	0.00077 (16)	−0.00733 (15)

Geometric parameters (Å, °)

C1—C2	1.400 (5)	C4—H4	0.9300
C1—C6	1.401 (5)	C5—C6	1.388 (5)
C1—C7	1.492 (5)	C5—H5	0.9300
C2—C3	1.392 (5)	C6—H6	0.9300
C2—Br10	1.901 (3)	C7—O8	1.217 (4)
C3—C4	1.389 (5)	C7—O9	1.319 (5)
C3—H3	0.9300	O9—H9	0.803 (19)
C4—C5	1.375 (5)		
C2—C1—C6	117.5 (3)	C3—C4—H4	119.8
C2—C1—C7	124.4 (3)	C4—C5—C6	119.8 (3)
C6—C1—C7	118.1 (3)	C4—C5—H5	120.1
C3—C2—C1	121.1 (3)	C6—C5—H5	120.1
C3—C2—Br10	115.6 (3)	C5—C6—C1	121.5 (3)
C1—C2—Br10	123.3 (2)	C5—C6—H6	119.2
C4—C3—C2	119.7 (3)	C1—C6—H6	119.2
C4—C3—H3	120.2	O8—C7—O9	122.8 (3)
C2—C3—H3	120.2	O8—C7—C1	124.3 (3)
C5—C4—C3	120.4 (3)	O9—C7—C1	112.9 (3)
C5—C4—H4	119.8	C7—O9—H9	113 (3)
C6—C1—C2—C3	−1.6 (5)	C4—C5—C6—C1	0.1 (6)
C7—C1—C2—C3	175.8 (3)	C2—C1—C6—C5	1.3 (5)
C6—C1—C2—Br10	177.6 (3)	C7—C1—C6—C5	−176.3 (3)
C7—C1—C2—Br10	−4.9 (5)	C2—C1—C7—O8	−17.1 (6)
C1—C2—C3—C4	0.5 (6)	C6—C1—C7—O8	160.4 (4)
Br10—C2—C3—C4	−178.8 (3)	C2—C1—C7—O9	164.8 (3)
C2—C3—C4—C5	1.0 (6)	C6—C1—C7—O9	−17.7 (5)
C3—C4—C5—C6	−1.3 (6)		

Hydrogen-bond geometry (Å, °)

<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 O8 ⁱ	0.81 (3)	1.84 (3)	2.643 (3)	177 (5)
C5—H5 \cdots O8 ⁱⁱ	0.93	2.65	3.514 (3)	153
C6—H6 \cdots O9 ⁱⁱⁱ	0.93	2.64	3.417 (3)	141

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