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Crystal and molecular structure of 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate)

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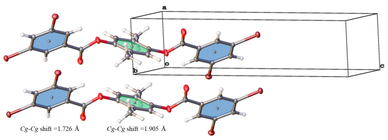
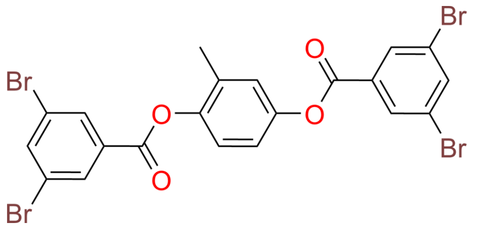
The aryl diester compound, 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate), $C_{21}H_{12}Br_4O_4$, was synthesized by esterification of methyl hydroquinone with 3,5-dibromobenzoic acid. A crystalline sample was obtained by cooling a sample of the melt (m.p. = 502 K/DSC) to room temperature. The molecular structure consists of a central benzene ring with *anti*-3,5-dibromobenzoate groups symmetrically attached at the 1 and 4 positions and a methyl group attached at the 2 position of the central ring. In the crystal structure (space group $P\overline{1}$), molecules of the title aryl diester are located on inversion centers imposing disorder of the methyl group and H atom across the central benzene ring. The crystal structure is consolidated by a network of C—H$\cdots$Br hydrogen bonds in addition to weaker and offset π–π interactions involving the central benzene rings as well as the rings of the attached 3,5-dibromobenzoate groups.



1. Chemical context

Inverse vulcanization (InV) polymerization is an important solvent-less process for the synthesis of elastomeric materials from elemental sulfur and thermally stable organic co-monomers, both of which are often found as waste products of the chemical industry (Chung *et al.*, 2013; Karunarathna *et al.*, 2020). Recently, aryl halide co-monomers, including the title aryl diester, were investigated for un-catalyzed InV chemistry, and shown to react *via* a radical aryl sulfur polymerization (RASP) mechanism at temperatures > 493 K (Karunarathna *et al.*, 2020; Thiounn *et al.*, 2020). An advantage of the title aryl diester as a co-monomer for InV reactions is reflected by its conjugated aromaticity and attendant exceptional thermal stability (T_d = 563 K/TGA). Further, a more recent study (Lauer *et al.*, 2024) demonstrated that successful InV reactions could be carried out at temperatures as low as 463 K, using the title aryl diester co-monomer in conjunction with a dithiocarbamate (DTC) catalyst. The catalyzed reaction data were significant because they provided evidence for the possible involvement of anionic sulfur intermediates and expanded the possible scope of the InV reactions to more thermally sensitive co-monomers (Lauer *et al.*, 2024).



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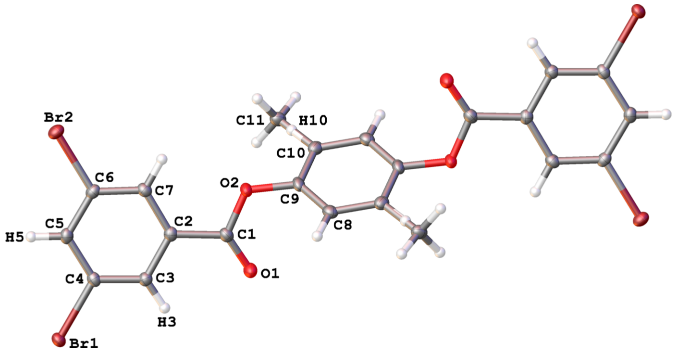

Figure 1
Molecular structure of 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate), depicting the *anti*-position of the 3,5-dibromobenzoate end groups. The methyl group is shown in both positions, disordered across the central benzene ring in space group $P\overline{1}$. Displacement ellipsoids are shown at the 50% probability level; non-labeled atoms are generated by symmetry operation $1 - x, 2 - y, -z$.

2. Structural commentary

The aryl diester compound, 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate), crystallizes in the space group $P\overline{1}$ with one half molecule per asymmetric unit. Molecules lie on crystallographic inversion centers that impose disorder of the methyl group (C11H$_3$) and an H atom (H10) across the central benzene ring (Fig. 1). The two 3,5-dibromobenzoate end groups are attached to the central benzene ring in an *anti* fashion, with the planes of the 3,5-dibromobenzoate rings inclined at a dihedral angle of 54.53 (9)° with respect to the plane of the central benzene ring (Fig. 1). The ester groups are nearly co-planar with their conjugated 3,5-dibromophenyl rings, making a dihedral angle of only 8.21 (11)°, but inclined at a dihedral angle of 62.58 (10)° with respect to the central benzene ring (Fig. 1). This compares well to the structure of the related 1,4-phenylene dibenzoate, with the end group rings and ester groups tipped with respect to the central 1,4-benzene ring at dihedral angles of 55.29 (8) and 60.31 (9)°, respectively, and the ester groups with their conjugated end group rings tipped at only a small dihedral angle of 5.94 (8)° (Ganaie *et al.*, 2016).

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
C5—H5$\cdots$Br1$^{\rm i}$	0.95 (1)	3.12 (2)	3.893 (2)	139 (2)
C3—H3$\cdots$Br1$^{\rm ii}$	0.95 (1)	3.02 (1)	3.956 (2)	172 (2)

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

3. Supramolecular features

Intermolecular contacts of the title aryl diester involve hydrogen-bonding and weaker ring π–π interactions. Complementary end-to-end hydrogen bonding C5—H5$\cdots$Br1 [3.12 (2) Å, Table 1] between the 3,5-dibromophenyl groups forms chains of aryl diester molecules that run parallel to [011] (Fig. 2). The planes between the 3,5-dibromophenyl rings on adjacent molecules in the chains are offset, giving a stair-step pattern of aryl diester molecular links in the chains (Fig. 2). Complementary C3—H3$\cdots$Br1 interactions [3.02 (1) Å, Table 1] extend along [100] and result in shorter side-to-side hydrogen bonding that cross-links the end-to-end chains forming a tri-periodic network (Fig. 2). This arrangement places the Br2 and H7 atoms in positions that point towards the central benzene rings of adjacent molecules and that are free of C—H$\cdots$Br hydrogen-bonding interactions (Fig. 2). The network of C—H$\cdots$Br hydrogen bonds between Br1 and H3/H5 leaves a side-to-side packing of molecules along [100] with all rings on adjacent molecules oriented parallel (Fig. 3). Weak π–π interactions are evident between these parallel rings with centroid-to-centroid ($Cg\cdots Cg$) distances of 3.8875 (1) Å, but with their centroids shifted by 1.726 Å (3,5-dibromophenyl rings) and 1.905 Å (central benzene rings). In the crystal structure of the related 1,4-phenylene dibenzoate, three C—H$\cdots\pi$ interactions and one displaced π–π interaction between the peripheral rings [$Cg\cdots Cg$ distance = 3.9590 (10) Å] were noted (Ganaie *et al.*, 2016). The presence of Br and the attendant network of stronger C—H$\cdots$Br hydrogen bonds in the title aryl diester structure precludes

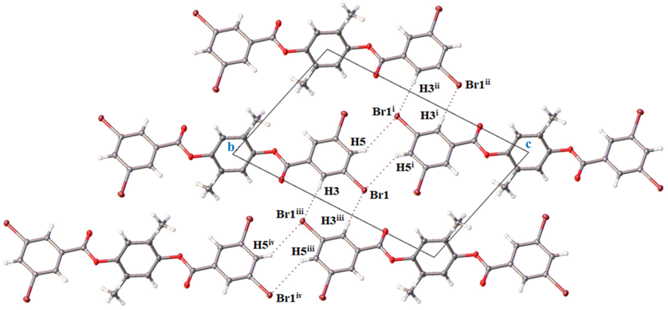

Figure 2
Hydrogen-bonding motif for 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate), depicting complementary end-to-end [C5—H5$\cdots$Br1, 3.12 (2) Å] and side-to-side [C3—H3$\cdots$Br1, 3.02 (1) Å] C—H$\cdots$Br interactions, in a view down [100]. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-1 + x, -1 + y, z$; (iii) $2 - x, 2 - y, 1 - z$; (iv) $1 + x, 1 + y, z$.]

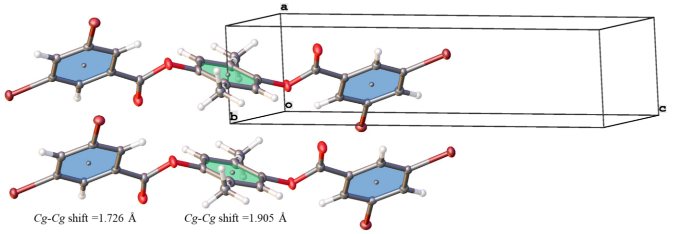

Figure 3
Unit-cell overlay and depiction of the π–π interactions along [100] in the crystal structure of 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate), giving parallel but slipped central 1,4-benzene rings (shaded green) and end group 3,5-dibromophenyl rings (shaded blue). The centroids of the central benzene rings lie on inversion centers, giving equal $Cg\cdots Cg$ distances that correspond to the a lattice parameter [3.8875 (1) Å] with ring centroids shifted by 1.905 Å (central benzene rings) and 1.726 Å (3,5-dibromophenyl rings). Displacement ellipsoids are shown at the 50% probability level.

C—H···π interactions, resulting in only displaced and weak π–π interactions between parallel rings.

4. Database survey

Five structurally related aryl ester compounds were found in the Cambridge Structure Database [CSD; web interface (CCDC 2017); Groom *et al.*, 2016]. Of the three aryl diesters reported, two contain a central 1,4-benzene ring bound at both positions to either an unsubstituted benzoate group [CSD entry NADMUD (deposition number 1407716); Ganaie *et al.*, 2016] or to a *p*-tolyl benzoate group [CSD entry TAJDEN (deposition number 1265699); Ciajolo *et al.*, 1991], and one contains a central 9,10-anthrahydroquinone ring bound at both positions to an unsubstituted benzoate group [CSD entry ANTHQB (deposition number 1103109); Iball & Mackay, 1962]. The remaining two hits are the monoesters, 4-bromophenyl benzoate [CSD entry QIXNER (deposition number 684565); Gowda *et al.*, 2008] and 4-methoxyphenyl benzoate [CSD entry TIGVUB (deposition number 657773); Gowda *et al.*, 2007]. Hydrogen bonding was not observed in the crystal structure of 4-bromophenyl benzoate (Gowda *et al.*, 2008).

5. Synthesis and crystallization

The synthesis of 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate) was carried out using a modified Steglich esterification procedure and was previously published (Lauer *et al.*, 2024; Jordan *et al.*, 2021). M.p. = 502 K/DSC, T_d = 563 K/TGA). A crystalline sample was obtained by melting a sample of a white powder of 2-methyl-1,4-phenylene bis(3,5-dibromobenzoate) in a glass vial on a hot plate. The melt was allowed to cool to room temperature, forming a crystalline solid. Crystals suitable for single crystal X-ray diffraction were obtained by cutting into the solidified crystalline melt sample.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms, except H3, H5 and H10, were placed using a riding model with their positions constrained relative to their parent C atom using the appropriate HFIX command in *SHELXL* (Sheldrick, 2015*b*). Hydrogen atoms involved in C—H···Br hydrogen-bonding, H3 and H5, as well as H10 were placed from the electron-density map, and their C—H distances restrained (DFIX, C—H range 0.94–0.95 Å) at 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. Electron density corresponding to the disordered methyl group (C11) and H atom (H10) positions was obvious in the electron-density map. The occupancies of disordered atoms, H10 and C11, were set to 0.5, and H atoms attached to C11 (H11*A*, H11*B*, and H11*C*) were placed using a riding model (HFIX 137).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{21}H_{12}Br_4O_4$
M_r	647.95
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, *b*, *c* (Å)	3.8875 (1), 9.3118 (2), 14.7772 (3)
α, β, γ (°)	104.228 (2), 93.211 (2), 98.219 (2)
V (Å^3)	510.87 (2)
Z	1
Radiation type	Cu *K*α
μ (mm^{-1})	9.85
Crystal size (mm)	0.13 × 0.06 × 0.01
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix3000
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2024)
T_{min}, T_{max}	0.543, 0.998
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9500, 1892, 1848
R_{int}	0.022
(sin θ/λ)$_{max}$ (Å^{-1})	0.605
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.048, 1.11
No. of reflections	1892
No. of parameters	147
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.49

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

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Computing details

2-Methyl-1,4-phenylene bis(3,5-dibromobenzoate)

Crystal data

$C_{21}H_{12}Br_4O_4$
$M_r = 647.95$
Triclinic, $P\overline{1}$
$a = 3.8875$ (1) Å
$b = 9.3118$ (2) Å
$c = 14.7772$ (3) Å
$\alpha = 104.228$ (2)°
$\beta = 93.211$ (2)°
$\gamma = 98.219$ (2)°
$V = 510.87$ (2) Å^3
$Z = 1$
$F(000) = 310$
$D_x = 2.106$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 8434 reflections
$\theta = 3.1$–68.8°
$\mu = 9.85$ mm^{-1}
$T = 100$ K
Plate, clear colourless
0.13 × 0.06 × 0.01 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix3000 diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Cu) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2024)
$T_{\min} = 0.543$, $T_{\max} = 0.998$
9500 measured reflections
1892 independent reflections
1848 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.022$
$\theta_{\max} = 68.9$°, $\theta_{\min} = 3.1$°
$h = -4 \rightarrow 4$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.048$
$S = 1.11$
1892 reflections
147 parameters
3 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 0.7349P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.49$ e Å^{-3}
Extinction correction: SHELXL (Sheldrick, 2015*b*), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00125 (19)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
Br1	0.70739 (6)	0.79521 (3)	0.55753 (2)	0.01735 (10)	
Br2	−0.10300 (6)	0.36527 (3)	0.25588 (2)	0.01878 (10)	
O1	0.7673 (5)	1.00485 (19)	0.24435 (12)	0.0222 (4)	
O2	0.3733 (4)	0.84273 (18)	0.13414 (11)	0.0195 (4)	
C1	0.5529 (6)	0.8933 (3)	0.22059 (16)	0.0171 (5)	
C2	0.4527 (6)	0.7893 (3)	0.28060 (16)	0.0154 (5)	
C3	0.5910 (6)	0.8343 (3)	0.37435 (16)	0.0152 (5)	
C4	0.5110 (6)	0.7388 (3)	0.43104 (16)	0.0151 (4)	
C5	0.3006 (6)	0.6000 (3)	0.39750 (17)	0.0165 (5)	
C6	0.1688 (6)	0.5579 (3)	0.30378 (17)	0.0154 (5)	
C7	0.2403 (6)	0.6506 (3)	0.24487 (16)	0.0156 (5)	
H7	0.146265	0.620309	0.181107	0.019*	
C8	0.3712 (6)	1.0708 (3)	0.08300 (17)	0.0185 (5)	
H8	0.282846	1.117184	0.139659	0.022*	
C9	0.4468 (6)	0.9264 (3)	0.06787 (16)	0.0176 (5)	
C10	0.5725 (6)	0.8531 (3)	−0.01344 (17)	0.0186 (5)	
H10	0.611 (18)	0.754 (3)	−0.019 (5)	0.022*	0.5
C11	0.6348 (14)	0.6943 (5)	−0.0242 (4)	0.0197 (10)	0.5
H11A	0.743277	0.660759	−0.082337	0.030*	0.5
H11B	0.411636	0.628836	−0.026516	0.030*	0.5
H11C	0.789947	0.689846	0.029312	0.030*	0.5
H5	0.249 (7)	0.535 (3)	0.4374 (17)	0.024*	
H3	0.742 (6)	0.9274 (18)	0.3950 (19)	0.024*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01993 (15)	0.01909 (14)	0.01311 (14)	0.00223 (10)	−0.00038 (9)	0.00523 (9)
Br2	0.01717 (15)	0.01470 (14)	0.02246 (15)	−0.00116 (9)	−0.00003 (10)	0.00357 (10)
O1	0.0260 (9)	0.0214 (9)	0.0175 (8)	−0.0055 (7)	−0.0024 (7)	0.0080 (7)
O2	0.0247 (9)	0.0187 (8)	0.0141 (8)	−0.0039 (7)	−0.0037 (7)	0.0077 (7)
C1	0.0191 (12)	0.0186 (12)	0.0141 (11)	0.0042 (10)	0.0014 (9)	0.0044 (9)
C2	0.0147 (11)	0.0160 (11)	0.0165 (11)	0.0039 (9)	0.0032 (9)	0.0051 (9)
C3	0.0148 (11)	0.0158 (11)	0.0153 (11)	0.0026 (9)	0.0019 (9)	0.0041 (9)
C4	0.0136 (11)	0.0193 (11)	0.0141 (11)	0.0045 (9)	0.0028 (9)	0.0058 (9)
C5	0.0172 (12)	0.0165 (11)	0.0180 (11)	0.0049 (9)	0.0037 (9)	0.0068 (9)
C6	0.0127 (11)	0.0138 (11)	0.0197 (12)	0.0018 (9)	0.0030 (9)	0.0041 (9)
C7	0.0141 (11)	0.0188 (11)	0.0142 (11)	0.0036 (9)	0.0006 (9)	0.0042 (9)
C8	0.0187 (12)	0.0204 (12)	0.0145 (11)	0.0005 (9)	−0.0020 (9)	0.0033 (9)

C9	0.0176 (12)	0.0209 (12)	0.0143 (11)	−0.0016 (9)	−0.0031 (9)	0.0084 (9)
C10	0.0192 (12)	0.0163 (11)	0.0189 (12)	0.0007 (9)	−0.0046 (9)	0.0047 (9)
C11	0.023 (3)	0.018 (2)	0.017 (2)	0.005 (2)	−0.0006 (19)	0.002 (2)

Geometric parameters (Å, º)

Br1—C4	1.896 (2)	C6—C7	1.381 (3)
Br2—C6	1.893 (2)	C7—H7	0.9500
O1—C1	1.199 (3)	C8—H8	0.9500
O2—C1	1.361 (3)	C8—C9	1.385 (3)
O2—C9	1.411 (3)	C8—C10$^{\text{i}}$	1.395 (3)
C1—C2	1.493 (3)	C9—C10	1.381 (3)
C2—C3	1.397 (3)	C10—H10	0.94 (2)
C2—C7	1.393 (3)	C10—C11	1.504 (5)
C3—C4	1.380 (3)	C11—H10	0.56 (2)
C3—H3	0.945 (10)	C11—H11A	0.9800
C4—C5	1.387 (3)	C11—H11B	0.9800
C5—C6	1.389 (3)	C11—H11C	0.9800
C5—H5	0.951 (10)		

C1—O2—C9	117.81 (18)	C9—C8—H8	120.6
O1—C1—O2	124.3 (2)	C9—C8—C10$^{\text{i}}$	118.7 (2)
O1—C1—C2	124.8 (2)	C10$^{\text{i}}$—C8—H8	120.6
O2—C1—C2	110.85 (19)	C8—C9—O2	120.2 (2)
C3—C2—C1	117.2 (2)	C10—C9—O2	116.5 (2)
C7—C2—C1	122.0 (2)	C10—C9—C8	123.1 (2)
C7—C2—C3	120.7 (2)	C8$^{\text{i}}$—C10—H10	124 (4)
C2—C3—H3	117.8 (18)	C8$^{\text{i}}$—C10—C11	122.9 (3)
C4—C3—C2	118.6 (2)	C9—C10—C8$^{\text{i}}$	118.2 (2)
C4—C3—H3	123.5 (18)	C9—C10—H10	118 (4)
C3—C4—Br1	119.26 (18)	C9—C10—C11	118.9 (3)
C3—C4—C5	122.0 (2)	C11—C10—H10	1 (4)
C5—C4—Br1	118.69 (17)	C10—C11—H10	1 (8)
C4—C5—C6	118.0 (2)	C10—C11—H11A	109.5
C4—C5—H5	120.9 (18)	C10—C11—H11B	109.5
C6—C5—H5	121.0 (18)	C10—C11—H11C	109.5
C5—C6—Br2	118.44 (17)	H10—C11—H11A	110.7
C7—C6—Br2	119.77 (18)	H10—C11—H11B	109.0
C7—C6—C5	121.8 (2)	H10—C11—H11C	108.8
C2—C7—H7	120.6	H11A—C11—H11B	109.5
C6—C7—C2	118.8 (2)	H11A—C11—H11C	109.5
C6—C7—H7	120.6	H11B—C11—H11C	109.5

Br1—C4—C5—C6	−177.72 (16)	C2—C3—C4—C5	0.5 (3)
Br2—C6—C7—C2	−177.37 (17)	C3—C2—C7—C6	−0.1 (3)
O1—C1—C2—C3	7.4 (3)	C3—C4—C5—C6	0.0 (3)
O1—C1—C2—C7	−170.4 (2)	C4—C5—C6—Br2	177.45 (17)
O2—C1—C2—C3	−173.95 (19)	C4—C5—C6—C7	−0.5 (3)

O2—C1—C2—C7	8.2 (3)	C5—C6—C7—C2	0.5 (3)
O2—C9—C10—C8^{i}	176.3 (2)	C7—C2—C3—C4	−0.4 (3)
O2—C9—C10—C11	−2.3 (4)	C8—C9—C10—C8^{i}	0.6 (4)
C1—O2—C9—C8	−65.1 (3)	C8—C9—C10—C11	−178.0 (3)
C1—O2—C9—C10	119.1 (2)	C9—O2—C1—O1	0.6 (3)
C1—C2—C3—C4	−178.3 (2)	C9—O2—C1—C2	−178.03 (19)
C1—C2—C7—C6	177.7 (2)	C10^{i}—C8—C9—O2	−176.1 (2)
C2—C3—C4—Br1	178.15 (16)	C10^{i}—C8—C9—C10	−0.6 (4)

Symmetry code: (i) −*x*+1, −*y*+2, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···Br1^{ii}	0.95 (1)	3.12 (2)	3.893 (2)	139 (2)
C3—H3···Br1^{iii}	0.95 (1)	3.02 (1)	3.956 (2)	172 (2)

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+2, −*y*+2, −*z*+1.