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Crystallographic and spectroscopic characterization of 2-bromo-*p*-tolualdehyde

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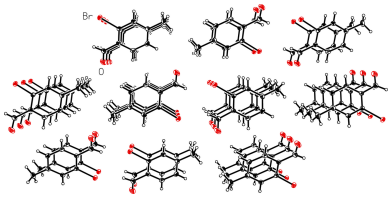
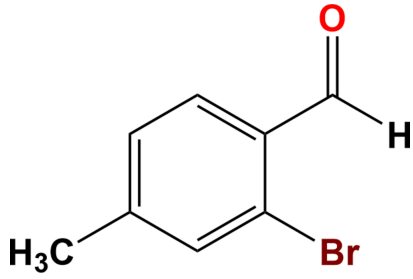


The title compound (systematic name: 2-bromo-4-methylbenzaldehyde), C_8H_7BrO, is a halogenated benzaldehyde derivative. The molecule contains an aldehyde moiety, *ortho* bromine, and *para* methyl group. Packing *via* van der Waals forces, the molecules are arranged with both offset face-to-face and an edge-to-face π-stacking interaction revealed by Hirshfeld surface characterization.

1. Chemical context

Benzaldehydes are a class of molecules commonly used as key ingredients in many natural fruit flavorings (Jabba *et al.*, 2020; Kosmider *et al.*, 2016). Benzaldehydes exhibit a wide range of properties; some of their derivatives have been investigated as potential carcinogens, particularly as flavor ingredients commonly found in e-cigarettes (Jabba *et al.*, 2020). Conversely, others have been researched for their anticancer properties (Saitoh & Saya, 2016; Takeuchi *et al.*, 1978). The title compound, 2-bromo-4-methylbenzaldehyde (I), more widely known as 2-bromo-*p*-tolualdehyde, is a benzaldehyde derivative with a bromine and methyl group. This compound may be synthesized by converting 2-bromo-4-methylaniline to the aldehyde *via* the benzenediazonium chloride (Jolad & Rajagopalan, 1966). The title compound has seen recent applications in the synthesis of non-linear optical materials (Rahman *et al.*, 2025), as the starting material in the preparation of a protein kinase inhibitor (Defois *et al.*, 2024), and in ruthenium-catalyzed aldehyde annulation to prepare indenes (Ma *et al.*, 2025).



2. Structural commentary

The molecular structure of the title compound (Fig. 1) shows the aldehyde group located at the *para* position relative to the methyl group on the aromatic ring. The aldehyde is oriented with the oxygen atom rotated opposite an *ortho* bromine atom to avoid electronic repulsion, resulting in an intramolecular Br···H1*A* interaction at 2.7895 (14) Å and an angle between

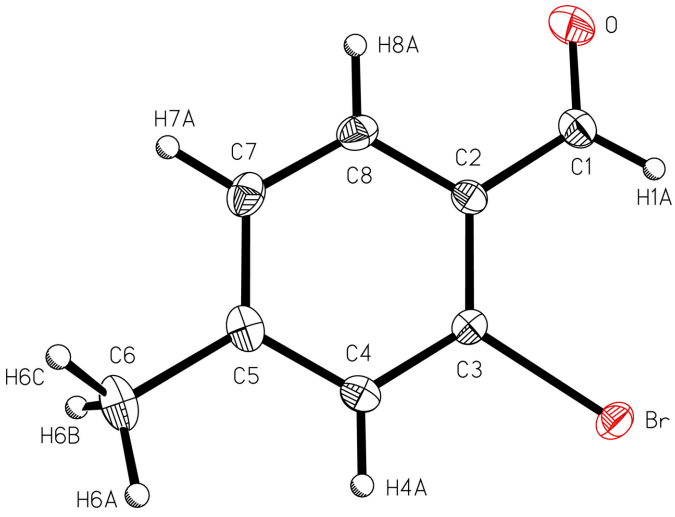


Figure 1
A view of 2-bromo-*p*-tolualdehyde (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

the aldehyde group and the plane of the aromatic ring of 10.60 (13)°.

3. Supramolecular features

The title compound packs together in the solid state *via* van der Waals forces (Fig. 2). The shortest distance between bromine atoms in adjacent molecules is 3.9641 (3) Å, which exceeds the sum of the van der Waals radii of bromine (3.70 Å; (Bondi, 1964). In an offset head-to-tail stacking motif running parallel to the crystallographic *b*-axis, the molecules of 2-bromo-*p*-tolualdehyde are arranged with the polar aldehyde and bromine groups in proximity to each other with a Br···$H_{aldehyde}$ interaction, Br···H1*A*, with H–acceptor distance of 3.0651 (14) Å, longer than the observed intramolecular Br···H interaction. The stacks further pack in an offset fashion to maximize hydrophobic-like interactions of the non-polar tolyl groups. Both face-to-face and edge-to-face π-stacking geometrical arrangement of the aromatic rings are apparent, although both are highly offset (Fig. 3). The face-to-face π-stacking arrangement is characterized by a ring centroid-to-centroid distance of 3.9641 (3) Å, centroid-to-

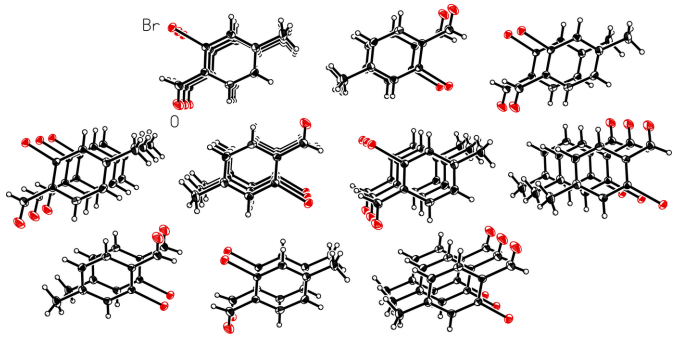


Figure 2
A view of the molecular packing in 2-bromo-*p*-tolualdehyde (I). Displacement ellipsoids are shown at the 50% probability level.

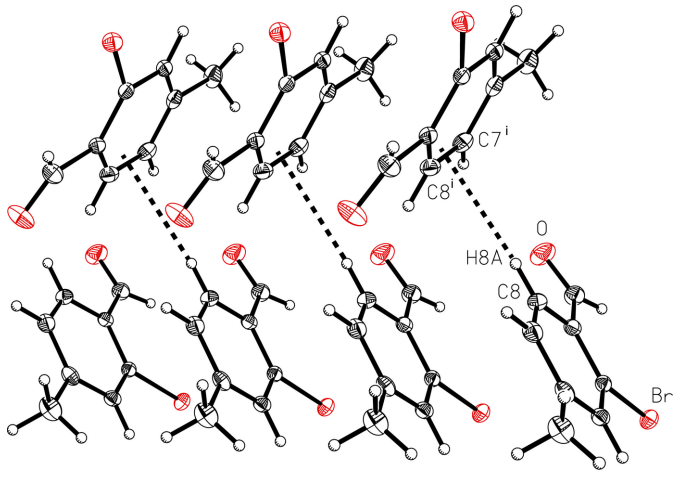


Figure 3
A view of the face-to-face and edge-to-face (C8—H8*A*···π^{i} shown *via* dashed lines) π-stacking geometrical arrangement in 2-bromo-*p*-tolualdehyde (I). Displacement ellipsoids are shown at the 50% probability level. Symmetry code: (i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$.

plane distance of 3.410 (1) Å, and ring-offset slippage parameter of 2.021 (2) Å. The edge-to-face π-stacking arrangement is revealed by the Hirshfeld surface calculated with *CrystalExplorer21* (Spackman *et al.*, 2021), mapped over d_{norm} in the range −0.0622 to 1.0811 a.u. (Fig. 4). The brighter red spot on the right of the surface indicates the offset edge-to-face C—H···π interaction of the C8—H8*A* proton directed towards the C7–C8 edge of the molecule within the surface, with an H8*A*···C7–C8 bond centroid distance of 2.770 Å. The red spot at the bottom of the surface represents the equivalent interaction originating from the molecule within the surface. The directionality of the C—H···π interaction is confirmed when the surface is mapped over d_e in the range 1.0656 to 2.3698 a.u. and d_i in the range 1.0646 to 2.3113 a.u. (Fig. 5), with a bright-red spot on the right of the surface when mapped over d_e indicating a short contact from the surface to the atom outside, and conversely a bright-red spot on the bottom of the surface when mapped over d_i indicating a short contact from

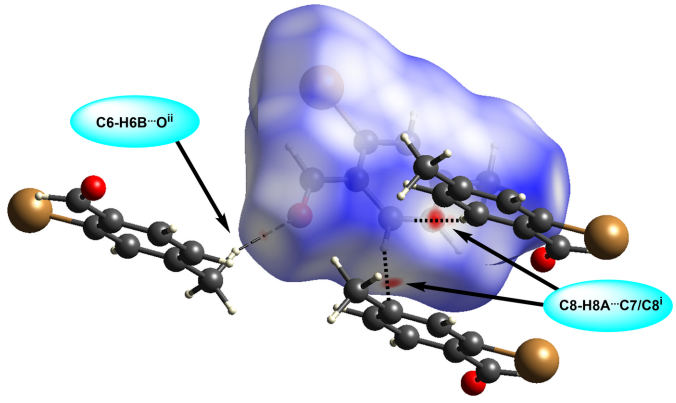


Figure 4
Hirshfeld surface of 2-bromo-*p*-tolualdehyde (I) mapped over d_{norm} showing *via* dashed lines the C8—H8*A*···π^{i} and C6—H6*B*···O^{ii} interactions. Symmetry codes: (i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

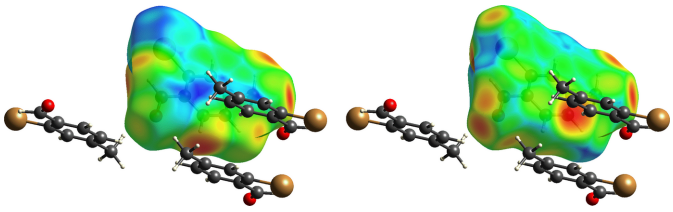


Figure 5
Hirshfeld surface of 2-bromo-*p*-tolualdehyde (I) mapped over d_i (left) and d_e (right) showing the C8—H8*A*···π^i interaction.

the surface to the atom inside. The less intense red spot on the left of the d_{norm} surface indicates a weak C—H···O interaction, C6—H6*B*···O, with an H–acceptor distance of 2.655 (10) Å. The two-dimensional fingerprint plots (Fig. 6) show that no single interaction dominates, the most important interatomic contacts, summing to 91.8%, being (*b*) H···H (34.6%), (*c*) Br···H/H···Br (20.4%), (*d*) O···H/H···O (17.1%), (*e*) C···H/H···C (13.0%) and (*f*) C···C (6.7%) contacts. Additionally, Br contacts with C, Br and O together contribute 5.7%, and with the contribution of 2.4% O···C contacts, the total reaches 99.9%.

4. Database survey

The Cambridge Structural Database (version 6.00, April 2025; Groom *et al.*, 2016) contains related aromatic bromobenzaldehydes. 4-Bromobenzaldehyde (CSD Refcode YICFEV01; Ndima *et al.*, 2021) crystallizes with two molecules in the asymmetric unit and features C—Br bond lengths of 1.891 and 1.895 Å, similar to the title compound at 1.9040 (13) Å, whereas the smaller angle between the aldehyde group and the plane of the aromatic rings of 0.85 and 2.07° in the related structure emphasizes in the impact of the *ortho* bromine regiochemistry in the title compound, which twists the aldehyde 10.60 (13)° out of the plane of the aromatic ring. Similarly to the title compound, related structure 1-bromo-2-naphthaldehyde (Refcode FADWIQ; Koppenhoefer & Bats, 1986) also has the aldehyde oriented with the oxygen atom rotated opposite the *ortho* bromine atom resulting in an intramolecular Br···H interaction at 2.653 Å, although the aldehyde carbonyl appears to be fully conjugated to the naphthyl, displaying an angle between the aldehyde group and the plane of the aromatic ring of 0°.

Table 1
Experimental details.

Crystal data	
Chemical formula	C_8H_7BrO
M_r	199.05
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	125
a, b, c (Å)	11.4432 (8), 3.9641 (3), 16.8225 (11)
β (°)	102.838 (1)
V (Å^3)	744.03 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.45
Crystal size (mm)	0.38 × 0.33 × 0.25
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.26, 0.34
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17211, 2269, 2159
R_{int}	0.023
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.017, 0.045, 1.08
No. of reflections	2269
No. of parameters	93
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.34

Computer programs: *Bruker Instrument Service*, *APEX3* and *SAINT* (Bruker, 2013), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2017/1* (Sheldrick, 2015*b*), *SHELXTL2014* (Sheldrick, 2008), *OLEX2* (Dolomanov *et al.*, 2009), and *Mercury* (Macrae *et al.*, 2020).

5. Synthesis and crystallization

2-Bromo-*p*-tolualdehyde (technical grade) was purchased from Aldrich Chemical Company, USA, and was used as received.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and refined using a riding model with: C—H = 0.95, 0.95 and 0.98 Å and U_{iso}(H) = 1.2, 1.2 and 1.5 × U_{eq}(C) of the aryl, aldehyde and methyl C-atoms, respectively.

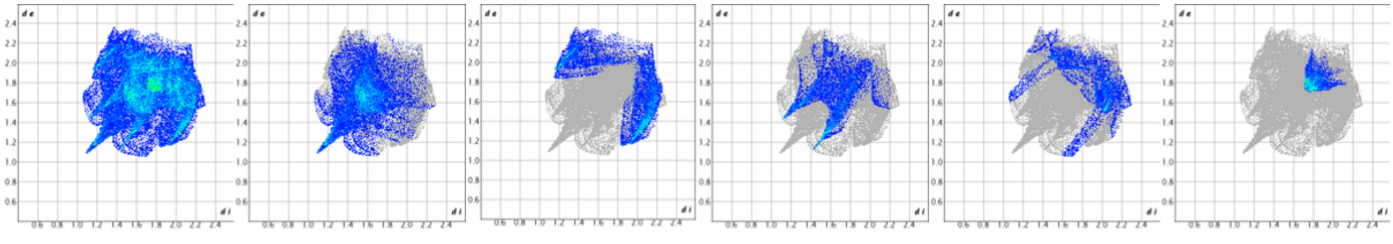


Figure 6
The (*a*) full two-dimensional fingerprint plot for 2-bromo-*p*-tolualdehyde (I) and individual fingerprint plots for (*b*) H···H (34.6%), (*c*) Br···H/H···Br (20.4%), (*d*) O···H/H···O (17.1%), (*e*) C···H/H···C (13.0%) and (*f*) C···C (6.7%) contacts.

7. Analytical Data

^{1}H NMR (Bruker Avance III HD 400 MHz, $CDCl_3$): δ 2.4 (*s*, 3H, CH_3), δ 7.23 (*dd*, 1H, C$_{aryl}H$, J_{ortho} = 7.8 Hz, J_{meta} = 0.8 Hz), δ 7.46 (*s*, 1H, C$_{aryl}H$), δ 7.82 (*d*, 1H, C$_{aryl}H$, J_{ortho} = 7.8 Hz), δ 10.32 (*s*, 1H, C*H*O). ^{13}C NMR (^{13}C{^{1}H}, 100.6 MHz, $CDCl_3$): δ 20.2 (*C*H$_3$), δ 127.0 (*C*$_{aryl}$), δ 128.9 (*C*$_{aryl}$H), δ 129.9 (*C*$_{aryl}$H), δ 131.2 (*C*$_{aryl}$), δ 134.1 (*C*$_{aryl}$H), δ 146.7 (*C*$_{aryl}$), δ 190.2 (*C*HO). IR (Thermo Nicolet iS50, ATR, cm^{-1}): 3029 (*w*, C$_{aryl}$H str), 2953 (*w*, C$_{alkyl}$H str), 2923 (*w*, C$_{alkyl}$H str), 2858 (*m*) and 2752 (*w*) (CHO Fermi doublet), 1683 (*s*, CO str), 1648 (*m*), 1598 (*s*), 1560 (*m*), 1499 (*w*), 1482 (*m*), 1445 (*m*), 1380 (*s*), 1292 (*w*), 1267 (*s*), 1207 (*s*), 1141 (*m*), 1038 (*s*), 998 (*m*), 873 (*m*), 864 (*s*), 818 (*s*), 780 (*s*), 693 (*s*), 672 (*m*), 611 (*s*), 532 (*m*), 440 (*s*), 434 (*s*). GC/MS (Hewlett-Packard MS 5975/GC 7890): *M*+ = 199 amu.

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Computing details

2-Bromo-4-methylbenzaldehyde

Crystal data

C_8H_7BrO
$M_r = 199.05$
Monoclinic, $P2_1/n$
$a = 11.4432$ (8) Å
$b = 3.9641$ (3) Å
$c = 16.8225$ (11) Å
$\beta = 102.838$ (1)°
$V = 744.03$ (9) Å^3
$Z = 4$
$F(000) = 392$
$D_x = 1.777$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9969 reflections
$\theta = 2.4$–30.5°
$\mu = 5.45$ mm^{-1}
$T = 125$ K
Plate, colourless
0.38 × 0.33 × 0.25 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed X-ray tube, Bruker APEX-II CCD
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.26$, $T_{max} = 0.34$
17211 measured reflections
2269 independent reflections
2159 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 30.5°$, $\theta_{min} = 2.0°$
$h = -16\rightarrow16$
$k = -5\rightarrow5$
$l = -23\rightarrow24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.045$
$S = 1.08$
2269 reflections
93 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2 + 0.4808P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL2017/1* (Sheldrick 2015b)
Extinction coefficient: 0.0085 (7)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.61962 (2)	0.86694 (3)	0.61166 (2)	0.01803 (5)
O	0.28890 (10)	0.2568 (3)	0.56866 (7)	0.0305 (2)
C1	0.37283 (12)	0.4513 (4)	0.58656 (8)	0.0204 (3)
H1A	0.40198	0.554074	0.543759	0.024*
C2	0.43181 (11)	0.5358 (3)	0.67170 (7)	0.0147 (2)
C3	0.53957 (11)	0.7144 (3)	0.69284 (8)	0.0138 (2)
C4	0.59307 (11)	0.7850 (3)	0.77369 (8)	0.0159 (2)
H4A	0.666864	0.904404	0.78654	0.019*
C5	0.53869 (12)	0.6811 (3)	0.83594 (8)	0.0173 (2)
C6	0.59545 (14)	0.7624 (4)	0.92352 (8)	0.0246 (3)
H6A	0.652269	0.948864	0.925516	0.037*
H6B	0.637915	0.563344	0.949925	0.037*
H6C	0.533058	0.827998	0.952079	0.037*
C7	0.43039 (12)	0.5029 (3)	0.81548 (8)	0.0188 (2)
H7A	0.392109	0.431425	0.857244	0.023*
C8	0.37879 (11)	0.4303 (3)	0.73479 (8)	0.0180 (2)
H8A	0.305944	0.306442	0.722046	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.01877 (7)	0.01856 (7)	0.01827 (7)	−0.00280 (4)	0.00737 (5)	0.00088 (4)
O	0.0269 (5)	0.0362 (6)	0.0245 (5)	−0.0129 (5)	−0.0029 (4)	−0.0015 (5)
C1	0.0202 (6)	0.0224 (6)	0.0171 (6)	−0.0019 (5)	0.0008 (5)	−0.0002 (5)
C2	0.0132 (5)	0.0148 (5)	0.0153 (5)	0.0013 (4)	0.0018 (4)	−0.0001 (4)
C3	0.0139 (5)	0.0127 (5)	0.0155 (5)	0.0013 (4)	0.0047 (4)	0.0000 (4)
C4	0.0144 (5)	0.0147 (5)	0.0176 (6)	0.0014 (4)	0.0016 (4)	−0.0014 (4)
C5	0.0201 (6)	0.0161 (5)	0.0153 (5)	0.0061 (4)	0.0028 (4)	−0.0007 (4)
C6	0.0315 (7)	0.0266 (7)	0.0145 (6)	0.0045 (6)	0.0024 (5)	−0.0029 (5)
C7	0.0192 (6)	0.0201 (6)	0.0189 (6)	0.0044 (5)	0.0082 (5)	0.0028 (5)
C8	0.0141 (5)	0.0191 (6)	0.0216 (6)	0.0004 (4)	0.0056 (4)	0.0013 (5)

Geometric parameters (Å, º)

Br—C3	1.9040 (13)	C5—C7	1.4013 (19)
O—C1	1.2162 (18)	C5—C6	1.5071 (19)
C1—C2	1.4796 (18)	C6—H6A	0.98
C1—H1A	0.95	C6—H6B	0.98
C2—C3	1.3977 (17)	C6—H6C	0.98

C2—C8	1.3984 (18)	C7—C8	1.3849 (19)
C3—C4	1.3904 (17)	C7—H7A	0.95
C4—C5	1.3941 (19)	C8—H8A	0.95
C4—H4A	0.95		

O—C1—C2	123.27 (13)	C7—C5—C6	120.89 (13)
O—C1—H1A	118.4	C5—C6—H6A	109.5
C2—C1—H1A	118.4	C5—C6—H6B	109.5
C3—C2—C8	117.74 (11)	H6A—C6—H6B	109.5
C3—C2—C1	123.22 (12)	C5—C6—H6C	109.5
C8—C2—C1	119.04 (12)	H6A—C6—H6C	109.5
C4—C3—C2	121.51 (12)	H6B—C6—H6C	109.5
C4—C3—Br	117.40 (9)	C8—C7—C5	120.44 (12)
C2—C3—Br	121.08 (9)	C8—C7—H7A	119.8
C3—C4—C5	120.15 (12)	C5—C7—H7A	119.8
C3—C4—H4A	119.9	C7—C8—C2	121.29 (12)
C5—C4—H4A	119.9	C7—C8—H8A	119.4
C4—C5—C7	118.85 (12)	C2—C8—H8A	119.4
C4—C5—C6	120.25 (13)		

O—C1—C2—C3	169.24 (14)	C3—C4—C5—C7	0.54 (19)
O—C1—C2—C8	−10.0 (2)	C3—C4—C5—C6	−178.96 (12)
C8—C2—C3—C4	0.20 (18)	C4—C5—C7—C8	0.30 (19)
C1—C2—C3—C4	−179.10 (12)	C6—C5—C7—C8	179.80 (13)
C8—C2—C3—Br	179.59 (9)	C5—C7—C8—C2	−0.9 (2)
C1—C2—C3—Br	0.29 (17)	C3—C2—C8—C7	0.65 (19)
C2—C3—C4—C5	−0.80 (19)	C1—C2—C8—C7	179.99 (12)
Br—C3—C4—C5	179.79 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···Br^{i}	0.95	3.07	3.5842 (14)	116

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