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2-(4-Bromophenyl)-2-oxoethyl 2-methylbenzoate

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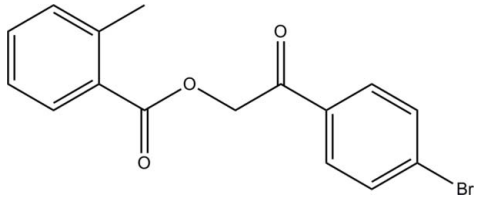
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.040; wR factor = 0.094; data-to-parameter ratio = 28.6.

In the title compound, $C_{16}H_{13}BrO_3$, the dihedral angle formed between the bromo- and methyl-substituted benzene rings is 66.66 (8)°. In the crystal, molecules are linked by intermolecular C—H···O hydrogen bonds, forming a two-dimensional network parallel to the *ac* plane. The crystal packing is further consolidated by C—H···π interactions.

Related literature

For background and applications of phenacyl benzoates, see: Rather & Reid (1919); Sheehan & Umezaw (1973); Ruzicka *et al.* (2002); Litera *et al.* (2006); Huang *et al.* (1996); Gandhi *et al.* (1995). For a related structure, see: Fun *et al.* (2011). For the synthesis, see: Judefind & Reid (1920). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{16}H_{13}BrO_3$
M_r = 333.17
Monoclinic, $P2_1/c$
a = 5.4519 (1) Å
b = 31.2382 (5) Å
c = 9.7206 (1) Å
β = 120.410 (1)°
V = 1427.74 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.88 mm^{-1}
T = 100 K
0.51 × 0.36 × 0.08 mm

‡ Thomson Reuters ResearcherID: A-3561-2009.

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.323, T_{max} = 0.811
20164 measured reflections
5211 independent reflections
4181 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.094
S = 1.04
5211 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C10–C15 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···O2^{i}	0.99	2.32	3.224 (2)	151
C8—H8B···O2^{ii}	0.99	2.52	3.447 (3)	156
C15—H15A···$Cg1^{iii}$	0.95	2.74	3.5472 (19)	143
C16—H16B···$Cg1^{iv}$	0.98	2.98	3.4909 (19)	114
C2—H2A···$Cg2^{v}$	0.95	2.91	3.5915 (19)	130

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2797).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2009). *SADABS*, *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Fun, H.-K., Loh, W.-S., Garudachari, B., Isloor, A. M. & Satyanarayan, M. N. (2011). *Acta Cryst.* E**67**, o1529.
Gandhi, S. S., Bell, K. L. & Gibson, M. S. (1995). *Tetrahedron*, **51**, 13301–13308.
Huang, W., Pian, J., Chen, B., Pei, W. & Ye, X. (1996). *Tetrahedron*, **52**, 10131–10136.
Judefind, W. L. & Reid, E. E. (1920). *J. Am. Chem. Soc.* **42**, 1043–1055.
Litera, J. K., Loya, A. D. & Klan, P. (2006). *J. Org. Chem.* **71**, 713–723.
Rather, J. B. & Reid, E. (1919). *J. Am. Chem. Soc.* **41**, 75–83.
Ruzicka, R., Zabadal, M. & Klan, P. (2002). *Synth. Commun.* **32**, 2581–2590.
Sheehan, J. C. & Umezaw, K. (1973). *J. Org. Chem.* **58**, 3771–3773.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supporting information

Acta Cryst. (2011). E**67**, o3119 [doi:10.1107/S1600536811044564]

2-(4-Bromophenyl)-2-oxoethyl 2-methylbenzoate

Hoong-Kun Fun, Chin Wei Ooi, B. Garudachari, Arun M. Isloor and M. N. Satyanarayan

S1. Comment

Phenacyl benzoate derivatives are very important in identification of organic acids (Rather & Reid, 1919), since they undergo photolysis in neutral and mild conditions (Sheehan & Umezaw, 1973; Ruzicka *et al.*, 2002; Litera *et al.*, 2006). They find applications in the field of synthetic chemistry for the synthesis of oxazoles, imidazoles (Huang *et al.*, 1996) and benzoxazepine (Gandhi *et al.*, 1995). We hereby report the crystal structure of 2-(4-bromophenyl)-2-oxoethyl 2-methylbenzoate which has potential commercial importance.

In the title compound (Fig. 1), the dihedral angle formed between the bromo-substituted (C1–C6) and the methyl-substituted (C10–C15) benzene rings is 66.66 (8)°. The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges and are comparable to the related structure (Fun *et al.*, 2011).

In the crystal packing (Fig. 2), the molecules are linked by intermolecular C8—H8A···O2 and C8—H8B···O2 hydrogen bonds (Table 1), forming a two-dimensional network parallel to the *ac* plane. The crystal packing is further consolidated by C—H···π interactions, involving the centroids of the bromo-substituted (C1–C6; *Cg*1; Table 1) and methyl-substituted benzene rings (C10–C15; *Cg*2; Table 1).

S2. Experimental

The mixture of 2-methylbenzoic acid (1.0 g, 0.0073 mol), potassium carbonate (1.10 g, 0.0080 mol) and 2-bromo-1-(4-bromophenyl)ethanone (2.02 g, 0.0073 mol) in dimethylformamide (10 ml) was stirred at room temperature for 2 h. On cooling, colourless needle-shaped crystals of 2-(4-bromophenyl)-2-oxoethyl 2-methylbenzoate began to separate out. It was collected by filtration and recrystallized from ethanol. Yield: 2.35 g, 96.3%. *M.p.*: 330–331 K (Judefind & Reid, 1920).

S3. Refinement

All the H atoms were positioned geometrically (C—H = 0.95, 0.98 or 0.99 Å) and refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). A rotating group model was applied to the methyl group. In the final refinement, one outliner (0 2 0) was omitted.

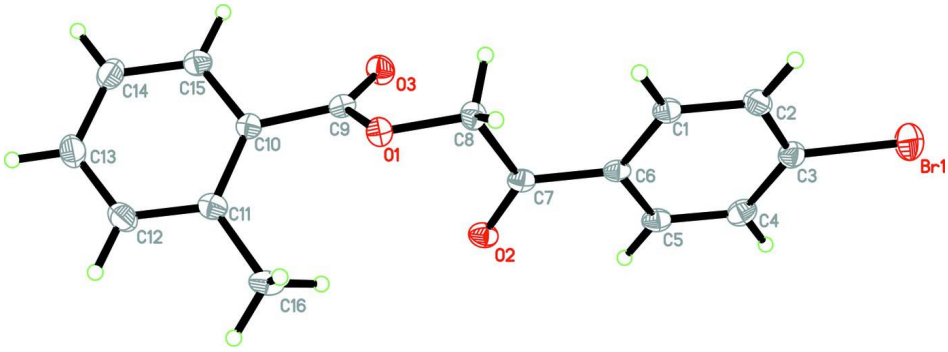

Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids.

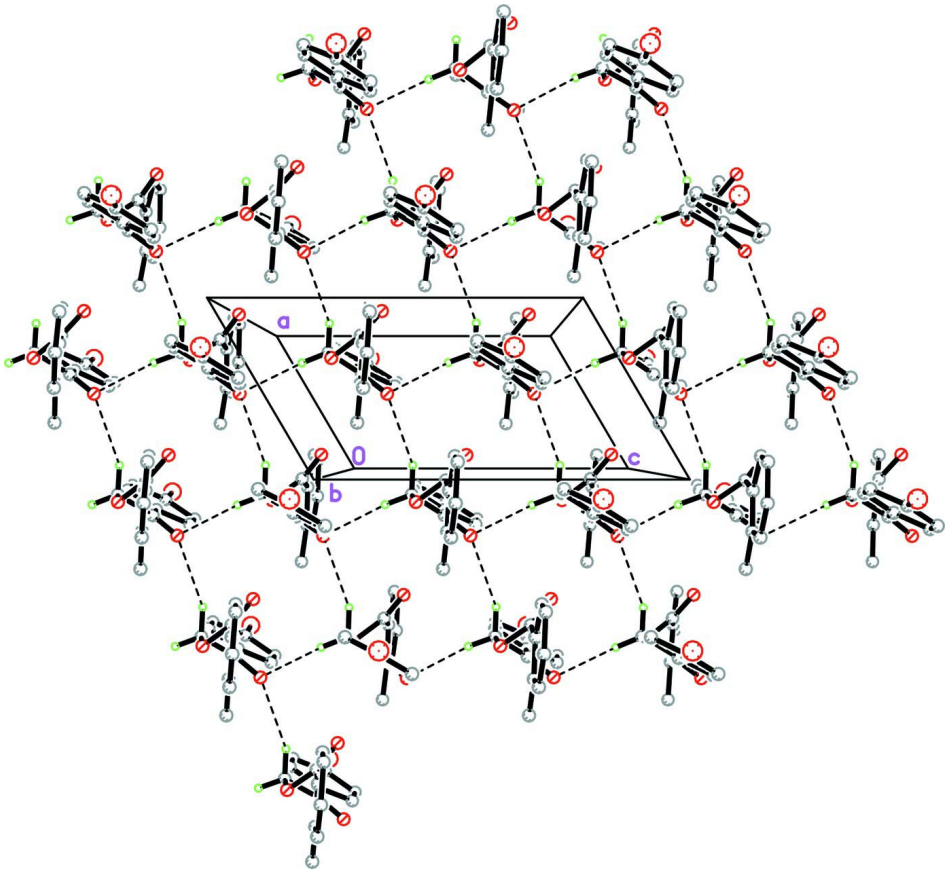

Figure 2

The crystal packing of the title compound. The dashed lines represent the hydrogen bonds.

2-(4-Bromophenyl)-2-oxoethyl 2-methylbenzoate

Crystal data

$C_{16}H_{13}BrO_3$
$M_r = 333.17$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 5.4519\ (1)$ Å
$b = 31.2382\ (5)$ Å
$c = 9.7206\ (1)$ Å
$\beta = 120.410\ (1)°$
$V = 1427.74\ (4)$ Å^3
$Z = 4$

$F(000) = 672$
$D_x = 1.550$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7724 reflections
$\theta = 2.6–32.6°$
$\mu = 2.88$ mm^{-1}
$T = 100$ K
Plate, colourless
0.51 × 0.36 × 0.08 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.323$, $T_{max} = 0.811$
20164 measured reflections
5211 independent reflections
4181 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 32.7°$, $\theta_{min} = 2.5°$
$h = -8 \rightarrow 8$
$k = -35 \rightarrow 47$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.094$
$S = 1.04$
5211 reflections
182 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
$w = 1/[\sigma^2(F_o^2) + (0.0391P)^2 + 0.9854P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.17278 (4)	0.970131 (6)	0.70447 (3)	0.03247 (7)
O1	0.2143 (2)	0.70425 (4)	0.82251 (14)	0.0169 (2)
O2	0.4582 (2)	0.75657 (4)	0.70793 (14)	0.0185 (2)
O3	−0.1113 (3)	0.70407 (4)	0.56018 (15)	0.0219 (3)
C1	0.1466 (3)	0.84316 (5)	0.81729 (19)	0.0167 (3)
H1A	0.0726	0.8273	0.8715	0.020*
C2	0.1160 (3)	0.88749 (6)	0.8057 (2)	0.0194 (3)
H2A	0.0232	0.9020	0.8526	0.023*
C3	0.2231 (3)	0.91002 (6)	0.7248 (2)	0.0197 (3)
C4	0.3636 (4)	0.88967 (6)	0.6568 (2)	0.0202 (3)

H4A	0.4370	0.9057	0.6024	0.024*
C5	0.3940 (3)	0.84555 (6)	0.6701 (2)	0.0177 (3)
H5A	0.4897	0.8312	0.6246	0.021*
C6	0.2854 (3)	0.82191 (5)	0.74968 (18)	0.0145 (3)
C7	0.3187 (3)	0.77446 (5)	0.75677 (18)	0.0147 (3)
C8	0.1688 (4)	0.74932 (5)	0.8257 (2)	0.0170 (3)
H8A	0.2405	0.7585	0.9371	0.020*
H8B	−0.0376	0.7554	0.7635	0.020*
C9	0.0627 (3)	0.68539 (5)	0.67839 (19)	0.0156 (3)
C10	0.1268 (3)	0.63882 (5)	0.68481 (19)	0.0154 (3)
C11	0.4045 (3)	0.62214 (6)	0.7696 (2)	0.0178 (3)
C12	0.4349 (4)	0.57773 (6)	0.7654 (2)	0.0234 (3)
H12A	0.6203	0.5657	0.8198	0.028*
C13	0.2030 (4)	0.55090 (6)	0.6846 (2)	0.0259 (4)
H13A	0.2306	0.5208	0.6866	0.031*
C14	−0.0708 (4)	0.56778 (6)	0.6002 (2)	0.0239 (3)
H14A	−0.2306	0.5495	0.5440	0.029*
C15	−0.1062 (3)	0.61174 (6)	0.5995 (2)	0.0191 (3)
H15A	−0.2917	0.6236	0.5400	0.023*
C16	0.6654 (3)	0.64980 (6)	0.8579 (2)	0.0223 (3)
H16A	0.8327	0.6338	0.8739	0.033*
H16B	0.6905	0.6579	0.9616	0.033*
H16C	0.6428	0.6757	0.7954	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03491 (11)	0.01766 (9)	0.04329 (13)	0.00216 (7)	0.01866 (9)	0.00472 (8)
O1	0.0187 (5)	0.0162 (5)	0.0144 (5)	0.0007 (4)	0.0074 (4)	−0.0001 (4)
O2	0.0168 (5)	0.0230 (6)	0.0175 (6)	0.0007 (4)	0.0101 (4)	−0.0028 (4)
O3	0.0182 (5)	0.0211 (6)	0.0189 (6)	0.0023 (4)	0.0038 (5)	0.0018 (5)
C1	0.0155 (7)	0.0202 (7)	0.0153 (7)	−0.0010 (6)	0.0085 (6)	−0.0001 (6)
C2	0.0162 (7)	0.0205 (8)	0.0207 (8)	0.0020 (6)	0.0086 (6)	−0.0017 (6)
C3	0.0161 (7)	0.0180 (7)	0.0214 (8)	−0.0003 (6)	0.0068 (6)	0.0011 (6)
C4	0.0191 (7)	0.0228 (8)	0.0190 (8)	−0.0032 (6)	0.0099 (6)	0.0020 (6)
C5	0.0149 (7)	0.0244 (8)	0.0157 (7)	−0.0013 (6)	0.0090 (6)	−0.0012 (6)
C6	0.0106 (6)	0.0193 (7)	0.0117 (6)	−0.0006 (5)	0.0044 (5)	−0.0008 (5)
C7	0.0111 (6)	0.0203 (7)	0.0094 (6)	−0.0006 (5)	0.0028 (5)	−0.0020 (5)
C8	0.0210 (7)	0.0163 (7)	0.0168 (7)	−0.0002 (6)	0.0118 (6)	−0.0016 (6)
C9	0.0135 (6)	0.0182 (7)	0.0151 (7)	−0.0016 (5)	0.0073 (5)	−0.0007 (5)
C10	0.0163 (7)	0.0168 (7)	0.0139 (7)	0.0002 (5)	0.0081 (6)	0.0007 (5)
C11	0.0173 (7)	0.0226 (8)	0.0154 (7)	0.0020 (6)	0.0096 (6)	0.0026 (6)
C12	0.0226 (8)	0.0229 (8)	0.0282 (9)	0.0072 (6)	0.0155 (7)	0.0058 (7)
C13	0.0307 (9)	0.0178 (8)	0.0343 (10)	0.0040 (7)	0.0203 (8)	0.0044 (7)
C14	0.0258 (8)	0.0201 (8)	0.0280 (9)	−0.0044 (7)	0.0152 (7)	−0.0018 (7)
C15	0.0168 (7)	0.0211 (8)	0.0185 (8)	−0.0005 (6)	0.0082 (6)	0.0000 (6)
C16	0.0140 (7)	0.0303 (9)	0.0204 (8)	0.0018 (6)	0.0072 (6)	−0.0009 (7)

Geometric parameters (Å, º)

Br1—C3	1.8935 (18)	C8—H8A	0.9900
O1—C9	1.3493 (19)	C8—H8B	0.9900
O1—C8	1.433 (2)	C9—C10	1.490 (2)
O2—C7	1.2170 (19)	C10—C15	1.397 (2)
O3—C9	1.207 (2)	C10—C11	1.407 (2)
C1—C2	1.392 (2)	C11—C12	1.400 (2)
C1—C6	1.396 (2)	C11—C16	1.507 (2)
C1—H1A	0.9500	C12—C13	1.383 (3)
C2—C3	1.386 (2)	C12—H12A	0.9500
C2—H2A	0.9500	C13—C14	1.393 (3)
C3—C4	1.393 (2)	C13—H13A	0.9500
C4—C5	1.386 (2)	C14—C15	1.386 (2)
C4—H4A	0.9500	C14—H14A	0.9500
C5—C6	1.399 (2)	C15—H15A	0.9500
C5—H5A	0.9500	C16—H16A	0.9800
C6—C7	1.491 (2)	C16—H16B	0.9800
C7—C8	1.512 (2)	C16—H16C	0.9800
C9—O1—C8	115.46 (13)	O3—C9—O1	123.39 (15)
C2—C1—C6	120.43 (15)	O3—C9—C10	124.51 (15)
C2—C1—H1A	119.8	O1—C9—C10	112.05 (13)
C6—C1—H1A	119.8	C15—C10—C11	120.62 (15)
C3—C2—C1	118.88 (15)	C15—C10—C9	116.27 (14)
C3—C2—H2A	120.6	C11—C10—C9	123.10 (14)
C1—C2—H2A	120.6	C12—C11—C10	117.24 (15)
C2—C3—C4	121.92 (16)	C12—C11—C16	119.55 (15)
C2—C3—Br1	118.84 (13)	C10—C11—C16	123.17 (15)
C4—C3—Br1	119.24 (13)	C13—C12—C11	121.96 (16)
C5—C4—C3	118.51 (15)	C13—C12—H12A	119.0
C5—C4—H4A	120.7	C11—C12—H12A	119.0
C3—C4—H4A	120.7	C12—C13—C14	120.28 (17)
C4—C5—C6	120.84 (15)	C12—C13—H13A	119.9
C4—C5—H5A	119.6	C14—C13—H13A	119.9
C6—C5—H5A	119.6	C15—C14—C13	118.89 (17)
C1—C6—C5	119.42 (15)	C15—C14—H14A	120.6
C1—C6—C7	122.24 (14)	C13—C14—H14A	120.6
C5—C6—C7	118.33 (14)	C14—C15—C10	120.96 (16)
O2—C7—C6	121.60 (15)	C14—C15—H15A	119.5
O2—C7—C8	121.25 (15)	C10—C15—H15A	119.5
C6—C7—C8	117.14 (13)	C11—C16—H16A	109.5
O1—C8—C7	111.25 (13)	C11—C16—H16B	109.5
O1—C8—H8A	109.4	H16A—C16—H16B	109.5
C7—C8—H8A	109.4	C11—C16—H16C	109.5
O1—C8—H8B	109.4	H16A—C16—H16C	109.5
C7—C8—H8B	109.4	H16B—C16—H16C	109.5
H8A—C8—H8B	108.0		

C6—C1—C2—C3	0.6 (2)	C8—O1—C9—O3	−3.7 (2)
C1—C2—C3—C4	−0.9 (3)	C8—O1—C9—C10	178.78 (12)
C1—C2—C3—Br1	178.42 (12)	O3—C9—C10—C15	−40.3 (2)
C2—C3—C4—C5	0.5 (3)	O1—C9—C10—C15	137.23 (15)
Br1—C3—C4—C5	−178.80 (12)	O3—C9—C10—C11	139.03 (17)
C3—C4—C5—C6	0.2 (2)	O1—C9—C10—C11	−43.5 (2)
C2—C1—C6—C5	0.0 (2)	C15—C10—C11—C12	−0.6 (2)
C2—C1—C6—C7	−178.94 (14)	C9—C10—C11—C12	−179.87 (15)
C4—C5—C6—C1	−0.4 (2)	C15—C10—C11—C16	177.21 (16)
C4—C5—C6—C7	178.59 (15)	C9—C10—C11—C16	−2.1 (2)
C1—C6—C7—O2	−174.45 (15)	C10—C11—C12—C13	−1.3 (3)
C5—C6—C7—O2	6.6 (2)	C16—C11—C12—C13	−179.19 (17)
C1—C6—C7—C8	6.2 (2)	C11—C12—C13—C14	1.8 (3)
C5—C6—C7—C8	−172.78 (14)	C12—C13—C14—C15	−0.3 (3)
C9—O1—C8—C7	−75.92 (17)	C13—C14—C15—C10	−1.6 (3)
O2—C7—C8—O1	−0.4 (2)	C11—C10—C15—C14	2.0 (3)
C6—C7—C8—O1	178.89 (12)	C9—C10—C15—C14	−178.63 (15)

Hydrogen-bond geometry (Å, º)

*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C10–C15 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8*A*···O2^{i}	0.99	2.32	3.224 (2)	151
C8—H8*B*···O2^{ii}	0.99	2.52	3.447 (3)	156
C15—H15*A*···*Cg*1^{iii}	0.95	2.74	3.5472 (19)	143
C16—H16*B*···*Cg*1^{iv}	0.98	2.98	3.4909 (19)	114
C2—H2*A*···*Cg*2^{v}	0.95	2.91	3.5915 (19)	130

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*−1, *y*, *z*; (iii) *x*−1, −*y*+1/2, *z*−3/2; (iv) *x*+1, −*y*+1/2, *z*−1/2; (v) *x*, −*y*+1/2, *z*−1/2.