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1-Allyloxy-2-bromo-3-(3-phenylallyloxy)benzene

Peter Kirsop, John M. D. Storey and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

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Key indicators

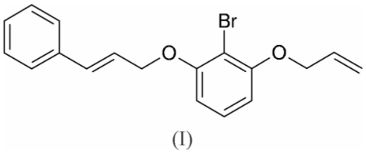
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.041
wR factor = 0.111
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{18}H_{17}BrO_2$, possesses normal geometrical parameters. A possible intramolecular C—H···O interaction is present. The crystal packing is influenced by π–π stacking.

Comment

The title compound, (I) (Fig. 1), arose during our studies to determine the philicity of aryl radicals by competitive cyclization (Kirsop *et al.*, 2004*a*,*b*).



(I)

Compound (I) possesses normal geometrical parameters. A *PLATON* (Spek, 2003) analysis of (I) indicated that an intramolecular C—H···O interaction (Table 1) may occur between an *exo* methylene C1—H1*A* group and acceptor O1, which may help to stabilize an essentially planar arrangement of the atoms C1, C2, C3 and O1 [C1—C2—C3—O1 = −3.0 (6)°]. The acute C—H···O bond angle of 100° is consistent with the intramolecular nature of this interaction.

As well as van der Waals forces, the crystal packing in (I) is influenced by π–π stacking interactions. Inversion symmetry results in dimeric associations of molecules of (I) with a $C_g\cdots C_g^{\,i}$ separation of 3.767 (3) Å [C_g is the geometric centroid of atoms C13–C18; symmetry code: (i) $-1-x, 2-y, -z$]. The ring planes are exactly parallel and separated by 3.55 (3) Å. The lateral displacement of $C_g^{\,i}$ relative to the perpendicular from C_g to the mean plane for the atoms C13^i–C18^i is 1.25 (8) Å. The packing of (I) is shown in Fig. 2.

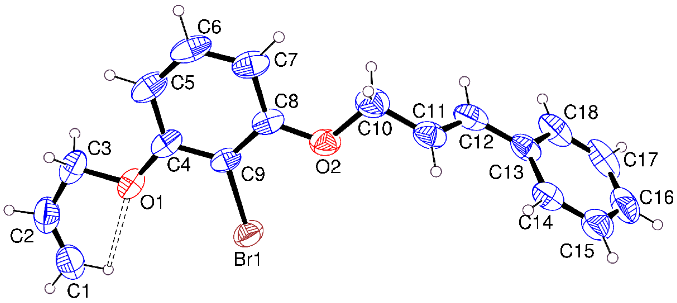


Figure 1
The molecular structure of (I) (30% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius and the possible intramolecular C—H···O interaction is shown as a dashed lines.

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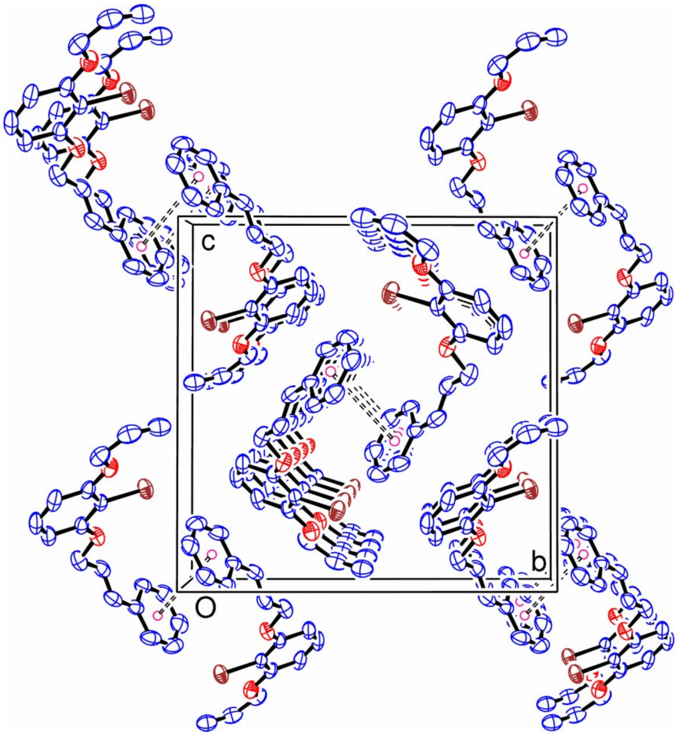

Figure 2
The packing in (I) projected on to (100), with π–π stacking interactions involving the C13–C18 phenyl rings indicated by dashed lines and all C—H H atoms omitted for clarity (30% displacement ellipsoids).

Experimental

2-Bromobenzene-1,3-diol (Kirsop *et al.*, 2004*b*; 5.00 g, 0.026 mol), allyl bromide (3.20 g, 0.026 mol) and potassium carbonate (8.00 g, 0.0579 mol) were added to 100 ml of dry acetone. The mixture was stirred at reflux under a nitrogen atmosphere for 3 h. After cooling, the mixture was filtered and the solvent removed at reduced pressure to give a dark brown oil (4.64 g, 78%). Thin-layer chromatography (4:1 hexane–ethyl acetate) showed three sharp spots: at $R_F = 0.24$ was unreacted starting material, at $R_F = 0.38$ was 3-allyloxy-2-bromophenol, and at $R_F = 0.52$ was 1,3-bis(allyloxy)-2-bromobenzene. These compounds were separated using flash column chromatography to give 3-allyloxy-2-bromophenol as a clear oil (1.85 g, 31%). ^{1}H NMR: δ_H ($CDCl_3$) 4.58 (2H, *d*, J = 4.9 Hz, CH_2), 5.30 (1H, *d*, J = 10.7 Hz, CH), 5.47 (1H, *d* J = 17.1 Hz, CH) 5.74 (1H, *s*, OH), 6.05 (1H, *m*, CH), 6.45 (1H, *d*, J = 8.2 Hz, Ar-H), 6.66 (1H, *d*, J = 9.8 Hz, Ar-H), 7.12 (1H, *t*, J = 8.2 Hz, Ar-H). ^{13}C NMR: δ_C 69.8, 100.6, 105.0, 108.6, 117.8, 128.6, 132.6, 153.6, 155.5. ν_{max} (KBr)/cm^{-1}: 3497, 2912, 1595, 1463, 1269, 1192, 1064, 767.

A mixture of 3-allyloxy-2-bromophenol (2.00 g, 0.009 mol), cinnamyl bromide (2.06 g, 0.011 mol) and potassium carbonate (8.0 g, 0.058 mol) was added to dry acetone (100 ml). The mixture was stirred at reflux under a nitrogen atmosphere for 12 h. After cooling, the mixture was filtered and the solvent removed at reduced pressure to give a dark brown oil (1.92 g, 68%). Thin-layer chromatography (4:1 hexane–ethyl acetate) showed 1-allyloxy-2-bromo-3-(3-phenylallyloxy) benzene (I) as a sharp spot at $R_F = 0.33$. The crude product was purified by flash column chromatography to give (I) as a white powder (1.56 g, 51%). A sample of this powder was recrystallized from hot hexane–ethyl acetate (20:1) to give translucent rhombs and slabs (m.p. 353–355 K). ^{1}H NMR: δ_H ($CDCl_3$) 4.58 (2H, d, J = 4.1 Hz, CH_2), 4.74 (2H, *d*, J = 3.9 Hz, CH_2), 5.26 (1H, *d*, J = 9.6 Hz, CH_2), 5.44 (1H, *d*, J = 17.0 Hz, CH_2), 6.01–6.08 (1H, *m*, CH), 6.37–6.41 (1H, *m*, CH), 6.53 (1H, *d*, J = 7.0 Hz, Ar-H), 6.58 (1H, *d*, J = 7.0 Hz, Ar-H), 6.75 (1H, *d*, J = 9.2 Hz, CH), 7.14 (1H, *t*, J = 8.1 Hz, CH), 7.23 (1H, *d*, J = 6.2 Hz, Ar-H), 7.29 (2H, *t*, J = 8.3 Hz, Ar-H), 7.38 (2H, *d*, J = 7.2 Hz, Ar-H). ^{13}C NMR: δ_C 70.0, 70.1, 102.7, 106.6, 106.7, 117.8, 124.2 (2 C), 126.8, 128.1, 128.2, 128.8 (2 C), 132.9, 133.1, 136.6, 156.6 (2 C). ν_{max} (KBr)/cm^{-1}: 1644, 1591, 1470, 1375, 1255, 1116, 1062, 767.

Crystal data

$C_{18}H_{17}BrO_2$
$M_r = 345.23$
Monoclinic, $P2_1/n$
$a = 7.2956$ (4) Å
$b = 14.8719$ (8) Å
$c = 14.7849$ (7) Å
$\beta = 95.171$ (1)°
$V = 1597.62$ (14) Å^3
$Z = 4$

$D_x = 1.435$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3898 reflections
$\theta = 2.7$–23.3°
$\mu = 2.57$ mm^{-1}
$T = 293$ (2) K
Slab, colourless
0.47 × 0.32 × 0.18 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.362$, $T_{max} = 0.628$
11903 measured reflections

3131 independent reflections
2142 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.0$°
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.111$
$S = 1.06$
3131 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1552P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O1	0.93	2.39	2.715 (5)	100

All the H atoms were positioned geometrically and refined as riding on their carrier C atoms (C—H = 0.93 Å for aromatic and sp^2-hybridized C atoms and C—H = 0.97 Å for sp^3-hybridized C atoms) with the the constraint $U_{iso}(H) = 1.2U_{eq}$(carrier atom) applied.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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supporting information

Acta Cryst. (2004). E**60**, o1147–o1148   [https://doi.org/10.1107/S1600536804013133]

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(I)

Crystal data

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Monoclinic, $P2_1/n$
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a = 7.2956 (4) Å
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β = 95.171 (1)°
V = 1597.62 (14) Å^3
Z = 4
$F(000)$ = 704
D_x = 1.435 Mg m^{-3}
Melting point: 353-355 K K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3898 reflections
θ = 2.7–23.3°
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Slab, colourless
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Graphite monochromator
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$R_{\rm int}$ = 0.025
$\theta_{\max}$ = 26.0°, $\theta_{\min}$ = 2.0°
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 18$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.111
S = 1.06
3131 reflections
190 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
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1552P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}

Special details

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	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.7164 (6)	0.9837 (4)	0.4453 (3)	0.1019 (14)
H1A	0.5955	0.9901	0.4204	0.122*
H1B	0.7707	1.0283	0.4828	0.122*
C2	0.8077 (6)	0.9138 (4)	0.4283 (3)	0.0988 (14)
H2	0.9279	0.9109	0.4550	0.119*
C3	0.7445 (5)	0.8372 (3)	0.3711 (3)	0.0866 (11)
H3A	0.8176	0.8325	0.3197	0.104*
H3B	0.7581	0.7819	0.4058	0.104*
C4	0.4709 (5)	0.7921 (2)	0.2806 (2)	0.0655 (9)
C5	0.5451 (6)	0.7111 (2)	0.2545 (3)	0.0843 (11)
H5	0.6620	0.6936	0.2782	0.101*
C6	0.4451 (6)	0.6577 (2)	0.1939 (3)	0.0904 (13)
H6	0.4964	0.6036	0.1772	0.109*
C7	0.2716 (5)	0.6796 (2)	0.1561 (3)	0.0813 (11)
H7	0.2073	0.6415	0.1147	0.098*
C8	0.1952 (5)	0.7604 (2)	0.1815 (2)	0.0651 (9)
C9	0.2946 (4)	0.81529 (19)	0.2437 (2)	0.0599 (8)
C10	−0.0783 (6)	0.7392 (2)	0.0806 (3)	0.0902 (11)
H10A	−0.1080	0.6809	0.1050	0.108*
H10B	−0.0082	0.7298	0.0287	0.108*
C11	−0.2497 (5)	0.7898 (2)	0.0529 (3)	0.0787 (10)
H11	−0.3270	0.8030	0.0978	0.094*
C12	−0.3003 (6)	0.8172 (3)	−0.0290 (3)	0.0832 (11)
H12	−0.2236	0.8021	−0.0736	0.100*
C13	−0.4657 (5)	0.8693 (2)	−0.0587 (2)	0.0714 (9)
C14	−0.6087 (5)	0.8823 (2)	−0.0051 (3)	0.0759 (10)
H14	−0.6035	0.8551	0.0517	0.091*
C15	−0.7564 (6)	0.9336 (3)	−0.0329 (3)	0.0943 (12)
H15	−0.8512	0.9407	0.0045	0.113*
C16	−0.7669 (7)	0.9751 (3)	−0.1160 (4)	0.1047 (14)
H16	−0.8677	1.0109	−0.1348	0.126*
C17	−0.6283 (9)	0.9635 (4)	−0.1706 (3)	0.1101 (17)
H17	−0.6344	0.9915	−0.2271	0.132*
C18	−0.4786 (7)	0.9101 (3)	−0.1426 (3)	0.0964 (14)
H18	−0.3856	0.9018	−0.1809	0.116*
O1	0.5548 (3)	0.85114 (16)	0.33997 (17)	0.0765 (7)
O2	0.0263 (3)	0.79109 (15)	0.14831 (17)	0.0765 (7)
Br1	0.19441 (5)	0.92522 (2)	0.27726 (3)	0.08017 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.091 (3)	0.132 (4)	0.080 (3)	−0.007 (3)	−0.005 (2)	0.003 (3)
C2	0.066 (3)	0.145 (5)	0.084 (3)	0.005 (3)	−0.002 (2)	0.021 (3)
C3	0.064 (2)	0.100 (3)	0.096 (3)	0.020 (2)	0.012 (2)	0.030 (3)
C4	0.063 (2)	0.0543 (18)	0.084 (2)	0.0068 (15)	0.0306 (18)	0.0191 (18)
C5	0.080 (2)	0.056 (2)	0.123 (3)	0.0145 (18)	0.041 (2)	0.023 (2)
C6	0.104 (3)	0.0459 (19)	0.129 (4)	0.013 (2)	0.054 (3)	0.007 (2)
C7	0.094 (3)	0.0520 (19)	0.103 (3)	−0.0017 (18)	0.038 (2)	−0.0010 (19)
C8	0.071 (2)	0.0481 (17)	0.080 (2)	0.0007 (15)	0.0282 (19)	0.0050 (17)
C9	0.065 (2)	0.0443 (16)	0.074 (2)	0.0052 (14)	0.0266 (18)	0.0068 (15)
C10	0.092 (3)	0.071 (2)	0.108 (3)	−0.011 (2)	0.012 (2)	−0.021 (2)
C11	0.084 (3)	0.071 (2)	0.083 (3)	−0.0210 (19)	0.019 (2)	−0.020 (2)
C12	0.093 (3)	0.088 (3)	0.073 (3)	−0.030 (2)	0.027 (2)	−0.029 (2)
C13	0.084 (3)	0.071 (2)	0.060 (2)	−0.0312 (18)	0.012 (2)	−0.0142 (18)
C14	0.089 (3)	0.079 (2)	0.060 (2)	−0.021 (2)	0.012 (2)	−0.0101 (19)
C15	0.092 (3)	0.097 (3)	0.094 (3)	−0.016 (2)	0.006 (3)	−0.021 (3)
C16	0.115 (4)	0.085 (3)	0.106 (4)	−0.020 (3)	−0.034 (3)	−0.018 (3)
C17	0.147 (5)	0.112 (4)	0.065 (3)	−0.056 (4)	−0.025 (3)	0.004 (3)
C18	0.113 (4)	0.115 (4)	0.062 (3)	−0.051 (3)	0.012 (2)	−0.016 (2)
O1	0.0589 (14)	0.0716 (15)	0.0984 (18)	0.0117 (11)	0.0044 (13)	0.0088 (14)
O2	0.0765 (16)	0.0618 (14)	0.0917 (17)	−0.0025 (12)	0.0096 (13)	−0.0180 (13)
Br1	0.0675 (3)	0.0665 (2)	0.1065 (3)	0.01149 (16)	0.0076 (2)	−0.0170 (2)

Geometric parameters (Å, º)

C1—C2	1.271 (6)	C10—O2	1.430 (4)
C1—H1A	0.9300	C10—C11	1.485 (5)
C1—H1B	0.9300	C10—H10A	0.9700
C2—C3	1.467 (6)	C10—H10B	0.9700
C2—H2	0.9300	C11—C12	1.298 (5)
C3—O1	1.434 (4)	C11—H11	0.9300
C3—H3A	0.9700	C12—C13	1.468 (6)
C3—H3B	0.9700	C12—H12	0.9300
C4—O1	1.348 (4)	C13—C18	1.377 (5)
C4—C5	1.390 (5)	C13—C14	1.380 (5)
C4—C9	1.395 (4)	C14—C15	1.353 (6)
C5—C6	1.358 (6)	C14—H14	0.9300
C5—H5	0.9300	C15—C16	1.371 (6)
C6—C7	1.376 (5)	C15—H15	0.9300
C6—H6	0.9300	C16—C17	1.361 (7)
C7—C8	1.389 (4)	C16—H16	0.9300
C7—H7	0.9300	C17—C18	1.383 (7)
C8—O2	1.363 (4)	C17—H17	0.9300
C8—C9	1.385 (5)	C18—H18	0.9300
C9—Br1	1.875 (3)		

C2—C1—H1A	120.0	O2—C10—H10A	110.2
C2—C1—H1B	120.0	C11—C10—H10A	110.2
H1A—C1—H1B	120.0	O2—C10—H10B	110.2
C1—C2—C3	127.3 (4)	C11—C10—H10B	110.2
C1—C2—H2	116.4	H10A—C10—H10B	108.5
C3—C2—H2	116.4	C12—C11—C10	125.3 (4)
O1—C3—C2	108.5 (3)	C12—C11—H11	117.4
O1—C3—H3A	110.0	C10—C11—H11	117.4
C2—C3—H3A	110.0	C11—C12—C13	127.0 (4)
O1—C3—H3B	110.0	C11—C12—H12	116.5
C2—C3—H3B	110.0	C13—C12—H12	116.5
H3A—C3—H3B	108.4	C18—C13—C14	117.5 (4)
O1—C4—C5	125.5 (3)	C18—C13—C12	119.4 (4)
O1—C4—C9	116.2 (3)	C14—C13—C12	123.1 (4)
C5—C4—C9	118.3 (4)	C15—C14—C13	121.8 (4)
C6—C5—C4	119.4 (4)	C15—C14—H14	119.1
C6—C5—H5	120.3	C13—C14—H14	119.1
C4—C5—H5	120.3	C14—C15—C16	120.3 (5)
C5—C6—C7	123.3 (3)	C14—C15—H15	119.8
C5—C6—H6	118.3	C16—C15—H15	119.8
C7—C6—H6	118.3	C17—C16—C15	119.3 (5)
C6—C7—C8	118.1 (4)	C17—C16—H16	120.3
C6—C7—H7	120.9	C15—C16—H16	120.3
C8—C7—H7	120.9	C16—C17—C18	120.3 (4)
O2—C8—C9	116.3 (3)	C16—C17—H17	119.9
O2—C8—C7	124.3 (3)	C18—C17—H17	119.9
C9—C8—C7	119.4 (3)	C13—C18—C17	120.7 (5)
C8—C9—C4	121.5 (3)	C13—C18—H18	119.6
C8—C9—Br1	119.8 (2)	C17—C18—H18	119.6
C4—C9—Br1	118.7 (3)	C4—O1—C3	118.9 (3)
O2—C10—C11	107.6 (3)	C8—O2—C10	118.6 (3)

C1—C2—C3—O1	−3.0 (6)	C11—C12—C13—C18	165.4 (4)
O1—C4—C5—C6	179.9 (3)	C11—C12—C13—C14	−12.4 (6)
C9—C4—C5—C6	0.4 (5)	C18—C13—C14—C15	−0.4 (5)
C4—C5—C6—C7	0.2 (6)	C12—C13—C14—C15	177.4 (3)
C5—C6—C7—C8	−0.2 (6)	C13—C14—C15—C16	−0.6 (6)
C6—C7—C8—O2	178.9 (3)	C14—C15—C16—C17	0.7 (6)
C6—C7—C8—C9	−0.3 (5)	C15—C16—C17—C18	0.1 (6)
O2—C8—C9—C4	−178.3 (3)	C14—C13—C18—C17	1.2 (5)
C7—C8—C9—C4	0.9 (5)	C12—C13—C18—C17	−176.7 (3)
O2—C8—C9—Br1	−0.2 (4)	C16—C17—C18—C13	−1.1 (6)
C7—C8—C9—Br1	179.1 (2)	C5—C4—O1—C3	8.6 (5)
O1—C4—C9—C8	179.5 (3)	C9—C4—O1—C3	−171.9 (3)
C5—C4—C9—C8	−1.0 (5)	C2—C3—O1—C4	175.2 (3)
O1—C4—C9—Br1	1.3 (4)	C9—C8—O2—C10	177.0 (3)
C5—C4—C9—Br1	−179.1 (2)	C7—C8—O2—C10	−2.2 (5)
O2—C10—C11—C12	120.8 (4)	C11—C10—O2—C8	−176.8 (3)

C10—C11—C12—C13	−178.3 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*A*···O1	0.93	2.39	2.715 (5)	100