Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 3,5-bis(allyloxy)-4-bromobenzoate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.006 Å
R factor = 0.052
wR factor = 0.084
Data-to-parameter ratio = 19.1

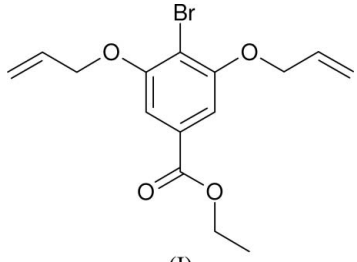
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 16 January 2007
Accepted 16 January 2007

The asymmetric molecular conformation of the title compound, $C_{15}H_{17}BrO_4$, may be be influenced by an intramolecular C—H···O interaction. The molecules form π–π stacks in the crystal structure.

Comment

The title compound, (I) (Fig. 1), was prepared as part of our studies to determine the philicity of aryl radicals by competitive cyclization reactions (Kirsop *et al.*, 2004).



(I)

Compound (I) possesses normal geometrical parameters. The dihedral angle between the mean plane of the C1–C6 benzene ring and the plane of the C7/O1/O2 group is 6.0 (5)°. The two —O—CH_2—CH=CH_2 side chains have very different conformations (Fig. 1), which may be attributable, at least in part, to an intramolecular C12—H12*A*···O3 interaction (Table 1). The molecules form π–π stacks in the crystal structure (Fig. 2), with alternating centroid-to-centroid

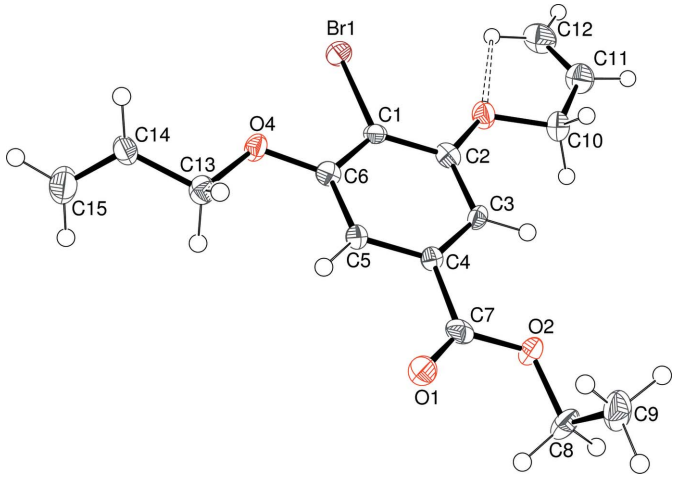


Figure 1
The molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. The intramolecular C—H···O interaction referred to in the *Comment* is indicated by a dashed line.

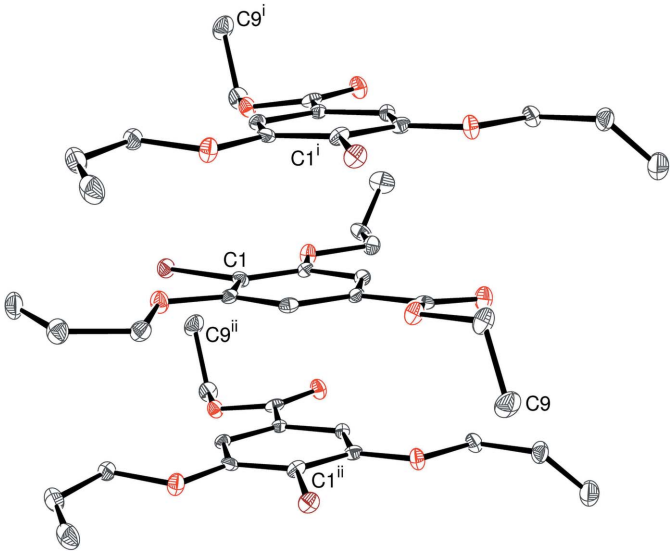


Figure 2
Part of a π–π stacked column of molecules (30% displacement ellipsoids and H atoms omitted). [Symmetry codes: (i) x, $-y$, $1-z$; (ii) x, $1-y$, $1-z$.]

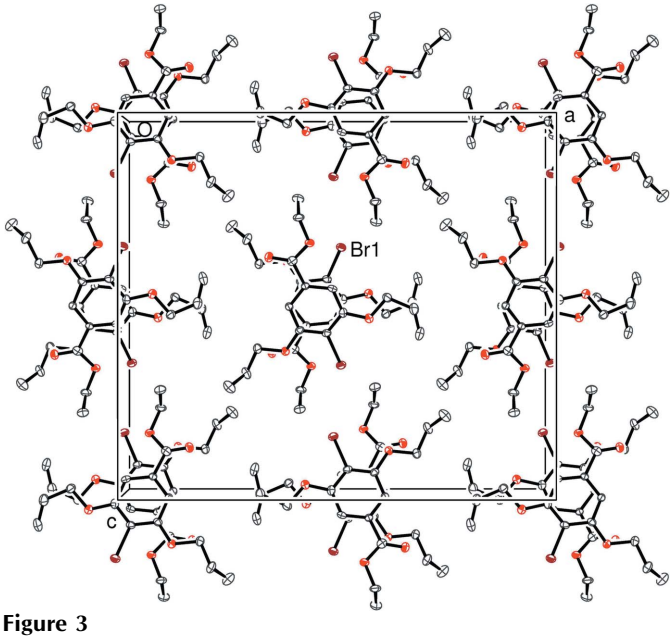


Figure 3
Unit-cell contents of (I), viewed down [010] (50% displacement ellipsoids and H atoms omitted).

separations between benzene rings [$Cg\cdots Cg^{i}$ = 3.626 (2), $Cg\cdots Cg^{ii}$ = 3.466 (2) Å; symmetry codes: (i) x, $-y$, $1-z$; (ii) x, $1-y$, $1-z$]. The stacking interactions give rise to columns of molecules along [010] (Fig. 3).

Experimental

4-Bromo-3,5-dihydroxybenzoic acid (6.8 g, 0.03 mol) was added to 100 ml of ethanol. Concentrated H_2SO_4 (1 ml) was added and the mixture was refluxed for 14 h. After cooling, the solvent was removed at reduced pressure to give a pale yellow oil. Diethyl ether (100 ml) was added and the mixture was neutralized by careful addition of a saturated $NaHCO_3$ solution (100 ml). The mixture was transferred to a separating funnel and the product extracted with diethyl ether (4 × 100 ml). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give 4-bromo-3,5-dihydroxybenzoic acid ethyl ester as a white powder (7.5 g, 96%). Ethyl 4-bromo-3,5-dihydroxybenzoate (3.00 g, 0.011 mol), allyl bromide (1.30 g, 0.011 mol) and K_2CO_3 (8.00 g, 0.0579 mol) were added to 100 ml of dry acetone. The mixture was stirred at room temperature under a nitrogen atmosphere for 14 h, then filtered and the solvent removed at reduced pressure to give a dark brown oil. Thin layer chromatography (4:1 hexane–ethyl acetate eluent) showed the title compound as a sharp spot at R_F = 0.52. The crude product was purified by flash column chromatography to yield a white powder (1.42 g, 38%). A sample of this powder was recrystallized from hot hexane to give translucent needles of (I) (m.p. 315–317 K).

Crystal data

$C_{15}H_{17}BrO_4$
M_r = 341.20
Orthorhombic, $C222_1$
a = 22.1421 (2) Å
b = 7.0559 (13) Å
c = 19.5604 (11) Å
V = 3056.0 (6) Å^3
Z = 8
D_x = 1.483 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.70 mm^{-1}
T = 120 (2) K
Needle, colourless
0.22 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.588, T_{max} = 0.948
10933 measured reflections
3495 independent reflections
2604 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.084
S = 1.01
3495 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), 1500 Friedel pairs
Flack parameter: 0.106 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12A···O3	0.95	2.39	2.715 (6)	100

H atoms were placed in idealized locations (C—H = 0.95–0.99 Å) and refined as riding atoms, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

We thank the EPSRC UK National Crystallography Service (University of Southampton) for the data collection.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kirsop, P., Storey, J. M. D. & Harrison, W. T. A. (2004). *Acta Cryst.* E**60**, o1147–o1148.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

Acta Cryst. (2007). E**63**, o833–o835 [https://doi.org/10.1107/S1600536807002383]

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$C_{15}H_{17}BrO_4$
$M_r = 341.20$
Orthorhombic, $C222_1$
Hall symbol: C 2c 2
$a = 22.1421$ (2) Å
$b = 7.0559$ (13) Å
$c = 19.5604$ (11) Å
$V = 3056.0$ (6) Å^3
$Z = 8$
$F(000) = 1392$
$D_x = 1.483$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1957 reflections
$\theta = 2.9$–$27.5°$
$\mu = 2.70$ mm^{-1}
$T = 120$ K
Needle, colourless
0.22 × 0.04 × 0.02 mm

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Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
$T_{min} = 0.588$, $T_{max} = 0.948$
10933 measured reflections
3495 independent reflections
2604 reflections with $I > 2\sigma(I)$
$R_{int} = 0.084$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -20 \rightarrow 28$
$k = -9 \rightarrow 9$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.084$
$S = 1.01$
3495 reflections
183 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
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Absolute structure: Flack (1983), 1500 Friedel pairs
Absolute structure parameter: 0.106 (13)

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_{iso}*/U_{eq}
C1	0.4754 (2)	0.3097 (5)	0.4289 (2)	0.0184 (11)
C2	0.5137 (2)	0.2603 (5)	0.4827 (2)	0.0185 (10)
C3	0.4891 (2)	0.2071 (5)	0.5457 (2)	0.0173 (10)
H3	0.5145	0.1745	0.5829	0.021*
C4	0.4267 (2)	0.2030 (6)	0.5526 (2)	0.0159 (10)
C5	0.3893 (2)	0.2505 (6)	0.4987 (2)	0.0171 (10)
H5	0.3467	0.2467	0.5046	0.021*
C6	0.4132 (2)	0.3035 (6)	0.4364 (2)	0.0184 (11)
C7	0.3970 (2)	0.1440 (6)	0.6178 (2)	0.0215 (11)
C8	0.4125 (2)	0.0183 (7)	0.7297 (2)	0.0278 (12)
H8A	0.4379	−0.0848	0.7484	0.033*
H8B	0.3713	−0.0323	0.7227	0.033*
C9	0.4103 (2)	0.1796 (7)	0.7799 (2)	0.0360 (14)
H9A	0.3918	0.1362	0.8226	0.054*
H9B	0.3863	0.2835	0.7607	0.054*
H9C	0.4514	0.2244	0.7891	0.054*
C10	0.6157 (2)	0.2438 (7)	0.5223 (2)	0.0246 (12)
H10A	0.6095	0.1206	0.5454	0.030*
H10B	0.6102	0.3462	0.5563	0.030*
C11	0.6776 (2)	0.2528 (7)	0.4924 (3)	0.0313 (12)
H11	0.7105	0.2476	0.5236	0.038*
C12	0.6911 (2)	0.2671 (7)	0.4278 (3)	0.0360 (13)
H12A	0.6598	0.2728	0.3946	0.043*
H12B	0.7321	0.2719	0.4138	0.043*
C13	0.3152 (2)	0.3480 (7)	0.3880 (2)	0.0235 (11)
H13A	0.3021	0.4327	0.4255	0.028*
H13B	0.3020	0.2174	0.3988	0.028*
C14	0.2884 (2)	0.4107 (6)	0.3224 (2)	0.0274 (12)
H14	0.2995	0.5312	0.3048	0.033*
C15	0.2503 (2)	0.3082 (7)	0.2876 (3)	0.0383 (15)
H15A	0.2385	0.1871	0.3042	0.046*
H15B	0.2343	0.3545	0.2458	0.046*
O1	0.34357 (14)	0.1487 (5)	0.62781 (15)	0.0253 (8)
O2	0.43720 (12)	0.0814 (4)	0.66439 (15)	0.0216 (7)
O3	0.57368 (14)	0.2653 (4)	0.46792 (16)	0.0251 (8)
O4	0.37974 (13)	0.3545 (4)	0.38091 (14)	0.0220 (7)
Br1	0.509124 (19)	0.38018 (6)	0.34421 (2)	0.02348 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.023 (3)	0.017 (2)	0.015 (2)	−0.0058 (18)	0.001 (2)	0.0005 (18)
C2	0.017 (3)	0.014 (2)	0.025 (3)	0.003 (2)	0.001 (2)	−0.0052 (17)
C3	0.024 (3)	0.0149 (19)	0.013 (2)	0.0015 (19)	−0.004 (2)	−0.0008 (16)
C4	0.017 (3)	0.016 (2)	0.014 (3)	0.0011 (18)	0.001 (2)	−0.0034 (18)
C5	0.016 (3)	0.018 (2)	0.017 (3)	0.0009 (19)	−0.001 (2)	−0.001 (2)
C6	0.021 (3)	0.019 (3)	0.016 (3)	−0.0008 (18)	0.003 (2)	−0.0041 (19)
C7	0.027 (3)	0.015 (2)	0.023 (3)	−0.006 (2)	0.002 (2)	−0.006 (2)
C8	0.032 (3)	0.037 (3)	0.014 (3)	0.005 (2)	0.002 (2)	0.005 (2)
C9	0.036 (3)	0.052 (4)	0.021 (3)	0.000 (2)	−0.003 (3)	−0.009 (2)
C10	0.023 (3)	0.029 (3)	0.022 (3)	0.003 (2)	−0.003 (2)	−0.004 (2)
C11	0.023 (3)	0.033 (3)	0.038 (3)	0.005 (2)	−0.002 (3)	0.002 (3)
C12	0.020 (3)	0.041 (3)	0.046 (4)	0.001 (2)	0.008 (3)	0.001 (3)
C13	0.019 (3)	0.025 (3)	0.026 (3)	0.004 (2)	−0.001 (2)	0.001 (2)
C14	0.023 (3)	0.024 (3)	0.035 (3)	−0.004 (2)	−0.010 (2)	0.002 (2)
C15	0.038 (4)	0.038 (3)	0.040 (4)	0.002 (2)	−0.015 (3)	0.002 (3)
O1	0.0175 (19)	0.033 (2)	0.0253 (18)	0.0034 (16)	0.0019 (14)	0.0034 (16)
O2	0.0218 (17)	0.0273 (17)	0.0157 (17)	0.0050 (12)	−0.0004 (14)	0.0030 (15)
O3	0.019 (2)	0.0346 (19)	0.0217 (19)	−0.0019 (14)	−0.0013 (17)	−0.0002 (16)
O4	0.0168 (18)	0.0308 (18)	0.0184 (17)	0.0035 (16)	−0.0010 (13)	0.0049 (15)
Br1	0.0254 (2)	0.0274 (2)	0.0176 (2)	−0.0024 (2)	0.0027 (2)	0.0011 (2)

Geometric parameters (Å, º)

C1—C6	1.386 (6)	C9—H9B	0.980
C1—C2	1.395 (6)	C9—H9C	0.980
C1—Br1	1.884 (4)	C10—O3	1.421 (5)
C2—O3	1.361 (5)	C10—C11	1.492 (6)
C2—C3	1.397 (6)	C10—H10A	0.990
C3—C4	1.389 (6)	C10—H10B	0.990
C3—H3	0.950	C11—C12	1.303 (6)
C4—C5	1.381 (6)	C11—H11	0.950
C4—C7	1.494 (6)	C12—H12A	0.950
C5—C6	1.381 (6)	C12—H12B	0.950
C5—H5	0.950	C13—O4	1.436 (5)
C6—O4	1.363 (5)	C13—C14	1.481 (6)
C7—O1	1.200 (5)	C13—H13A	0.990
C7—O2	1.348 (5)	C13—H13B	0.990
C8—O2	1.459 (5)	C14—C15	1.303 (6)
C8—C9	1.504 (6)	C14—H14	0.950
C8—H8A	0.990	C15—H15A	0.950
C8—H8B	0.990	C15—H15B	0.950
C9—H9A	0.980		
C6—C1—C2	121.0 (4)	C8—C9—H9C	109.5
C6—C1—Br1	119.7 (3)	H9A—C9—H9C	109.5

C2—C1—Br1	119.2 (3)	H9B—C9—H9C	109.5
O3—C2—C1	115.2 (4)	O3—C10—C11	107.7 (4)
O3—C2—C3	125.1 (4)	O3—C10—H10A	110.2
C1—C2—C3	119.7 (4)	C11—C10—H10A	110.2
C4—C3—C2	118.6 (4)	O3—C10—H10B	110.2
C4—C3—H3	120.7	C11—C10—H10B	110.2
C2—C3—H3	120.7	H10A—C10—H10B	108.5
C5—C4—C3	121.1 (4)	C12—C11—C10	126.3 (5)
C5—C4—C7	117.1 (4)	C12—C11—H11	116.8
C3—C4—C7	121.7 (4)	C10—C11—H11	116.8
C4—C5—C6	120.6 (4)	C11—C12—H12A	120.0
C4—C5—H5	119.7	C11—C12—H12B	120.0
C6—C5—H5	119.7	H12A—C12—H12B	120.0
O4—C6—C5	124.5 (4)	O4—C13—C14	107.8 (4)
O4—C6—C1	116.6 (4)	O4—C13—H13A	110.1
C5—C6—C1	118.9 (4)	C14—C13—H13A	110.1
O1—C7—O2	123.4 (4)	O4—C13—H13B	110.1
O1—C7—C4	124.4 (4)	C14—C13—H13B	110.1
O2—C7—C4	112.3 (4)	H13A—C13—H13B	108.5
O2—C8—C9	110.6 (4)	C15—C14—C13	123.1 (5)
O2—C8—H8A	109.5	C15—C14—H14	118.5
C9—C8—H8A	109.5	C13—C14—H14	118.5
O2—C8—H8B	109.5	C14—C15—H15A	120.0
C9—C8—H8B	109.5	C14—C15—H15B	120.0
H8A—C8—H8B	108.1	H15A—C15—H15B	120.0
C8—C9—H9A	109.5	C7—O2—C8	116.4 (3)
C8—C9—H9B	109.5	C2—O3—C10	118.5 (3)
H9A—C9—H9B	109.5	C6—O4—C13	117.1 (3)

C6—C1—C2—O3	177.6 (3)	C5—C4—C7—O1	−5.7 (6)
Br1—C1—C2—O3	−1.0 (5)	C3—C4—C7—O1	175.3 (4)
C6—C1—C2—C3	−1.2 (6)	C5—C4—C7—O2	173.3 (4)
Br1—C1—C2—C3	−179.7 (3)	C3—C4—C7—O2	−5.6 (6)
O3—C2—C3—C4	−177.9 (3)	O3—C10—C11—C12	−3.5 (7)
C1—C2—C3—C4	0.7 (5)	O4—C13—C14—C15	123.9 (5)
C2—C3—C4—C5	−0.1 (6)	O1—C7—O2—C8	−0.3 (6)
C2—C3—C4—C7	178.8 (4)	C4—C7—O2—C8	−179.3 (3)
C3—C4—C5—C6	0.0 (7)	C9—C8—O2—C7	−91.1 (5)
C7—C4—C5—C6	−179.0 (4)	C1—C2—O3—C10	171.0 (4)
C4—C5—C6—O4	−179.3 (4)	C3—C2—O3—C10	−10.3 (6)
C4—C5—C6—C1	−0.5 (6)	C11—C10—O3—C2	179.5 (3)
C2—C1—C6—O4	180.0 (4)	C5—C6—O4—C13	−1.4 (6)
Br1—C1—C6—O4	−1.5 (5)	C1—C6—O4—C13	179.8 (4)
C2—C1—C6—C5	1.1 (6)	C14—C13—O4—C6	179.3 (3)
Br1—C1—C6—C5	179.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12*A*···O3	0.95	2.39	2.715 (6)	100