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Crystal structure of 4-bromophenyl-2-oxo-2*H*-chromene-3-carboxylate

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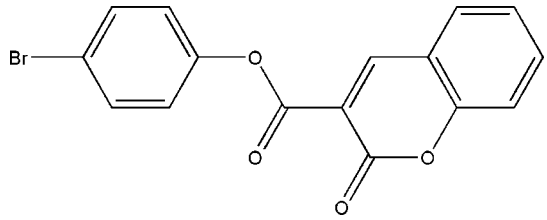
In the title compound, $C_{16}H_9BrO_4$, the coumarin ring system is approximately planar, with an r.m.s deviation of the ten fitted non-H atoms of 0.031 Å, and forms a dihedral angle of 25.85 (10)° with the bromobenzene ring. The carbonyl atoms are *syn*. In the crystal, molecules are connected along [001] *via* C—H···O interactions, forming *C*(6) chains. Neighbouring *C*(6) chains are connected *via* several π–π interactions [range of centroid–centroid distances = 3.7254 (15)–3.7716 (16) Å], leading to sheets propagating in the *bc* plane.

Keywords: crystal structure; 2-oxo-2*H*-chromene; hydrogen bonding; π–π interactions.

CCDC reference: 1057743

1. Related literature

For related structures, see: Sreenivasa *et al.* (2013); Palakshamurthy, Sreenivasa *et al.* (2013); Palakshamurthy, Devarajegowda *et al.* (2013); Devarajegowda *et al.* (2013). For the biological activity and other applications of 2-oxo-2*H*-chromene derivatives, see: Abdel-Aziz *et al.* (2013); Kostova (2006); Chandrasekharan & Kelly (2002).



2. Experimental

2.1. Crystal data

$C_{16}H_9BrO_4$
M_r = 345.14
Monoclinic, $P2_1/c$
a = 16.0782 (10) Å
b = 7.2618 (4) Å
c = 12.7396 (8) Å
β = 113.311 (4)°
V = 1366.01 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.02 mm^{-1}
T = 296 K
0.24 × 0.18 × 0.16 mm

2.2. Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.526, T_{max} = 0.617
20483 measured reflections
2395 independent reflections
1831 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.079
S = 1.01
2395 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···O3^{i}	0.93	2.40	3.124 (3)	134

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5362).

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supporting information

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Crystal structure of 4-bromophenyl-2-oxo-2*H*-chromene-3-carboxylate

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S1. Chemical context

Hetero cyclic compounds of 2-oxo-2*H*-chromenes display wide range of biological activities such as anti-HIV (Kostova, *et al.*, 2006), anti-cancer (Abdel-Aziz *et al.*,2013), etc. They also play a significant role as chemical sensors, fluorescent probes and laser dyes (Chandrasekharan *et al.*, 2002). In continuation of our work on 2-oxo-2*H*-chromene derivatives (Sreenivasa *et al.*, 2013; Palakshamurthy, Sreenivasa *et al.*, 2013; Palakshamurthy, Devarajegowda *et al.*, 2013; Devarajegowda, *et al.*,2013), in the present work we report the synthesis and crystal structure of 4-bromophenyl-2-oxo-2*H*-chromene-3-carboxylate (I), an intermediate compound obtained during synthesis of coumarin–based Liquid Crystals (LCs).

S2. Structural commentary

The dihedral angle between the coumarin ring and the bromobenzene ring in (I) is 25.85 (10)°. Compared to this, the dihedral angle is 22.95 (11)° in 4′-cyanobiphenyl-4-yl-7-diethylamino-2-oxo-2*H*-chromene-3-carboxylate (II) (Sreenivasa *et al.*, 2013), 62.97 (2)° in 4-(decyloxy)phenyl 2-oxo-7-trifluoromethyl-2*H*-chromene-3-carboxylate (III) (Palakshamurthy, Sreenivasa *et al.*, 2013), 21.00 (1)° in 4-(octyloxy)phenyl 2-oxo-2*H*-chromene-3-carboxylate (IV) (Palakshamurthy, Devarajegowda *et al.*, 2013) and 54.46 (17)° in 4-[4-(heptyloxy)benzoyloxy] phenyl 2-oxo-7-trifluoromethyl-2*H*-chromene-3-carboxylate (V) (Devarajegowda, *et al.*, 2013). Further, in (I), the torsions C9—C8—C10—O3, O3—C10—O4—C11 and C12—C11—O4—C10 have values 27.6 (4), 6.3 (3) and 124.6 (2)°, respectively.

S3. Supramolecular features

In the crystal structure, the molecules are connected along [001] via C12—H12···O3 interactions forming C(6) chains (Fig 2., Table 2). Further, neighbouring C(6) chains are interlocked via $\pi\cdots\pi$ interactions (Fig. 3), namely, Cg1··· Cg3^{i} [3.7254 (15) Å, i: 1-x, 1/2+y, 1/2-z] and Cg2··· Cg3^{i,ii} [3.7303 (16) and 3.7716 (16) Å, ii: 1-x, 1/2+y, 1/2-z], where Cg1, Cg2 and Cg3 are the centroids of the C6/C7/C8/C9/O1/C1, C1–C6 and C11–C16 rings, respectively). Overall, a two-dimensional architecture is observed in the *bc* plane.

S4. Synthesis and crystallization

Coumarin 3-carboxylic acid (1.0 mmol), 4-bromophenol (1.0 mmol) and a catalytic amount of N,N-dimethylamino-pyrimidine (DMAP) were dissolved in anhydrous CH_2Cl_2. To this solution, a solution of dicyclohexylcarbodimide (DCC) in dried CH_2Cl_2 was added and stirred. After 24 h of stirring, dicyclohexylurea was filtered off and the solution was concentrated. The solid residue obtained was purified by column chromatography on silica gel using $CHCl_3$ as the eluent. Single crystals suitable for X-ray studies were grown by slow evaporation technique at room temperature using ethanol as the solvent.

S5. Refinement

The H atoms were positioned with idealized geometry using a riding model with C—H = 0.93Å, and with 1.2U_{eq}(C). Owing to poor agreement, several reflections, *i.e.* (0 2 5), (-1 0 2), (-2 0 8), (7 0 0) and (-7 2 5), were omitted from the final cycles of refinement.

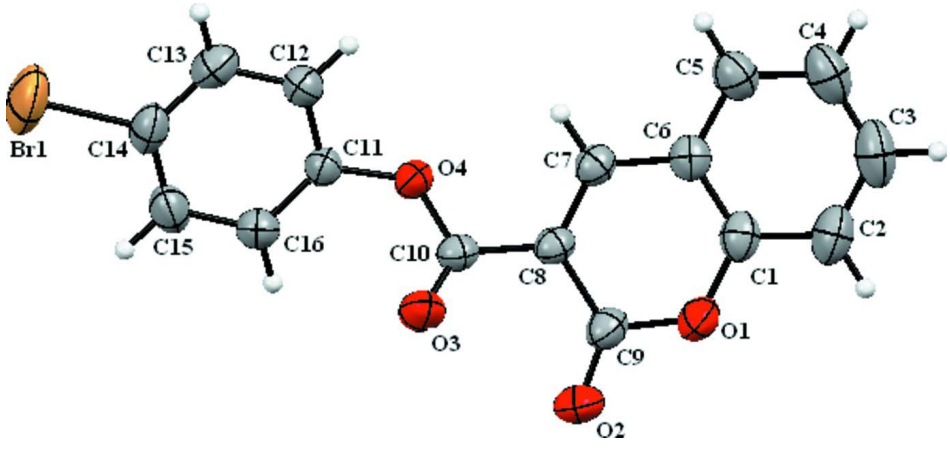

Figure 1

The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

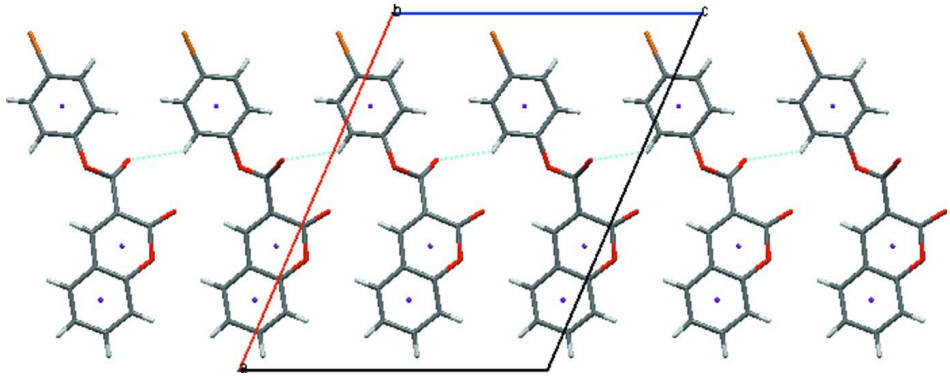

Figure 2

The crystal packing of the title compound *via* C—H···O interactions along [001]. Hydrogen bonds are shown as dashed lines.

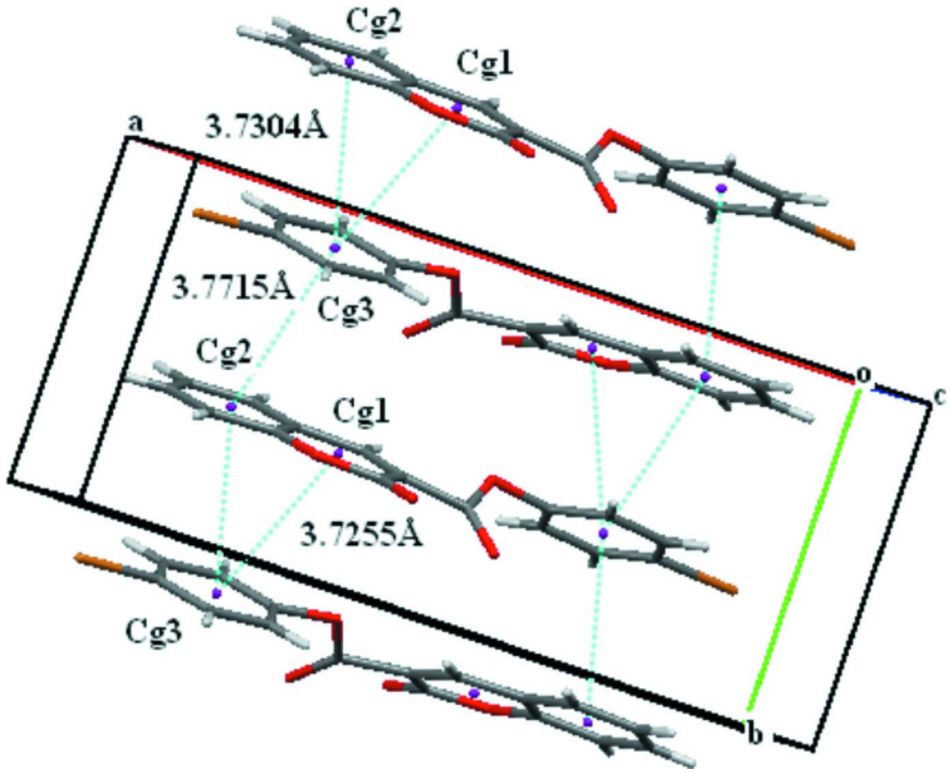

Figure 3

Various π–π interactions observed in the crystal packing

4-Bromophenyl-2-oxo-2*H*-chromene-3-carboxylate

Crystal data

$C_{16}H_9BrO_4$
M_r = 345.14
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 16.0782 (10) Å
b = 7.2618 (4) Å
c = 12.7396 (8) Å
β = 113.311 (4)°
V = 1366.01 (15) Å^3
Z = 4
F(000) = 688

Prism
D_x = 1.678 Mg m^{-3}
Melting point: 523 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2395 reflections
θ = 2.8–25.0°
μ = 3.02 mm^{-1}
T = 296 K
Prism, colourless
0.24 × 0.18 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 2.01 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.526, T_{max} = 0.617

20483 measured reflections
2395 independent reflections
1831 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 25.0°, θ_{min} = 2.8°
h = −19→19
k = −8→8
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.079$
$S = 1.01$
2395 reflections
191 parameters
0 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.8274P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0062 (6)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.94359 (2)	0.14526 (6)	0.64830 (3)	0.0907 (2)
O1	0.31144 (12)	0.1686 (2)	−0.06316 (14)	0.0517 (5)
O2	0.44603 (13)	0.1964 (3)	−0.06745 (15)	0.0612 (5)
O3	0.58965 (12)	0.2657 (3)	0.15291 (14)	0.0556 (5)
O4	0.56890 (11)	0.0734 (2)	0.27929 (13)	0.0428 (4)
C1	0.25543 (17)	0.1424 (3)	−0.0061 (2)	0.0460 (6)
C2	0.1631 (2)	0.1504 (4)	−0.0694 (3)	0.0613 (8)
H2	0.1403	0.1720	−0.1477	0.074*
C3	0.1059 (2)	0.1257 (4)	−0.0142 (3)	0.0709 (9)
H3	0.0436	0.1322	−0.0558	0.085*
C4	0.1389 (2)	0.0915 (4)	0.1017 (3)	0.0673 (9)
H4	0.0990	0.0734	0.1372	0.081*
C5	0.23074 (18)	0.0840 (4)	0.1648 (3)	0.0547 (7)
H5	0.2530	0.0613	0.2429	0.066*
C6	0.29078 (17)	0.1108 (3)	0.1108 (2)	0.0413 (6)
C7	0.38706 (16)	0.1145 (3)	0.1709 (2)	0.0394 (6)
H7	0.4122	0.0939	0.2493	0.047*
C8	0.44200 (16)	0.1472 (3)	0.11609 (19)	0.0364 (6)
C9	0.40485 (18)	0.1736 (3)	−0.0079 (2)	0.0440 (6)
C10	0.54071 (17)	0.1702 (3)	0.18007 (19)	0.0385 (6)
C11	0.65769 (16)	0.0988 (3)	0.36007 (19)	0.0370 (5)
C12	0.66608 (17)	0.1487 (3)	0.4677 (2)	0.0433 (6)
H12	0.6149	0.1711	0.4827	0.052*
C13	0.75178 (19)	0.1654 (4)	0.5536 (2)	0.0517 (7)
H13	0.7590	0.2000	0.6270	0.062*
C14	0.82608 (18)	0.1301 (4)	0.5288 (2)	0.0499 (7)

C15	0.81735 (18)	0.0805 (4)	0.4214 (2)	0.0538 (7)
H15	0.8686	0.0581	0.4065	0.065*
C16	0.73210 (17)	0.0637 (4)	0.3352 (2)	0.0452 (6)
H16	0.7251	0.0293	0.2619	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0491 (2)	0.1081 (3)	0.0795 (3)	−0.01632 (19)	−0.01221 (17)	0.0173 (2)
O1	0.0460 (11)	0.0681 (12)	0.0343 (9)	0.0056 (9)	0.0087 (8)	−0.0015 (8)
O2	0.0622 (13)	0.0888 (15)	0.0368 (10)	0.0067 (11)	0.0240 (10)	0.0059 (10)
O3	0.0497 (11)	0.0724 (13)	0.0443 (10)	−0.0097 (10)	0.0181 (9)	0.0127 (9)
O4	0.0364 (9)	0.0547 (10)	0.0336 (9)	−0.0038 (8)	0.0100 (7)	0.0081 (8)
C1	0.0401 (15)	0.0421 (15)	0.0489 (15)	0.0008 (11)	0.0102 (13)	−0.0059 (12)
C2	0.0473 (18)	0.0615 (19)	0.0576 (18)	0.0004 (14)	0.0020 (15)	−0.0034 (14)
C3	0.0383 (17)	0.064 (2)	0.096 (3)	−0.0063 (14)	0.0115 (18)	−0.0058 (18)
C4	0.0465 (18)	0.064 (2)	0.094 (3)	−0.0078 (15)	0.0305 (18)	−0.0008 (18)
C5	0.0470 (17)	0.0564 (17)	0.0636 (17)	−0.0055 (14)	0.0250 (15)	0.0011 (14)
C6	0.0403 (14)	0.0363 (14)	0.0455 (14)	0.0000 (11)	0.0150 (12)	−0.0028 (11)
C7	0.0421 (14)	0.0375 (13)	0.0367 (13)	0.0018 (11)	0.0135 (11)	−0.0006 (10)
C8	0.0421 (14)	0.0352 (13)	0.0316 (12)	0.0027 (10)	0.0144 (11)	−0.0010 (10)
C9	0.0464 (15)	0.0485 (15)	0.0335 (13)	0.0059 (12)	0.0121 (12)	−0.0013 (11)
C10	0.0433 (14)	0.0409 (14)	0.0336 (13)	0.0007 (11)	0.0178 (11)	−0.0006 (10)
C11	0.0333 (13)	0.0405 (13)	0.0354 (12)	−0.0006 (11)	0.0117 (10)	0.0040 (10)
C12	0.0401 (15)	0.0506 (15)	0.0407 (14)	0.0037 (12)	0.0177 (12)	0.0031 (11)
C13	0.0576 (18)	0.0535 (16)	0.0374 (14)	−0.0025 (13)	0.0120 (13)	0.0006 (12)
C14	0.0381 (15)	0.0502 (16)	0.0487 (16)	−0.0054 (12)	0.0036 (12)	0.0084 (12)
C15	0.0375 (15)	0.0610 (17)	0.0630 (18)	0.0030 (13)	0.0200 (14)	0.0106 (14)
C16	0.0445 (15)	0.0535 (16)	0.0399 (13)	0.0011 (12)	0.0192 (12)	0.0023 (12)

Geometric parameters (Å, º)

Br1—C14	1.903 (3)	C5—H5	0.9300
O1—C1	1.376 (3)	C6—C7	1.430 (3)
O1—C9	1.384 (3)	C7—C8	1.346 (3)
O2—C9	1.200 (3)	C7—H7	0.9300
O3—C10	1.198 (3)	C8—C9	1.463 (3)
O4—C10	1.358 (3)	C8—C10	1.479 (3)
O4—C11	1.403 (3)	C11—C12	1.372 (3)
C1—C2	1.382 (4)	C11—C16	1.377 (3)
C1—C6	1.387 (4)	C12—C13	1.385 (4)
C2—C3	1.373 (5)	C12—H12	0.9300
C2—H2	0.9300	C13—C14	1.375 (4)
C3—C4	1.380 (5)	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.368 (4)
C4—C5	1.374 (4)	C15—C16	1.381 (4)
C4—H4	0.9300	C15—H15	0.9300
C5—C6	1.402 (4)	C16—H16	0.9300

C1—O1—C9	122.67 (19)	C9—C8—C10	118.1 (2)
C10—O4—C11	118.88 (18)	O2—C9—O1	116.2 (2)
O1—C1—C2	117.5 (2)	O2—C9—C8	127.5 (2)
O1—C1—C6	121.0 (2)	O1—C9—C8	116.3 (2)
C2—C1—C6	121.5 (3)	O3—C10—O4	123.6 (2)
C3—C2—C1	118.6 (3)	O3—C10—C8	126.2 (2)
C3—C2—H2	120.7	O4—C10—C8	110.2 (2)
C1—C2—H2	120.7	C12—C11—C16	121.9 (2)
C2—C3—C4	121.3 (3)	C12—C11—O4	115.9 (2)
C2—C3—H3	119.4	C16—C11—O4	122.1 (2)
C4—C3—H3	119.4	C11—C12—C13	119.1 (2)
C5—C4—C3	120.2 (3)	C11—C12—H12	120.4
C5—C4—H4	119.9	C13—C12—H12	120.4
C3—C4—H4	119.9	C14—C13—C12	119.0 (2)
C4—C5—C6	119.8 (3)	C14—C13—H13	120.5
C4—C5—H5	120.1	C12—C13—H13	120.5
C6—C5—H5	120.1	C15—C14—C13	121.6 (2)
C1—C6—C5	118.7 (2)	C15—C14—Br1	119.5 (2)
C1—C6—C7	117.9 (2)	C13—C14—Br1	118.9 (2)
C5—C6—C7	123.3 (2)	C14—C15—C16	119.7 (2)
C8—C7—C6	121.3 (2)	C14—C15—H15	120.2
C8—C7—H7	119.4	C16—C15—H15	120.2
C6—C7—H7	119.4	C11—C16—C15	118.7 (2)
C7—C8—C9	120.8 (2)	C11—C16—H16	120.7
C7—C8—C10	121.0 (2)	C15—C16—H16	120.7

C9—O1—C1—C2	176.4 (2)	C7—C8—C9—O1	2.0 (3)
C9—O1—C1—C6	−3.1 (4)	C10—C8—C9—O1	−173.9 (2)
O1—C1—C2—C3	−179.7 (2)	C11—O4—C10—O3	6.3 (3)
C6—C1—C2—C3	−0.2 (4)	C11—O4—C10—C8	−170.71 (19)
C1—C2—C3—C4	−0.7 (4)	C7—C8—C10—O3	−148.3 (3)
C2—C3—C4—C5	0.9 (5)	C9—C8—C10—O3	27.6 (4)
C3—C4—C5—C6	−0.2 (4)	C7—C8—C10—O4	28.7 (3)
O1—C1—C6—C5	−179.7 (2)	C9—C8—C10—O4	−155.5 (2)
C2—C1—C6—C5	0.9 (4)	C10—O4—C11—C12	124.6 (2)
O1—C1—C6—C7	2.8 (3)	C10—O4—C11—C16	−59.7 (3)
C2—C1—C6—C7	−176.7 (2)	C16—C11—C12—C13	0.4 (4)
C4—C5—C6—C1	−0.7 (4)	O4—C11—C12—C13	176.2 (2)
C4—C5—C6—C7	176.7 (3)	C11—C12—C13—C14	−0.5 (4)
C1—C6—C7—C8	−0.1 (3)	C12—C13—C14—C15	0.5 (4)
C5—C6—C7—C8	−177.6 (2)	C12—C13—C14—Br1	−177.94 (19)
C6—C7—C8—C9	−2.2 (3)	C13—C14—C15—C16	−0.5 (4)
C6—C7—C8—C10	173.5 (2)	Br1—C14—C15—C16	178.0 (2)
C1—O1—C9—O2	179.7 (2)	C12—C11—C16—C15	−0.3 (4)
C1—O1—C9—C8	0.7 (3)	O4—C11—C16—C15	−175.9 (2)
C7—C8—C9—O2	−176.9 (3)	C14—C15—C16—C11	0.4 (4)
C10—C8—C9—O2	7.3 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···O3^{i}	0.93	2.40	3.124 (3)	134

Symmetry code: (i) x, $-y+1/2$, $z+1/2$.