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Synthesis and structure of 4-bromo-2-chlorophenyl 4′-methoxy-[1,1′-biphenyl]-4-carboxylate featuring short halogen···oxygen contacts

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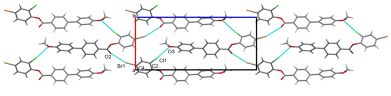
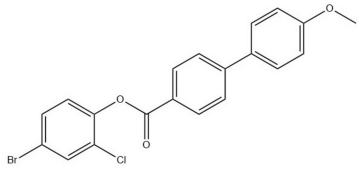
In the title compound, $C_{20}H_{14}BrClO_3$, the dihedral angles between the aromatic ring of the 4-bromo-2-chlorophenyl and the immediate neighbour and second aromatic ring of the biphenyl moiety are 80.59 (2) and 75.42 (2)°, respectively. The dihedral angle between the rings within the biphenyl moiety is 24.57 (4)°. The torsion angle associated with the ester group linking the biphenyl ring and the 4-bromo-2-chlorophenyl group is −166.6 (2)°. The extended structure features short halogen···oxygen contacts [Cl···O = 2.991 (3), Br···O = 3.139 (2) Å], forming molecular sheets lying parallel to (101). The Hirshfeld surface analysis reveals that the major contributions to the intermolecular interactions are from C···H/H···C (32.2%), H···H/H···H (26.3%), Br···H/H···Br (10.7%), O···H/H···O (10.4%) and Cl···H/H···Cl (7.5%) contacts.

1. Chemical context

Biphenyl derivates exhibit medicinal properties such as anti-hypertensive (Sharma *et al.*, 2010), anti-diabetic (Sachan *et al.*, 2009), anti-bacterial (Trivedi *et al.*, 2009), antifungal (Zhao *et al.*, 2017) and anticancer (Mukherjee *et al.*, 2016) effects. The drug obtained from the piperidine derivative of biphenyl-4-carboxylate selectively kills the bacterial persisters that are resistant to antibiotic treatments (Kim *et al.*, 2011). Some biphenyl-carboxylic acid derivatives act as antiresorptive drugs (Van't Hof *et al.*, 2004; Idris *et al.*, 2009) by stopping or slowing down bone loss in osteoporosis. It is found that biphenyl compounds substituted with a heterocyclic ring can act as anti-tyrosinase agents (Kwong *et al.*, 2017) that reduce the activity of tyrosinase enzyme. Biphenyl-4-carboxylic acid derivatives inhibit tubulin polymerization to act as anticancer agents (Mahale *et al.*, 2014). 4-Bromo-2-chlorophenyl-based compounds exhibit significant *in vitro* inhibitory effects on plasmodium falciparum against malaria parasites (Vallone *et al.*, 2018, Kos *et al.*, 2022). The presence of a halogen atom in the phenyl moiety of 4-bromo-2-chlorophenyl derivatives is found to induce antimicrobial properties in the compounds (Radwan *et al.*, 2014).





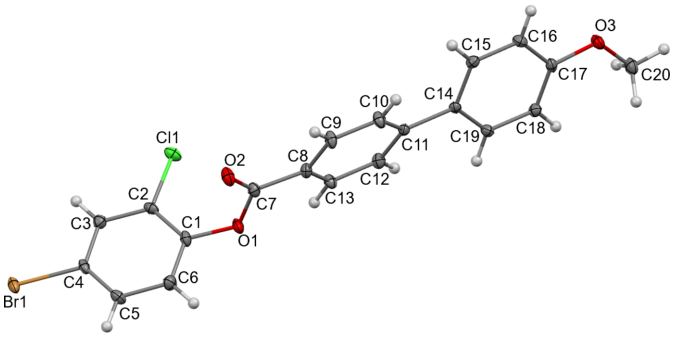


Figure 1
The molecular structure of (**I**) showing displacement ellipsoids drawn at the 50% probability level.

As part of our studies in this area, we now present the synthesis and crystal structure of the title compound, $C_{20}H_{14}BrClO_3$ (**I**).

2. Structural commentary

The molecular structure of (**I**) is shown in Fig. 1. The dihedral angle between the aromatic ring (C1–C6) of the 4-bromo-2-chlorophenyl group and the C8–C13 and C14–C19 rings of the methoxy-biphenyl-carboxylate moiety are 80.59 (2) and 75.42 (2)°, respectively. The dihedral angle between the aromatic rings in the biphenyl moiety (C8–C13 and C14–C19) is 24.57 (4)°. The torsion angle in the ester group (C1—O1—C7—C8) linking the 4-bromo-2-chlorophenyl group with the biphenyl moiety is −166.6 (2)°.

3. Supramolecular features

The crystal packing features short C2—Cl1···O3 and C4—Br1···O2 interactions with a Cl1···O3 distance of 2.991 (3) Å and a Br1···O2 distance of 3.139 (2) Å, forming molecular sheets propagating in the (101) plane, as shown in Fig. 2. The van der Waals separations of Cl and O atoms and Br and O atoms are 3.27 and 3.37 Å, respectively. Two weak C—H···π interactions also occur (Table 1).

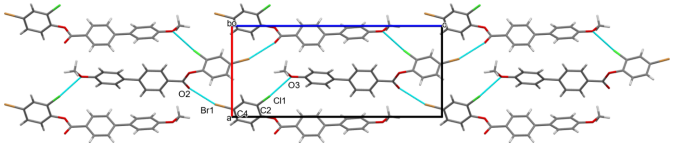


Figure 2
The packing of (**I**) with dashed lines indicating Cl···O and Br···O contacts.

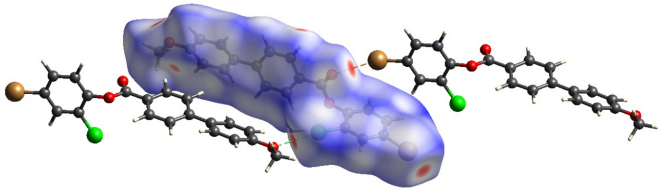


Figure 3
The Hirshfeld surface of (**I**) mapped over d_{norm} with red spots corresponding to Cl···O and Br···O short contacts.

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

*Cg*3 is the centroid of the C14–C19 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···*Cg*3^{i}	0.93	2.65	3.459 (3)	147
C10—H10···*Cg*3^{ii}	0.93	2.85	3.577 (3)	136

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

4. Hirshfeld surface analysis

A Hirshfeld surface analysis for (**I**) was performed to quantify and visualize the intermolecular interaction present in the molecules using *Crystal-Explorer17* (Turner *et al.*, 2017). The Hirshfeld surface (Spackman & Jayatilaka, 2009) mapped over normalised contact distance d_{norm} (Fig. 3) shows the presence of red spots on the iso-surface that correspond to the existence of the short halogen···oxygen type interactions noted above. The two-dimensional fingerprint plots (McKinnon *et al.*, 2007)

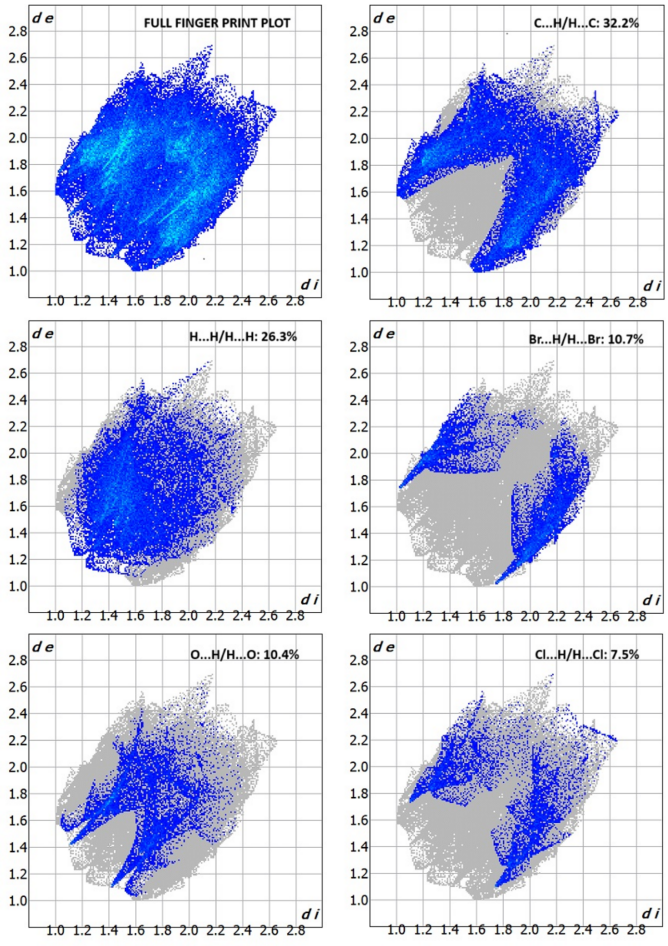


Figure 4
The two-dimensional fingerprint plots of the major contributors to intermolecular interactions in (**I**).

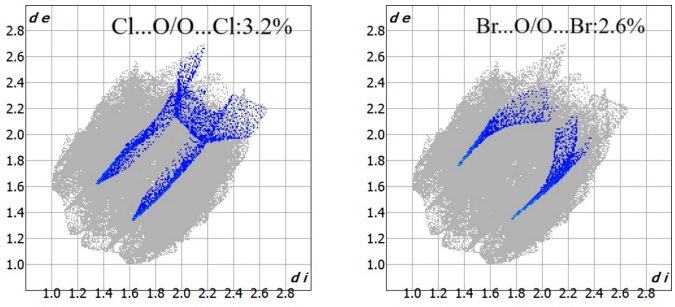


Figure 5
Fingerprints plots for the Cl···O/O···Cl and Br···O/O···Br contacts in (**I**).

are shown in Fig. 4. The major contributions for the intermolecular interactions are from C···H/H···C (32.2%), H···H (26.3%), Br···H/H···Br (10.7%), O···H/H···O (10.4%) and Cl···H/H···Cl (7.5%). The sharp spikes in the fingerprint plots for Cl···O and Br···O contacts (Fig. 5) confirm the existence of the directional halogen···oxygen interactions.

5. Database survey

A search of the Cambridge Structural Database (CSD version 2.0.4, December 2019; Groom *et al.*, 2016) for molecules containing a [1,1′-biphenyl]-4-carboxylate fragment resulted in more than thirty matches, but six compounds were identified with a substitution at the oxygen atom of the ester group similar to the title compound. In five of the compounds, namely CSD refcodes PUGZUP (Chen *et al.*, 2020), ESEMAT (Wang *et al.*, 2021), FIRYIR(Royal *et al.*, 2019), JOCVAB (Chen *et al.*, 2019) and JOCVEF (Chen *et al.*, 2019), the dihedral angles between the aromatic rings of the biphenyl carboxylic acid range between 29.42 (2) and 38.39 (3)° whereas in NEKPAK (Wang *et al.*, 2017), the dihedral angle is 12.42 (2)°. The conformations of the ester groups (C—O—C—C), which link the biphenyl ring and the functional group in the above compounds and (**I**), are all *anti*.

6. Synthesis and crystallization

A mixture of 4-bromo-2-chlorophenol (0.208 g, 1.00 mmol) and 4′-methoxy-[1,1′-biphenyl]-4-carboxylic acid (0.228 g, 1.00 mmol) was suspended in anhydrous chloroform (10 ml). To this were added *N*,*N*-dicyclohexylcarbodiimide (0.206 g, 1.00 mmol) and 4-*N*,*N*-dimethylamino pyridine (5 mg) and the mixture was stirred overnight at room temperature. The *N*,*N*-dicyclohexyl urea formed was filtered off and the filtrate diluted with chloroform (25 ml). This solution was washed successively with 5% aqueous acetic acid solution (2 × 25 ml) and water (2 × 25 ml) and dried over sodium sulfate. The residue obtained on removal of the solvent was chromatographed on silica gel using chloroform as the eluent. Removal of solvent from the eluate afforded a white material, which was recrystallized from the mixed solvents of chloroform and petroleum ether to yield colourless prisms of (**I**). Yield 78%.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{14}BrClO_3$
M_r	417.67
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	296
a, b, c (Å)	8.8347 (4), 9.4124 (5), 20.5526 (11)
V (Å^3)	1709.07 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.58
Crystal size (mm)	0.40 × 0.35 × 0.29
Data collection	
Diffractometer	Bruker SMART APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.371, 0.475
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28805, 4264, 4012
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.054, 1.04
No. of reflections	4264
No. of parameters	228
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.23
Absolute structure	Flack parameter
Absolute structure parameter	0.011 (8)

Computer programs: *APEX2* and *SAINT* (Bruker, 2017), *SHELXL2018/3* and *SHELXL2019/2* (Sheldrick, 2015*b*), *SHELXT2018/2* (Sheldrick, 2015*a*) and *Mercury* (Macrae *et al.*, 2020).

Elemental analysis calculated: C, 57.51; H, 3.38; Br, 19.13; Cl, 8.49; O, 11.49% found is C, 57.56; H, 3.39; Br, 19.15; Cl, 8.53%, m.p. 338–340 K.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned with idealized geometry and refined using a riding model with C—H = 0.93–0.96 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

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Synthesis and structure of 4-bromo-2-chlorophenyl 4′-methoxy-[1,1′-biphenyl]-4-carboxylate featuring short halogen···oxygen contacts

B. S. Palakshamurthy, H. Anil Kumar, H. C. Devarajegowda, H.T. Srinivasa and M. Harish Kumar

Computing details

4-Bromo-2-chlorophenyl 4′-methoxy-[1,1′-biphenyl]-4-carboxylate

Crystal data

$C_{20}H_{14}BrClO_3$
M_r = 417.67
Orthorhombic, $P2_12_12_1$
a = 8.8347 (4) Å
b = 9.4124 (5) Å
c = 20.5526 (11) Å
V = 1709.07 (15) Å^3
Z = 4
$F(000)$ = 840
prism
D_x = 1.623 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4264 reflections
θ = 2.5–28.5°
μ = 2.58 mm^{-1}
T = 296 K
Prism, colourless
0.40 × 0.35 × 0.29 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 1.02 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.371, T_{max} = 0.475
28805 measured reflections
4264 independent reflections
4012 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 28.4°, θ_{min} = 2.0°
h = −11→11
k = −12→11
l = −27→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.054
S = 1.04
4264 reflections
228 parameters
0 restraints
0 constraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0209P)^2 + 0.2511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.005
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack parameter
Absolute structure parameter: 0.011 (8)

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.

Refinement. Refined as a 2-component inversion twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.36294 (3)	0.65415 (3)	1.07977 (2)	0.02179 (8)
Cl1	0.27206 (8)	0.77586 (8)	0.82023 (3)	0.02310 (15)
O1	0.5178 (2)	0.5732 (2)	0.79614 (9)	0.0205 (4)
O2	0.6829 (2)	0.7562 (2)	0.79511 (9)	0.0237 (4)
O3	0.5585 (2)	0.6213 (2)	0.28240 (9)	0.0200 (4)
C1	0.4892 (3)	0.5971 (3)	0.86220 (13)	0.0170 (5)
C2	0.3733 (3)	0.6880 (3)	0.87978 (12)	0.0162 (5)
C3	0.3367 (3)	0.7066 (3)	0.94475 (13)	0.0179 (5)
H3	0.260073	0.768730	0.957100	0.021*
C4	0.4174 (3)	0.6301 (3)	0.99101 (12)	0.0163 (5)
C5	0.5330 (3)	0.5395 (3)	0.97413 (13)	0.0192 (6)
H5	0.586627	0.490548	1.005954	0.023*
C6	0.5685 (3)	0.5224 (3)	0.90840 (13)	0.0200 (6)
H6	0.645518	0.460749	0.895960	0.024*
C7	0.6090 (3)	0.6712 (3)	0.76569 (12)	0.0173 (5)
C8	0.6024 (3)	0.6556 (3)	0.69402 (12)	0.0162 (5)
C9	0.7052 (3)	0.7323 (3)	0.65671 (13)	0.0193 (5)
H9	0.776532	0.789750	0.677077	0.023*
C10	0.7022 (3)	0.7237 (3)	0.58936 (13)	0.0199 (5)
H10	0.772926	0.773917	0.565012	0.024*
C11	0.5936 (3)	0.6401 (3)	0.55758 (12)	0.0137 (5)
C12	0.4918 (3)	0.5638 (3)	0.59588 (12)	0.0181 (6)
H12	0.419557	0.507014	0.575668	0.022*
C13	0.4953 (3)	0.5702 (3)	0.66334 (13)	0.0171 (5)
H13	0.426611	0.517802	0.687867	0.021*
C14	0.5846 (3)	0.6327 (3)	0.48544 (12)	0.0137 (5)
C15	0.6389 (3)	0.7435 (3)	0.44582 (12)	0.0163 (5)
H15	0.682792	0.822772	0.465137	0.020*
C16	0.6283 (3)	0.7369 (3)	0.37886 (12)	0.0172 (5)
H16	0.664628	0.811468	0.353630	0.021*
C17	0.5634 (3)	0.6189 (3)	0.34898 (12)	0.0160 (5)
C18	0.5083 (3)	0.5085 (3)	0.38685 (12)	0.0163 (5)
H18	0.464090	0.429602	0.367308	0.020*
C19	0.5197 (3)	0.5164 (3)	0.45424 (13)	0.0158 (5)
H19	0.482771	0.441679	0.479239	0.019*
C20	0.4945 (4)	0.5005 (3)	0.25032 (13)	0.0238 (6)
H20A	0.509264	0.509222	0.204215	0.036*
H20B	0.388077	0.495699	0.259587	0.036*

H20C	0.543054	0.415659	0.265624	0.036*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03127 (14)	0.02241 (13)	0.01170 (11)	−0.00941 (12)	0.00389 (11)	−0.00150 (11)
Cl1	0.0232 (3)	0.0267 (3)	0.0194 (3)	0.0006 (3)	−0.0048 (3)	0.0066 (3)
O1	0.0279 (10)	0.0228 (10)	0.0107 (9)	−0.0050 (8)	0.0038 (8)	0.0002 (8)
O2	0.0236 (10)	0.0321 (11)	0.0153 (9)	−0.0082 (9)	0.0012 (8)	−0.0034 (8)
O3	0.0248 (10)	0.0231 (11)	0.0120 (9)	−0.0039 (8)	−0.0019 (8)	0.0016 (7)
C1	0.0160 (12)	0.0222 (13)	0.0128 (12)	−0.0036 (11)	0.0030 (10)	−0.0014 (10)
C2	0.0160 (11)	0.0177 (13)	0.0147 (11)	−0.0027 (10)	−0.0046 (10)	0.0035 (9)
C3	0.0180 (13)	0.0174 (12)	0.0182 (12)	−0.0007 (10)	0.0023 (10)	−0.0003 (10)
C4	0.0190 (12)	0.0196 (14)	0.0104 (11)	−0.0076 (11)	0.0023 (9)	0.0008 (10)
C5	0.0181 (13)	0.0243 (14)	0.0152 (13)	−0.0012 (12)	−0.0015 (10)	0.0057 (11)
C6	0.0173 (12)	0.0231 (14)	0.0197 (14)	0.0030 (11)	0.0033 (11)	0.0010 (11)
C7	0.0150 (12)	0.0210 (13)	0.0160 (11)	−0.0002 (11)	0.0021 (10)	0.0002 (10)
C8	0.0161 (12)	0.0191 (12)	0.0134 (11)	0.0003 (11)	0.0015 (9)	−0.0029 (11)
C9	0.0179 (12)	0.0258 (14)	0.0142 (12)	−0.0077 (12)	0.0001 (10)	−0.0041 (11)
C10	0.0192 (12)	0.0250 (13)	0.0157 (14)	−0.0067 (11)	0.0034 (11)	0.0000 (11)
C11	0.0143 (11)	0.0141 (12)	0.0127 (11)	0.0015 (10)	−0.0003 (9)	−0.0010 (10)
C12	0.0163 (12)	0.0204 (13)	0.0177 (13)	−0.0028 (11)	−0.0014 (10)	−0.0020 (10)
C13	0.0163 (12)	0.0193 (13)	0.0158 (13)	−0.0041 (11)	0.0031 (10)	0.0017 (10)
C14	0.0124 (11)	0.0160 (13)	0.0128 (11)	0.0036 (10)	−0.0008 (9)	0.0011 (10)
C15	0.0167 (11)	0.0144 (12)	0.0179 (12)	0.0008 (11)	−0.0014 (11)	−0.0019 (9)
C16	0.0173 (11)	0.0176 (12)	0.0168 (12)	−0.0012 (12)	0.0004 (11)	0.0045 (9)
C17	0.0151 (12)	0.0214 (14)	0.0114 (12)	0.0030 (10)	−0.0002 (10)	−0.0008 (9)
C18	0.0177 (12)	0.0152 (13)	0.0162 (13)	−0.0005 (10)	−0.0037 (10)	−0.0018 (10)
C19	0.0161 (12)	0.0160 (13)	0.0154 (12)	0.0010 (11)	−0.0004 (10)	0.0029 (10)
C20	0.0287 (14)	0.0283 (16)	0.0143 (13)	−0.0021 (13)	−0.0031 (11)	−0.0035 (11)

Geometric parameters (Å, º)

Br1—C4	1.900 (2)	C10—C11	1.402 (4)
Cl1—C2	1.727 (3)	C10—H10	0.9300
O1—C7	1.375 (3)	C11—C12	1.395 (4)
O1—C1	1.399 (3)	C11—C14	1.487 (3)
O2—C7	1.196 (3)	C12—C13	1.388 (4)
O3—C17	1.369 (3)	C12—H12	0.9300
O3—C20	1.431 (3)	C13—H13	0.9300
C1—C6	1.374 (4)	C14—C19	1.392 (4)
C1—C2	1.382 (4)	C14—C15	1.408 (3)
C2—C3	1.385 (4)	C15—C16	1.381 (3)
C3—C4	1.389 (4)	C15—H15	0.9300
C3—H3	0.9300	C16—C17	1.392 (4)
C4—C5	1.375 (4)	C16—H16	0.9300
C5—C6	1.396 (4)	C17—C18	1.387 (4)
C5—H5	0.9300	C18—C19	1.391 (3)

C6—H6	0.9300	C18—H18	0.9300
C7—C8	1.482 (3)	C19—H19	0.9300
C8—C9	1.391 (4)	C20—H20A	0.9600
C8—C13	1.393 (4)	C20—H20B	0.9600
C9—C10	1.387 (4)	C20—H20C	0.9600
C9—H9	0.9300		

C7—O1—C1	116.1 (2)	C11—C10—H10	119.6
C17—O3—C20	117.4 (2)	C12—C11—C10	117.9 (2)
C6—C1—C2	120.9 (2)	C12—C11—C14	120.3 (2)
C6—C1—O1	119.7 (2)	C10—C11—C14	121.9 (2)
C2—C1—O1	119.1 (2)	C13—C12—C11	121.8 (2)
C6—C1—O1	119.7 (2)	C13—C12—H12	119.1
C2—C1—O1	119.1 (2)	C11—C12—H12	119.1
C1—C2—C3	120.2 (2)	C12—C13—C8	119.5 (2)
C1—C2—Cl1	119.6 (2)	C12—C13—H13	120.3
C3—C2—Cl1	120.1 (2)	C8—C13—H13	120.3
C2—C3—C4	118.3 (2)	C19—C14—C15	117.2 (2)
C2—C3—H3	120.8	C19—C14—C11	121.3 (2)
C4—C3—H3	120.8	C15—C14—C11	121.6 (2)
C5—C4—C3	122.0 (2)	C16—C15—C14	121.3 (2)
C5—C4—Br1	120.3 (2)	C16—C15—H15	119.3
C3—C4—Br1	117.7 (2)	C14—C15—H15	119.3
C4—C5—C6	118.9 (3)	C15—C16—C17	120.2 (2)
C4—C5—H5	120.6	C15—C16—H16	119.9
C6—C5—H5	120.6	C17—C16—H16	119.9
C1—C6—C5	119.7 (3)	O3—C17—C18	124.2 (2)
C1—C6—H6	120.2	O3—C17—C16	116.1 (2)
C5—C6—H6	120.2	C18—C17—C16	119.6 (2)
O2—C7—O1	122.5 (2)	C17—C18—C19	119.6 (2)
O2—C7—O1	122.5 (2)	C17—C18—H18	120.2
O2—C7—C8	126.2 (2)	C19—C18—H18	120.2
O1—C7—C8	111.3 (2)	C18—C19—C14	122.1 (3)
O1—C7—C8	111.3 (2)	C18—C19—H19	119.0
C9—C8—C13	119.6 (2)	C14—C19—H19	119.0
C9—C8—C7	118.1 (2)	O3—C20—H20A	109.5
C13—C8—C7	122.3 (2)	O3—C20—H20B	109.5
C10—C9—C8	120.5 (2)	H20A—C20—H20B	109.5
C10—C9—H9	119.8	O3—C20—H20C	109.5
C8—C9—H9	119.8	H20A—C20—H20C	109.5
C9—C10—C11	120.7 (2)	H20B—C20—H20C	109.5
C9—C10—H10	119.6		

O1—O1—C1—C6	0.0 (6)	O2—C7—C8—C13	−169.1 (3)
C7—O1—C1—C6	−100.4 (3)	O1—C7—C8—C13	11.1 (4)
O1—O1—C1—C2	0.0 (6)	O1—C7—C8—C13	11.1 (4)
C7—O1—C1—C2	84.4 (3)	C13—C8—C9—C10	−0.3 (4)
C7—O1—C1—O1	0 (34)	C7—C8—C9—C10	−178.8 (3)

C6—C1—C2—C3	0.9 (4)	C8—C9—C10—C11	1.4 (4)
O1—C1—C2—C3	176.0 (2)	C9—C10—C11—C12	−1.5 (4)
O1—C1—C2—C3	176.0 (2)	C9—C10—C11—C14	178.0 (2)
C6—C1—C2—Cl1	−178.0 (2)	C10—C11—C12—C13	0.6 (4)
O1—C1—C2—Cl1	−2.8 (3)	C14—C11—C12—C13	−178.9 (2)
O1—C1—C2—Cl1	−2.8 (3)	C11—C12—C13—C8	0.4 (4)
C1—C2—C3—C4	−1.1 (4)	C9—C8—C13—C12	−0.6 (4)
Cl1—C2—C3—C4	177.7 (2)	C7—C8—C13—C12	177.8 (2)
C2—C3—C4—C5	1.2 (4)	C12—C11—C14—C19	−24.4 (4)
C2—C3—C4—Br1	−178.8 (2)	C10—C11—C14—C19	156.1 (3)
C3—C4—C5—C6	−1.1 (4)	C12—C11—C14—C15	154.5 (3)
Br1—C4—C5—C6	178.9 (2)	C10—C11—C14—C15	−25.0 (4)
C2—C1—C6—C5	−0.7 (4)	C19—C14—C15—C16	−0.1 (4)
O1—C1—C6—C5	−175.8 (2)	C11—C14—C15—C16	−179.1 (3)
O1—C1—C6—C5	−175.8 (2)	C14—C15—C16—C17	−0.2 (4)
C4—C5—C6—C1	0.8 (4)	C20—O3—C17—C18	−1.1 (4)
O1—O1—C7—O2	0.0 (5)	C20—O3—C17—C16	179.1 (2)
C1—O1—C7—O2	13.6 (4)	C15—C16—C17—O3	−179.7 (3)
C1—O1—C7—O1	0 (67)	C15—C16—C17—C18	0.5 (4)
O1—O1—C7—C8	0.0 (4)	O3—C17—C18—C19	179.7 (3)
C1—O1—C7—C8	−166.6 (2)	C16—C17—C18—C19	−0.5 (4)
O2—C7—C8—C9	9.3 (4)	C17—C18—C19—C14	0.2 (4)
O1—C7—C8—C9	−170.5 (2)	C15—C14—C19—C18	0.1 (4)
O1—C7—C8—C9	−170.5 (2)	C11—C14—C19—C18	179.1 (2)

Hydrogen-bond geometry (Å, º)

*Cg*3 is the centroid of the C14–C19 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···*Cg*3^{i}	0.93	2.65	3.459 (3)	147
C10—H10···*Cg*3^{ii}	0.93	2.85	3.577 (3)	136

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

Parameter	**SCXRD**	**DFT**
Br1—C4	1.900 (2)	1.9148
Cl1—C2	1.727 (3)	1.7468
O1—C7	1.375 (3)	1.3831
O1—C1	1.399 (3)	1.3848
O2—C7	1.196 (3)	1.2025
O3—C17	1.369 (3)	1.3619
C7—O1—C1	116.1 (2)	117.908
C17—O3—C20	117.4 (2)	118.693
C6—C1—C2	120.9 (2)	119.670
C6—C1—O1	119.7 (2)	119.844
O2—C7—O1	122.5 (2)	122.388
O2—C7—C8	126.2 (2)	126.007
C1—O1—C7—C8	-166.6 (2	-179.143

C7—O1—C1—C6	-100.4 (3)	-88.445
O1—C1—C2—Cl1	-2.8 (3)	-3.598