



Crystal structure of 4,4'-dibromo-2',5'-dimethoxy-[1,1'-biphenyl]-2,5-dione (BrHBQBr)

Joseph E. Meany,^a Steven P. Kelley,^a Robert M. Metzger,^a Robin D. Rogers^b and Stephen A. Woski^{a*}

Received 25 September 2015
Accepted 28 October 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; molecular rectifier; hemibiquinone; π - π stacking interactions; hydrogen bonding; Br \cdots Br halogen bonding

CCDC reference: 1433845

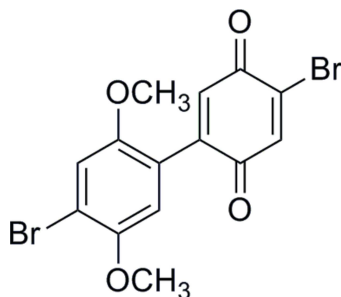
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336, USA, and ^bDepartment of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada, H3A 0B8. *Correspondence e-mail: swoski@ua.edu

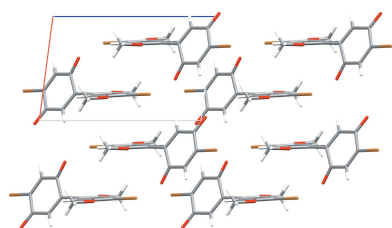
In the title compound, C₁₄H₁₀Br₂O₄, the dihedral angle between the aromatic rings is 67.29 (19)°. Both methoxy-group C atoms lie close to the plane of their attached ring [deviations = -0.130 (4) and 0.005 (5) Å]. In the crystal, molecules pack in a centrosymmetric fashion and interact *via* a mixture of weak π - π stacking interactions [centroid-centroid separations = 4.044 (2) and 4.063 (3) Å], weak C-H \cdots O hydrogen bonding, and Br \cdots Br halogen bonding. This induces a geometry quite different than that predicted by theory.

1. Chemical context

Biphenyl derivatives have recently been investigated as conductors for single molecule electronic systems (Venkataraman *et al.*, 2006). Researchers have shown that as the equilibrium twist angle θ between the two rings increases, conduction through the molecule decreases as $\cos^2(\theta)$. This effect is rationalized as a loss of overlap between two π systems. Interrupting conjugation is a prerequisite for the design of unimolecular rectifiers (Aviram & Ratner, 1974). Biphenyl derivatives with one electron-rich and one electron-deficient ring may be able to bias the direction of electron flow through the molecule, thus acting as a molecular diode. To this end we propose a dimethoxybenzene-quinone structure ('hemibiquinone', HBQ) as a potential unimolecular device. The asymmetric biphenyl structure should allow for high conductivity through each of the rings, while the dihedral angle between the two rings decreases orbital overlap and allows for partial isolation of the electron-rich donor and electron-poor acceptor moieties.



Two HBQ structures have been previously reported by Taylor *et al.* (2007) and Zeng & Becker (2004). The molecule described herein is unique in that it possesses bromine substituents on each ring (Fig. 1). The distal halogens allow for high synthetic versatility: these groups can be elaborated sequentially with functional groups to allow deposition in a predictable manner onto a variety of substrates. Originally this



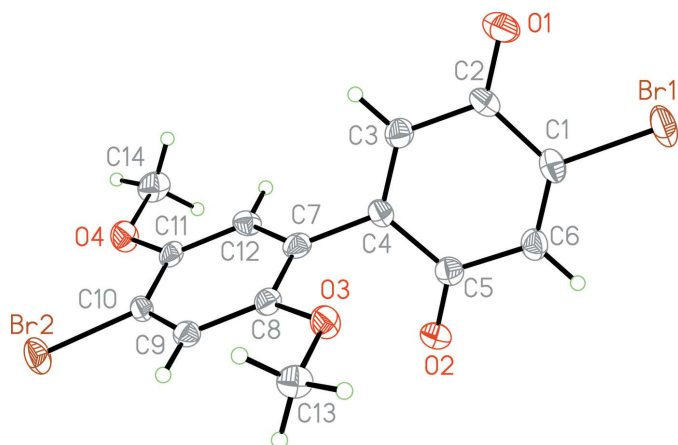


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level.

molecule was proposed by Love *et al.* (2009) as an impurity in the synthesis of 4,4'-dibromodiquinone; however, characterization of this compound was not reported. We have developed a selective synthesis for this hemibiquinone that is scalable to gram quantities.

2. Structural commentary

Because of the crucial role that the twist angle between the rings plays in the electronic properties of the molecule, the determination of the C12–C7–C4–C5 torsion angle is the key observation in this structural analysis. This angle measures $-110.9(4)^\circ$ in the crystal structure. DFT (B3LYP-DGDZVP) calculations performed on the target molecule in the gas phase predict an angle of -38.54° . This significant discrepancy is probably due to packing interactions in the solid phase.

Substituents on the HBQ system behave as expected. The C–Br bond distances reflect the natures of the electron-deficient quinone and electron-rich dimethoxybenzene rings: the C1–Br1 bond distance is 1.872(5) Å, while the C10–Br2 bond is 1.897(4) Å. Thus Br1 has a slightly stronger π -donating character into the quinone moiety, strengthening the bond relative to the C10–Br2 bond of the dimethoxybenzene

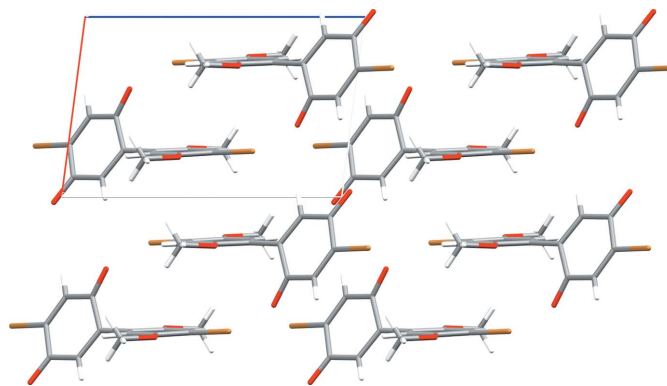


Figure 2
The unit-cell packing of the title compound, viewed down the *b* axis.

ring. The methoxy substituents are nearly coplanar to the benzene ring, with a C12–C11–O4–C14 torsion angle of $1.5(6)^\circ$ and a C9–C8–O3–C13 torsion angle of $-4.4(5)^\circ$. The methyl portions of each of these groups point away from the sterically restricting groups *ortho* to these positions. Finally, the quinone ring is slightly buckled (r.m.s. deviation = 0.064 Å), probably due to supramolecular packing effects.

3. Supramolecular features

Each molecule is surrounded by eight neighboring molecules, which interact through hydrogen bonding, halogen bonding, and π – π interactions (Figs. 2 and 3). The strongest interactions appear to be between functional groups on the quinone ring of one molecule with those on the dimethoxybenzene ring of another. These include especially short but non-directional C–H \cdots O hydrogen bonds (Table 1) between the quinone carbonyl groups and dimethoxybenzene ring hydrogen atoms of two neighbors. Interactions between like parts of neighboring molecules include edge-to-edge stacking of quinone rings with quinone rings, dimethoxybenzene rings with dimethoxybenzene rings, and dimeric hydrogen bonding between methoxy groups. Quinone rings on adjacent molecules along the *c* axis show some face-to-face π -stacking.

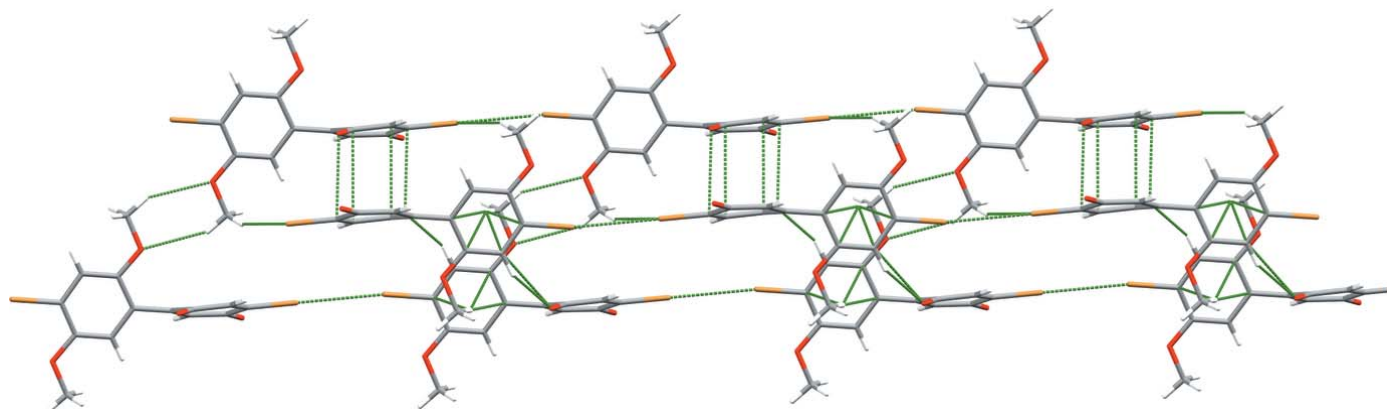


Figure 3
Packing diagram showing the stacking of parallel halogen-bonded chains. The view is down the *a* axis.

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the C1–C6 and C7–C12 rings, respectively.

D–H...A	D–H	H...A	D...A	D–H...A
C9–H9A...O2 ⁱ	0.95	2.40	3.270 (5)	151
C12–H12A...O1 ⁱⁱ	0.95	2.62	3.461 (5)	148
C13–H13A...O4 ⁱⁱⁱ	0.98	2.65	3.525 (5)	149
C13–H13B...Cg2 ⁱ	0.98	2.57	3.443 (5)	148
C14–H14A...Cg1 ^{iv}	0.98	3.00	3.695 (5)	129

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y + 2, -z + 2$; (iii) $x, y - 1, z$; (iv) $x, y + 1, z$.

Along the *a* axis, the benzene rings ‘nestle’ closely to one another in an antiparallel geometry, where one quinone points up and the layer behind it points down. Within the *cb* plane, the benzene rings are coplanar; hydrogen atoms from C14 on one molecule project closely to O3 on the adjacent molecule and *vice versa* for a hydrogen atom attached to C13 to the adjacent O4 (Fig. 2). Symmetric C–H... π short contacts exist between pairs of C13–H13C...dimethoxybenzene (Table 1).

Molecules are aligned linearly in a head-to-tail manner where the bromine atoms participate in Br...Br halogen bonding (Fig. 3). As discussed above, Br1 is electron deficient with respect to Br2, and a distinct halogen bond forms along the molecular *x*-axis (the C7–C4 biphenyl bond). The Br1...Br2 separation is 3.4204 (8) Å, with almost linear C1–Br1...Br2 and C10–Br2...Br1 angles of 178.2 (4) and 170.9 (4)°, respectively. Equivalent rings from molecules packed along this axis are parallel to one another; the quinone and benzene rings aligned coplanar to the corresponding ring in the next molecule.

4. Synthesis and crystallization

Cerium(IV) ammonium nitrate (0.956 g, 1.75 mmol, 1.75 eq) was dissolved in 30 ml of H₂O. A solution of 2-bromo-1,4-dimethoxybenzene (0.253 g, 1.17 mmol) in 25 ml of acetonitrile was quickly added with vigorous stirring. After three hours, the product had precipitated as a grey–green powder. The precipitate was filtered, washed with water, and dried. The crude product was purified using flash chromatography (silica gel, chloroform), yielding 0.0959 g of the desired product (20.3%). Crystals were obtained by slow evaporation of a solution in chloroform.

5. Refinement

Hydrogen atoms were placed in calculated positions, and their coordinates and displacement parameters were constrained to ride on the carrier atom [C–H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms, C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for other H atoms]. Hydrogen atoms on methyl groups were refined with a riding rotating model. Crystal data,

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₄ H ₁₀ Br ₂ O ₄
M_r	402.04
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0909 (6), 9.2120 (8), 10.7056 (10)
α , β , γ (°)	90.989 (3), 97.098 (3), 101.909 (3)
<i>V</i> (Å ³)	678.35 (10)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	5.98
Crystal size (mm)	0.10 × 0.07 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>AXScale</i> ; Bruker, 2010)
T_{min} , T_{max}	0.561, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7453, 2714, 2180
R_{int}	0.036
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.630
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.043, 0.148, 1.04
No. of reflections	2714
No. of parameters	183
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.67, -1.06

Computer programs: *APEX2* and *SAINT* (Bruker, 2010), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

data collection and structure refinement details are summarized in Table 2.

Acknowledgements

This research was supported by the National Science Foundation (CHE-08-48206). One of us (JEM) is grateful to the Department of Education’s Graduate Assistance in Areas of National Need (GAANN) Program for fellowship support. We appreciate the assistance of Professor David Dixon, Dr Monica Vasiliu and Dr Edward Garner in performing the DFT calculations.

References

- Aviram, A. & Ratner, M. A. (1974). *Chem. Phys. Lett.* **29**, 277–283.
- Bruker (2010). *APEX2*, *AXScale* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Love, B. E., Bonner-Stewart, J. & Forrest, L. A. (2009). *Synlett*, pp. 813–817.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Taylor, S. R., Ung, A. T., Pyne, S. G., Skelton, B. W. & White, A. H. (2007). *Tetrahedron*, **63**, 11377–11385.
- Venkataraman, L., Klare, J. E., Nuckolls, C., Hybertsen, M. S. & Steigerwald, M. L. (2006). *Nature*, **442**, 904–907.
- Zeng, C. & Becker, J. Y. (2004). *J. Org. Chem.* **69**, 1053–1059.

supporting information

Acta Cryst. (2015). E71, 1454-1456 [https://doi.org/10.1107/S2056989015020472]

Crystal structure of 4,4'-dibromo-2',5'-dimethoxy-[1,1'-biphenyl]-2,5-dione (BrHBQBr)

Joseph E. Meany, Steven P. Kelley, Robert M. Metzger, Robin D. Rogers and Stephen A. Woski

Computing details

Data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINTE* (Bruker, 2010); data reduction: *SAINTE* (Bruker, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

4,4'-Dibromo-2',5'-dimethoxy-[1,1'-biphenyl]-2,5-dione

Crystal data

$C_{14}H_{10}Br_2O_4$

$M_r = 402.04$

Triclinic, $P\bar{1}$

$a = 7.0909$ (6) Å

$b = 9.2120$ (8) Å

$c = 10.7056$ (10) Å

$\alpha = 90.989$ (3)°

$\beta = 97.098$ (3)°

$\gamma = 101.909$ (3)°

$V = 678.35$ (10) Å³

$Z = 2$

$F(000) = 392$

$D_x = 1.968$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3169 reflections

$\theta = 3.0$ – 26.5 °

$\mu = 5.98$ mm⁻¹

$T = 173$ K

Fragment, brown

$0.10 \times 0.07 \times 0.06$ mm

Data collection

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(*AXScale*; Bruker, 2010)

$T_{\min} = 0.561$, $T_{\max} = 0.745$

7453 measured reflections

2714 independent reflections

2180 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 26.6$ °, $\theta_{\min} = 1.9$ °

$h = -8 \rightarrow 8$

$k = -11 \rightarrow 11$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.148$

$S = 1.04$

2714 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

$w = 1/[\sigma^2(F_o^2) + (0.1053P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.67$ e Å⁻³

$\Delta\rho_{\min} = -1.06$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.28348 (7)	0.59976 (6)	1.11818 (5)	0.0442 (2)
Br2	0.25434 (6)	1.33646 (5)	0.34039 (4)	0.0308 (2)
O1	-0.0292 (5)	0.7668 (4)	1.0260 (3)	0.0365 (8)
O2	0.5998 (4)	0.9672 (4)	0.8081 (3)	0.0282 (7)
O3	0.2720 (4)	0.8360 (3)	0.5689 (3)	0.0246 (6)
O4	0.2214 (4)	1.4265 (3)	0.6021 (3)	0.0272 (7)
C1	0.2910 (6)	0.7438 (5)	0.9966 (4)	0.0258 (9)
C2	0.1101 (6)	0.8048 (5)	0.9676 (4)	0.0239 (9)
C3	0.1079 (6)	0.9086 (5)	0.8659 (4)	0.0240 (9)
H3A	-0.0054	0.9476	0.8449	0.029*
C4	0.2593 (6)	0.9515 (4)	0.8004 (4)	0.0189 (8)
C5	0.4475 (6)	0.9059 (5)	0.8446 (4)	0.0223 (9)
C6	0.4464 (6)	0.7913 (5)	0.9381 (4)	0.0243 (9)
H6A	0.5583	0.7501	0.9572	0.029*
C7	0.2536 (5)	1.0448 (5)	0.6908 (4)	0.0215 (9)
C8	0.2612 (5)	0.9822 (4)	0.5715 (4)	0.0196 (8)
C9	0.2575 (5)	1.0693 (4)	0.4676 (4)	0.0196 (8)
H9A	0.2624	1.0282	0.3864	0.024*
C10	0.2465 (5)	1.2161 (5)	0.4825 (4)	0.0200 (8)
C11	0.2352 (5)	1.2807 (4)	0.5986 (4)	0.0193 (8)
C12	0.2373 (5)	1.1929 (5)	0.7029 (4)	0.0207 (8)
H12A	0.2275	1.2340	0.7833	0.025*
C13	0.2659 (6)	0.7645 (5)	0.4477 (4)	0.0241 (9)
H13A	0.2659	0.6590	0.4580	0.036*
H13B	0.3801	0.8112	0.4087	0.036*
H13C	0.1476	0.7745	0.3938	0.036*
C14	0.2129 (7)	1.4946 (5)	0.7220 (5)	0.0305 (10)
H14A	0.1988	1.5974	0.7109	0.046*
H14B	0.3327	1.4938	0.7781	0.046*
H14C	0.1013	1.4394	0.7590	0.046*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0440 (3)	0.0453 (4)	0.0449 (4)	0.0096 (2)	0.0080 (2)	0.0305 (3)
Br2	0.0436 (3)	0.0247 (3)	0.0258 (3)	0.0094 (2)	0.0065 (2)	0.01177 (19)
O1	0.0362 (17)	0.037 (2)	0.041 (2)	0.0078 (14)	0.0193 (15)	0.0106 (15)
O2	0.0248 (14)	0.0329 (18)	0.0288 (18)	0.0059 (12)	0.0101 (12)	0.0073 (13)
O3	0.0345 (16)	0.0171 (15)	0.0247 (17)	0.0089 (12)	0.0075 (12)	0.0024 (12)

O4	0.0369 (16)	0.0190 (16)	0.0287 (18)	0.0109 (12)	0.0071 (13)	0.0038 (13)
C1	0.031 (2)	0.020 (2)	0.025 (2)	0.0029 (17)	0.0031 (17)	0.0069 (18)
C2	0.027 (2)	0.023 (2)	0.022 (2)	0.0014 (16)	0.0082 (16)	0.0036 (17)
C3	0.0241 (19)	0.019 (2)	0.029 (3)	0.0056 (16)	0.0047 (17)	0.0031 (17)
C4	0.0259 (19)	0.016 (2)	0.016 (2)	0.0052 (15)	0.0046 (15)	0.0002 (15)
C5	0.026 (2)	0.021 (2)	0.020 (2)	0.0059 (16)	0.0037 (16)	-0.0010 (16)
C6	0.028 (2)	0.026 (2)	0.019 (2)	0.0078 (17)	0.0007 (16)	0.0027 (17)
C7	0.0158 (17)	0.019 (2)	0.030 (2)	0.0029 (14)	0.0052 (15)	0.0037 (17)
C8	0.0177 (17)	0.015 (2)	0.026 (2)	0.0034 (14)	0.0042 (15)	0.0040 (16)
C9	0.0176 (17)	0.019 (2)	0.023 (2)	0.0038 (14)	0.0047 (15)	0.0035 (16)
C10	0.0157 (17)	0.025 (2)	0.019 (2)	0.0036 (15)	0.0024 (14)	0.0079 (17)
C11	0.0169 (17)	0.0135 (19)	0.028 (2)	0.0048 (14)	0.0035 (15)	0.0052 (16)
C12	0.0210 (18)	0.016 (2)	0.025 (2)	0.0017 (14)	0.0068 (15)	0.0011 (16)
C13	0.026 (2)	0.019 (2)	0.027 (2)	0.0031 (16)	0.0047 (16)	-0.0037 (17)
C14	0.035 (2)	0.020 (2)	0.039 (3)	0.0101 (18)	0.0077 (19)	-0.003 (2)

Geometric parameters (Å, °)

Br1—C1	1.872 (5)	C6—H6A	0.9500
Br2—C10	1.897 (4)	C7—C12	1.398 (6)
O1—C2	1.227 (5)	C7—C8	1.404 (6)
O2—C5	1.224 (5)	C8—C9	1.384 (6)
O3—C8	1.365 (5)	C9—C10	1.378 (6)
O3—C13	1.437 (5)	C9—H9A	0.9500
O4—C11	1.367 (5)	C10—C11	1.388 (6)
O4—C14	1.433 (6)	C11—C12	1.390 (6)
C1—C6	1.334 (6)	C12—H12A	0.9500
C1—C2	1.504 (6)	C13—H13A	0.9800
C2—C3	1.462 (6)	C13—H13B	0.9800
C3—C4	1.349 (6)	C13—H13C	0.9800
C3—H3A	0.9500	C14—H14A	0.9800
C4—C7	1.468 (6)	C14—H14B	0.9800
C4—C5	1.504 (6)	C14—H14C	0.9800
C5—C6	1.467 (6)		
C8—O3—C13	117.3 (3)	C9—C8—C7	119.4 (4)
C11—O4—C14	117.8 (3)	C10—C9—C8	119.7 (4)
C6—C1—C2	121.0 (4)	C10—C9—H9A	120.2
C6—C1—Br1	122.8 (4)	C8—C9—H9A	120.2
C2—C1—Br1	116.2 (3)	C9—C10—C11	122.4 (4)
O1—C2—C3	122.1 (4)	C9—C10—Br2	119.1 (3)
O1—C2—C1	121.0 (4)	C11—C10—Br2	118.5 (3)
C3—C2—C1	116.8 (4)	O4—C11—C10	117.4 (4)
C4—C3—C2	123.1 (4)	O4—C11—C12	124.6 (4)
C4—C3—H3A	118.5	C10—C11—C12	118.0 (4)
C2—C3—H3A	118.5	C11—C12—C7	120.7 (4)
C3—C4—C7	123.8 (4)	C11—C12—H12A	119.7
C3—C4—C5	118.4 (4)	C7—C12—H12A	119.7

C7—C4—C5	117.8 (3)	O3—C13—H13A	109.5
O2—C5—C6	120.5 (4)	O3—C13—H13B	109.5
O2—C5—C4	121.1 (4)	H13A—C13—H13B	109.5
C6—C5—C4	118.3 (4)	O3—C13—H13C	109.5
C1—C6—C5	121.2 (4)	H13A—C13—H13C	109.5
C1—C6—H6A	119.4	H13B—C13—H13C	109.5
C5—C6—H6A	119.4	O4—C14—H14A	109.5
C12—C7—C8	119.8 (4)	O4—C14—H14B	109.5
C12—C7—C4	121.3 (4)	H14A—C14—H14B	109.5
C8—C7—C4	118.9 (3)	O4—C14—H14C	109.5
O3—C8—C9	125.2 (4)	H14A—C14—H14C	109.5
O3—C8—C7	115.4 (4)	H14B—C14—H14C	109.5

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the C1–C6 and C7–C12 rings, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C9—H9 <i>A</i> ...O2 ⁱ	0.95	2.40	3.270 (5)	151
C12—H12 <i>A</i> ...O1 ⁱⁱ	0.95	2.62	3.461 (5)	148
C13—H13 <i>A</i> ...O4 ⁱⁱⁱ	0.98	2.65	3.525 (5)	149
C13—H13 <i>B</i> ...Cg2 ⁱ	0.98	2.57	3.443 (5)	148
C14—H14 <i>A</i> ...Cg1 ^{iv}	0.98	3.00	3.695 (5)	129

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y+2, -z+2$; (iii) $x, y-1, z$; (iv) $x, y+1, z$.