research communications

Crystal structure of 4′-bromo-2′,5′-dimethoxy-2,5-dioxo-[1,1′-biphenyl]-3,4-dicarbonitrile [BrHBQ(CN)₂] benzene hemisolvate

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In the crystal of the title compound, $C_{16}H_9BrN_2O_4 \cdot 0.5C_6H_6$, the molecules stack in a centrosymmetric unit cell in a 2:1 stoichiometry with co-crystallized benzene solvent molecules and interact *via* various weak interactions. This induces a geometry different from that predicted by theory, and is unique among the hemibiquinones heretofore reported.

1. Chemical context

A new class of molecules, dubbed hemibiquinones (HBQs), has been developed and reported as potential molecular rectifiers. Biphenyl derivatives have garnered great attention to themselves as conductors of electricity (Venkataraman *et al.*, 2006). Thus, control over the molecular equilibrium geometry, and therefore the overlap of the π orbitals, allows for control over the governing electrical characteristics. The efficiency of conduction through a given molecule is dependent on the torsion angle between adjacent electrophores.
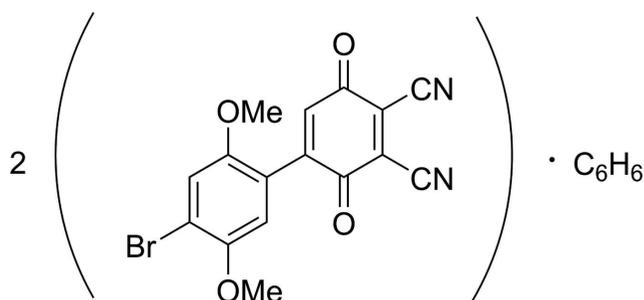
The title hemibiquinone (HBQ) molecule, 4′-bromo-2′,5′-dimethoxy-2,5-dioxo-[1,1′-biphenyl]-3,4-dicarbonitrile **1** (Fig. 1), has been isolated as a molecule that will self-assemble on a gold surface as a potential unimolecular rectifier. HBQ **1** is predicted to act as a molecular diode due to the linking of the electron-rich 4′-bromo-2′,5′-dimethoxybenzene donor with an electron-poor 3,4-dicarbonitrile quinone acceptor. This follows the scheme outlined by Aviram & Ranter (1974), where an electron-rich donor and an electron-poor acceptor are covalently bonded through an isolating saturated bridge. In HBQs, the predicted dihedral twist away from coplanarity of the two rings would decrease orbital overlap and allow for partial isolation of the donor and acceptor moieties. We have developed a selective synthesis for this hemibiquinone derivative that is scalable to gram quantities.
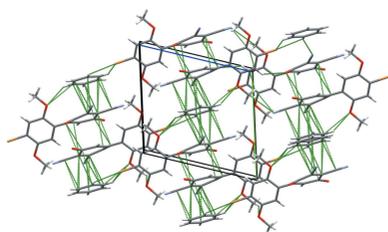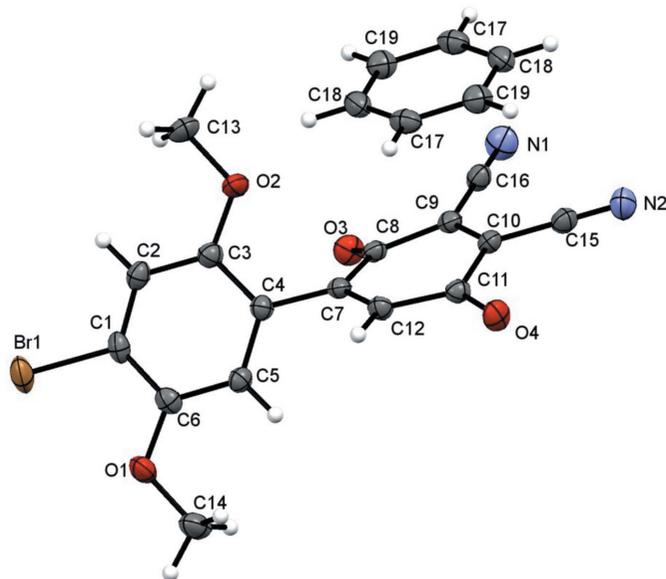
Figure 1
The molecular structure of HBQ **1** showing the atom-numbering scheme. Ellipsoids are displayed at the 50% probability level. Hydrogen atoms are displayed as calculated.

2. Structural commentary

As in the other reported HBQ molecules (Meany *et al.*, 2015), we seek to use and compare the inter-ring torsion angles in the crystals as a guide against gas-phase calculated values. However, crystallized benzene solvent molecules in the crystal structure prevent us from drawing direct conclusions about the geometry. Packing effects distort the biphenyl molecule out of plane in the opposite direction as the hydroquinone starting material [BrHBQH$_2$(CN)$_2$], Fig. 2. The C—C biphenyl bond [1.482 (2) Å] in **1** is comparable to that in the hydroquinone [1.481 (2) Å]. In this molecule, the C5—C4—C7—C8 torsion is 125.3 (2)°, compared to the hydroquinone torsion angle of −126.50°, (Meany, 2015). DFT (B3LYP-DGDZVP)
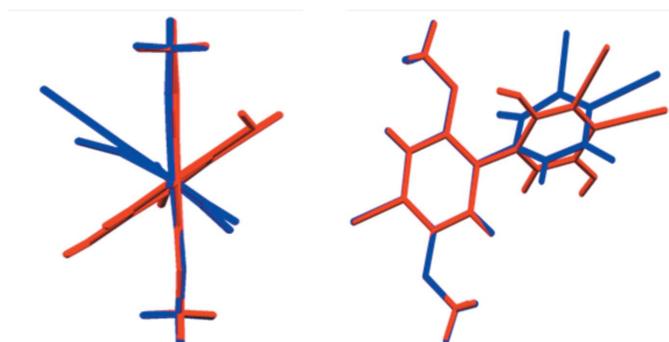

Figure 2
Molecular overlay of **1** (blue) with the reduced precursor hydroquinone (BrHBQH$_2$(CN)$_2$, red). Viewed along the plane of the dimethoxybenzene ring and the C—C biphenyl bond (left), and parallel to the plane of the dimethoxybenzene ring (right). The overlay is meant to show the divergent geometry between the precursor and the title molecule, based on the different solid-state interactions.

calculations performed on the target molecule in the gas phase predict an angle of −39.71°. This significant discrepancy is due to packing interactions in the solid phase, especially from benzene. Finally, the quinone ring is slightly buckled, likely due to supramolecular packing effects.

As in other structures, the methoxy groups are aligned nearly in-plane with the benzene ring, C2—C3—O2—C13 being bent out of plane by 2.9 (3)° and C5—C6—O1—C14 bent out of plane by −7.0 (3)°. The methoxy group bond angle C3—O2—C13 is measured at 117.4 (1)°, and C6—O1—C14 is measured at 117.3 (1)°. The methyl portions of each of these groups point away from the sterically restricting groups *ortho* to these positions, typical for this class.

Continuing the trend from the hydroquinone, the C9—C10 bond in **1** [1.346 (2) Å] is shorter than than the corresponding hydroquinone C9—C10 bond [1.408 (2) Å] and the C1—C6 bond [1.334 (6) Å] of BrHBQBr (Meany, 2015). The stronger polarization of **1** due to the dicyanoquinone relative to the starting materials weakens the bond through repulsive effects. The Br1—C1 bond is slightly longer in **1** [1.893 (2) Å] compared to the same bond in the hydroquinone precursor [1.885 (1) Å], but is still shorter than that of the starting material BrHBQBr [1.898 (4) Å; Meany, 2015]. The calculated dipole moment (B3LYP-DGDZVP) of BrHBQH$_2$(CN)$_2$ is only 6.17 D, compared to a dipole moment of 7.78 D for compound **1**.

3. Supramolecular features

The molecule packs in space group $P\bar{1}$ with two HBQ molecules and one solvent molecule, the latter completed by a crystallographic inversion centre. The molecules align anti-parallel to one another in the unit cell, primarily along the *c* crystallographic axis. The quinone rings are mostly parallel to the *ac* plane and sandwich, in a 2:1 ratio, a benzene solvent molecule. The plane of the dimethoxybenzene ring aligns with the diagonal of the *ab* plane.

Analysis of the short contacts shows an off-center donor–acceptor-type π–π interaction between benzene and the HBQ molecule. Fig3. 3 and 4 show the great extent of π-overlap between benzene and HBQ **1**. It is readily apparent that the benzene ring, rather than being centered between the quinone rings exactly, is actually slightly off-center. Instead, the electron density of the benzene is centered over the slightly electropositive C9—C10 bond.

Each HBQ molecule interacts with a total of three benzene molecules by short contacts. As mentioned above, one molecule of benzene is sandwiched between two quinone rings. Additionally, the 3-substituted nitrile group accepts a C—H$\cdots$N hydrogen bond from a solvent molecule (H$\cdots$N = 2.81 Å, C—H$\cdots$N = 147°). The third benzene molecule exhibits short contacts to the 4′-bromine atom on the opposite end of the molecule, where H17 and H18 link to Br1 almost symmetrically (H17$\cdots$Br1 = 3.05 Å, C17—H17$\cdots$Br1 = 127°; H18$\cdots$Br1 = 3.04 Å, C18—H178$\cdots$Br1 = 128°). Since the benzene molecule π-stacks parallel to the quinones, the benzene molecule is oriented in the same direction relative to
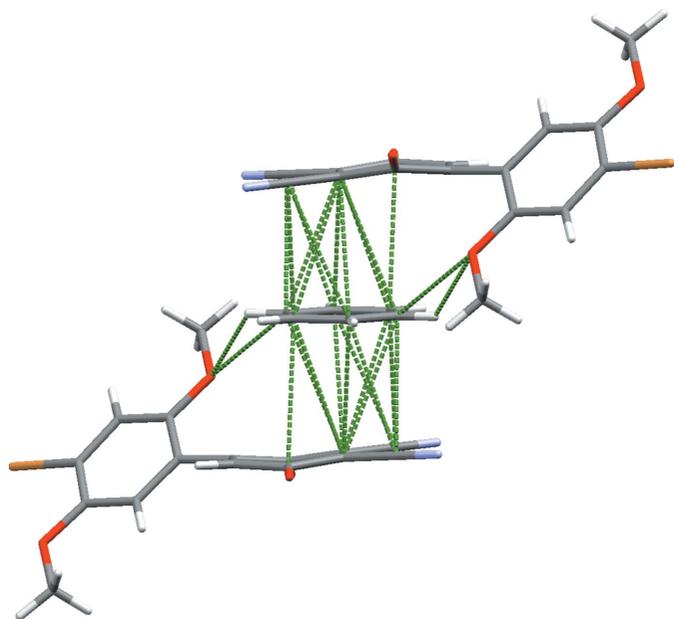
Figure 3
Packing diagram showing the off-center π–π short contacts of **1** with the intercalated solvent benzene. Weak hydrogen bonds from O2 project closely to the benzene protons.

the dimethoxybenzene ring. Although, in previous HBQ crystals the 4 and 4′ groups show evidence of intermolecular halogen bonding, due to the excess electron density around the aryl bromine atoms and the nitrile groups, an attractive interaction is not possible, rather a slightly repulsive interaction is favored. Instead, the protons on C17 and C18 bifurcate to Br1 as an acceptor, forming slightly asymmetric hydrogen bonds between the dimethoxybenzene ring and the benzene solvent molecule. As discussed above, the quinone carbonyl groups are deflected from perfect planarity. In
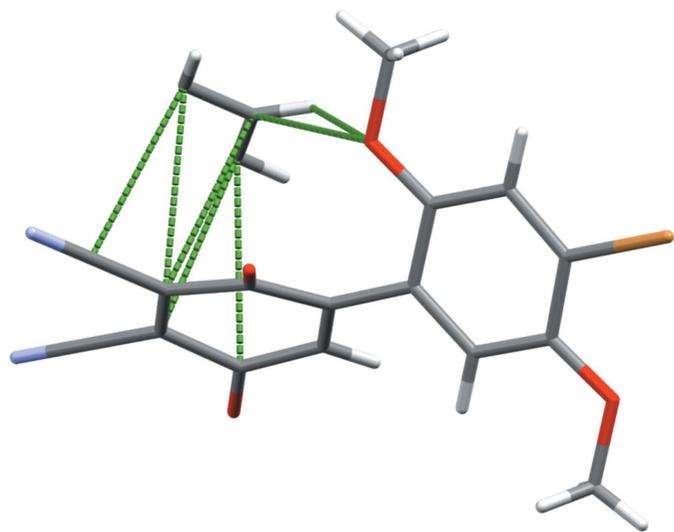

Figure 4
Packing diagram showing the off-center π–π short contacts of **1** with the intercalated solvent benzene as the asymmetric unit to only one HBQ. Weak hydrogen bonds from O2 project close to the benzene protons.
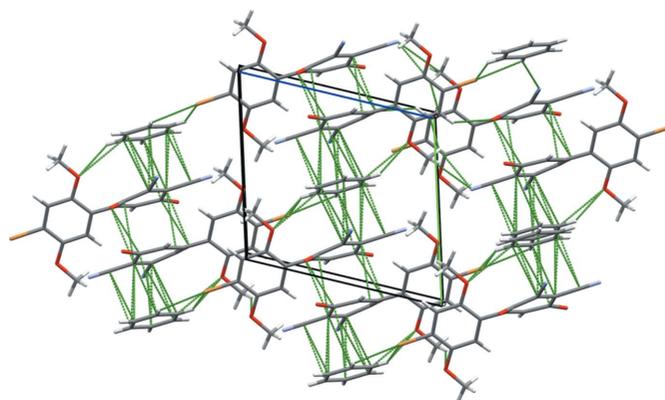

Figure 5
Packing diagram showing the *b* directional π-stacks and the weak *c* directional halogen bonds. Viewed along the *a* axis.

previous structures, methoxy oxygen atoms tended to deflect the carbonyl groups through repulsive effects. However, this structure contains some attractive intermolecular hydrogen bonding character, including the C14—H14*B*···O4 contact, which is a moderate interaction at 2.57 Å and a bond angle of 157°. A second weaker interaction occurs between the C5—H5 dimethoxybenzene grouping and O4 (2.64 Å and 134°). Projection of the O4 carbonyl atom to a neighboring quinoid proton H12 is also evident at a bond length of 2.65 Å and a C12—H12···O4 angle of 147°. There is a fourth and weakest interaction with O4, *viz.* C16≡N1···O4 with an N1···O4 bond length of 3.159 (2) Å and a bond angle of 129.91 (1)°. Two contacts are made with O3: a C2—H2···O3 (2.65 Å and 142°) bond and weak π-contacts [C10···O3 and C11···O3 = 3.251 (2) and 3.187 (2) Å, respectively]. Additionally, there is a short contact between C10 and C8, at 3.486 (3) Å. The N2 nitrile atom possibly accepts a very weak interaction from the methoxy C13 and H13*A* pair (2.82 Å and 97°). There is a long C13···N2 [(3.101 (3) Å] interaction as well. Even longer than those interactions, H13 also has a weak H···π interaction with the dimethoxybenzene ring on an adjacent molecule (H···π = 2.88 Å). The packing is shown in Fig. 5.

4. Synthesis and crystallization

4′-Bromo-2,5-dihydroxy-2′,5′-dimethoxy-[1,1′-biphenyl]-3,4-dicarbonitrile (0.126 g, 0.337 mmol) was suspended in a mixture of 100 mL of H_2O and 100 mL of benzene. $FeCl_3$ (0.340 g, 2.09 mmol) was added in one portion. The resulting mixture was capped and stirred overnight. The resulting phases were separated, and the organic phase was washed with water and dried over anhydrous Na_2SO_4. Evaporation of the solvent produced a crude product. The pure product was precipitated from a chloroform solution by addition of hexane, yielding 0.0460 g (36.7%). Black, block-shaped crystals of **1** were grown from chloroform solution with residual benzene at 296 K. ^{1}H NMR (360 MHz, CDCl$_3$) δ = 7.22 (*s*, 1H, ArH), 7.12 (*s*, 1H, ArH), 6.71 (*s*, 1H, ArH), 3.87 (*s*, 3H, OCH$_3$), 3.76 (*s*, 3H, OCH$_3$).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_9BrN_2O_4 \cdot 0.5C_6H_6$
M_r	412.22
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	173
a, b, c (Å)	8.0427 (17), 10.343 (2), 11.007 (2)
α, β, γ (°)	104.469 (2), 95.120 (2), 102.851 (2)
V (Å³)	854.1 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	2.43
Crystal size (mm)	$0.21 \times 0.11 \times 0.06$
Data collection	
Diffractometer	Bruker AXS *SMART* APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.600, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11856, 3957, 3382
R_{int}	0.022
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.653
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.028, 0.068, 1.06
No. of reflections	3957
No. of parameters	237
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.40, −0.35

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b) *SHELXLE* (Hübschle et al., 2011), *Mercury* (Macrae et al., 2006) and *SHELXTL* (Sheldrick, 2008).

5. Refinement

H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with C— H-bond distances of 0.95 Å for aromatic C—H, 1.00, 0.99 and 0.98 Å for aliphatic CH_3, 0.88 Å. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3. Crystal data, data collection and structure refinement details are summarized in Table 1.

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supporting information

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015b) *SHELXLE* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

4′-Bromo-2′,5′-dimethoxy-2,5-dioxo-[1,1′-biphenyl]-3,4-dicarbonitrile benzene hemisolvate

Crystal data

$C_{16}H_9BrN_2O_4 \cdot 0.5C_6H_6$	$Z = 2$
$M_r = 412.22$	$F(000) = 414$
Triclinic, $P\bar{1}$	$D_x = 1.603$ Mg m^{-3}
$a = 8.0427$ (17) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.343$ (2) Å	Cell parameters from 5182 reflections
$c = 11.007$ (2) Å	$\theta = 2.9$–27.4°
$\alpha = 104.469$ (2)°	$\mu = 2.43$ mm^{-1}
$\beta = 95.120$ (2)°	$T = 173$ K
$\gamma = 102.851$ (2)°	Block, black
$V = 854.1$ (3) Å^3	$0.21 \times 0.11 \times 0.06$ mm

Data collection

Bruker AXS SMART APEXII CCD diffractometer	3957 independent reflections
Radiation source: sealed X-ray tube	3382 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{int} = 0.022$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$\theta_{max} = 27.6°$, $\theta_{min} = 2.9°$
$T_{min} = 0.600$, $T_{max} = 0.746$	$h = -10 \rightarrow 10$
11856 measured reflections	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.028$	
$wR(F^2) = 0.068$	Hydrogen site location: inferred from neighbouring sites
$S = 1.06$	
3957 reflections	H-atom parameters constrained
237 parameters	
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.3076P]$

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

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

$\Delta\rho_{max} = 0.40$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.1145 (2)	−0.15670 (19)	−0.05223 (15)	0.0248 (4)
C2	0.2309 (2)	−0.02953 (19)	−0.02559 (16)	0.0249 (4)
H2	0.2677	0.0071	−0.0925	0.030*
C3	0.2939 (2)	0.04468 (18)	0.10043 (16)	0.0240 (4)
C4	0.2382 (2)	−0.01088 (18)	0.19817 (15)	0.0216 (3)
C5	0.1153 (2)	−0.13776 (18)	0.16872 (15)	0.0219 (3)
H5	0.0746	−0.1731	0.2353	0.026*
C6	0.0521 (2)	−0.21285 (18)	0.04302 (16)	0.0235 (4)
C7	0.3088 (2)	0.06338 (17)	0.33278 (15)	0.0207 (3)
C8	0.5003 (2)	0.10333 (17)	0.36973 (15)	0.0207 (3)
C9	0.5736 (2)	0.19577 (17)	0.50147 (15)	0.0207 (3)
C10	0.4713 (2)	0.21563 (17)	0.59112 (15)	0.0212 (3)
C11	0.2798 (2)	0.15131 (17)	0.55889 (16)	0.0215 (3)
C12	0.2090 (2)	0.08304 (18)	0.42447 (16)	0.0224 (3)
H12	0.0872	0.0513	0.4011	0.027*
C13	0.4568 (3)	0.2362 (2)	0.04085 (19)	0.0327 (4)
H13A	0.5171	0.1797	−0.0155	0.049*
H13B	0.5338	0.3282	0.0801	0.049*
H13C	0.3540	0.2445	−0.0084	0.049*
C14	−0.1132 (3)	−0.4035 (2)	0.10228 (19)	0.0356 (4)
H14A	−0.1932	−0.4943	0.0630	0.053*
H14B	−0.1695	−0.3463	0.1616	0.053*
H14C	−0.0097	−0.4148	0.1483	0.053*
C15	0.5379 (2)	0.29235 (19)	0.72153 (16)	0.0260 (4)
C16	0.7587 (2)	0.24907 (19)	0.52856 (16)	0.0257 (4)
C17	0.3212 (2)	0.45790 (19)	0.48189 (19)	0.0298 (4)
H17	0.1988	0.4292	0.4699	0.036*
C18	0.4079 (3)	0.43078 (19)	0.37931 (18)	0.0301 (4)
H18	0.3454	0.3836	0.2969	0.036*
C19	0.5876 (3)	0.4731 (2)	0.39738 (18)	0.0306 (4)
H19	0.6478	0.4547	0.3271	0.037*
N1	0.9050 (2)	0.2909 (2)	0.55007 (17)	0.0393 (4)
N2	0.5915 (2)	0.35262 (19)	0.82435 (15)	0.0399 (4)
O1	−0.06536 (16)	−0.33788 (13)	0.00550 (12)	0.0311 (3)
O2	0.40645 (18)	0.17220 (13)	0.13801 (12)	0.0327 (3)
O3	0.59685 (17)	0.05565 (14)	0.30356 (12)	0.0308 (3)

O4	0.19158 (16)	0.15713 (14)	0.64297 (12)	0.0303 (3)
Br1	0.04198 (3)	−0.26003 (2)	−0.22428 (2)	0.03965 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0214 (8)	0.0332 (10)	0.0170 (8)	0.0076 (7)	0.0021 (6)	0.0015 (7)
C2	0.0256 (9)	0.0318 (10)	0.0200 (8)	0.0081 (8)	0.0074 (7)	0.0098 (7)
C3	0.0254 (9)	0.0231 (9)	0.0231 (8)	0.0045 (7)	0.0069 (7)	0.0062 (7)
C4	0.0235 (8)	0.0217 (9)	0.0190 (8)	0.0055 (7)	0.0057 (6)	0.0042 (6)
C5	0.0225 (8)	0.0242 (9)	0.0194 (8)	0.0058 (7)	0.0062 (6)	0.0059 (7)
C6	0.0180 (8)	0.0256 (9)	0.0248 (8)	0.0044 (7)	0.0040 (6)	0.0035 (7)
C7	0.0242 (8)	0.0165 (8)	0.0211 (8)	0.0021 (7)	0.0053 (6)	0.0065 (6)
C8	0.0230 (8)	0.0193 (8)	0.0212 (8)	0.0033 (7)	0.0081 (6)	0.0085 (6)
C9	0.0208 (8)	0.0199 (8)	0.0229 (8)	0.0041 (7)	0.0039 (6)	0.0093 (7)
C10	0.0239 (8)	0.0208 (9)	0.0195 (8)	0.0034 (7)	0.0048 (6)	0.0080 (6)
C11	0.0223 (8)	0.0208 (8)	0.0220 (8)	0.0048 (7)	0.0068 (6)	0.0065 (6)
C12	0.0205 (8)	0.0226 (9)	0.0218 (8)	0.0015 (7)	0.0047 (6)	0.0051 (7)
C13	0.0354 (10)	0.0330 (10)	0.0332 (10)	0.0033 (9)	0.0115 (8)	0.0182 (8)
C14	0.0371 (11)	0.0271 (10)	0.0350 (10)	−0.0038 (9)	0.0107 (8)	0.0037 (8)
C15	0.0250 (9)	0.0292 (10)	0.0240 (9)	0.0031 (8)	0.0054 (7)	0.0108 (7)
C16	0.0256 (9)	0.0307 (10)	0.0227 (8)	0.0059 (8)	0.0056 (7)	0.0114 (7)
C17	0.0237 (9)	0.0242 (9)	0.0399 (10)	0.0022 (8)	0.0026 (8)	0.0105 (8)
C18	0.0329 (10)	0.0237 (9)	0.0293 (9)	0.0030 (8)	−0.0015 (8)	0.0053 (7)
C19	0.0329 (10)	0.0282 (10)	0.0322 (10)	0.0088 (8)	0.0098 (8)	0.0083 (8)
N1	0.0243 (9)	0.0536 (12)	0.0407 (10)	0.0062 (8)	0.0046 (7)	0.0181 (9)
N2	0.0457 (10)	0.0428 (10)	0.0235 (8)	−0.0013 (8)	0.0018 (7)	0.0077 (7)
O1	0.0283 (7)	0.0286 (7)	0.0267 (6)	−0.0046 (6)	0.0027 (5)	0.0013 (5)
O2	0.0445 (8)	0.0254 (7)	0.0232 (6)	−0.0044 (6)	0.0095 (6)	0.0078 (5)
O3	0.0284 (7)	0.0338 (7)	0.0307 (7)	0.0086 (6)	0.0142 (5)	0.0058 (6)
O4	0.0271 (7)	0.0380 (8)	0.0241 (6)	0.0055 (6)	0.0113 (5)	0.0054 (5)
Br1	0.03537 (12)	0.05225 (15)	0.01873 (10)	−0.00172 (9)	0.00001 (7)	0.00002 (8)

Geometric parameters (Å, º)

C1—C2	1.379 (3)	C11—O4	1.213 (2)
C1—C6	1.399 (2)	C11—C12	1.470 (2)
C1—Br1	1.8928 (17)	C12—H12	0.9500
C2—C3	1.393 (2)	C13—O2	1.434 (2)
C2—H2	0.9500	C13—H13A	0.9800
C3—O2	1.364 (2)	C13—H13B	0.9800
C3—C4	1.403 (2)	C13—H13C	0.9800
C4—C5	1.399 (2)	C14—O1	1.436 (2)
C4—C7	1.482 (2)	C14—H14A	0.9800
C5—C6	1.392 (2)	C14—H14B	0.9800
C5—H5	0.9500	C14—H14C	0.9800
C6—O1	1.362 (2)	C15—N2	1.138 (2)
C7—C12	1.349 (2)	C16—N1	1.141 (2)

C7—C8	1.493 (2)	C17—C18	1.382 (3)
C8—O3	1.212 (2)	C17—C19[i]	1.390 (3)
C8—C9	1.506 (2)	C17—H17	0.9500
C9—C10	1.346 (2)	C18—C19	1.394 (3)
C9—C16	1.443 (2)	C18—H18	0.9500
C10—C15	1.443 (2)	C19—C17[i]	1.390 (3)
C10—C11	1.506 (2)	C19—H19	0.9500
C2—C1—C6	122.44 (15)	O4—C11—C10	119.64 (15)
C2—C1—Br1	118.35 (13)	C12—C11—C10	117.32 (14)
C6—C1—Br1	119.19 (13)	C7—C12—C11	123.04 (15)
C1—C2—C3	119.35 (15)	C7—C12—H12	118.5
C1—C2—H2	120.3	C11—C12—H12	118.5
C3—C2—H2	120.3	O2—C13—H13A	109.5
O2—C3—C2	124.46 (15)	O2—C13—H13B	109.5
O2—C3—C4	115.94 (15)	H13A—C13—H13B	109.5
C2—C3—C4	119.59 (16)	O2—C13—H13C	109.5
C5—C4—C3	119.93 (15)	H13A—C13—H13C	109.5
C5—C4—C7	119.47 (14)	H13B—C13—H13C	109.5
C3—C4—C7	120.60 (15)	O1—C14—H14A	109.5
C6—C5—C4	120.83 (15)	O1—C14—H14B	109.5
C6—C5—H5	119.6	H14A—C14—H14B	109.5
C4—C5—H5	119.6	O1—C14—H14C	109.5
O1—C6—C5	124.89 (15)	H14A—C14—H14C	109.5
O1—C6—C1	117.32 (15)	H14B—C14—H14C	109.5
C5—C6—C1	117.79 (16)	N2—C15—C10	179.5 (2)
C12—C7—C4	123.16 (15)	N1—C16—C9	179.8 (2)
C12—C7—C8	118.87 (15)	C18—C17—C19[i]	120.29 (17)
C4—C7—C8	117.58 (14)	C18—C17—H17	119.9
O3—C8—C7	123.21 (15)	C19[i]—C17—H17	119.9
O3—C8—C9	118.80 (15)	C17—C18—C19	119.66 (17)
C7—C8—C9	117.66 (14)	C17—C18—H18	120.2
C10—C9—C16	122.54 (15)	C19—C18—H18	120.2
C10—C9—C8	120.68 (15)	C17[i]—C19—C18	120.05 (18)
C16—C9—C8	116.49 (14)	C17[i]—C19—H19	120.0
C9—C10—C15	122.68 (15)	C18—C19—H19	120.0
C9—C10—C11	120.23 (15)	C6—O1—C14	117.33 (14)
C15—C10—C11	117.03 (14)	C3—O2—C13	117.42 (14)
O4—C11—C12	123.04 (16)		
C6—C1—C2—C3	2.2 (3)	C4—C7—C8—C9	171.61 (14)
Br1—C1—C2—C3	−176.22 (13)	O3—C8—C9—C10	−158.87 (16)
C1—C2—C3—O2	−178.67 (17)	C7—C8—C9—C10	14.8 (2)
C1—C2—C3—C4	0.0 (3)	O3—C8—C9—C16	15.1 (2)
O2—C3—C4—C5	176.45 (16)	C7—C8—C9—C16	−171.25 (14)
C2—C3—C4—C5	−2.3 (3)	C16—C9—C10—C15	0.3 (3)
O2—C3—C4—C7	−3.8 (2)	C8—C9—C10—C15	173.92 (15)
C2—C3—C4—C7	177.44 (16)	C16—C9—C10—C11	−176.80 (15)

C3—C4—C5—C6	2.5 (3)	C8—C9—C10—C11	−3.2 (2)
C7—C4—C5—C6	−177.20 (15)	C9—C10—C11—O4	171.98 (16)
C4—C5—C6—O1	178.97 (16)	C15—C10—C11—O4	−5.3 (2)
C4—C5—C6—C1	−0.4 (3)	C9—C10—C11—C12	−7.8 (2)
C2—C1—C6—O1	178.57 (16)	C15—C10—C11—C12	174.96 (15)
Br1—C1—C6—O1	−3.0 (2)	C4—C7—C12—C11	177.18 (15)
C2—C1—C6—C5	−2.0 (3)	C8—C7—C12—C11	4.5 (2)
Br1—C1—C6—C5	176.44 (12)	O4—C11—C12—C7	−172.59 (17)
C5—C4—C7—C12	−47.4 (2)	C10—C11—C12—C7	7.1 (2)
C3—C4—C7—C12	132.83 (18)	C19ⁱ—C17—C18—C19	0.0 (3)
C5—C4—C7—C8	125.34 (17)	C17—C18—C19—C17ⁱ	0.0 (3)
C3—C4—C7—C8	−54.4 (2)	C5—C6—O1—C14	−7.0 (3)
C12—C7—C8—O3	158.02 (17)	C1—C6—O1—C14	172.39 (16)
C4—C7—C8—O3	−15.1 (2)	C2—C3—O2—C13	2.9 (3)
C12—C7—C8—C9	−15.3 (2)	C4—C3—O2—C13	−175.80 (16)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.