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# Crystal structure of 4'-bromo-2,5-dihydroxy-2',5'-dimethoxy-[1,1'-biphenyl]-3,4-dicarbonitrile

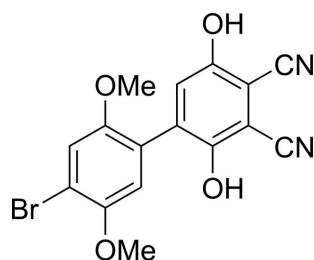
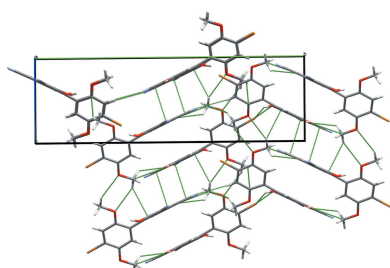
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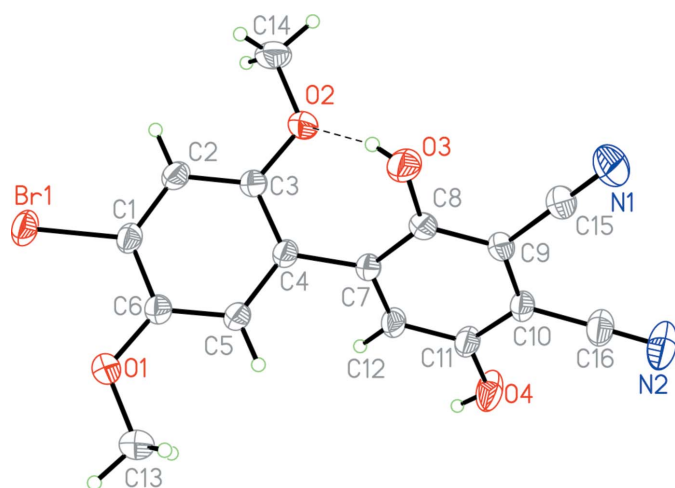
In the crystal of the title substituted hemibiquinone derivative, C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>4</sub> or [BrHBQH<sub>2</sub>(CN)<sub>2</sub>], the substituted benzene rings are rotated about the central C—C bond, forming a dihedral angle of 53.59 (7)°. The ring systems interact through an intramolecular O—H···O<sub>methoxy</sub> hydrogen bond, which induces a geometry quite different from those in previously reported hemibiquinone structures. In the crystal, the molecules associate through an intermolecular O—H···N<sub>nitrile</sub> hydrogen bond, forming chains which extend along [100] and are interlinked through very weak C—H···N hydrogen bonds, giving a overall two-dimensional structure lying parallel to (010).

## 1. Chemical context

Recently, a new class of molecules (hemibiquinones, HBQs) has been reported as potential molecular rectifiers (Meany *et al.*, 2015). Biphenyl derivatives have garnered great attention as conductors of electricity (Venkataraman *et al.*, 2006). The symmetric nature of the biphenyl and polyphenyl derivatives studied so far allows for reasonable conduction through the  $\pi$  orbitals. Biphenyl derivatives with one electron-rich and one electron-deficient ring may be able to preferentially bias the direction of electron flow through the molecule, thus acting as a molecular diode. The donor–bridge–acceptor model has long been accepted as a basis for the design of molecular rectifiers (Aviram & Ratner, 1974). The asymmetric biphenyl structure should allow for 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. The efficiency of conduction through a given molecule can be tuned depending on the torsion angle between the two rings.



As one of the series of molecules made for testing rectification through HBQs, the title compound, C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>4</sub>, [BrHBQH<sub>2</sub>(CN)<sub>2</sub>], (I) has been isolated as an intermediate in the preparation of an HBQ derivative which can self-assemble on a gold surface. We have developed a selective synthesis for



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are displayed at the 50% probability level. The intramolecular O3—H···O2 hydrogen bond is shown as a dashed line.

this reduced hemibiquinone derivative that is scalable to gram quantities. Molecule (I) is predicted not to act as a molecular diode itself because both rings act as donor moieties. The oxidation of the hydroquinone ring of (I) would produce a potential rectifier.

Dicyano-functionalized hydroquinones are known for their ability to form hydrogen-bonded networks (Reddy *et al.*, 1996) and charge-transfer complexes (Bock *et al.*, 1996), sometimes both at once (Ghorai & Mani, 2014). They have also been used as rigid ligands in coordination polymers (Kuroda-Sowa *et al.*, 1997). However, there are no crystal structures in which a dicyano-functionalized hydroquinone moiety has been appended to another aromatic ring. The present study affords an opportunity to investigate the mutual effects of these two functionalized ring systems on both the geometry of the molecule and its intermolecular interactions.

## 2. Structural commentary

In the title compound (Fig. 1), the benzene rings are twisted out of a common plane, forming a dihedral angle of 53.59 (7)°, which appears to optimize the 2.7576 (18) Å O3—H···O2 intramolecular hydrogen bond (Table 1). The rings are essentially planar although the O3—H group, which participates in the intramolecular hydrogen bond, is displaced slightly out of the plane. Also, the rings are not co-axial with the C4—C7 bond that bridges them. This can be seen in torsion angles involving three carbon atoms from one ring and the bridging carbon atom from the other, which deviate from linearity by *ca* 5° [C2—C3—C4—C7 = 173.88 (14)°, C6—C5—C4—C7 = −175.45 (14)°, C4—C7—C8—C9 = 174.94 (13)°, C4—C7—C12—C11 = −175.62 (13)°]. This bending of the molecule about its long axis may also be due to hydrogen bonding as it causes the methoxy group to approach the OH group more closely. The aromatic C—C bonds of both rings have a narrow range of distances [from 1.387 (2) to

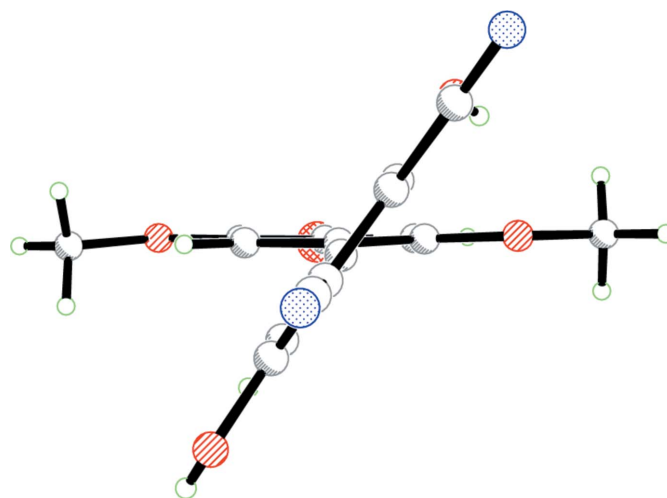
**Table 1**  
Hydrogen-bond geometry (Å, °).

| <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> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O3—H3A···O2               | 0.72 (3)    | 2.11 (3)      | 2.7576 (18)           | 152 (3)                 |
| O4—H4A···N1 <sup>i</sup>  | 0.79 (2)    | 2.03 (2)      | 2.8189 (18)           | 172 (2)                 |
| C2—H2A···N2 <sup>ii</sup> | 0.93        | 2.72          | 3.638 (2)             | 168                     |

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

1.412 (2) Å]. The C—C, C—O, C—N, and C≡N distances for the molecule are similar to the corresponding distances in 2,3,5,6-tetracyanohydroquinone (Bock *et al.*, 1993). The C—C bond distances around the bromodimethoxybenzene ring are close to those in the other hemibiquinone molecules containing this ring (Meany *et al.*, 2015, 2016). The C9—C10 bond in (I) [1.408 (2) Å] is longer than the corresponding C1—C6 bond in BrHBQBr (1.334 Å; Meany *et al.*, 2015). The stronger polarization of (I) relative to the starting material should weaken the bond through repulsive effects. The Br1—C1 bond is slightly shorter in (I) [1.885 (1) Å] compared to the starting material [1.898 (4) Å] as well, also suggesting decreased electron density on the dimethoxybenzene ring due to increased polarization. The calculated dipole (B3LYP-DGDZVP) of BrHBQBr is only 1.33 D, compared to 6.17 D for (I).

As in the other reported hemibiquinone molecules (Meany *et al.*, 2015), we seek to use and compare the inter-ring torsion angles in the crystals as a guide compared to gas-phase calculated values. The intramolecular hydrogen bond from the C8 phenol to the O2 methoxy group causes a greater torsion angle than that in the starting HBQ (Meany *et al.*, 2015). In (I), the C5—C4—C7—C8 torsion angle is −126.5 (2)°, compared to −110.9 (5)° in HBQ. DFT (B3LYP-DGDZVP) calculations performed on the target molecule in the gas phase predict an angle of 48.85°. This significant discrepancy is due to packing interactions in the solid phase as well as the additional hydrogen bond. The hydrogen bond is indicated in Fig. 1, while the relative orientations of the rings can be seen in Fig. 2.



**Figure 2**  
Ball-and-stick plot of (I), viewed down the C4—C7 bond.

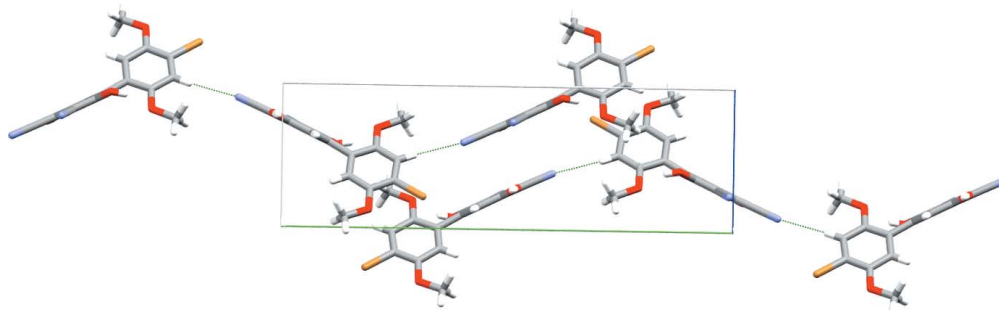


Figure 3

Short (less than the sum of the van der Waals radii) contact environment around  $[\text{BrHBOH}_2(\text{CN})_2]$ . Dashed green lines indicate short contacts. Axes are color coded: red =  $a$  axis, green =  $b$  axis and blue =  $c$  axis.

The  $\text{O3}-\text{H}\cdots\text{O2}$  intramolecular hydrogen bond points toward the non-bonded electrons on O2 with a total bond angle of  $152(3)^\circ$ . As a result of the influence of other short contacts and supramolecular interactions (see below), the phenolic  $\text{C}-\text{O}-\text{H}$  bond angles deviate when compared to the methoxy  $\text{C}-\text{O}-\text{C}$  bond angles:  $\text{C8}-\text{O3}-\text{H}$  is  $108(2)^\circ$ ,  $\text{C11}-\text{O4}-\text{H}$  is  $112.3(2)^\circ$ ,  $\text{C3}-\text{O2}-\text{C14}$  is  $117.9(1)^\circ$ , and  $\text{C6}-\text{O1}-\text{C13}$  is  $117.2(1)^\circ$ . As in other structures, the methoxy groups are aligned mostly in-plane with the benzene ring,  $\text{C5}-\text{C6}-\text{O1}-\text{C13}$  being bent out of plane by  $-4.5(2)^\circ$  and  $\text{C2}-\text{C3}-\text{O2}-\text{C14}$  bent out of plane by  $-1.3(2)^\circ$ . The  $\text{C12}-\text{C11}-\text{O4}-\text{H}$  phenol group is also nearly planar, being bent out of plane by  $1.3^\circ$ . However, the hydrogen-bonded phenol is unsurprisingly bent out of plane,  $\text{C7}-\text{C8}-\text{O3}-\text{H} = 38(2)^\circ$ . The methoxy methyl groups point away from the sterically restricting groups *ortho* to these positions.

### 3. Supramolecular features

Each molecule makes short (less than the sum of the van der Waals radii) contacts to six neighboring molecules (Fig. 3). As in previously reported HBQ structures, rings of like identity

are all aligned in parallel planes. All short contacts are associated with Lewis acid–base interactions of some kind, and for each interaction there is one neighboring molecule that acts as a donor and second that acts as an acceptor. Two central molecules in the unit cell stack antiparallel to one another, the quinone rings shifted off-center from one another in the  $a$ -axis direction. Both nitrile groups are involved in intermolecular hydrogen-bonding interactions, the first one ( $\text{O4}-\text{H}\cdots\text{N1}$ ) strong, the second one ( $\text{C2}-\text{H}\cdots\text{N2}$ ) weaker but still highly directional. For details, see Table 1. These interactions link molecules along the crystallographic  $a$ - and  $b$ -axis directions, respectively, forming sheets parallel to (010) (Fig. 4). The quinone rings are aligned parallel to the  $bc$  plane diagonal.

The remaining two molecules in the unit cell are oriented orthogonally to the central molecules. These molecules are antiparallel to each other, where the dimethoxybenzene rings stack with those of the central pair. Slightly repulsive  $\pi$ -interactions between molecules along  $b$  and stacking along  $c$  can be seen in Fig. 5. Intercentroid distances for the rings are longer than expected for close  $\pi$ - $\pi$  interactions at  $4.107(1) \text{ \AA}$ . However, since the rings are slightly offset from one another, this is not the correct centroid to use. Instead, a close  $3.598(1) \text{ \AA}$   $\pi$ -interaction between two intermolecular  $\text{C9}-\text{C10}$  centroids exists. A centroid calculated for the  $\text{C7}-\text{C8}-$

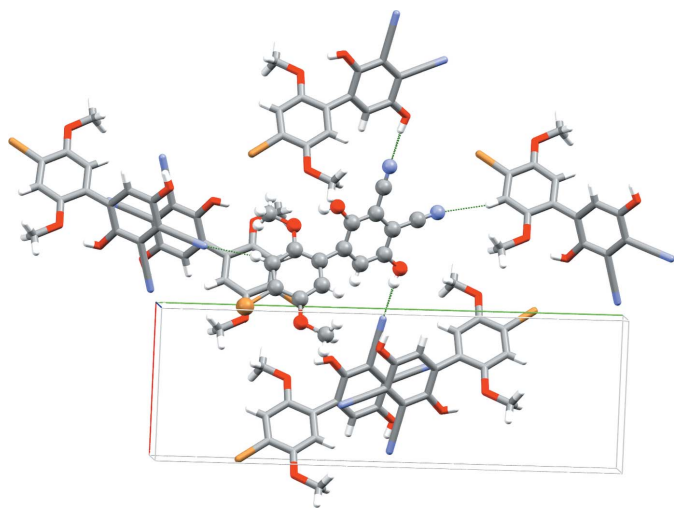


Figure 4

Hydrogen-bonded sheets along  $ab$ . Dashed green lines indicate short contacts. Axes are color coded: red =  $a$  axis, green =  $b$  axis and blue =  $c$  axis.

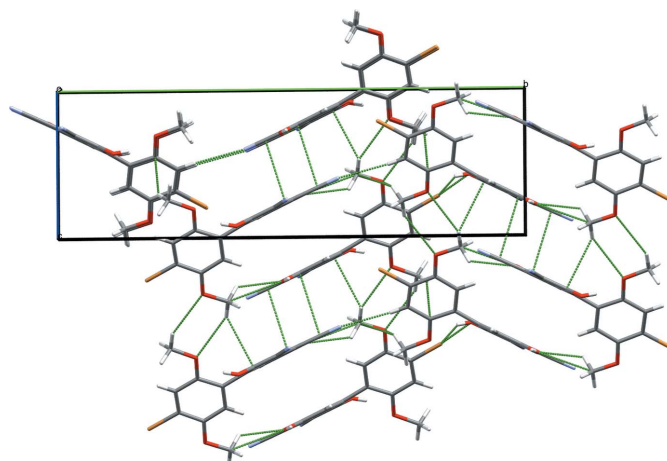


Figure 5

Unit-cell packing of (I), viewed along the  $a$  axis. Short contacts show the long ring stacking along the  $c$  axis.

**Table 2**  
Experimental details.

|  |  |
|--|--|
| Crystal data   |  |
| Chemical formula   | C <sub>16</sub> H <sub>11</sub> BrN <sub>2</sub> O <sub>4</sub>        |
| <i>M</i> <sub>r</sub>  | 375.18   |
| Crystal system, space group  | Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>                         |
| Temperature (K)  | 296  |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)   | 8.4726 (3), 23.7748 (8), 8.0833 (3)                                    |
| β (°)  | 111.6985 (17)  |
| <i>V</i> (Å <sup>3</sup> )   | 1512.88 (9)  |
| <i>Z</i>   | 4  |
| Radiation type   | Mo <i>K</i> α  |
| μ (mm <sup>-1</sup> )  | 2.74   |
| Crystal size (mm)  | 0.35 × 0.20 × 0.09   |
| Data collection  |  |
| Diffractometer   | Bruker APEXII CCD  |
| Absorption correction  | Multi-scan ( <i>SADABS</i> ; Bruker, 2010)                             |
| <i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>  | 0.428, 0.747   |
| No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections                             | 65083, 6269, 4739  |
| <i>R</i> <sub>int</sub>  | 0.037  |
| (sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )  | 0.796  |
| Refinement   |  |
| <i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i> | 0.035, 0.089, 1.03   |
| No. of reflections   | 6269   |
| No. of parameters  | 216  |
| H-atom treatment   | H atoms treated by a mixture of independent and constrained refinement |
| Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )   | 0.59, -0.26  |

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

C9—C11—C12 ring sits 3.574 (1) Å from a centroid for N1—C15—C9—C10—C16—N2, which may be explained by the electron-donating character of the hydroquinone as compared to the dinitrile substituents. The planes of the dimethoxybenzene rings are oriented parallel to the short diagonal of the *ac* plane.

#### 4. Synthesis and crystallization

2-Bromo-5-(4-bromo-2,5-dimethoxyphenyl)cyclohexa-2,5-diene-1,4-dione, BrHBQBr, (0.300 g, 0.744 mmol) was dissolved in 350 mL of acetonitrile. In a separate beaker, potassium cyanide (0.124 g, 1.90 mmol) was dissolved in 50 mL of H<sub>2</sub>O. Upon pouring the aqueous solution into the organic solution, the mixture immediately changed from a vibrant red to a deep purple. After stirring for 1 h, 50 μL of concentrated HCl solution was added, changing the color of the mixture from purple to bright orange. The mixture was diluted with 50 mL of water and the acetonitrile was removed by rotary evaporation. A tan powder precipitated, which was

recovered by filtration and washed with water to yield the crude product. This material was recrystallized from acetone giving 0.196 g (70.4%) of pure material as yellow–orange prisms. <sup>1</sup>H NMR (360 MHz, *d*<sub>6</sub>-acetone) δ = 10.02 (*s*, 1H, ArOH), 8.75 (*s*, 1H, ArOH), 7.34 (*s*, 1H, ArH), 7.24 (*s*, 1H, ArH), 7.05 (*s*, 1H, ArH), 3.88 (*s*, 3H, OCH<sub>3</sub>), 3.82 (*s*, 3H, OCH<sub>3</sub>).

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydroxyl hydrogen atoms were located from the difference map and their coordinates were refined while the thermal parameters were constrained to ride on the carrier atom with *U*<sub>iso</sub> = 1.5*U*<sub>eq</sub>(O). Hydrogen atoms bonded to carbon were placed in calculated positions with C—H = 0.93 Å (aromatic) or 0.96 Å (methyl) and their coordinates and thermal parameters were constrained to ride on the carrier atom, with *U*<sub>iso</sub> = 1.5*U*<sub>eq</sub>(aromatic C) or 1.5*U*<sub>eq</sub>(methyl C).

#### Acknowledgements

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## supporting information

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## Crystal structure of 4'-bromo-2,5-dihydroxy-2',5'-dimethoxy-[1,1'-biphenyl]-3,4-dicarbonitrile

Joseph E. Meany, Steven P. Kelley, 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'-Bromo-2,5-dihydroxy-2',5'-dimethoxy-[1,1'-biphenyl]-3,4-dicarbonitrile

#### Crystal data

$C_{16}H_{11}BrN_2O_4$

$M_r = 375.18$

Monoclinic,  $P2_1/c$

$a = 8.4726$  (3) Å

$b = 23.7748$  (8) Å

$c = 8.0833$  (3) Å

$\beta = 111.6985$  (17)°

$V = 1512.88$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 752$

$D_x = 1.647$  Mg m<sup>-3</sup>

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

Cell parameters from 9370 reflections

$\theta = 2.6$ – $29.9$ °

$\mu = 2.74$  mm<sup>-1</sup>

$T = 296$  K

Tablet, yellow-orange

$0.35 \times 0.20 \times 0.09$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2010)

$T_{\min} = 0.428$ ,  $T_{\max} = 0.747$

65083 measured reflections

6269 independent reflections

4739 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\max} = 34.5$ °,  $\theta_{\min} = 1.7$ °

$h = -13$ → $13$

$k = -37$ → $37$

$l = -12$ → $12$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.089$

$S = 1.03$

6269 reflections

216 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.4609P]$

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

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

$\Delta\rho_{\max} = 0.59$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.26$  e Å<sup>-3</sup>



*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 ( $\text{\AA}^2$ )*

|      | <i>x</i>      | <i>y</i>    | <i>z</i>      | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|-------------|---------------|----------------------------------|
| Br1  | 0.00177 (2)   | 0.18718 (2) | 0.27906 (3)   | 0.03808 (6)                      |
| O1   | 0.09291 (15)  | 0.30658 (4) | 0.37344 (17)  | 0.0372 (3)                       |
| O2   | -0.52102 (14) | 0.29007 (5) | -0.19615 (17) | 0.0400 (3)                       |
| O3   | -0.65570 (14) | 0.38022 (5) | -0.07840 (19) | 0.0393 (3)                       |
| H3A  | -0.639 (3)    | 0.3515 (11) | -0.093 (3)    | 0.059*                           |
| O4   | -0.25442 (16) | 0.52226 (5) | -0.2911 (2)   | 0.0502 (4)                       |
| H4A  | -0.163 (3)    | 0.5103 (10) | -0.276 (3)    | 0.050*                           |
| N1   | -0.92239 (18) | 0.49008 (7) | -0.2525 (3)   | 0.0524 (4)                       |
| N2   | -0.6248 (3)   | 0.59864 (7) | -0.3963 (3)   | 0.0594 (5)                       |
| C1   | -0.12247 (17) | 0.25158 (6) | 0.1689 (2)    | 0.0269 (3)                       |
| C2   | -0.27623 (17) | 0.24472 (6) | 0.0277 (2)    | 0.0290 (3)                       |
| H2A  | -0.3187       | 0.2089      | -0.0098       | 0.035*                           |
| C3   | -0.36583 (17) | 0.29233 (6) | -0.0569 (2)   | 0.0277 (3)                       |
| C4   | -0.30049 (16) | 0.34595 (5) | -0.00356 (19) | 0.0258 (2)                       |
| C5   | -0.14639 (17) | 0.35126 (6) | 0.1413 (2)    | 0.0276 (3)                       |
| H5A  | -0.1032       | 0.3870      | 0.1789        | 0.033*                           |
| C6   | -0.05661 (18) | 0.30449 (6) | 0.2301 (2)    | 0.0271 (3)                       |
| C7   | -0.38125 (16) | 0.39804 (5) | -0.09918 (19) | 0.0258 (2)                       |
| C8   | -0.55087 (16) | 0.41297 (6) | -0.1289 (2)   | 0.0269 (3)                       |
| C9   | -0.61363 (16) | 0.46445 (6) | -0.20684 (19) | 0.0270 (3)                       |
| C10  | -0.51175 (16) | 0.50206 (6) | -0.2583 (2)   | 0.0283 (3)                       |
| C11  | -0.34649 (17) | 0.48643 (6) | -0.2341 (2)   | 0.0312 (3)                       |
| C12  | -0.28382 (17) | 0.43499 (6) | -0.1544 (2)   | 0.0300 (3)                       |
| H12A | -0.1728       | 0.4251      | -0.1377       | 0.036*                           |
| C13  | 0.1665 (2)    | 0.36036 (8) | 0.4267 (3)    | 0.0523 (5)                       |
| H13A | 0.2725        | 0.3563      | 0.5253        | 0.078*                           |
| H13B | 0.0908        | 0.3832      | 0.4618        | 0.078*                           |
| H13C | 0.1860        | 0.3780      | 0.3291        | 0.078*                           |
| C14  | -0.5909 (2)   | 0.23599 (7) | -0.2582 (3)   | 0.0411 (4)                       |
| H14A | -0.6967       | 0.2403      | -0.3568       | 0.062*                           |
| H14B | -0.6098       | 0.2161      | -0.1638       | 0.062*                           |
| H14C | -0.5131       | 0.2151      | -0.2957       | 0.062*                           |
| C15  | -0.78630 (18) | 0.47882 (7) | -0.2331 (2)   | 0.0346 (3)                       |
| C16  | -0.5754 (2)   | 0.55568 (7) | -0.3358 (2)   | 0.0368 (3)                       |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$     | $U^{12}$    | $U^{13}$    | $U^{23}$    |
|-----|-------------|-------------|--------------|-------------|-------------|-------------|
| Br1 | 0.03661 (8) | 0.02562 (8) | 0.05028 (11) | 0.00760 (5) | 0.01403 (7) | 0.01143 (6) |

|     |             |            |             |             |             |             |
|-----|-------------|------------|-------------|-------------|-------------|-------------|
| O1  | 0.0332 (5)  | 0.0295 (5) | 0.0380 (6)  | 0.0005 (4)  | 0.0002 (5)  | 0.0032 (4)  |
| O2  | 0.0303 (5)  | 0.0276 (5) | 0.0480 (7)  | -0.0015 (4) | -0.0019 (5) | -0.0029 (5) |
| O3  | 0.0287 (5)  | 0.0312 (5) | 0.0611 (8)  | -0.0015 (4) | 0.0201 (5)  | 0.0066 (5)  |
| O4  | 0.0361 (6)  | 0.0334 (6) | 0.0905 (11) | 0.0093 (5)  | 0.0344 (7)  | 0.0259 (6)  |
| N1  | 0.0283 (7)  | 0.0508 (9) | 0.0779 (12) | 0.0084 (6)  | 0.0192 (7)  | 0.0051 (8)  |
| N2  | 0.0674 (11) | 0.0381 (8) | 0.0724 (12) | 0.0203 (8)  | 0.0255 (10) | 0.0161 (8)  |
| C1  | 0.0264 (6)  | 0.0219 (6) | 0.0334 (7)  | 0.0039 (4)  | 0.0122 (5)  | 0.0046 (5)  |
| C2  | 0.0286 (6)  | 0.0202 (6) | 0.0380 (8)  | 0.0004 (4)  | 0.0120 (6)  | 0.0003 (5)  |
| C3  | 0.0233 (5)  | 0.0233 (6) | 0.0342 (7)  | 0.0003 (4)  | 0.0079 (5)  | 0.0003 (5)  |
| C4  | 0.0238 (5)  | 0.0205 (5) | 0.0325 (7)  | 0.0019 (4)  | 0.0098 (5)  | 0.0025 (5)  |
| C5  | 0.0261 (6)  | 0.0208 (5) | 0.0341 (7)  | 0.0007 (4)  | 0.0090 (5)  | 0.0009 (5)  |
| C6  | 0.0254 (5)  | 0.0251 (6) | 0.0296 (7)  | 0.0018 (5)  | 0.0088 (5)  | 0.0024 (5)  |
| C7  | 0.0223 (5)  | 0.0206 (5) | 0.0322 (7)  | 0.0021 (4)  | 0.0073 (5)  | 0.0005 (5)  |
| C8  | 0.0211 (5)  | 0.0249 (6) | 0.0330 (7)  | -0.0002 (4) | 0.0082 (5)  | -0.0005 (5) |
| C9  | 0.0208 (5)  | 0.0251 (6) | 0.0330 (7)  | 0.0031 (4)  | 0.0073 (5)  | -0.0011 (5) |
| C10 | 0.0259 (6)  | 0.0229 (6) | 0.0354 (8)  | 0.0052 (4)  | 0.0105 (5)  | 0.0035 (5)  |
| C11 | 0.0262 (6)  | 0.0232 (6) | 0.0462 (9)  | 0.0034 (5)  | 0.0158 (6)  | 0.0067 (6)  |
| C12 | 0.0226 (5)  | 0.0243 (6) | 0.0433 (8)  | 0.0044 (4)  | 0.0122 (5)  | 0.0060 (5)  |
| C13 | 0.0467 (10) | 0.0336 (8) | 0.0546 (11) | -0.0069 (7) | -0.0069 (8) | -0.0022 (8) |
| C14 | 0.0353 (7)  | 0.0336 (8) | 0.0483 (10) | -0.0086 (6) | 0.0083 (7)  | -0.0100 (7) |
| C15 | 0.0262 (6)  | 0.0302 (7) | 0.0455 (9)  | 0.0038 (5)  | 0.0109 (6)  | -0.0008 (6) |
| C16 | 0.0364 (8)  | 0.0297 (7) | 0.0453 (9)  | 0.0088 (6)  | 0.0165 (7)  | 0.0063 (6)  |

*Geometric parameters (Å, °)*

|            |             |            |             |
|------------|-------------|------------|-------------|
| Br1—C1     | 1.8848 (13) | C5—C6      | 1.3878 (19) |
| O1—C6      | 1.3655 (18) | C5—H5A     | 0.9300      |
| O1—C13     | 1.418 (2)   | C7—C12     | 1.3876 (19) |
| O2—C3      | 1.3799 (17) | C7—C8      | 1.4120 (18) |
| O2—C14     | 1.4266 (19) | C8—C9      | 1.3892 (19) |
| O3—C8      | 1.3528 (17) | C9—C10     | 1.408 (2)   |
| O3—H3A     | 0.72 (3)    | C9—C15     | 1.4396 (19) |
| O4—C11     | 1.3464 (18) | C10—C11    | 1.3907 (18) |
| O4—H4A     | 0.79 (2)    | C10—C16    | 1.434 (2)   |
| N1—C15     | 1.137 (2)   | C11—C12    | 1.3927 (19) |
| N2—C16     | 1.143 (2)   | C12—H12A   | 0.9300      |
| C1—C2      | 1.388 (2)   | C13—H13A   | 0.9600      |
| C1—C6      | 1.3909 (19) | C13—H13B   | 0.9600      |
| C2—C3      | 1.3933 (19) | C13—H13C   | 0.9600      |
| C2—H2A     | 0.9300      | C14—H14A   | 0.9600      |
| C3—C4      | 1.3933 (19) | C14—H14B   | 0.9600      |
| C4—C5      | 1.4004 (19) | C14—H14C   | 0.9600      |
| C4—C7      | 1.4860 (18) |            |             |
| C6—O1—C13  | 117.15 (12) | C9—C8—C7   | 119.57 (12) |
| C3—O2—C14  | 117.91 (12) | C8—C9—C10  | 121.32 (12) |
| C8—O3—H3A  | 108 (2)     | C8—C9—C15  | 118.27 (13) |
| C11—O4—H4A | 112.3 (17)  | C10—C9—C15 | 120.41 (13) |

|              |              |                 |              |
|--------------|--------------|-----------------|--------------|
| C2—C1—C6     | 121.99 (12)  | C11—C10—C9      | 118.94 (12)  |
| C2—C1—Br1    | 118.91 (10)  | C11—C10—C16     | 119.68 (13)  |
| C6—C1—Br1    | 119.09 (10)  | C9—C10—C16      | 121.38 (12)  |
| C1—C2—C3     | 118.92 (12)  | O4—C11—C10      | 117.60 (13)  |
| C1—C2—H2A    | 120.5        | O4—C11—C12      | 122.95 (12)  |
| C3—C2—H2A    | 120.5        | C10—C11—C12     | 119.45 (13)  |
| O2—C3—C4     | 115.96 (12)  | C7—C12—C11      | 122.30 (12)  |
| O2—C3—C2     | 123.42 (13)  | C7—C12—H12A     | 118.8        |
| C4—C3—C2     | 120.62 (12)  | C11—C12—H12A    | 118.8        |
| C3—C4—C5     | 118.83 (12)  | O1—C13—H13A     | 109.5        |
| C3—C4—C7     | 123.21 (12)  | O1—C13—H13B     | 109.5        |
| C5—C4—C7     | 117.87 (12)  | H13A—C13—H13B   | 109.5        |
| C6—C5—C4     | 121.56 (13)  | O1—C13—H13C     | 109.5        |
| C6—C5—H5A    | 119.2        | H13A—C13—H13C   | 109.5        |
| C4—C5—H5A    | 119.2        | H13B—C13—H13C   | 109.5        |
| O1—C6—C5     | 124.67 (12)  | O2—C14—H14A     | 109.5        |
| O1—C6—C1     | 117.32 (12)  | O2—C14—H14B     | 109.5        |
| C5—C6—C1     | 118.01 (13)  | H14A—C14—H14B   | 109.5        |
| C12—C7—C8    | 118.37 (12)  | O2—C14—H14C     | 109.5        |
| C12—C7—C4    | 118.74 (11)  | H14A—C14—H14C   | 109.5        |
| C8—C7—C4     | 122.82 (12)  | H14B—C14—H14C   | 109.5        |
| O3—C8—C9     | 117.39 (12)  | N1—C15—C9       | 179.5 (2)    |
| O3—C8—C7     | 122.99 (13)  | N2—C16—C10      | 179.4 (2)    |
|              |              |                 |              |
| C13—O1—C6—C1 | 175.14 (15)  | C4—C5—C6—O1     | -179.10 (15) |
| C13—O1—C6—C5 | -4.5 (2)     | C4—C5—C6—C1     | 1.2 (2)      |
| C14—O2—C3—C2 | -1.3 (2)     | C4—C7—C8—O3     | -2.4 (2)     |
| C14—O2—C3—C4 | 178.48 (15)  | C4—C7—C8—C9     | 174.94 (13)  |
| Br1—C1—C2—C3 | -178.26 (12) | C12—C7—C8—O3    | -179.24 (14) |
| C6—C1—C2—C3  | 1.0 (2)      | C12—C7—C8—C9    | -1.9 (2)     |
| Br1—C1—C6—O1 | -2.8 (2)     | C4—C7—C12—C11   | -175.62 (13) |
| Br1—C1—C6—C5 | 176.93 (12)  | C8—C7—C12—C11   | 1.4 (2)      |
| C2—C1—C6—O1  | 177.95 (14)  | O3—C8—C9—C10    | 177.94 (14)  |
| C2—C1—C6—C5  | -2.4 (2)     | O3—C8—C9—C15    | -1.7 (2)     |
| C1—C2—C3—O2  | -178.78 (14) | C7—C8—C9—C10    | 0.5 (2)      |
| C1—C2—C3—C4  | 1.5 (2)      | C7—C8—C9—C15    | -179.13 (13) |
| O2—C3—C4—C5  | 177.70 (14)  | C8—C9—C10—C11   | 1.6 (2)      |
| O2—C3—C4—C7  | -5.9 (2)     | C8—C9—C10—C16   | -178.84 (14) |
| C2—C3—C4—C5  | -2.6 (2)     | C15—C9—C10—C11  | -178.81 (14) |
| C2—C3—C4—C7  | 173.88 (14)  | C15—C9—C10—C16  | 0.8 (2)      |
| C3—C4—C5—C6  | 1.2 (2)      | C9—C10—C11—O4   | 177.38 (14)  |
| C7—C4—C5—C6  | -175.45 (14) | C9—C10—C11—C12  | -2.1 (2)     |
| C3—C4—C7—C8  | 57.1 (2)     | C16—C10—C11—O4  | -2.2 (2)     |
| C3—C4—C7—C12 | -126.09 (16) | C16—C10—C11—C12 | 178.27 (14)  |
| C5—C4—C7—C8  | -126.50 (16) | O4—C11—C12—C7   | -178.82 (14) |
| C5—C4—C7—C12 | 50.37 (19)   | C10—C11—C12—C7  | 0.7 (2)      |



*Hydrogen-bond geometry (Å, °)*

| <i>D</i> —H $\cdots$ <i>A</i>    | <i>D</i> —H | H $\cdots$ <i>A</i> | <i>D</i> $\cdots$ <i>A</i> | <i>D</i> —H $\cdots$ <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O3—H3A $\cdots$ O2               | 0.72 (3)    | 2.11 (3)            | 2.7576 (18)                | 152 (3)                       |
| O4—H4A $\cdots$ N1 <sup>i</sup>  | 0.79 (2)    | 2.03 (2)            | 2.8189 (18)                | 172 (2)                       |
| C2—H2A $\cdots$ N2 <sup>ii</sup> | 0.93        | 2.72                | 3.638 (2)                  | 168                           |

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