



# Crystal structures of *p*-substituted derivatives of 2,6-dimethylbromobenzene with $\frac{1}{2} \leq Z' \leq 4$

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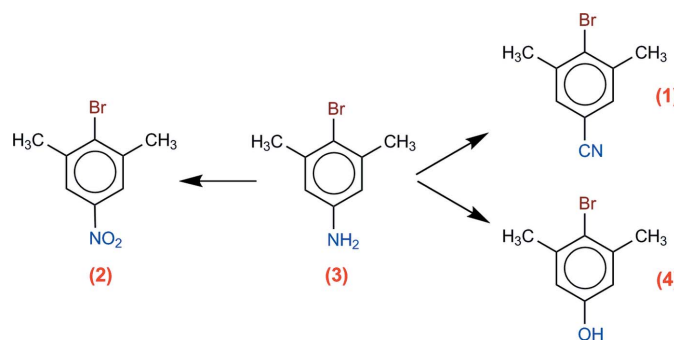
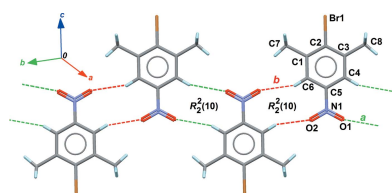
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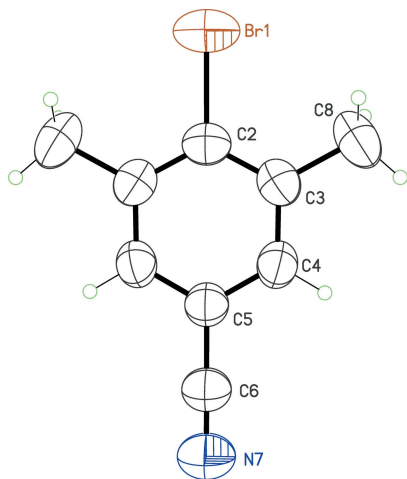
The crystal structures of four bromoarenes based on 2,6-dimethylbromobenzene are reported, which are differentiated according the functional group  $X$  placed *para* to the Br atom:  $X = \text{CN}$  (4-bromo-3,5-dimethylbenzonitrile,  $\text{C}_9\text{H}_8\text{BrN}$ ), **(1)**,  $X = \text{NO}_2$  (2-bromo-1,3-dimethyl-5-nitrobenzene,  $\text{C}_8\text{H}_8\text{BrNO}_2$ ), **(2)**,  $X = \text{NH}_2$  (4-bromo-3,5-dimethylaniline,  $\text{C}_8\text{H}_{10}\text{BrN}$ ), **(3)** and  $X = \text{OH}$  (4-bromo-3,5-dimethylphenol,  $\text{C}_8\text{H}_9\text{BrO}$ ), **(4)**. The content of the asymmetric unit is different in each crystal,  $Z' = \frac{1}{2}$  ( $X = \text{CN}$ ),  $Z' = 1$  ( $X = \text{NO}_2$ ),  $Z' = 2$  ( $X = \text{NH}_2$ ), and  $Z' = 4$  ( $X = \text{OH}$ ), and is related to the molecular symmetry and the propensity of  $X$  to be involved in hydrogen bonding. In none of the studied compounds does the crystal structure feature other non-covalent interactions, such as  $\pi$ - $\pi$ ,  $\text{C}-\text{H} \cdots \pi$  or  $\text{C}-\text{Br} \cdots \text{Br}$  contacts.

## 1. Chemical context

Our group is interested in the design of chemical model systems for studying polar- $\pi$  interactions (Cozzi *et al.*, 2008). In order to achieve this objective, it is necessary to prepare a variety of arylboronic esters as suitable substrates for Suzuki-Miyaura cross-coupling reactions (Ishiyama *et al.*, 1995; Kotha *et al.*, 2002). We obtained these boronic derivatives starting from functionalized bromoarenes. The present communication is about the synthesis and crystallography of a series of such bromoarenes, namely, *para*-substituted derivatives of 2,6-dimethylbromobenzene, for which the *p*-substituent is  $X = \text{CN}$  **(1)**,  $X = \text{NO}_2$  **(2)**,  $X = \text{NH}_2$  **(3)**, or  $X = \text{OH}$  **(4)**.



The crystallized molecules are closely related to one another from the chemical and structural points of view. However, very different crystal structures were obtained, with different compositions for the asymmetric units. Once again, this evidences that small chemical modifications for a given compound may induce dramatic changes in its crystal structure, even in the case of hydrogen/deuterium exchange, which is the smallest possible modification of a molecule (Vasylyeva

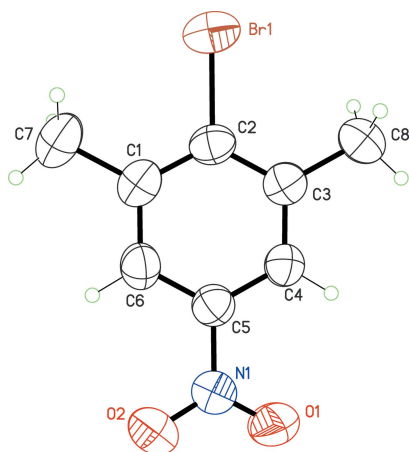

**Figure 1**

The molecular structure of (1), with displacement ellipsoids for non-H atoms at the 50% probability level. Unlabelled atoms are generated by the symmetry operation  $(x, \frac{3}{2} - y, z)$ .

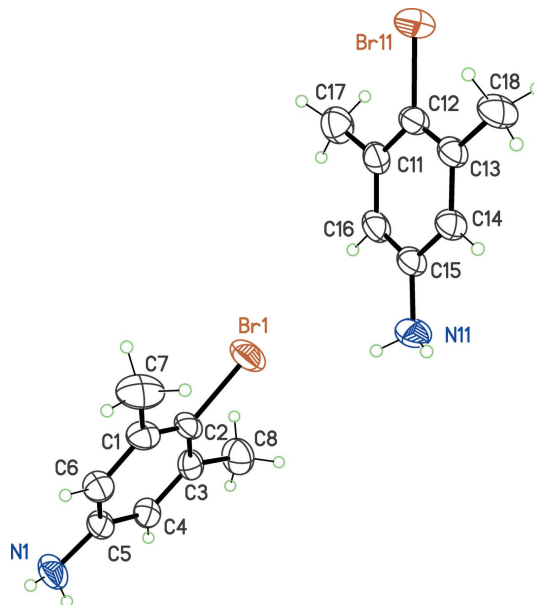
*et al.*, 2010). As a consequence, the blind tests of organic crystal-structure prediction hosted by the CCDC (Reilly *et al.*, 2016) certainly have a bright future ahead of them.

## 2. Structural commentary

No unusual bond lengths or angles are observed in the four molecules (Figs. 1–4). For example, the C–Br bond lengths span a narrow range, from 1.900 (4) to 1.910 (2) Å. The substituent *X* in the position *para* to the C–Br bond thus has no influence on the geometry of the bromobenzene core, even if very different *X* groups are used, namely, strongly electron-withdrawing groups ( $X = \text{CN}$ ,  $\text{NO}_2$ ) and strongly electron-donating groups ( $X = \text{NH}_2$ ,  $\text{OH}$ ). Another structural invariant over the studied series is the minimization of steric crowding effects between the Br atom and the methyl groups in *ortho* positions. The methyl groups are systematically rotated in such a way that the C–Br bond is staggered with a  $\text{CH}_2$  fragment of


**Figure 2**

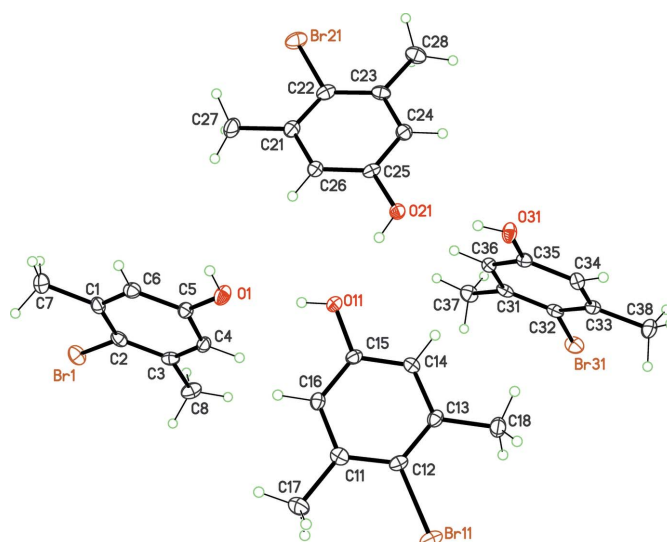
The molecular structure of (2), with displacement ellipsoids for non-H atoms at the 50% probability level.


**Figure 3**

The asymmetric unit of compound (3), with displacement ellipsoids for non-H atoms at the 30% probability level.

the methyl group. As a consequence, the endocyclic angle at the Br-bearing C atom is always the largest one in the benzene ring, varying from 121.8 (3)° in (3) to 123.9 (4)° in (1).

The point of interest regarding the molecular structures is that four different values of  $Z'$  are obtained for the four compounds. Molecule (1) ( $X = \text{CN}$ ) has the highest potential molecular symmetry,  $C_{2v}$ , assuming a linear C–C≡N group. Omitting H atoms, this symmetry is actually reached, with the C–Br and C–C≡N fragments lying on the mirror plane in space group  $P2_1/m$  (Fig. 1). The asymmetric unit then contains a half-molecule, and  $Z' = \frac{1}{2}$ . In (2), with  $X = \text{NO}_2$ , the latent symmetry  $C_{2v}$  is broken because the nitro group is tilted


**Figure 4**

The asymmetric unit of compound (4), with displacement ellipsoids for non-H atoms at the 50% probability level.

slightly with respect to the benzene ring by an angle of  $13.0(4)^\circ$ . For this crystal,  $Z' = 1$  in space group  $P\bar{1}$  (Fig. 2). Finally, for (3) and (4), which are isoelectronic molecules [ $X = \text{NH}_2$ , (3) and  $X = \text{OH}$ , (4)], despite the molecular symmetry being close to  $C_{2v}$ , the asymmetric units contain more than one molecule:  $Z' = 2$  for (3) (Fig. 3) and  $Z' = 4$  for (4) (Fig. 4), in space groups  $P2_1/n$  and  $Pbca$ , respectively.

The increasing size of the asymmetric unit, reflected in the increasing value of  $Z'$ , may be rationalized on the basis of two key parameters. First, a higher molecular symmetry obviously favours the crystallization of low  $Z'$  crystals, as in (1). This has been observed in many symmetrically substituted benzene derivatives, for example, in 4-bromo-benzonitrile in space group  $Cm$  (Britton *et al.*, 1977; see also Desiraju & Harlow, 1989), or 2,6-dibromo-4-chlorobenzonitrile in space group  $P2_1/m$  (Britton, 2005). The standard asymmetric unit with  $Z' = 1$  is obtained for (2), for which the molecular symmetry is lowered to  $C_1$ . Secondly, the introduction of efficient donor groups for hydrogen bonding, such as  $\text{NH}_2$  and  $\text{OH}$  groups, is an enabling factor for crystal structures having  $Z' > 1$ , as observed for (3) and (4). A search in the organic subset of the CSD (Groom *et al.*, 2016) reflects such a trend: for example, comparing nitrobenzene and aniline derivatives, the former class is characterized by 12.5% of crystals with  $Z' > 1$ , and this fraction is increased to 15.6% in the latter. In the same way, phenol derivatives with  $Z' = 4$  are not uncommon (Dey *et al.*, 2005; Mukherjee & Desiraju, 2011).

### 3. Supramolecular features

As expected, compound (1) is featureless regarding the packing of the molecules. No short contacts such as halogen bonds are formed, and  $\pi$ - $\pi$  interactions are insignificant, the shortest separation between benzene ring being defined by cell translations along the short cell axis,  $a = 4.0382(1) \text{ \AA}$ .

For (2), two pairs of weak  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds link the molecules to form two centrosymmetric first-level ring motifs of  $R_2^2(10)$ , with the participation of the nitro group as acceptor (Table 1). The nitro group participates with two contacts to two rings, generating a chain of  $R$  motifs along

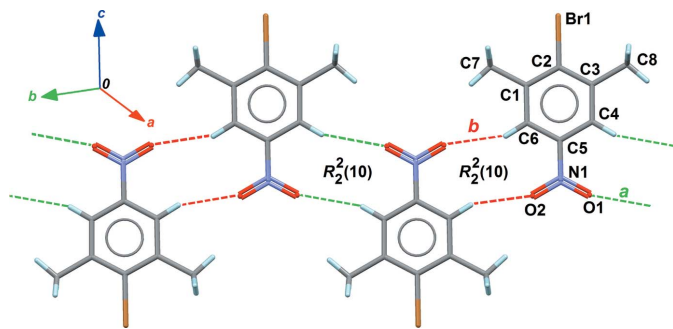


Figure 5

Part of the crystal structure of (2), showing  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds (dashed lines) forming  $R$  motifs in the crystals. Hydrogen bonds  $a$  (green) and  $b$  (red) correspond to entries 1 and 2 in Table 1. Atoms belonging to the asymmetric unit are labelled.

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (2).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C4}-\text{H4A}\cdots\text{O1}^i$	0.93	2.51	3.377 (5)	156
$\text{C6}-\text{H6A}\cdots\text{O2}^{ii}$	0.93	2.55	3.351 (5)	144

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

$[\bar{1}10]$  (Fig. 5). As for (1), slipped  $\pi$ -stacking interactions are insignificant, the benzene-to-benzene distance being, again, determined by the cell axis  $a = 4.0502(5) \text{ \AA}$ .

Although compounds (3) and (4) are isoelectronic, they present different crystal structures. This is because their donor groups for hydrogen bonding are of a different nature: the  $\text{N}-\text{H}$  bond is a poorer donor compared to the  $\text{O}-\text{H}$  bond, on the basis of the polarity of these bonds, estimated with the differences of electronegativity  $\chi_{\text{N}} - \chi_{\text{H}} = 0.84$  and  $\chi_{\text{O}} - \chi_{\text{H}} = 1.24$  (Pauling's scale is used for  $\chi$ ). Moreover, the  $\text{NH}_2$  group is potentially involved in two hydrogen bonds, while the  $\text{OH}$  group is expected to form a single, stronger contact, at least as long as bifurcated hydrogen bonds are not considered.

Both compounds (3) and (4) have a supramolecular structure based on chains oriented along a screw  $2_1$  axis (Fig. 6). For (3), two discrete contacts  $D(2)$  are formed between the two independent molecules (Table 2). These contacts involve only one  $\text{N}-\text{H}$  bond for a given  $\text{NH}_2$  group, and the acceptor atom is the  $\text{N}$  site of the connected molecule, with the  $\text{N}-\text{H}\cdots\text{N}$

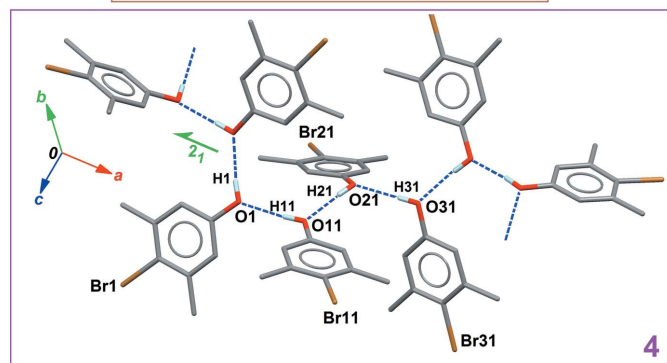
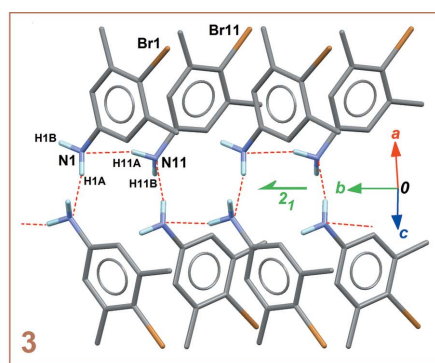


Figure 6

Part of the crystal structures of (3) (top) and (4) (bottom), showing  $\text{N}-\text{H}\cdots\text{N}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds (red and blue dashed lines, respectively). In each case, the asymmetric unit comprises the molecules with labelled atoms.

**Table 2**  
Hydrogen-bond geometry (Å, °) for (3).

<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>
N1—H1A...N1 <sup>i</sup>	0.88 (2)	2.41 (3)	3.212 (6)	152 (5)
N11—H11A...N1 <sup>ii</sup>	0.90 (2)	2.52 (3)	3.365 (6)	157 (4)

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

**Table 3**  
Hydrogen-bond geometry (Å, °) for (4).

<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>
O11—H11...O1	0.78 (3)	1.90 (3)	2.681 (3)	173 (4)
O21—H21...O11	0.76 (3)	1.92 (3)	2.682 (3)	176 (3)
O31—H31...O21	0.77 (3)	1.95 (3)	2.714 (2)	175 (3)
O1—H1...O31 <sup>i</sup>	0.78 (3)	1.95 (3)	2.729 (3)	172 (3)

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

contact oriented toward the lone pair of the acceptor N atom. A second level motif  $C_2^2(4)$  is formed using the discrete contacts, and the chain of connected molecules runs along [010] (Fig. 6, top).

A similar framework of *D* and *C* motifs appears in (4), this time starting from a  $Z' = 4$  asymmetric unit: three discrete motifs *D*(2) are formed within the asymmetric unit, and a fourth *D*(2) motif connects the first independent molecule with a symmetry-related molecule in the crystal (Table 3). As a consequence,  $C_4^4(8)$  chains are formed, propagating parallel to [100] (Fig. 6, bottom). As mentioned above, the hydrogen bonds in (4) are much more efficient than those observed in (3): all O—H...O bonds have short H...O distances of *ca* 1.9 Å and O—H...O angles are close to 180° (Table 3).

It is worth noting that none of the observed 1D supramolecular structures in (2)–(4) include  $\pi$ – $\pi$  or C—H... $\pi$  contacts, nor C—Br...Br halogen bonds. The arrangement of the molecules in the crystal over the studied series of compounds is thus mainly determined by the absence of, the presence of weak, or strong hydrogen bonds, respectively, in (1), (2) and (3), or (4).

#### 4. Database survey

Polysubstituted benzene systems are ubiquitous in the crystallographic literature. Limiting a survey to 2,6-dimethylbromobenzene, only two derivatives closely related to the series we have studied may be found, with *X* = <sup>t</sup>Bu (Field *et al.*, 2003) and *X* = I (Liu *et al.*, 2008), which do not present obvious supramolecular features. Both form  $Z' = \frac{1}{2}$  crystals, as for (1).

#### 5. Synthesis and crystallization

Compound (3) was purchased from Oakwood Chemical Co. and was the starting material for the synthesis of (2) by oxidation with *m*-CPBA, and (1) and (4) *via* a Sandmeyer reaction. Single crystals of (3) were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution.

Compound (1) was prepared by modification of the reported procedure (Xu *et al.*, 2000). A solution of NaNO<sub>2</sub>

(0.36 g, 5.2 mmol) in water (5 ml) was added dropwise to a suspension of 4-bromo-3,5-dimethylaniline (1 g, 5 mmol) in aqueous HCl (2 ml, 12 M), and water (2 ml) at 273 K. The mixture was stirred at 273 K for 30 min and then neutralized with NaHCO<sub>3</sub>. Separately, a solution of CuCN (0.54 g, 6 mmol), and KCN (0.81 g, 12 mmol) in water (10 ml) was heated at 343 K. This solution was added dropwise to the diazotization solution previously prepared. The mixture was kept at 343 K for 30 min with stirring and then cooled at room temperature. The product was extracted with toluene (3 × 30 ml). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc, 95:5) to obtain compound (1) as orange needles (0.77 g, 73%); m.p. 408–410 K; IR: 3022 (C—H Ar), 2354 (C≡N), 1498 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 (*s*, 2H), 2.44 (*s*, 6H) p.p.m.; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ : 140.0, 133.2, 131.1, 118.4, 110.7, 23.8 p.p.m.; GC–MS (EI): *m/z* = 209 (100%) [*M*<sup>+</sup>], 211 (97%) [*M*<sup>+</sup> + 2] amu. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution.

Compound (2) was prepared by modification of the reported procedure (Gilbert & Borden, 1979). A solution of 4-bromo-3,5-dimethylaniline and 3-chloroperoxybenzoic acid (4 g, 23 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (35 ml) was heated at 323 K for 2 h. After cooling at room temperature, the precipitate was filtered off and the liquid phase was washed with NaOH (1 M, 3 × 50 ml). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was dissolved in glacial acetic acid (10 ml), and a solution of H<sub>2</sub>O<sub>2</sub> (5 ml, 33% aq. solution) and glacial acetic acid (5 ml) was added at room temperature. Then, conc. HNO<sub>3</sub> (0.5 ml) was slowly added and the mixture was heated to 363 K for 4 h. After cooling, the crude was treated with water (50 ml), and was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 ml). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude was purified on a silica gel column chromatography (petroleum ether) to give compound (2) as bright-yellow crystals (0.51 g, 44%); m.p. 478–483 K; IR: 2988 (C—H Aliph), 1558, 1340 (N—O) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.92 (*s*, 2H), 2.51 (*s*, 6H) p.p.m.; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  146.3, 140.1, 134.8, 122.5, 24.1 p.p.m.; GC–MS (EI): *m/z* = 229 (100%) [*M*<sup>+</sup>], 231 (97%) [*M*<sup>+</sup> + 2] amu. Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of an ether solution.

Preparation of (4): A solution of 4-bromo-3,5-dimethylaniline (1 g, 5 mmol) in conc. H<sub>2</sub>SO<sub>4</sub> (25 ml) and water (5 ml) was cooled to 273 K. Then a solution of NaNO<sub>2</sub> (0.35 g, 5 mmol) in water (10 ml) was added dropwise under stirring. After additional 30 min the solution was refluxed for 30 min. The mixture was cooled and extracted with EtOAc (3 × 50 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude was purified by silica gel column chromatography (petroleum ether/EtOAc, 9:1) to provide the product (4) as pale-orange crystals (0.56 g, 55%); m.p. 386–388 K; IR: 3620 (O—H), 2987

**Table 4**  
Experimental details.

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	C <sub>9</sub> H <sub>8</sub> BrN	C <sub>8</sub> H <sub>8</sub> BrNO <sub>2</sub>	C <sub>8</sub> H <sub>10</sub> BrN	C <sub>8</sub> H <sub>9</sub> BrO
<i>M<sub>r</sub></i>	210.07	230.06	200.08	201.06
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>m</i>	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Orthorhombic, <i>Pbca</i>
Temperature (K)	296	296	296	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.0382 (1), 8.9362 (4), 12.1015 (4)	4.0502 (5), 9.3817 (6), 12.1823 (5)	10.48314 (15), 6.10173 (10), 26.6195 (5)	14.65213 (17), 17.9520 (2), 24.0079 (3)
$\alpha$ , $\beta$ , $\gamma$ (°)	90, 93.763 (3), 90	93.498 (4), 99.284 (4), 101.722 (5)	90, 100.0731 (16), 90	90, 90, 90
<i>V</i> (Å <sup>3</sup> )	435.76 (3)	445.20 (7)	1676.48 (5)	6314.94 (12)
<i>Z</i>	2	2	8	32
Radiation type	Cu <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$	Cu <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	5.87	5.98	6.06	6.50
Crystal size (mm)	0.21 × 0.15 × 0.12	0.80 × 0.60 × 0.10	0.30 × 0.12 × 0.10	0.23 × 0.20 × 0.18
Data collection				
Diffractometer	Rigaku OD SuperNova AtlasS2	Rigaku OD SuperNova AtlasS2	Rigaku OD SuperNova AtlasS2	Rigaku OD SuperNova AtlasS2
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> <sub>min</sub> – <i>T</i> <sub>max</sub>	0.615, 1.000	0.304, 1.000	0.593, 1.000	0.601, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	2457, 883, 771	5640, 1697, 1503	39830, 3276, 2716	22136, 6110, 5342
<i>R</i> <sub>int</sub>	0.027	0.038	0.093	0.033
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.615	0.616	0.620	0.615
Refinement				
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.044, 0.147, 1.08	0.045, 0.128, 1.07	0.054, 0.165, 1.11	0.026, 0.065, 1.02
No. of reflections	883	1697	3276	6110
No. of parameters	59	111	197	381
No. of restraints	0	0	6	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.51, -0.46	0.63, -0.59	0.44, -1.11	0.56, -0.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008) and *CifTab* (Sheldrick, 2008).

(C–H aliph), 1590 (C=C Ar), 1120 (C–O) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.57 (*s*, 2H), 4.99 (*s*, 1H), 2.34 (*s*, 6H) p.p.m.; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  153.9, 139.5, 118.3, 115.2, 23.8 p.p.m.; GC–MS (EI): *m/z* = 200 (100%) [*M*<sup>+</sup>], 202 (97%) [*M*<sup>+</sup> + 2] amu. Crystals suitable for diffraction were obtained by slow evaporation of an EtOAc solution.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. At room temperature, compound (3) decomposes after a few minutes under Mo *K* $\alpha$  irradiation, but is stable for hours under Cu *K* $\alpha$  irradiation. For compound (3), H atoms of NH<sub>2</sub> groups were located in a difference Fourier map and were refined with restraints of N–H = 0.89 (2) Å and H $\cdots$ H = 1.52 (2) Å. For (4), H atoms of OH groups were found in a difference map and refined freely. All other H atoms in (1)–(4) were refined as riding.

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## supporting information

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## Crystal structures of *p*-substituted derivatives of 2,6-dimethylbromobenzene with $\frac{1}{2} \leq Z' \leq 4$

Angélica Navarrete Guitérrez, Gerardo Aguirre Hernández and Sylvain Bernès

### Computing details

For all compounds, data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *CifTab* (Sheldrick, 2008).

(1)

#### Crystal data

C<sub>9</sub>H<sub>8</sub>BrN

$M_r = 210.07$

Monoclinic,  $P2_1/m$

$a = 4.0382$  (1) Å

$b = 8.9362$  (4) Å

$c = 12.1015$  (4) Å

$\beta = 93.763$  (3)°

$V = 435.76$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 208$

$D_x = 1.601$  Mg m<sup>-3</sup>

Melting point: 408 K

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 1415 reflections

$\theta = 3.7\text{--}71.2^\circ$

$\mu = 5.87$  mm<sup>-1</sup>

$T = 296$  K

Needle, orange

0.21 × 0.15 × 0.12 mm

#### Data collection

Rigaku OD SuperNova AtlasS2

diffractometer

Radiation source: micro-focus sealed X-ray

tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 5.1980 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Rigaku OD, 2015)

$T_{\min} = 0.615$ ,  $T_{\max} = 1.000$

2457 measured reflections

883 independent reflections

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

$R_{\text{int}} = 0.027$

$\theta_{\max} = 71.4^\circ$ ,  $\theta_{\min} = 3.7^\circ$

$h = -3 \rightarrow 4$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.147$

$S = 1.08$

883 reflections

59 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from  
neighbouring sites  
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0947P)^2 + 0.0077P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

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	0.11810 (14)	0.7500	0.05285 (4)	0.0896 (4)
C2	0.3504 (11)	0.7500	0.1947 (4)	0.0588 (10)
C3	0.4270 (8)	0.6133 (4)	0.2438 (3)	0.0616 (8)
C4	0.6007 (9)	0.6158 (3)	0.3467 (3)	0.0615 (7)
H4A	0.6616	0.5261	0.3814	0.074*
C5	0.6843 (12)	0.7500	0.3980 (4)	0.0592 (10)
C6	0.8701 (14)	0.7500	0.5047 (4)	0.0697 (12)
N7	1.0181 (16)	0.7500	0.5880 (5)	0.0920 (15)
C8	0.3447 (12)	0.4662 (5)	0.1894 (4)	0.0890 (12)
H8A	0.4147	0.4671	0.1151	0.133*
H8B	0.1095	0.4499	0.1878	0.133*
H8C	0.4573	0.3873	0.2305	0.133*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0749 (5)	0.1338 (7)	0.0588 (5)	0.000	-0.0053 (3)	0.000
C2	0.053 (2)	0.072 (3)	0.052 (2)	0.000	0.0056 (17)	0.000
C3	0.0654 (18)	0.0579 (17)	0.0622 (18)	-0.0049 (13)	0.0085 (14)	-0.0070 (13)
C4	0.0739 (19)	0.0499 (15)	0.0613 (17)	0.0023 (13)	0.0087 (14)	0.0037 (12)
C5	0.067 (3)	0.058 (2)	0.053 (2)	0.000	0.006 (2)	0.000
C6	0.077 (3)	0.075 (3)	0.056 (3)	0.000	-0.001 (2)	0.000
N7	0.104 (4)	0.104 (4)	0.066 (3)	0.000	-0.012 (3)	0.000
C8	0.107 (3)	0.068 (2)	0.092 (3)	-0.015 (2)	0.007 (2)	-0.026 (2)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br1—C2	1.902 (5)	C5—C6	1.450 (7)
C2—C3	1.384 (4)	C6—N7	1.138 (7)
C3—C4	1.389 (5)	C8—H8A	0.9600
C3—C8	1.498 (5)	C8—H8B	0.9600
C4—C5	1.383 (4)	C8—H8C	0.9600
C4—H4A	0.9300		
C3 <sup>i</sup> —C2—C3	123.9 (4)	C4—C5—C6	119.8 (2)
C3—C2—Br1	118.1 (2)	N7—C6—C5	179.5 (6)
C2—C3—C4	117.2 (3)	C3—C8—H8A	109.5
C2—C3—C8	123.3 (3)	C3—C8—H8B	109.5
C4—C3—C8	119.5 (3)	H8A—C8—H8B	109.5
C5—C4—C3	120.7 (3)	C3—C8—H8C	109.5



C5—C4—H4A	119.6	H8A—C8—H8C	109.5
C3—C4—H4A	119.6	H8B—C8—H8C	109.5
C4 <sup>i</sup> —C5—C4	120.3 (4)		
C3 <sup>i</sup> —C2—C3—C4	-2.2 (7)	C2—C3—C4—C5	1.6 (5)
Br1—C2—C3—C4	179.1 (3)	C8—C3—C4—C5	179.1 (4)
C3 <sup>i</sup> —C2—C3—C8	-179.6 (4)	C3—C4—C5—C4 <sup>i</sup>	-1.1 (7)
Br1—C2—C3—C8	1.8 (5)	C3—C4—C5—C6	-179.1 (4)

Symmetry code: (i)  $x, -y+3/2, z$ .

## (2) 2-Bromo-1,3-dimethyl-5-nitrobenzene

### Crystal data

$C_8H_8BrNO_2$

$M_r = 230.06$

Triclinic,  $P\bar{1}$

$a = 4.0502$  (5) Å

$b = 9.3817$  (6) Å

$c = 12.1823$  (5) Å

$\alpha = 93.498$  (4)°

$\beta = 99.284$  (4)°

$\gamma = 101.722$  (5)°

$V = 445.20$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 228$

$D_x = 1.716$  Mg m<sup>-3</sup>

Melting point: 478 K

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$  Å

Cell parameters from 2941 reflections

$\theta = 3.7$ – $71.5$ °

$\mu = 5.98$  mm<sup>-1</sup>

$T = 296$  K

Block, pale yellow

$0.80 \times 0.60 \times 0.10$  mm

### Data collection

Rigaku OD SuperNova AtlasS2  
diffractometer

Radiation source: micro-focus sealed X-ray  
tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 5.1980 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2015)

$T_{\min} = 0.304$ ,  $T_{\max} = 1.000$

5640 measured reflections

1697 independent reflections

1503 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 71.7$ °,  $\theta_{\min} = 3.7$ °

$h = -4 \rightarrow 4$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 14$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.128$

$S = 1.07$

1697 reflections

111 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 0.2116P]$

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

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

$\Delta\rho_{\max} = 0.63$  e Å<sup>-3</sup>

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.11600 (12)	0.72052 (5)	0.45994 (3)	0.0787 (2)

N1	0.2977 (9)	0.7622 (4)	-0.0226 (3)	0.0628 (8)
O1	0.4131 (11)	0.6691 (4)	-0.0677 (3)	0.0899 (10)
O2	0.2182 (11)	0.8634 (4)	-0.0707 (3)	0.0947 (11)
C1	0.1468 (9)	0.8635 (4)	0.2627 (3)	0.0565 (8)
C2	0.1714 (9)	0.7332 (4)	0.3086 (3)	0.0534 (8)
C3	0.2324 (9)	0.6117 (4)	0.2500 (3)	0.0548 (8)
C4	0.2752 (9)	0.6237 (4)	0.1406 (3)	0.0530 (8)
H4A	0.3211	0.5459	0.0991	0.064*
C5	0.2495 (9)	0.7520 (4)	0.0932 (3)	0.0533 (8)
C6	0.1846 (10)	0.8718 (4)	0.1517 (3)	0.0571 (8)
H6A	0.1667	0.9564	0.1173	0.069*
C7	0.0874 (12)	0.9962 (5)	0.3270 (4)	0.0779 (12)
H7A	-0.1068	0.9678	0.3630	0.117*
H7B	0.0445	1.0676	0.2765	0.117*
H7C	0.2867	1.0373	0.3824	0.117*
C8	0.2502 (13)	0.4705 (5)	0.3008 (4)	0.0724 (11)
H8A	0.4026	0.4907	0.3716	0.109*
H8B	0.3335	0.4077	0.2517	0.109*
H8C	0.0257	0.4232	0.3114	0.109*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0850 (4)	0.0998 (4)	0.0536 (3)	0.0207 (3)	0.0197 (2)	0.0041 (2)
N1	0.073 (2)	0.0602 (17)	0.0567 (17)	0.0151 (15)	0.0126 (15)	0.0087 (14)
O1	0.132 (3)	0.093 (2)	0.0637 (18)	0.051 (2)	0.0380 (19)	0.0117 (16)
O2	0.147 (3)	0.084 (2)	0.071 (2)	0.049 (2)	0.031 (2)	0.0291 (17)
C1	0.0481 (17)	0.060 (2)	0.059 (2)	0.0150 (15)	0.0028 (14)	-0.0057 (16)
C2	0.0472 (17)	0.066 (2)	0.0475 (17)	0.0139 (14)	0.0087 (13)	0.0035 (15)
C3	0.0521 (18)	0.0584 (19)	0.0536 (18)	0.0132 (15)	0.0070 (14)	0.0044 (15)
C4	0.0570 (19)	0.0500 (17)	0.0541 (19)	0.0158 (14)	0.0103 (14)	0.0044 (14)
C5	0.0533 (18)	0.0539 (18)	0.0513 (18)	0.0103 (14)	0.0069 (14)	0.0040 (14)
C6	0.061 (2)	0.0497 (18)	0.061 (2)	0.0169 (15)	0.0044 (16)	0.0045 (15)
C7	0.084 (3)	0.072 (3)	0.078 (3)	0.027 (2)	0.010 (2)	-0.016 (2)
C8	0.090 (3)	0.068 (2)	0.064 (2)	0.023 (2)	0.016 (2)	0.0195 (19)

*Geometric parameters (Å, °)*

Br1—C2	1.900 (4)	C4—C5	1.382 (5)
N1—O1	1.214 (4)	C4—H4A	0.9300
N1—O2	1.217 (4)	C5—C6	1.388 (5)
N1—C5	1.460 (5)	C6—H6A	0.9300
C1—C6	1.389 (6)	C7—H7A	0.9600
C1—C2	1.390 (5)	C7—H7B	0.9600
C1—C7	1.512 (5)	C7—H7C	0.9600
C2—C3	1.394 (5)	C8—H8A	0.9600
C3—C4	1.379 (5)	C8—H8B	0.9600
C3—C8	1.506 (5)	C8—H8C	0.9600

O1—N1—O2	122.2 (4)	C6—C5—N1	118.9 (3)
O1—N1—C5	119.0 (3)	C5—C6—C1	118.9 (3)
O2—N1—C5	118.7 (3)	C5—C6—H6A	120.5
C6—C1—C2	117.7 (3)	C1—C6—H6A	120.5
C6—C1—C7	118.6 (4)	C1—C7—H7A	109.5
C2—C1—C7	123.7 (4)	C1—C7—H7B	109.5
C1—C2—C3	123.8 (3)	H7A—C7—H7B	109.5
C1—C2—Br1	117.9 (3)	C1—C7—H7C	109.5
C3—C2—Br1	118.4 (3)	H7A—C7—H7C	109.5
C4—C3—C2	117.4 (3)	H7B—C7—H7C	109.5
C4—C3—C8	119.8 (3)	C3—C8—H8A	109.5
C2—C3—C8	122.8 (4)	C3—C8—H8B	109.5
C3—C4—C5	119.7 (3)	H8A—C8—H8B	109.5
C3—C4—H4A	120.2	C3—C8—H8C	109.5
C5—C4—H4A	120.2	H8A—C8—H8C	109.5
C4—C5—C6	122.5 (3)	H8B—C8—H8C	109.5
C4—C5—N1	118.6 (3)		
C6—C1—C2—C3	0.2 (5)	C3—C4—C5—C6	0.6 (6)
C7—C1—C2—C3	-178.8 (4)	C3—C4—C5—N1	179.7 (3)
C6—C1—C2—Br1	-179.5 (3)	O1—N1—C5—C4	-12.0 (5)
C7—C1—C2—Br1	1.6 (5)	O2—N1—C5—C4	167.5 (4)
C1—C2—C3—C4	1.0 (5)	O1—N1—C5—C6	167.1 (4)
Br1—C2—C3—C4	-179.4 (3)	O2—N1—C5—C6	-13.4 (5)
C1—C2—C3—C8	-178.6 (4)	C4—C5—C6—C1	0.6 (6)
Br1—C2—C3—C8	1.1 (5)	N1—C5—C6—C1	-178.5 (3)
C2—C3—C4—C5	-1.3 (5)	C2—C1—C6—C5	-0.9 (5)
C8—C3—C4—C5	178.2 (3)	C7—C1—C6—C5	178.1 (4)

*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>
C4—H4A $\cdots$ O1 <sup>i</sup>	0.93	2.51	3.377 (5)	156
C6—H6A $\cdots$ O2 <sup>ii</sup>	0.93	2.55	3.351 (5)	144

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

(3)

*Crystal data*C<sub>8</sub>H<sub>10</sub>BrN*M<sub>r</sub>* = 200.08Monoclinic, *P*2<sub>1</sub>/*n**a* = 10.48314 (15) Å*b* = 6.10173 (10) Å*c* = 26.6195 (5) Å $\beta$  = 100.0731 (16)°*V* = 1676.48 (5) Å<sup>3</sup>*Z* = 8*F*(000) = 800*D<sub>x</sub>* = 1.585 Mg m<sup>-3</sup>

Melting point: 346 K

Cu *K* $\alpha$  radiation,  $\lambda$  = 1.54184 Å

Cell parameters from 14036 reflections

 $\theta$  = 3.4–71.4° $\mu$  = 6.06 mm<sup>-1</sup>

$T = 296$  K  $0.30 \times 0.12 \times 0.10$  mm  
 Needle, colourless

*Data collection*

Rigaku OD SuperNova AtlasS2 diffractometer	$T_{\min} = 0.593$ , $T_{\max} = 1.000$
Radiation source: micro-focus sealed X-ray tube, SuperNova (Cu) X-ray Source	39830 measured reflections
Mirror monochromator	3276 independent reflections
Detector resolution: $5.1980$ pixels $\text{mm}^{-1}$	2716 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.093$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)	$\theta_{\max} = 72.8^\circ$ , $\theta_{\min} = 3.4^\circ$
	$h = -12 \rightarrow 12$
	$k = -7 \rightarrow 7$
	$l = -32 \rightarrow 32$

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.054$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.165$	$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 1.0194P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
3276 reflections	$(\Delta/\sigma)_{\max} < 0.001$
197 parameters	$\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
6 restraints	$\Delta\rho_{\min} = -1.11 \text{ e } \text{\AA}^{-3}$
0 constraints	
Primary atom site location: structure-invariant direct methods	

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.24694 (5)	0.23484 (10)	0.15702 (3)	0.1038 (3)
N1	-0.1935 (4)	0.7889 (7)	0.20733 (16)	0.0868 (12)
H1A	-0.201 (5)	0.787 (7)	0.2398 (9)	0.104*
H1B	-0.202 (5)	0.918 (5)	0.1918 (15)	0.104*
C1	0.0703 (3)	0.5931 (7)	0.14294 (14)	0.0673 (9)
C2	0.1125 (3)	0.4160 (6)	0.17418 (14)	0.0618 (8)
C3	0.0613 (3)	0.3673 (6)	0.21759 (14)	0.0616 (8)
C4	-0.0384 (3)	0.4981 (6)	0.22843 (12)	0.0601 (8)
H4A	-0.0745	0.4684	0.2572	0.072*
C5	-0.0852 (3)	0.6715 (7)	0.19735 (13)	0.0608 (8)
C6	-0.0292 (4)	0.7188 (6)	0.15532 (15)	0.0673 (9)
H6A	-0.0593	0.8382	0.1349	0.081*
C7	0.1289 (6)	0.6536 (10)	0.0969 (2)	0.1049 (17)
H7A	0.2212	0.6663	0.1067	0.157*
H7B	0.0938	0.7910	0.0834	0.157*
H7C	0.1091	0.5419	0.0713	0.157*
C8	0.1109 (5)	0.1815 (8)	0.2535 (2)	0.0951 (14)
H8A	0.1029	0.0456	0.2351	0.143*
H8B	0.0611	0.1745	0.2805	0.143*
H8C	0.2003	0.2068	0.2678	0.143*
Br11	0.72828 (6)	-0.22871 (10)	-0.00212 (2)	0.0996 (3)
N11	0.6186 (4)	0.3496 (7)	0.17122 (14)	0.0816 (10)

H11A	0.658 (4)	0.480 (5)	0.1713 (19)	0.098*
H11B	0.536 (2)	0.356 (7)	0.1745 (18)	0.098*
C11	0.5864 (3)	-0.0934 (7)	0.07484 (15)	0.0681 (9)
C12	0.6933 (3)	-0.0488 (7)	0.05224 (13)	0.0652 (9)
C13	0.7753 (3)	0.1285 (7)	0.06764 (13)	0.0652 (9)
C14	0.7478 (4)	0.2596 (6)	0.10694 (14)	0.0648 (9)
H14A	0.8018	0.3773	0.1180	0.078*
C15	0.6412 (4)	0.2187 (7)	0.13007 (14)	0.0649 (9)
C16	0.5626 (3)	0.0413 (7)	0.11379 (14)	0.0688 (10)
H16A	0.4918	0.0122	0.1295	0.083*
C17	0.4956 (5)	-0.2818 (8)	0.0571 (2)	0.0917 (14)
H17A	0.4340	-0.2971	0.0796	0.138*
H17B	0.5447	-0.4147	0.0572	0.138*
H17C	0.4507	-0.2530	0.0231	0.138*
C18	0.8907 (5)	0.1869 (9)	0.04352 (18)	0.0884 (13)
H18A	0.8643	0.1973	0.0072	0.133*
H18B	0.9558	0.0755	0.0513	0.133*
H18C	0.9254	0.3251	0.0567	0.133*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0617 (3)	0.1074 (5)	0.1481 (6)	0.0103 (2)	0.0348 (3)	-0.0438 (3)
N1	0.066 (2)	0.117 (3)	0.082 (2)	0.034 (2)	0.0268 (18)	0.008 (2)
C1	0.0627 (19)	0.081 (2)	0.066 (2)	-0.0104 (18)	0.0315 (16)	-0.0087 (18)
C2	0.0408 (14)	0.068 (2)	0.080 (2)	0.0016 (14)	0.0206 (14)	-0.0159 (18)
C3	0.0466 (16)	0.065 (2)	0.072 (2)	-0.0036 (14)	0.0078 (14)	0.0020 (17)
C4	0.0478 (16)	0.079 (2)	0.0569 (17)	-0.0032 (15)	0.0185 (13)	0.0057 (17)
C5	0.0479 (16)	0.079 (2)	0.0584 (18)	0.0061 (16)	0.0183 (14)	-0.0009 (17)
C6	0.071 (2)	0.077 (2)	0.0575 (19)	0.0061 (18)	0.0207 (16)	0.0090 (17)
C7	0.122 (4)	0.118 (4)	0.093 (3)	-0.022 (3)	0.070 (3)	-0.009 (3)
C8	0.099 (3)	0.079 (3)	0.104 (4)	0.014 (3)	0.008 (3)	0.018 (3)
Br11	0.1085 (5)	0.1057 (5)	0.0899 (4)	0.0198 (3)	0.0326 (3)	-0.0249 (3)
N11	0.075 (2)	0.105 (3)	0.073 (2)	0.000 (2)	0.0369 (17)	-0.018 (2)
C11	0.0536 (17)	0.077 (2)	0.072 (2)	0.0145 (17)	0.0074 (15)	0.0043 (19)
C12	0.0644 (19)	0.078 (2)	0.0551 (17)	0.0193 (18)	0.0154 (15)	0.0002 (17)
C13	0.0575 (18)	0.086 (3)	0.0557 (18)	0.0144 (18)	0.0199 (15)	0.0073 (18)
C14	0.059 (2)	0.081 (3)	0.059 (2)	0.0026 (16)	0.0219 (16)	0.0020 (17)
C15	0.0562 (19)	0.085 (3)	0.0566 (18)	0.0134 (17)	0.0197 (15)	0.0017 (17)
C16	0.0485 (17)	0.090 (3)	0.072 (2)	0.0096 (17)	0.0224 (15)	0.006 (2)
C17	0.072 (3)	0.089 (3)	0.114 (4)	-0.003 (2)	0.014 (3)	-0.007 (3)
C18	0.084 (3)	0.115 (4)	0.078 (3)	0.003 (3)	0.046 (2)	0.001 (3)

*Geometric parameters (Å, °)*

Br1—C2	1.908 (3)	Br11—C12	1.902 (3)
N1—C5	1.407 (5)	N11—C15	1.409 (5)
N1—H1A	0.881 (18)	N11—H11A	0.897 (18)

N1—H1B	0.886 (18)	N11—H11B	0.884 (18)
C1—C6	1.380 (5)	C11—C16	1.380 (5)
C1—C2	1.388 (6)	C11—C12	1.389 (5)
C1—C7	1.510 (5)	C11—C17	1.514 (6)
C2—C3	1.389 (5)	C12—C13	1.398 (6)
C3—C4	1.385 (5)	C13—C14	1.387 (5)
C3—C8	1.515 (6)	C13—C18	1.508 (5)
C4—C5	1.379 (5)	C14—C15	1.390 (5)
C4—H4A	0.9300	C14—H14A	0.9300
C5—C6	1.382 (5)	C15—C16	1.383 (6)
C6—H6A	0.9300	C16—H16A	0.9300
C7—H7A	0.9600	C17—H17A	0.9600
C7—H7B	0.9600	C17—H17B	0.9600
C7—H7C	0.9600	C17—H17C	0.9600
C8—H8A	0.9600	C18—H18A	0.9600
C8—H8B	0.9600	C18—H18B	0.9600
C8—H8C	0.9600	C18—H18C	0.9600
C5—N1—H1A	113 (3)	C15—N11—H11A	111 (3)
C5—N1—H1B	113 (3)	C15—N11—H11B	114 (3)
H1A—N1—H1B	117 (3)	H11A—N11—H11B	115 (3)
C6—C1—C2	117.7 (3)	C16—C11—C12	118.3 (4)
C6—C1—C7	119.3 (4)	C16—C11—C17	120.0 (4)
C2—C1—C7	123.0 (4)	C12—C11—C17	121.6 (4)
C1—C2—C3	122.4 (3)	C11—C12—C13	121.8 (3)
C1—C2—Br1	118.6 (3)	C11—C12—Br11	119.6 (3)
C3—C2—Br1	119.0 (3)	C13—C12—Br11	118.6 (3)
C4—C3—C2	117.8 (3)	C14—C13—C12	118.0 (3)
C4—C3—C8	119.2 (4)	C14—C13—C18	118.2 (4)
C2—C3—C8	123.0 (4)	C12—C13—C18	123.8 (4)
C5—C4—C3	121.3 (3)	C13—C14—C15	121.3 (4)
C5—C4—H4A	119.4	C13—C14—H14A	119.3
C3—C4—H4A	119.4	C15—C14—H14A	119.3
C4—C5—C6	119.3 (3)	C16—C15—C14	118.9 (3)
C4—C5—N1	119.5 (3)	C16—C15—N11	121.0 (3)
C6—C5—N1	121.2 (4)	C14—C15—N11	120.0 (4)
C1—C6—C5	121.5 (4)	C11—C16—C15	121.7 (3)
C1—C6—H6A	119.2	C11—C16—H16A	119.2
C5—C6—H6A	119.2	C15—C16—H16A	119.2
C1—C7—H7A	109.5	C11—C17—H17A	109.5
C1—C7—H7B	109.5	C11—C17—H17B	109.5
H7A—C7—H7B	109.5	H17A—C17—H17B	109.5
C1—C7—H7C	109.5	C11—C17—H17C	109.5
H7A—C7—H7C	109.5	H17A—C17—H17C	109.5
H7B—C7—H7C	109.5	H17B—C17—H17C	109.5
C3—C8—H8A	109.5	C13—C18—H18A	109.5
C3—C8—H8B	109.5	C13—C18—H18B	109.5
H8A—C8—H8B	109.5	H18A—C18—H18B	109.5

C3—C8—H8C	109.5	C13—C18—H18C	109.5
H8A—C8—H8C	109.5	H18A—C18—H18C	109.5
H8B—C8—H8C	109.5	H18B—C18—H18C	109.5
C6—C1—C2—C3	-2.1 (6)	C16—C11—C12—C13	-0.6 (5)
C7—C1—C2—C3	177.4 (4)	C17—C11—C12—C13	178.3 (4)
C6—C1—C2—Br1	178.4 (3)	C16—C11—C12—Br11	-179.3 (3)
C7—C1—C2—Br1	-2.1 (5)	C17—C11—C12—Br11	-0.4 (5)
C1—C2—C3—C4	2.1 (5)	C11—C12—C13—C14	0.7 (5)
Br1—C2—C3—C4	-178.4 (3)	Br11—C12—C13—C14	179.3 (3)
C1—C2—C3—C8	-176.8 (4)	C11—C12—C13—C18	-178.5 (4)
Br1—C2—C3—C8	2.6 (5)	Br11—C12—C13—C18	0.2 (5)
C2—C3—C4—C5	-0.2 (5)	C12—C13—C14—C15	-0.8 (6)
C8—C3—C4—C5	178.8 (4)	C18—C13—C14—C15	178.4 (4)
C3—C4—C5—C6	-1.7 (6)	C13—C14—C15—C16	0.9 (6)
C3—C4—C5—N1	174.7 (4)	C13—C14—C15—N11	177.6 (4)
C2—C1—C6—C5	0.1 (6)	C12—C11—C16—C15	0.8 (6)
C7—C1—C6—C5	-179.4 (4)	C17—C11—C16—C15	-178.2 (4)
C4—C5—C6—C1	1.7 (6)	C14—C15—C16—C11	-0.9 (6)
N1—C5—C6—C1	-174.6 (4)	N11—C15—C16—C11	-177.5 (4)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ N11 <sup>i</sup>	0.88 (2)	2.41 (3)	3.212 (6)	152 (5)
N11—H11A $\cdots$ N1 <sup>ii</sup>	0.90 (2)	2.52 (3)	3.365 (6)	157 (4)

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

## (4) 4-Bromo-3,5-dimethylphenol

## Crystal data

 $C_8H_9BrO$  $M_r = 201.06$ Orthorhombic,  $Pbca$  $a = 14.65213$  (17)  $\text{\AA}$  $b = 17.9520$  (2)  $\text{\AA}$  $c = 24.0079$  (3)  $\text{\AA}$  $V = 6314.94$  (12)  $\text{\AA}^3$  $Z = 32$  $F(000) = 3200$  $D_x = 1.692$   $\text{Mg m}^{-3}$ 

Melting point: 386 K

Cu  $K\alpha$  radiation,  $\lambda = 1.54184$   $\text{\AA}$ 

Cell parameters from 10448 reflections

 $\theta = 3.7\text{--}71.4^\circ$  $\mu = 6.50$   $\text{mm}^{-1}$  $T = 100$  K

Block, yellow

 $0.23 \times 0.20 \times 0.18$  mm

## Data collection

Rigaku OD SuperNova AtlasS2

diffractometer

Radiation source: micro-focus sealed X-ray

tube, SuperNova (Cu) X-ray Source

Mirror monochromator

Detector resolution: 5.1980 pixels  $\text{mm}^{-1}$  $\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2015)

 $T_{\min} = 0.601$ ,  $T_{\max} = 1.000$ 

22136 measured reflections

6110 independent reflections

5342 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.033$  $\theta_{\max} = 71.6^\circ$ ,  $\theta_{\min} = 3.7^\circ$  $h = -17 \rightarrow 13$  $k = -21 \rightarrow 22$  $l = -29 \rightarrow 28$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.026$  $wR(F^2) = 0.065$  $S = 1.02$ 

6110 reflections

381 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 3.051P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.002$  $\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$ *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	0.22468 (2)	0.59654 (2)	0.78001 (2)	0.02219 (7)
O1	0.46483 (12)	0.75860 (10)	0.61587 (8)	0.0196 (4)
H1	0.436 (2)	0.7751 (18)	0.5913 (14)	0.029*
C1	0.25870 (16)	0.69235 (13)	0.68779 (10)	0.0161 (5)
C2	0.30052 (17)	0.65022 (13)	0.72925 (10)	0.0162 (5)
C3	0.39536 (17)	0.64366 (13)	0.73399 (10)	0.0159 (5)
C4	0.44884 (16)	0.68140 (13)	0.69532 (10)	0.0151 (5)
H4A	0.5135	0.6785	0.6976	0.018*
C5	0.40869 (16)	0.72306 (13)	0.65365 (10)	0.0145 (5)
C6	0.31470 (16)	0.72865 (13)	0.64976 (10)	0.0164 (5)
H6A	0.2882	0.7576	0.6208	0.020*
C7	0.15740 (17)	0.69908 (16)	0.68248 (11)	0.0234 (6)
H7A	0.1318	0.7172	0.7177	0.035*
H7B	0.1313	0.6502	0.6737	0.035*
H7C	0.1427	0.7342	0.6526	0.035*
C8	0.44007 (18)	0.59541 (14)	0.77743 (11)	0.0219 (5)
H8A	0.5061	0.5944	0.7711	0.033*
H8B	0.4157	0.5447	0.7749	0.033*
H8C	0.4274	0.6157	0.8145	0.033*
Br11	0.90409 (2)	0.88537 (2)	0.75012 (2)	0.02282 (7)
O11	0.64155 (12)	0.73224 (11)	0.59470 (8)	0.0230 (4)
H11	0.590 (2)	0.7371 (19)	0.6026 (14)	0.034*
C11	0.72728 (16)	0.84371 (13)	0.71234 (10)	0.0159 (5)
C12	0.81977 (16)	0.83541 (13)	0.70215 (10)	0.0151 (5)
C13	0.85456 (16)	0.79230 (13)	0.65883 (10)	0.0152 (5)
C14	0.79235 (16)	0.75794 (14)	0.62345 (10)	0.0164 (5)
H14A	0.8137	0.7281	0.5935	0.020*
C15	0.69938 (16)	0.76692 (13)	0.63161 (10)	0.0146 (5)
C16	0.66644 (16)	0.80871 (13)	0.67584 (10)	0.0145 (5)
H16A	0.6025	0.8136	0.6814	0.017*
C17	0.69077 (19)	0.88894 (15)	0.76024 (11)	0.0230 (6)
H17A	0.7141	0.8687	0.7954	0.034*
H17B	0.6239	0.8867	0.7603	0.034*



H17C	0.7105	0.9408	0.7563	0.034*
C18	0.95504 (16)	0.78010 (15)	0.65044 (11)	0.0207 (5)
H18A	0.9646	0.7475	0.6182	0.031*
H18B	0.9810	0.7567	0.6838	0.031*
H18C	0.9851	0.8281	0.6439	0.031*
Br21	0.42678 (2)	0.47389 (2)	0.39094 (2)	0.02459 (7)
O21	0.69191 (12)	0.69370 (10)	0.49124 (7)	0.0175 (4)
H21	0.677 (2)	0.7063 (18)	0.5200 (13)	0.026*
C21	0.47716 (16)	0.59328 (14)	0.46321 (10)	0.0167 (5)
C22	0.51005 (17)	0.54353 (13)	0.42327 (10)	0.0175 (5)
C23	0.60053 (17)	0.54233 (13)	0.40577 (10)	0.0167 (5)
C24	0.66009 (17)	0.59418 (13)	0.42934 (10)	0.0163 (5)
H24A	0.7221	0.5953	0.4179	0.020*
C25	0.62964 (16)	0.64384 (13)	0.46920 (10)	0.0144 (5)
C26	0.53944 (16)	0.64363 (13)	0.48600 (10)	0.0158 (5)
H26A	0.5195	0.6782	0.5134	0.019*
C27	0.37892 (17)	0.59441 (16)	0.48179 (11)	0.0233 (6)
H27A	0.3712	0.6316	0.5113	0.035*
H27B	0.3620	0.5452	0.4960	0.035*
H27C	0.3397	0.6072	0.4501	0.035*
C28	0.63566 (19)	0.48676 (14)	0.36405 (11)	0.0221 (5)
H28A	0.6999	0.4974	0.3558	0.033*
H28B	0.5998	0.4903	0.3297	0.033*
H28C	0.6302	0.4364	0.3794	0.033*
Br31	1.07251 (2)	0.46757 (2)	0.62030 (2)	0.02168 (7)
O31	0.87558 (12)	0.69132 (10)	0.47660 (7)	0.0176 (4)
H31	0.823 (2)	0.6897 (17)	0.4800 (13)	0.026*
C31	0.91446 (17)	0.53218 (13)	0.57080 (10)	0.0154 (5)
C32	1.00912 (17)	0.53671 (13)	0.57385 (10)	0.0155 (5)
C33	1.06015 (16)	0.59008 (14)	0.54511 (10)	0.0158 (5)
C34	1.01266 (16)	0.64133 (13)	0.51263 (10)	0.0152 (5)
H34A	1.0451	0.6784	0.4925	0.018*
C35	0.91818 (16)	0.63854 (13)	0.50948 (10)	0.0139 (5)
C36	0.86927 (16)	0.58457 (13)	0.53791 (10)	0.0147 (5)
H36A	0.8046	0.5832	0.5350	0.018*
C37	0.86046 (18)	0.47289 (13)	0.60069 (11)	0.0200 (5)
H37A	0.8724	0.4760	0.6408	0.030*
H37B	0.8787	0.4237	0.5870	0.030*
H37C	0.7952	0.4804	0.5937	0.030*
C38	1.16258 (16)	0.59329 (15)	0.54722 (11)	0.0217 (5)
H38A	1.1841	0.6362	0.5256	0.033*
H38B	1.1879	0.5474	0.5314	0.033*
H38C	1.1825	0.5984	0.5860	0.033*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.02410 (15)	0.02111 (14)	0.02136 (14)	-0.00353 (10)	0.00837 (10)	0.00205 (10)

O1	0.0138 (9)	0.0259 (10)	0.0191 (9)	-0.0019 (7)	-0.0014 (7)	0.0086 (7)
C1	0.0150 (12)	0.0148 (11)	0.0187 (12)	0.0004 (9)	0.0032 (9)	-0.0035 (9)
C2	0.0195 (12)	0.0137 (11)	0.0155 (11)	-0.0036 (9)	0.0044 (9)	-0.0027 (9)
C3	0.0212 (13)	0.0125 (11)	0.0139 (11)	-0.0008 (9)	-0.0033 (9)	-0.0019 (9)
C4	0.0115 (11)	0.0152 (11)	0.0187 (12)	-0.0007 (9)	-0.0012 (9)	-0.0021 (9)
C5	0.0134 (11)	0.0144 (11)	0.0156 (11)	-0.0028 (9)	0.0013 (9)	0.0000 (9)
C6	0.0189 (12)	0.0161 (12)	0.0141 (11)	0.0021 (9)	-0.0019 (9)	0.0009 (9)
C7	0.0162 (13)	0.0303 (15)	0.0238 (13)	0.0005 (11)	0.0036 (10)	-0.0007 (11)
C8	0.0244 (14)	0.0216 (13)	0.0198 (13)	-0.0047 (10)	-0.0062 (10)	0.0041 (11)
Br11	0.02236 (14)	0.02426 (14)	0.02183 (14)	-0.00606 (10)	-0.00779 (10)	-0.00253 (11)
O11	0.0123 (9)	0.0369 (11)	0.0197 (9)	-0.0031 (8)	-0.0010 (7)	-0.0103 (8)
C11	0.0207 (13)	0.0113 (11)	0.0158 (11)	0.0024 (9)	0.0002 (9)	0.0014 (9)
C12	0.0164 (12)	0.0145 (11)	0.0145 (11)	-0.0021 (9)	-0.0044 (9)	0.0016 (9)
C13	0.0131 (12)	0.0169 (12)	0.0156 (11)	-0.0007 (9)	-0.0017 (9)	0.0033 (9)
C14	0.0166 (12)	0.0189 (12)	0.0136 (11)	0.0009 (9)	0.0013 (9)	-0.0036 (9)
C15	0.0142 (12)	0.0157 (11)	0.0139 (11)	-0.0030 (9)	-0.0023 (9)	-0.0004 (9)
C16	0.0121 (11)	0.0150 (11)	0.0163 (11)	0.0013 (9)	0.0000 (9)	0.0019 (9)
C17	0.0261 (14)	0.0223 (13)	0.0205 (13)	0.0005 (11)	0.0016 (11)	-0.0068 (10)
C18	0.0141 (12)	0.0274 (13)	0.0206 (13)	0.0002 (10)	0.0011 (10)	0.0021 (10)
Br21	0.02642 (15)	0.02282 (14)	0.02452 (15)	-0.00989 (11)	-0.00721 (11)	-0.00050 (11)
O21	0.0134 (8)	0.0209 (9)	0.0182 (9)	-0.0034 (7)	0.0007 (7)	-0.0071 (7)
C21	0.0153 (12)	0.0186 (12)	0.0163 (12)	-0.0024 (9)	-0.0006 (9)	0.0057 (10)
C22	0.0196 (13)	0.0158 (11)	0.0170 (12)	-0.0046 (9)	-0.0050 (10)	0.0043 (9)
C23	0.0235 (13)	0.0142 (11)	0.0122 (11)	0.0005 (10)	-0.0019 (10)	0.0014 (9)
C24	0.0164 (12)	0.0174 (12)	0.0151 (11)	-0.0016 (9)	0.0005 (9)	0.0020 (9)
C25	0.0157 (12)	0.0133 (11)	0.0142 (11)	-0.0024 (9)	-0.0050 (9)	0.0015 (9)
C26	0.0145 (12)	0.0174 (11)	0.0156 (11)	0.0011 (9)	-0.0008 (9)	-0.0009 (9)
C27	0.0140 (13)	0.0306 (14)	0.0252 (14)	-0.0046 (10)	0.0000 (10)	0.0023 (11)
C28	0.0299 (15)	0.0174 (12)	0.0191 (13)	-0.0002 (11)	0.0006 (11)	-0.0035 (10)
Br31	0.02599 (15)	0.02241 (14)	0.01663 (13)	0.00797 (10)	-0.00221 (10)	0.00384 (10)
O31	0.0120 (8)	0.0197 (9)	0.0211 (9)	0.0029 (7)	0.0013 (7)	0.0071 (7)
C31	0.0226 (13)	0.0134 (11)	0.0101 (11)	-0.0013 (9)	0.0026 (9)	-0.0020 (9)
C32	0.0206 (12)	0.0155 (12)	0.0104 (11)	0.0045 (9)	-0.0003 (9)	-0.0011 (9)
C33	0.0163 (12)	0.0178 (12)	0.0133 (11)	0.0002 (9)	-0.0008 (9)	-0.0031 (9)
C34	0.0148 (12)	0.0147 (11)	0.0160 (11)	0.0003 (9)	0.0028 (9)	0.0002 (9)
C35	0.0156 (12)	0.0142 (11)	0.0119 (11)	0.0009 (9)	-0.0009 (9)	-0.0001 (9)
C36	0.0139 (12)	0.0168 (12)	0.0133 (11)	-0.0010 (9)	0.0005 (9)	-0.0006 (9)
C37	0.0249 (14)	0.0173 (12)	0.0178 (12)	-0.0030 (10)	0.0026 (10)	0.0033 (10)
C38	0.0135 (12)	0.0265 (14)	0.0252 (14)	0.0020 (10)	-0.0009 (10)	-0.0016 (11)

*Geometric parameters (Å, °)*

Br1—C2	1.910 (2)	Br21—C22	1.912 (2)
O1—C5	1.381 (3)	O21—C25	1.383 (3)
O1—H1	0.78 (3)	O21—H21	0.76 (3)
C1—C6	1.390 (3)	C21—C22	1.396 (4)
C1—C2	1.392 (3)	C21—C26	1.396 (3)
C1—C7	1.495 (3)	C21—C27	1.507 (3)

C2—C3	1.399 (3)	C22—C23	1.391 (4)
C3—C4	1.391 (3)	C23—C24	1.396 (3)
C3—C8	1.506 (3)	C23—C28	1.504 (3)
C4—C5	1.381 (3)	C24—C25	1.382 (3)
C4—H4A	0.9500	C24—H24A	0.9500
C5—C6	1.384 (3)	C25—C26	1.382 (3)
C6—H6A	0.9500	C26—H26A	0.9500
C7—H7A	0.9800	C27—H27A	0.9800
C7—H7B	0.9800	C27—H27B	0.9800
C7—H7C	0.9800	C27—H27C	0.9800
C8—H8A	0.9800	C28—H28A	0.9800
C8—H8B	0.9800	C28—H28B	0.9800
C8—H8C	0.9800	C28—H28C	0.9800
Br11—C12	1.912 (2)	Br31—C32	1.910 (2)
O11—C15	1.375 (3)	O31—C35	1.382 (3)
O11—H11	0.78 (3)	O31—H31	0.77 (3)
C11—C12	1.385 (3)	C31—C32	1.391 (3)
C11—C16	1.399 (3)	C31—C36	1.395 (3)
C11—C17	1.506 (3)	C31—C37	1.508 (3)
C12—C13	1.393 (3)	C32—C33	1.398 (3)
C13—C14	1.391 (3)	C33—C34	1.392 (3)
C13—C18	1.502 (3)	C33—C38	1.503 (3)
C14—C15	1.386 (3)	C34—C35	1.387 (3)
C14—H14A	0.9500	C34—H34A	0.9500
C15—C16	1.387 (3)	C35—C36	1.385 (3)
C16—H16A	0.9500	C36—H36A	0.9500
C17—H17A	0.9800	C37—H37A	0.9800
C17—H17B	0.9800	C37—H37B	0.9800
C17—H17C	0.9800	C37—H37C	0.9800
C18—H18A	0.9800	C38—H38A	0.9800
C18—H18B	0.9800	C38—H38B	0.9800
C18—H18C	0.9800	C38—H38C	0.9800
C5—O1—H1	110 (2)	C25—O21—H21	111 (2)
C6—C1—C2	117.7 (2)	C22—C21—C26	117.2 (2)
C6—C1—C7	119.5 (2)	C22—C21—C27	122.8 (2)
C2—C1—C7	122.8 (2)	C26—C21—C27	120.0 (2)
C1—C2—C3	122.7 (2)	C23—C22—C21	123.1 (2)
C1—C2—Br1	118.31 (18)	C23—C22—Br21	118.39 (19)
C3—C2—Br1	118.90 (18)	C21—C22—Br21	118.48 (18)
C4—C3—C2	117.7 (2)	C22—C23—C24	117.6 (2)
C4—C3—C8	119.8 (2)	C22—C23—C28	122.5 (2)
C2—C3—C8	122.5 (2)	C24—C23—C28	119.9 (2)
C5—C4—C3	120.5 (2)	C25—C24—C23	120.6 (2)
C5—C4—H4A	119.8	C25—C24—H24A	119.7
C3—C4—H4A	119.8	C23—C24—H24A	119.7
C4—C5—O1	118.2 (2)	C26—C25—C24	120.6 (2)
C4—C5—C6	120.8 (2)	C26—C25—O21	121.4 (2)

O1—C5—C6	121.0 (2)	C24—C25—O21	118.0 (2)
C5—C6—C1	120.6 (2)	C25—C26—C21	120.8 (2)
C5—C6—H6A	119.7	C25—C26—H26A	119.6
C1—C6—H6A	119.7	C21—C26—H26A	119.6
C1—C7—H7A	109.5	C21—C27—H27A	109.5
C1—C7—H7B	109.5	C21—C27—H27B	109.5
H7A—C7—H7B	109.5	H27A—C27—H27B	109.5
C1—C7—H7C	109.5	C21—C27—H27C	109.5
H7A—C7—H7C	109.5	H27A—C27—H27C	109.5
H7B—C7—H7C	109.5	H27B—C27—H27C	109.5
C3—C8—H8A	109.5	C23—C28—H28A	109.5
C3—C8—H8B	109.5	C23—C28—H28B	109.5
H8A—C8—H8B	109.5	H28A—C28—H28B	109.5
C3—C8—H8C	109.5	C23—C28—H28C	109.5
H8A—C8—H8C	109.5	H28A—C28—H28C	109.5
H8B—C8—H8C	109.5	H28B—C28—H28C	109.5
C15—O11—H11	113 (3)	C35—O31—H31	111 (2)
C12—C11—C16	117.7 (2)	C32—C31—C36	117.6 (2)
C12—C11—C17	122.7 (2)	C32—C31—C37	122.6 (2)
C16—C11—C17	119.6 (2)	C36—C31—C37	119.7 (2)
C11—C12—C13	123.3 (2)	C31—C32—C33	123.2 (2)
C11—C12—Br11	118.38 (18)	C31—C32—Br31	118.53 (18)
C13—C12—Br11	118.27 (18)	C33—C32—Br31	118.27 (18)
C14—C13—C12	117.6 (2)	C34—C33—C32	117.5 (2)
C14—C13—C18	119.7 (2)	C34—C33—C38	119.5 (2)
C12—C13—C18	122.7 (2)	C32—C33—C38	123.0 (2)
C15—C14—C13	120.4 (2)	C35—C34—C33	120.4 (2)
C15—C14—H14A	119.8	C35—C34—H34A	119.8
C13—C14—H14A	119.8	C33—C34—H34A	119.8
O11—C15—C14	117.5 (2)	O31—C35—C36	121.8 (2)
O11—C15—C16	121.6 (2)	O31—C35—C34	117.2 (2)
C14—C15—C16	120.9 (2)	C36—C35—C34	121.0 (2)
C15—C16—C11	120.0 (2)	C35—C36—C31	120.3 (2)
C15—C16—H16A	120.0	C35—C36—H36A	119.8
C11—C16—H16A	120.0	C31—C36—H36A	119.8
C11—C17—H17A	109.5	C31—C37—H37A	109.5
C11—C17—H17B	109.5	C31—C37—H37B	109.5
H17A—C17—H17B	109.5	H37A—C37—H37B	109.5
C11—C17—H17C	109.5	C31—C37—H37C	109.5
H17A—C17—H17C	109.5	H37A—C37—H37C	109.5
H17B—C17—H17C	109.5	H37B—C37—H37C	109.5
C13—C18—H18A	109.5	C33—C38—H38A	109.5
C13—C18—H18B	109.5	C33—C38—H38B	109.5
H18A—C18—H18B	109.5	H38A—C38—H38B	109.5
C13—C18—H18C	109.5	C33—C38—H38C	109.5
H18A—C18—H18C	109.5	H38A—C38—H38C	109.5
H18B—C18—H18C	109.5	H38B—C38—H38C	109.5

C6—C1—C2—C3	0.3 (4)	C26—C21—C22—C23	0.0 (4)
C7—C1—C2—C3	179.6 (2)	C27—C21—C22—C23	179.8 (2)
C6—C1—C2—Br1	-177.41 (17)	C26—C21—C22—Br21	-179.83 (17)
C7—C1—C2—Br1	1.9 (3)	C27—C21—C22—Br21	-0.1 (3)
C1—C2—C3—C4	0.2 (4)	C21—C22—C23—C24	-0.6 (4)
Br1—C2—C3—C4	177.91 (17)	Br21—C22—C23—C24	179.23 (17)
C1—C2—C3—C8	-177.3 (2)	C21—C22—C23—C28	178.0 (2)
Br1—C2—C3—C8	0.4 (3)	Br21—C22—C23—C28	-2.2 (3)
C2—C3—C4—C5	-0.6 (3)	C22—C23—C24—C25	1.0 (3)
C8—C3—C4—C5	177.0 (2)	C28—C23—C24—C25	-177.7 (2)
C3—C4—C5—O1	-179.1 (2)	C23—C24—C25—C26	-0.7 (4)
C3—C4—C5—C6	0.6 (4)	C23—C24—C25—O21	179.7 (2)
C4—C5—C6—C1	0.0 (4)	C24—C25—C26—C21	0.1 (4)
O1—C5—C6—C1	179.6 (2)	O21—C25—C26—C21	179.6 (2)
C2—C1—C6—C5	-0.4 (3)	C22—C21—C26—C25	0.3 (3)
C7—C1—C6—C5	-179.7 (2)	C27—C21—C26—C25	-179.5 (2)
C16—C11—C12—C13	-2.2 (4)	C36—C31—C32—C33	-1.0 (4)
C17—C11—C12—C13	178.4 (2)	C37—C31—C32—C33	178.1 (2)
C16—C11—C12—Br11	178.05 (17)	C36—C31—C32—Br31	178.17 (17)
C17—C11—C12—Br11	-1.4 (3)	C37—C31—C32—Br31	-2.7 (3)
C11—C12—C13—C14	1.9 (4)	C31—C32—C33—C34	0.8 (4)
Br11—C12—C13—C14	-178.34 (18)	Br31—C32—C33—C34	-178.28 (17)
C11—C12—C13—C18	-176.2 (2)	C31—C32—C33—C38	-178.1 (2)
Br11—C12—C13—C18	3.6 (3)	Br31—C32—C33—C38	2.7 (3)
C12—C13—C14—C15	0.0 (4)	C32—C33—C34—C35	0.0 (3)
C18—C13—C14—C15	178.2 (2)	C38—C33—C34—C35	179.0 (2)
C13—C14—C15—O11	179.2 (2)	C33—C34—C35—O31	179.8 (2)
C13—C14—C15—C16	-1.6 (4)	C33—C34—C35—C36	-0.7 (4)
O11—C15—C16—C11	-179.5 (2)	O31—C35—C36—C31	-179.9 (2)
C14—C15—C16—C11	1.3 (4)	C34—C35—C36—C31	0.6 (4)
C12—C11—C16—C15	0.6 (3)	C32—C31—C36—C35	0.2 (3)
C17—C11—C16—C15	-180.0 (2)	C37—C31—C36—C35	-178.9 (2)

*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>
O11—H11...O1	0.78 (3)	1.90 (3)	2.681 (3)	173 (4)
O21—H21...O11	0.76 (3)	1.92 (3)	2.682 (3)	176 (3)
O31—H31...O21	0.77 (3)	1.95 (3)	2.714 (2)	175 (3)
O1—H1...O31 <sup>i</sup>	0.78 (3)	1.95 (3)	2.729 (3)	172 (3)

Symmetry code: (i)  $x-1/2, -y+3/2, -z+1$ .