

# Different supramolecular interactions mediated by bromine atoms in the crystal structures of three anisole derivates

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## Abstract

Three anisole building blocks featuring bishydroxymethyl or bisbromomethyl pendants have analyzed with regard to their molecular structure and packing behaviour. A typical supramolecular pattern we found were C—H··· $\pi$  interactions responsible for the generation of molecular stacks.  $\pi$ ··· $\pi$  Interactions were only observed in the absence of bromine indicating a striking influence on the distances between adjacent aromatic moieties. When comparing the bishydroxymethyl compound with the respective bisbromomethyl compound we found that the strong O—H···O in the zigzag arrangement in the first is replaced by C—H···Br interactions in the second without changing the general packing.

## 1. Introduction

Phenols and their ethers are important building blocks for the a large variety of target compounds. Of crucial importance in this respect is their activation in order to allow the desired reactions. One way of preparing suited phenol monomers is the introduction of hydroxymethyl residues, which can be done by applying formaldehyde under basic conditions. For further use, the alcoholic OH groups can be transformed into bromomethyl groups (Moran *et al.*, 1952).

During our studies on phenolic macrocycles we prepared the three title compounds, (I)-(III) and determined their molecular structures. All three are important educts for a wide range of molecules and materials. Title compound (I) has been used in the synthesis of selenacalixarenes (Thomas *et al.*, 2012), title compounds (II) and (III) in the preparation of rotaxanes (Hirose *et al.*, 2007a; Hirose *et al.*, 2007b), supramolecular ligands (Li *et al.*, 1988; Xu *et al.*, 2012; Sookcharoenpinyo *et al.*, 2012), cyclophanes (Yamato *et al.*, 2002; Yamato *et al.*, 2006; Shimizu *et al.*, 2009), macrocycles (Akine *et al.*, 2000; Sharghi *et al.*, 2001; Akine *et al.*, 2005), crown ethers (Hirose *et al.*, 2003) and pyrene derivatives (Tashiro *et al.*, 1989).

## 2. Experimental

### 2.1. Synthesis and crystallization

Ethyl 3,5-bis(hydroxymethyl)-4-methoxy-benzoate, (I), has been synthesized from ethylparaben (Haba *et al.*, 2005; Thomas *et al.*, 2012). Title compounds (II), 4-bromo-2,6-bis(hydroxymethyl)anisole, and (III), 4-bromo-2,6-bis(bromomethyl)anisole, have been prepared from 4-bromophenol according to literature procedures (Leroy *et al.*, 1988; Tashiro *et al.*, 1989; González-Bulnes *et al.*, 2013). Crystals suitable for X-ray diffraction were obtained by crystallization of the title compounds from the respective solvents at room temperature [(I): ethanol, m.p. 67 °C; (II): water, m.p. 127 °C; (III): ethanol, m.p. 85 °C].

### 2.2. Refinement

Data collection was performed at different temperatures [(I): 203 K, (II): 173 K, (III): 153 K] due to instability of the single crystals and to avoid unintended ice formation during the measurements. Crystal data, data collection and structure refinement details are summarized in Table 1.

### 3. Results and discussion

The title compounds (I-III) were found to crystallise with one molecule in the asymmetric part of the unit cell. While (I) crystallised in the triclinic space group  $P\bar{1}$ , (II) was detected in the noncentrosymmetric orthorhombic space group  $Pna2_1$  and (III) in the monoclinic group  $C2/c$ . For all crystal structures no solvent accessible area was found (Spek, 2009). The packing indices were calculated to 71.1 (I), 70.5 (II), and 70.2 (III) using Platon software (Spek, 2009). As expected the value slightly decreases with a higher number of bromine atoms.

First, the carbonyl group in the structure of (I) is more or less coplanar with the aromatic unit [dihedral angle of  $6.69(15)^\circ$ ]. The methoxy group is not coplanar and shows torsion angles of  $83.7(2)^\circ$  and  $-101.3(2)^\circ$  (see Table 2 for selected torsion angles). In contrast, both  $\text{CH}_2\text{OH}$  substituents differ in their position relative to the benzene core. While the hydroxymethylene unit of O1 is almost coplanar [ $4.6(3)^\circ$  and  $-173.24(17)^\circ$ ], the group of O3 gives a small torsion of about  $-22.3(3)^\circ$  and  $155.76^\circ$ . This is similar to the orientation of the  $\text{CH}_2\text{OH}$  groups in the structure of the free acid with torsion angles of  $1.2^\circ/-179.1^\circ$ , and  $-41.6^\circ/138.4^\circ$  for the second  $\text{CH}_2\text{OH}$  group, respectively (Kohmoto *et al.*, 2009). An inversed situation for one  $\text{CH}_2\text{OH}$  group is observed in the crystal structure of methyl 3,5-bis(hydroxymethyl)benzoate (Katzsch *et al.*, 2012). In here the torsion angles are  $-174.7^\circ/5.8^\circ$ , and  $-47.9^\circ/131.6^\circ$  for the second  $\text{CH}_2\text{OH}$  group. In the crystal structure of bromoanisole (II), the hydroxymethylene and methoxy substituents are orientated like described for (I) with slight differences. The corresponding torsion angles are given in Table 3. The molecular geometry of compound (III) is described by the same orientation of the methoxy group as observed for (I) and (II). In contrast, the bromomethyl moieties point to different directions, ("trans" form). The first methylene unit at Br1 is orientated as  $\text{CH}_2\text{OH}$  of O1 in (I) but with a greater torsion (Table 4). The second methylene moiety at Br3 shows an inversed orientation with a greater torsion compared to O2 in (I). A similar situation is found in related compounds such as 1-bromo-3,5-bis(bromomethyl)benzene with torsion angles of  $77.4^\circ/-103.5^\circ$  and  $106^\circ/-74.8^\circ$  (Jones *et al.*, 2012) or 1,3-bis(bromomethyl)benzene with an inversed orientation but torsion angles of  $-83.3^\circ/97.5^\circ$  and  $-82.9^\circ/96.2^\circ$  (Jones & Kus, 2007).

All three compounds (I)-(III) bear a methoxy group being able to form weak intermolecular hydrogen bonds. While (I) and (II) have two additional  $\text{CH}_2\text{OH}$  groups being known to give strong hydrogen bond networks, (III) does not. Furthermore, (I) possesses a  $\text{COOEt}$  group which could participate in  $\text{C}-\text{H}\cdots\text{O}$  or  $\text{O}-\text{H}\cdots\text{O}$  interactions. Indeed, the carbonyl oxygen atom O4 interacts in an  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond [ $\text{O3}-\text{H3O}\cdots\text{O4}$ :  $1.83(3) \text{ \AA}$ , Table 3] connecting two adjacent stacking like chains. These stacks arise as follows. Two molecules of (I) are connected via  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the two hydroxyl functionalities [ $\text{O1}-\text{H1O}\cdots\text{O3}$ :  $1.87(3) \text{ \AA}$ , Table 3] to form discrete dimers, which are stabilized by  $\pi\cdots\pi$  stacking interactions [ $d = 3.4815(16) \text{ \AA}$ ] (Fig. 1b). These dimers are connected via  $\text{C}-\text{H}\cdots\pi$  interaction of  $2.92 \text{ \AA}$  resulting in a chain-like stacking along the crystallographic  $a$ -axis. A weak  $\text{C}-\text{H}\cdots\text{O}$  contact of  $2.65 \text{ \AA}$  (Table 3) further stabilizes the molecular packing.

By way of contrast, as a consequence of the inversed orientation of the  $\text{CH}_2\text{OH}$  group in methyl 3,5-bis(hydroxymethyl)benzoate (Katzsch *et al.*, 2012), the hydrogen bonding pattern changes from discrete dimers to a continuous hydrogen bonding. The crystal structure of the free acid of (I) is dominated by the dimers resulting from the  $\text{COOH}$  group.

The molecule of the structure of (II) has two  $\text{CH}_2\text{OH}$  groups being able to interact in hydrogen bonds as observed in (I). In contrast to (I), no discrete dimers are formed but both hydroxyl groups are involved in linear  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. While  $\text{O1}-\text{H1}\cdots\text{O3}$  leads to a chain along the crystallographic  $a$ -axis, the combination with  $\text{O3}-\text{H3}\cdots\text{O1}$  results in a layerlike arrangement of stacked molecules within the  $ac$ -plane.  $\text{C}-\text{H}\cdots\pi$  interactions of  $2.82 \text{ \AA}$  support the stacking along the  $c$ -axis. Adjacent layers are connected via  $\text{Br}\cdots\text{Br}$  contacts and weak  $\text{C}-\text{H}\cdots\text{O}$  contacts ( $>2.8 \text{ \AA}$ ). Very weak  $\text{C}-\text{H}\cdots\text{Br}$  contacts are observed in addition to the  $\text{O1}-\text{H1}\cdots\text{O3}$  hydrogen bond supporting the formation of

chains. In contrast to (I),  $\pi \cdots \pi$  stacking interactions with distances between adjacent centres of the aromatic units of  $>4.4$  Å are not involved in the molecular packing of (II).

When comparing the structure of title compound (II) with the structure of the free phenol, *i.e.* 4-bromo-2,6-bis(hydroxymethyl)phenol (Crisp *et al.*, 2000), the overall packing behaviour is similar. In both cases, the arene units form continuous stacks in which the anisol units of (II) have the same orientation in every layer, whereas in the phenol every second molecule is rotated by  $180^\circ$ . This feature allows the phenolic hydroxyl group to take part in a combination of linear and branched hydrogen bonds, though prevents Br $\cdots$ Br contacts as found in (II).

In the packing of (III) stacks along the crystallographic *b*-axis are observed. These stacks are generated by C—H $\cdots$  $\pi$  (2.88 Å,  $117^\circ$ ) and C—H $\cdots$ Br (2.94 Å,  $155.3^\circ$ ) interactions, and are connected to an adjacent stack via an additional C—H $\cdots$ Br contact along the *c*-axis (2.99 Å,  $154.2^\circ$ ). This chain along the *c*-axis is supported by a very weak Br $\cdots$ Br contact [C1—Br2 $\cdots$ Br3—C9: 3.7187 (8) Å,  $x, -y+1, z-1/2$ ] resulting in a bifurcation at Br3. According to the respective angles of  $96.02$  ( $13^\circ$ ) and  $169.89$  ( $13^\circ$ ) it is a rather clear type II interaction (Mukherjee *et al.*, 2014). As observed in the structure of (II),  $\pi \cdots \pi$  stacking interactions are involved in the formation of the stacks. Additionally, the methoxy group in (III) leads to a reduced number and longer bromine $\cdots$ bromine contacts in comparison to 1-bromo-3,5-bis(bromomethyl)-benzene. In both cases, the aromatic bound Br is involved. Worthnoting, (II) and (III) display rather similar packing motifs. The aromatic units are piled up connected via C—H $\cdots$  $\pi$  interactions, while the interconnection is facilitated by either O—H $\cdots$ O or C—H $\cdots$ Br interactions (Fig. 5).

In summary, we have analyzed the molecular structure and the packing behaviour of three arene building blocks featuring *bis*(hydroxymethyl) or *bis*(bromomethyl) substituents. In all structures C—H $\cdots$  $\pi$  interactions are responsible for the generation of stacks. Therefore a typical supramolecular pattern the C—H $\cdots$  $\pi$  interaction can be considered, but in combination with strong O—H $\cdots$ O hydrogen bonds between the hydroxyl groups. For the *bis*(bromomethyl) derivative (III) the O—H $\cdots$ O interactions in the zigzag arrangement seems to be replaced by C—H $\cdots$ Br interactions without changing the general packing mode. Finally,  $\pi \cdots \pi$  interactions were only observed in the absence of bromine (I) indicating that the larger bromine atom enlarges the distances between adjacent aromatic moieties.

**Table 1**

Experimental details

	(I)	(II)	(III)
Crystal data			
Chemical formula	C <sub>12</sub> H <sub>16</sub> O <sub>5</sub>	C <sub>9</sub> H <sub>11</sub> BrO <sub>3</sub>	C <sub>9</sub> H <sub>9</sub> Br <sub>3</sub> O
<i>M<sub>r</sub></i>	240.25	247.09	372.89
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>	Monoclinic, <i>C2/c</i>
Temperature (K)	203	173	153
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.8601 (10), 8.2489 (11), 10.7883 (14)	13.1596 (7), 16.2514 (9), 4.4735 (2)	33.315 (4), 4.3913 (3), 15.9655 (17)
$\alpha$ , $\beta$ , $\gamma$ (°)	81.538 (11), 72.352 (10), 61.930 (9)	90, 90, 90	90, 110.142 (8), 90
<i>V</i> (Å <sup>3</sup> )	588.15 (14)	956.71 (9)	2192.9 (4)
<i>Z</i>	2	4	8
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.11	4.27	11.00
Crystal size (mm)	0.35 $\times$ 0.32 $\times$ 0.28	0.45 $\times$ 0.27 $\times$ 0.15	0.50 $\times$ 0.11 $\times$ 0.09

Data collection

Diffractometer	STOE <i>IPDS 2</i> diffractometer	STOE <i>IPDS 2</i> diffractometer	STOE <i>IPDS 2T</i> diffractometer
Absorption correction	–	Integration <i>X-AREA</i> (STOE)	Integration <i>X-AREA</i> (STOE)
$T_{\min}$ , $T_{\max}$	–	0.283, 0.564	0.008, 0.076
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4748, 2188, 1705	4183, 1904, 1647	5754, 2197, 1834
$R_{\text{int}}$	0.052	0.074	0.087
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.606	0.627	0.622
Refinement			
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.050, 0.140, 1.12	0.065, 0.190, 1.10	0.033, 0.088, 1.10
No. of reflections	2188	1904	2197
No. of parameters	164	127	119
No. of restraints	0	1	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	0.23, –0.26	0.82, –1.22	0.63, –0.60
Absolute structure	–	Classical Flack method preferred over Parsons because s.u. lower.	–
Absolute structure parameter–	–	0.01 (5)	–

Computer programs: STOE *X-AREA*, STOE *X-RED*, *SHELXL2012* (Sheldrick, 2012), *SHELXL2014* (Sheldrick, 2015), *XP* (Sheldrick, 2008), *WinGX* (Farrugia, 2012), *pubCIF* (Westrip, 2010), *SHELXLE* (Hübschle *et al.*, 2011).

**Table 2**

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$O1\text{---}H1O\cdots O3^i$	0.92 (3)	1.87 (3)	2.788 (2)	176 (3)
$O3\text{---}H3O\cdots O4^{ii}$	0.91 (3)	1.83 (3)	2.725 (2)	167 (3)
$C9\text{---}H9B\cdots O3^{iii}$	0.99	2.65	3.555 (3)	153

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

**Table 3**

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$C8\text{---}H8A\cdots Br1^i$	0.98	3.11	3.773 (13)	126
$C8\text{---}H8B\cdots Br1^{ii}$	0.98	3.11	3.917 (19)	140
$O1\text{---}H1\cdots O3^{ii}$	1.0 (2)	1.8 (2)	2.687 (13)	146 (20)
$O3\text{---}H3\cdots O1^{iii}$	0.76 (16)	1.95 (17)	2.685 (13)	160 (18)

Symmetry codes: (i)  $-x+1/2, y+1/2, z+1/2$ ; (ii)  $x-1/2, -y+3/2, z$ ; (iii)  $x+1/2, -y+3/2, z-1$ .

**Table 4**

Hydrogen-bond geometry (Å, °) for (III)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots Br3^i$	0.95	2.99	3.863 (5)	154
$C7-H7A\cdots Br2^{ii}$	0.99	2.94	3.866 (5)	155

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

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**References**

- Akine, S., Goto, K. & Kawashima, T. (2000). *Tetrahedron Lett.* **41**, 897–901.
- Akine, S., Goto, K. & Kawashima, T. (2005). *Bull. Chem. Soc. Jpn.* **78**, 169–179.
- Crisp, G. T., Turner, P. D. & Tiekink, E. R. T. (2000). *Z. Kristallogr. - New Cryst. Struct.* **215**, 443–444.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- González-Bulnes, L., Ibáñez, I., Bedoya, L. M., Beltrán, M., Catalán, S., Alcamí, J., Fustero, S. & Gallego, J. (2013). *Angew. Chem. Int. Ed.* **52**, 13405–13409.
- Haba, K., Popkov, M., Shamis, M., Lerner, R. A., Barbas, C. F. & Shabat, D. (2005). *Angew. Chem.* **117**, 726–730.
- Hirose, K., Fujiwara, A., Matsunaga, K., Aoki, N. & Tobe, Y. (2003). *Tetrahedron: Asymmetry* **14**, 555–566.
- Hirose, K., Ishibashi, K., Shiba, Y., Doi, Y. & Tobe, Y. (2007b). *Chem. Lett.* **36**, 810–811.
- Hirose, K., Nishihara, K., Harada, N., Nakamura, Y., Masuda, D., Araki, M. & Tobe, Y. (2007a). *Org. Lett.* **9**, 2969–2972.
- Hübschle, C. B., Sheldrick, G. M. & Dittrich, B. (2011). *J. Appl. Cryst.* **44**, 1281–1284.
- Jones, P. G. & Kus, P. (2007). *Z. Naturforsch. B Chem. Sci.* **62**, 725–731.
- Jones, P. G., Kus, P. & Dix, I. (2012). *Z. Naturforsch. B Chem. Sci.* **67**, 1273–1281.
- Katzsch, F., Eissmann, D. & Weber, E. (2012). *Struct. Chem.* **23**, 245–255.
- Kohmoto, S., Kuroda, Y., Someya, Y., Kishikawa, K., Masu, H., Yamaguchi, K. & Azumaya, I. (2009). *Cryst. Growth Des.* **9**, 3457–3462.
- Leroy, J., Wakselman, C., Lacroix, P. & Kahn, O. (1988). *J. Fluorine Chem.* **40**, 23–32.
- Li, Y., Wu, D., Zhu, J. & Zhao, H. (1988). *Youji Huaxue* **8**, 158–61.
- Moran, W. J., Schreiber, E. C., Engel, E., Behn, D. C. & Yamins, J. L. (1952). *J. Am. Chem. Soc.* **74**, 127–129.
- Mukherjee, A., Tothadi, S. & Desiraju, G. R. (2014). *Acc. Chem. Res.* **47**, 2514–2524.
- Sharghi, H., Ali Nasser, M. & Niknam, K. (2001). *J. Org. Chem.* **66**, 7287–7293.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
- Shimizu, T., Maeda, T., Hida, K. & Yamato, T. (2009). *J. Chem. Res.* **8**, 515–519.
- Sookcharoenpinyo, B., Klein, E., Ferrand, Y., Walker, D. B., Brotherhood, P. R., Ke, C., Crump, M. P. & Davis, A. P. (2012). *Angew. Chem., Int. Ed.* **51**, 4586–4590.

Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

Tashiro, M., Mataka, S., Takezaki, Y., Takeshita, M., Arimura, T., Tsuge, A. & Yamato, T. (1989). *J. Org. Chem.* **54**, 451–458.

Thomas, J., Dobrzanska, L., van Hecke, K., Sonawane, M. P., Robeyns, K., van Meervelt, L., Wozniak, K., Smet, M., Maes, W. & Dehaen, W. (2012). *Org. Biomol. Chem.* **10**, 6526–6536.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Xu, L., Li, Y., Yu, Y., Liu, T., Cheng, S., Liu, H. & Li, Y. (2012). *Org. Biomol. Chem.* **10**, 4375–4380.

Yamato, T., Okabe, R., Miyamoto, S. & Miyazaki, M. (2006). *J. Chem. Res.* **9**, 593–595.

Yamato, T., Tsuchihashi, K., Nakamura, N., Hirahara, M. & Tanaka, K. (2002). *Can. J. Chem.* **80**, 510–516.

### Figure 1

Perspective views of (I)–(III) showing 50% probability displacement ellipsoids for the non-H atoms and the used numbering.

### Figure 2

Least-squares overlays of a) (II) (black lines) and (I) (blue lines), b) (I) (black lines) and (III) (blue lines) and c) (II) (black lines) and (III) (blue lines) with the following r.m.s. deviations: a) 0.0198 Å, b) 0.0220 Å and c) 0.0122 Å for an overlay of the following atoms: C1–C6. All hydrogen atoms not bonded to oxygen are omitted for clarity. Relevant atoms are labelled with a) A (II) and B (I), b) A (I) and B (III) and c) A (II) and B (III).

### Figure 3

Packing of I

### Figure 4

Packing of II Packing of III

### Figure 5

Schematic non-covalent interactions in the packing of (II) and (III).

## supporting information

## Different supramolecular interactions mediated by bromine atoms in the crystal structures of three anisole derivates

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### Computing details

For all compounds, data collection: STOE *X-AREA*; cell refinement: STOE *X-AREA*; data reduction: STOE *X-RED*; program(s) used to solve structure: *SHELXL2012* (Sheldrick, 2012); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010), *SHELXLE* (Hübschle *et al.*, 2011).

### (I)

#### Crystal data

$C_{12}H_{16}O_5$   
 $M_r = 240.25$   
 Triclinic,  $P\bar{1}$   
 $a = 7.8601$  (10) Å  
 $b = 8.2489$  (11) Å  
 $c = 10.7883$  (14) Å  
 $\alpha = 81.538$  (11)°  
 $\beta = 72.352$  (10)°  
 $\gamma = 61.930$  (9)°  
 $V = 588.15$  (14) Å<sup>3</sup>  
 $Z = 2$

$F(000) = 256$   
 $D_x = 1.357$  Mg m<sup>-3</sup>  
 Melting point: 340.15 K  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 2183 reflections  
 $\theta = 2.0$ – $27.4$ °  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 203$  K  
 Piece, colorless  
 $0.35 \times 0.32 \times 0.28$  mm

#### Data collection

STOE IPDS 2  
 diffractometer  
 Radiation source: sealed X-ray tube, 12 x 0.4 mm  
 long-fine focus  
 Plane graphite monochromator  
 Detector resolution: 6.67 pixels mm<sup>-1</sup>  
 rotation method scans  
 4748 measured reflections

2188 independent reflections  
 1705 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.052$   
 $\theta_{max} = 25.5$ °,  $\theta_{min} = 2.0$ °  
 $h = -9 \rightarrow 9$   
 $k = -9 \rightarrow 9$   
 $l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.050$   
 $wR(F^2) = 0.140$   
 $S = 1.12$   
 2188 reflections  
 164 parameters  
 0 restraints

Hydrogen site location: mixed  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.2206P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.23$  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.

*Refinement.* H atoms were positioned geometrically and allowed to ride on their parent atoms, C–H = 0.95–0.98 %A and U<sub>iso</sub>(H) = 1.2–1.5 U<sub>eq</sub> (parent atom). Hydrogen atoms bonded to O were located via electron density. Individual reflections were considered as outliers and therefore omitted.

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

	x	y	z	U <sub>iso</sub> */U <sub>eq</sub>
O1	0.6177 (2)	0.0793 (2)	0.74711 (15)	0.0381 (4)
H1O	0.725 (5)	0.106 (4)	0.714 (3)	0.063 (9)*
O2	0.1535 (2)	0.6048 (2)	0.72607 (14)	0.0332 (4)
O3	0.0670 (2)	0.8314 (2)	0.36301 (15)	0.0375 (4)
H3O	−0.053 (5)	0.906 (4)	0.345 (3)	0.068 (9)*
O4	0.7377 (2)	0.0287 (2)	0.27189 (14)	0.0337 (4)
O5	0.5225 (2)	0.2543 (2)	0.17245 (13)	0.0333 (4)
C1	0.4636 (3)	0.2861 (3)	0.39511 (18)	0.0242 (4)
C2	0.5062 (3)	0.2150 (3)	0.51367 (19)	0.0257 (4)
H2	0.6094	0.0941	0.5179	0.031*
C3	0.3986 (3)	0.3202 (3)	0.62487 (19)	0.0263 (4)
C4	0.2463 (3)	0.4967 (3)	0.61648 (19)	0.0253 (4)
C5	0.1989 (3)	0.5687 (3)	0.49936 (19)	0.0255 (4)
C6	0.3094 (3)	0.4616 (3)	0.38892 (19)	0.0256 (4)
H6	0.2797	0.5082	0.3081	0.031*
C7	0.4465 (3)	0.2513 (3)	0.7539 (2)	0.0329 (5)
H7A	0.4672	0.3432	0.7887	0.040*
H7B	0.3298	0.2412	0.8159	0.040*
C8	−0.0362 (4)	0.6174 (4)	0.7980 (3)	0.0515 (7)
H8A	−0.0781	0.6774	0.8814	0.077*
H8B	−0.0270	0.4938	0.8139	0.077*
H8C	−0.1345	0.6897	0.7486	0.077*
C9	0.0352 (3)	0.7610 (3)	0.4921 (2)	0.0324 (5)
H9A	−0.0962	0.7595	0.5193	0.039*
H9B	0.0336	0.8418	0.5523	0.039*
C10	0.5892 (3)	0.1750 (3)	0.27619 (19)	0.0270 (4)
C11	0.6403 (4)	0.1645 (4)	0.0483 (2)	0.0429 (6)
H11A	0.5509	0.1828	−0.0057	0.051*
H11B	0.7165	0.0308	0.0621	0.051*
C12	0.7810 (5)	0.2422 (5)	−0.0196 (3)	0.0652 (8)
H12A	0.8573	0.1841	−0.1049	0.098*
H12B	0.8732	0.2188	0.0324	0.098*
H12C	0.7052	0.3749	−0.0312	0.098*

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

	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>12</sup>	U <sup>13</sup>	U <sup>23</sup>
O1	0.0355 (8)	0.0385 (9)	0.0355 (9)	−0.0116 (7)	−0.0154 (7)	0.0076 (7)
O2	0.0290 (7)	0.0382 (8)	0.0299 (8)	−0.0135 (6)	−0.0024 (6)	−0.0106 (6)



O3	0.0285 (8)	0.0354 (8)	0.0375 (9)	-0.0061 (6)	-0.0116 (6)	0.0070 (7)
O4	0.0285 (7)	0.0314 (8)	0.0322 (8)	-0.0042 (6)	-0.0094 (6)	-0.0047 (6)
O5	0.0330 (8)	0.0359 (8)	0.0234 (7)	-0.0083 (6)	-0.0095 (6)	-0.0007 (6)
C1	0.0228 (9)	0.0250 (10)	0.0248 (10)	-0.0111 (8)	-0.0062 (7)	0.0002 (8)
C2	0.0222 (9)	0.0250 (10)	0.0279 (10)	-0.0086 (8)	-0.0081 (8)	0.0011 (8)
C3	0.0260 (10)	0.0297 (10)	0.0263 (10)	-0.0146 (8)	-0.0089 (8)	0.0019 (8)
C4	0.0226 (9)	0.0289 (10)	0.0259 (10)	-0.0138 (8)	-0.0032 (7)	-0.0036 (8)
C5	0.0236 (9)	0.0237 (10)	0.0300 (10)	-0.0104 (8)	-0.0086 (8)	0.0001 (8)
C6	0.0261 (9)	0.0264 (10)	0.0262 (10)	-0.0123 (8)	-0.0103 (8)	0.0030 (8)
C7	0.0321 (11)	0.0362 (12)	0.0266 (11)	-0.0115 (9)	-0.0097 (8)	0.0014 (9)
C8	0.0346 (12)	0.0760 (19)	0.0401 (14)	-0.0267 (12)	0.0064 (10)	-0.0185 (13)
C9	0.0298 (10)	0.0266 (11)	0.0337 (11)	-0.0083 (8)	-0.0071 (8)	0.0013 (8)
C10	0.0244 (9)	0.0300 (11)	0.0264 (10)	-0.0121 (9)	-0.0069 (8)	0.0004 (8)
C11	0.0477 (13)	0.0480 (14)	0.0236 (11)	-0.0126 (11)	-0.0083 (9)	-0.0084 (10)
C12	0.0626 (18)	0.081 (2)	0.0404 (15)	-0.0330 (16)	0.0070 (13)	-0.0083 (14)

*Geometric parameters (Å, °) for (I)*

O1—C7	1.415 (3)	C5—C6	1.384 (3)
O1—H10	0.92 (3)	C5—C9	1.511 (3)
O2—C4	1.379 (2)	C6—H6	0.9500
O2—C8	1.419 (3)	C7—H7A	0.9900
O3—C9	1.423 (3)	C7—H7B	0.9900
O3—H3O	0.91 (3)	C8—H8A	0.9800
O4—C10	1.216 (2)	C8—H8B	0.9800
O5—C10	1.332 (2)	C8—H8C	0.9800
O5—C11	1.447 (3)	C9—H9A	0.9900
C1—C6	1.393 (3)	C9—H9B	0.9900
C1—C2	1.395 (3)	C11—C12	1.486 (4)
C1—C10	1.479 (3)	C11—H11A	0.9900
C2—C3	1.381 (3)	C11—H11B	0.9900
C2—H2	0.9500	C12—H12A	0.9800
C3—C4	1.396 (3)	C12—H12B	0.9800
C3—C7	1.512 (3)	C12—H12C	0.9800
C4—C5	1.395 (3)		
C7—O1—H10	105 (2)	O2—C8—H8A	109.5
C4—O2—C8	115.78 (17)	O2—C8—H8B	109.5
C9—O3—H3O	110 (2)	H8A—C8—H8B	109.5
C10—O5—C11	117.40 (16)	O2—C8—H8C	109.5
C6—C1—C2	120.16 (17)	H8A—C8—H8C	109.5
C6—C1—C10	120.83 (17)	H8B—C8—H8C	109.5
C2—C1—C10	118.96 (17)	O3—C9—C5	110.39 (17)
C3—C2—C1	120.11 (17)	O3—C9—H9A	109.6
C3—C2—H2	119.9	C5—C9—H9A	109.6
C1—C2—H2	119.9	O3—C9—H9B	109.6
C2—C3—C4	118.91 (18)	C5—C9—H9B	109.6
C2—C3—C7	121.67 (18)	H9A—C9—H9B	108.1
C4—C3—C7	119.38 (17)	O4—C10—O5	123.23 (18)
O2—C4—C5	120.26 (17)	O4—C10—C1	124.56 (18)
O2—C4—C3	117.72 (18)	O5—C10—C1	112.21 (16)

C5—C4—C3	121.82 (17)	O5—C11—C12	109.7 (2)
C6—C5—C4	118.35 (17)	O5—C11—H11A	109.7
C6—C5—C9	120.67 (18)	C12—C11—H11A	109.7
C4—C5—C9	120.96 (18)	O5—C11—H11B	109.7
C5—C6—C1	120.63 (18)	C12—C11—H11B	109.7
C5—C6—H6	119.7	H11A—C11—H11B	108.2
C1—C6—H6	119.7	C11—C12—H12A	109.5
O1—C7—C3	114.12 (17)	C11—C12—H12B	109.5
O1—C7—H7A	108.7	H12A—C12—H12B	109.5
C3—C7—H7A	108.7	C11—C12—H12C	109.5
O1—C7—H7B	108.7	H12A—C12—H12C	109.5
C3—C7—H7B	108.7	H12B—C12—H12C	109.5
H7A—C7—H7B	107.6		
C6—C1—C2—C3	-1.5 (3)	C9—C5—C6—C1	178.35 (18)
C10—C1—C2—C3	176.25 (17)	C2—C1—C6—C5	1.1 (3)
C1—C2—C3—C4	0.7 (3)	C10—C1—C6—C5	-176.65 (17)
C1—C2—C3—C7	-177.19 (18)	C2—C3—C7—O1	4.6 (3)
C8—O2—C4—C5	83.8 (2)	C4—C3—C7—O1	-173.27 (18)
C8—O2—C4—C3	-101.3 (2)	C6—C5—C9—O3	-22.3 (3)
C2—C3—C4—O2	-174.23 (16)	C4—C5—C9—O3	155.81 (18)
C7—C3—C4—O2	3.7 (3)	C11—O5—C10—O4	-3.3 (3)
C2—C3—C4—C5	0.6 (3)	C11—O5—C10—C1	176.13 (17)
C7—C3—C4—C5	178.51 (18)	C6—C1—C10—O4	172.68 (19)
O2—C4—C5—C6	173.67 (17)	C2—C1—C10—O4	-5.1 (3)
C3—C4—C5—C6	-1.0 (3)	C6—C1—C10—O5	-6.7 (3)
O2—C4—C5—C9	-4.5 (3)	C2—C1—C10—O5	175.55 (17)
C3—C4—C5—C9	-179.19 (18)	C10—O5—C11—C12	-93.5 (3)
C4—C5—C6—C1	0.2 (3)		

Hydrogen-bond geometry (Å, °) for (I)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O3 <sup>i</sup>	0.92 (3)	1.87 (3)	2.788 (2)	176 (3)
O3—H3O···O4 <sup>ii</sup>	0.91 (3)	1.83 (3)	2.725 (2)	167 (3)
C9—H9B···O3 <sup>iii</sup>	0.99	2.65	3.555 (3)	153

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

(II)

Crystal data

C<sub>9</sub>H<sub>11</sub>BrO<sub>3</sub>  
*M<sub>r</sub>* = 247.09  
 Orthorhombic, *Pna*2<sub>1</sub>  
*a* = 13.1596 (7) Å  
*b* = 16.2514 (9) Å  
*c* = 4.4735 (2) Å  
*V* = 956.71 (9) Å<sup>3</sup>  
*Z* = 4  
*F*(000) = 496

*D<sub>x</sub>* = 1.715 Mg m<sup>-3</sup>  
 Melting point: 400.15 K  
 Mo *K*α radiation, λ = 0.71073 Å  
 Cell parameters from 5411 reflections  
 θ = 2.0–27.2°  
 μ = 4.27 mm<sup>-1</sup>  
*T* = 173 K  
 Piece, colorless  
 0.45 × 0.27 × 0.15 mm

*Data collection*

STOE IPDS 2	$T_{\min} = 0.283$ , $T_{\max} = 0.564$
diffractometer	4183 measured reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm	1904 independent reflections
long-fine focus	1647 reflections with $I > 2\sigma(I)$
Plane graphite monochromator	$R_{\text{int}} = 0.074$
Detector resolution: 6.67 pixels $\text{mm}^{-1}$	$\theta_{\max} = 26.5^\circ$ , $\theta_{\min} = 2.5^\circ$
rotation method scans	$h = -13 \rightarrow 16$
Absorption correction: integration	$k = -20 \rightarrow 17$
<i>X-AREA</i> (STOE)	$l = -5 \rightarrow 5$

*Refinement*

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.123P)^2 + 3.1968P]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.190$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.10$	$\Delta\rho_{\max} = 0.82 \text{ e } \text{\AA}^{-3}$
1904 reflections	$\Delta\rho_{\min} = -1.22 \text{ e } \text{\AA}^{-3}$
127 parameters	Absolute structure: Classical Flack method preferred
1 restraint	over Parsons because s.u. lower.
Hydrogen site location: mixed	Absolute structure parameter: 0.01 (5)

*Special details*

*Geometry.* All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Refinement.* H atoms were positioned geometrically and allowed to ride on their parent atoms, C–H = 0.95–0.98 %A and Uiso(H) = 1.2–1.5 Ueq (parent atom). Hydrogen atoms bonded to O were located via electron density. Individual reflections were considered as outliers and therefore omitted.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.47945 (7)	0.58610 (5)	0.1742 (5)	0.0274 (4)
O1	0.1690 (7)	0.6471 (6)	0.924 (2)	0.0309 (18)
O2	0.2989 (7)	0.8804 (5)	0.7961 (19)	0.0284 (18)
O3	0.5787 (7)	0.9079 (5)	0.424 (2)	0.0248 (17)
C1	0.4222 (8)	0.6800 (6)	0.371 (2)	0.019 (2)
C2	0.3384 (9)	0.6688 (7)	0.554 (3)	0.023 (2)
H2	0.3111	0.6155	0.5870	0.028*
C3	0.2954 (7)	0.7370 (6)	0.689 (4)	0.0215 (19)
C4	0.3399 (8)	0.8139 (6)	0.640 (3)	0.019 (2)
C5	0.4253 (8)	0.8240 (6)	0.462 (2)	0.021 (2)
C6	0.4652 (8)	0.7551 (7)	0.321 (3)	0.023 (2)
H6	0.5220	0.7602	0.1915	0.027*
C7	0.2037 (9)	0.7300 (8)	0.889 (3)	0.027 (2)
H7A	0.2206	0.7529	1.0878	0.032*
H7B	0.1479	0.7636	0.8040	0.032*
C8	0.2333 (12)	0.9311 (9)	0.627 (5)	0.049 (5)
H8A	0.2158	0.9801	0.7438	0.073*
H8B	0.1713	0.9005	0.5787	0.073*
H8C	0.2674	0.9477	0.4420	0.073*

C9	0.4713 (10)	0.9082 (6)	0.411 (4)	0.029 (3)
H9A	0.4498	0.9286	0.2120	0.035*
H9B	0.4447	0.9467	0.5632	0.035*
H1	0.13 (2)	0.608 (14)	0.79 (5)	0.10 (9)*
H3	0.591 (14)	0.888 (10)	0.27 (4)	0.04 (5)*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0282 (6)	0.0184 (5)	0.0357 (6)	0.0039 (3)	0.0029 (8)	-0.0012 (7)
O1	0.029 (4)	0.040 (5)	0.024 (4)	-0.012 (4)	0.008 (3)	0.004 (4)
O2	0.030 (4)	0.025 (4)	0.030 (4)	0.004 (4)	0.002 (3)	-0.011 (3)
O3	0.021 (4)	0.022 (4)	0.031 (5)	-0.003 (3)	0.003 (3)	-0.004 (3)
C1	0.014 (5)	0.020 (5)	0.022 (5)	-0.005 (4)	0.000 (4)	0.000 (4)
C2	0.029 (6)	0.022 (5)	0.020 (4)	-0.007 (4)	-0.002 (4)	0.005 (4)
C3	0.021 (4)	0.022 (4)	0.021 (5)	0.001 (3)	-0.001 (7)	-0.001 (5)
C4	0.020 (4)	0.023 (4)	0.015 (5)	0.009 (4)	0.001 (4)	-0.005 (4)
C5	0.020 (5)	0.016 (5)	0.026 (5)	0.001 (4)	-0.002 (4)	0.001 (4)
C6	0.019 (5)	0.023 (5)	0.026 (6)	0.006 (4)	0.005 (4)	0.003 (5)
C7	0.021 (5)	0.037 (6)	0.023 (6)	-0.004 (5)	0.006 (4)	0.004 (4)
C8	0.035 (7)	0.038 (6)	0.074 (15)	0.017 (6)	0.002 (8)	-0.005 (8)
C9	0.032 (8)	0.010 (5)	0.046 (8)	-0.002 (4)	0.001 (5)	0.000 (4)

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

Br1—C1	1.916 (11)	C3—C7	1.506 (16)
O1—C7	1.431 (15)	C4—C5	1.387 (15)
O1—H1	1.0 (2)	C5—C6	1.388 (15)
O2—C4	1.396 (13)	C5—C9	1.513 (14)
O2—C8	1.411 (19)	C6—H6	0.9500
O3—C9	1.415 (17)	C7—H7A	0.9900
O3—H3	0.76 (16)	C7—H7B	0.9900
C1—C6	1.364 (15)	C8—H8A	0.9800
C1—C2	1.387 (15)	C8—H8B	0.9800
C2—C3	1.382 (17)	C8—H8C	0.9800
C2—H2	0.9500	C9—H9A	0.9900
C3—C4	1.397 (14)	C9—H9B	0.9900
C7—O1—H1	132 (10)	C5—C6—H6	120.3
C4—O2—C8	114.8 (11)	O1—C7—C3	113.1 (9)
C9—O3—H3	101 (10)	O1—C7—H7A	109.0
C6—C1—C2	123.0 (10)	C3—C7—H7A	109.0
C6—C1—Br1	118.3 (8)	O1—C7—H7B	109.0
C2—C1—Br1	118.7 (8)	C3—C7—H7B	109.0
C3—C2—C1	118.6 (10)	H7A—C7—H7B	107.8
C3—C2—H2	120.7	O2—C8—H8A	109.5
C1—C2—H2	120.7	O2—C8—H8B	109.5
C2—C3—C4	118.5 (11)	H8A—C8—H8B	109.5
C2—C3—C7	121.7 (9)	O2—C8—H8C	109.5
C4—C3—C7	119.8 (10)	H8A—C8—H8C	109.5
C5—C4—O2	120.6 (9)	H8B—C8—H8C	109.5

C5—C4—C3	122.4 (9)	O3—C9—C5	113.0 (9)
O2—C4—C3	116.9 (10)	O3—C9—H9A	109.0
C4—C5—C6	118.1 (10)	C5—C9—H9A	109.0
C4—C5—C9	121.2 (10)	O3—C9—H9B	109.0
C6—C5—C9	120.6 (11)	C5—C9—H9B	109.0
C1—C6—C5	119.4 (10)	H9A—C9—H9B	107.8
C1—C6—H6	120.3		
C6—C1—C2—C3	1.2 (17)	C2—C1—C6—C5	0.9 (17)
Br1—C1—C2—C3	-178.1 (10)	Br1—C1—C6—C5	-179.8 (8)
C1—C2—C3—C4	-1.6 (18)	C4—C5—C6—C1	-2.5 (17)
C1—C2—C3—C7	179.4 (11)	C9—C5—C6—C1	-179.9 (11)
C8—O2—C4—C5	83.0 (14)	C2—C3—C7—O1	0.9 (17)
C8—O2—C4—C3	-101.3 (13)	C4—C3—C7—O1	-178.1 (12)
C2—C3—C4—C5	0.0 (19)	C4—C5—C9—O3	137.6 (12)
C7—C3—C4—C5	179.0 (11)	C6—C5—C9—O3	-45.0 (17)
C2—C3—C4—O2	-175.6 (11)	C2—C3—C7—O1	0.9 (17)
C7—C3—C4—O2	3.5 (17)	C4—C3—C7—O1	-178.1 (12)
O2—C4—C5—C6	177.5 (10)	C6—C5—C9—O3	-45.0 (17)
C3—C4—C5—C6	2.1 (18)	C4—C5—C9—O3	137.6 (12)
O2—C4—C5—C9	-5.1 (17)	C3—C4—O2—C8	-101.3 (13)
C3—C4—C5—C9	179.5 (12)	C5—C4—O2—C8	83.0 (14)

Hydrogen-bond geometry (Å, °) for (II)

<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>
C8—H8 <i>A</i> $\cdots$ Br1 <sup>i</sup>	0.98	3.11	3.773 (13)	126
C8—H8 <i>B</i> $\cdots$ Br1 <sup>ii</sup>	0.98	3.11	3.917 (19)	140
O1—H1 $\cdots$ O3 <sup>iii</sup>	1.0 (2)	1.8 (2)	2.687 (13)	146 (20)
O3—H3 $\cdots$ O1 <sup>iii</sup>	0.76 (16)	1.95 (17)	2.685 (13)	160 (18)

Symmetry codes: (i)  $-x+1/2, y+1/2, z+1/2$ ; (ii)  $x-1/2, -y+3/2, z$ ; (iii)  $x+1/2, -y+3/2, z-1$ .

**(III) 4-Bromo-2,6-bis(bromomethyl)anisole**

Crystal data

C<sub>9</sub>H<sub>9</sub>Br<sub>3</sub>O  
*M<sub>r</sub>* = 372.89  
 Monoclinic, *C*2/*c*  
*a* = 33.315 (4) Å  
*b* = 4.3913 (3) Å  
*c* = 15.9655 (17) Å  
 $\beta$  = 110.142 (8)°  
*V* = 2192.9 (4) Å<sup>3</sup>  
*Z* = 8  
*F*(000) = 1408

*D<sub>x</sub>* = 2.259 Mg m<sup>-3</sup>  
 Melting point: 358.15 K  
 Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 6186 reflections  
 $\theta$  = 2.5–27.1°  
 $\mu$  = 11.00 mm<sup>-1</sup>  
*T* = 153 K  
 Piece, colorless  
 0.50 × 0.11 × 0.09 mm

Data collection

STOE IPDS 2T  
 diffractometer  
 Radiation source: sealed X-ray tube, 12 x 0.4 mm  
 long-fine focus  
 Plane graphite monochromator

Detector resolution: 6.67 pixels mm<sup>-1</sup>  
 rotation method scans  
 Absorption correction: integration  
*X-AREA* (STOE)  
*T<sub>min</sub>* = 0.008, *T<sub>max</sub>* = 0.076

5754 measured reflections  
 2197 independent reflections  
 1834 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.087$

$\theta_{\text{max}} = 26.2^\circ$ ,  $\theta_{\text{min}} = 2.6^\circ$   
 $h = -33 \rightarrow 40$   
 $k = -5 \rightarrow 4$   
 $l = -19 \rightarrow 19$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.088$   
 $S = 1.10$   
 2197 reflections  
 119 parameters  
 0 restraints

Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 2.9694P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.60 \text{ e } \text{\AA}^{-3}$

*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.

*Refinement.* H atoms were positioned geometrically and allowed to ride on their parent atoms, C–H = 0.95–0.98 %A and  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}(\text{parent atom})$ .

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.47987 (2)	0.49550 (12)	0.35631 (3)	0.03202 (15)
Br2	0.29357 (2)	0.25013 (12)	0.15688 (3)	0.03636 (16)
Br3	0.42282 (2)	0.06192 (11)	0.65117 (3)	0.03003 (14)
O1	0.32003 (9)	0.0508 (7)	0.4161 (2)	0.0277 (7)
C1	0.42990 (12)	0.3516 (10)	0.3754 (3)	0.0221 (8)
C2	0.39000 (13)	0.4533 (10)	0.3190 (3)	0.0244 (9)
H2	0.3880	0.5895	0.2715	0.029*
C3	0.35315 (12)	0.3527 (10)	0.3331 (3)	0.0205 (8)
C4	0.35679 (12)	0.1583 (9)	0.4038 (3)	0.0195 (8)
C5	0.39681 (13)	0.0557 (9)	0.4607 (3)	0.0208 (8)
C6	0.43327 (12)	0.1556 (10)	0.4443 (3)	0.0199 (8)
H6	0.4607	0.0868	0.4813	0.024*
C7	0.31004 (14)	0.4628 (11)	0.2722 (3)	0.0295 (10)
H7A	0.3112	0.6848	0.2625	0.035*
H7B	0.2883	0.4250	0.3004	0.035*
C8	0.30694 (14)	0.2317 (11)	0.4772 (3)	0.0296 (10)
H8A	0.2805	0.1481	0.4817	0.044*
H8B	0.3020	0.4419	0.4555	0.044*
H8C	0.3294	0.2284	0.5361	0.044*
C9	0.40141 (14)	−0.1557 (11)	0.5363 (3)	0.0273 (9)
H9A	0.4215	−0.3212	0.5359	0.033*
H9B	0.3733	−0.2488	0.5291	0.033*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0210 (2)	0.0455 (3)	0.0322 (3)	−0.00607 (19)	0.01262 (19)	−0.0037 (2)

Br2	0.0317 (2)	0.0407 (3)	0.0278 (3)	0.0014 (2)	-0.00112 (19)	-0.0017 (2)
Br3	0.0344 (2)	0.0322 (2)	0.0236 (3)	0.00105 (19)	0.01019 (19)	0.00098 (19)
O1	0.0219 (14)	0.0262 (15)	0.0382 (18)	-0.0063 (13)	0.0143 (14)	-0.0061 (15)
C1	0.0188 (18)	0.026 (2)	0.022 (2)	-0.0070 (17)	0.0084 (16)	-0.0090 (19)
C2	0.023 (2)	0.026 (2)	0.024 (2)	-0.0003 (17)	0.0084 (17)	-0.0005 (18)
C3	0.0182 (17)	0.0199 (19)	0.022 (2)	-0.0008 (17)	0.0051 (15)	-0.0056 (18)
C4	0.0204 (18)	0.0167 (17)	0.024 (2)	-0.0038 (16)	0.0106 (16)	-0.0088 (18)
C5	0.025 (2)	0.0151 (18)	0.024 (2)	-0.0018 (16)	0.0107 (17)	-0.0072 (17)
C6	0.0143 (16)	0.025 (2)	0.0174 (18)	0.0029 (17)	0.0021 (14)	-0.0061 (18)
C7	0.023 (2)	0.030 (2)	0.030 (2)	0.0078 (19)	0.0033 (19)	0.000 (2)
C8	0.023 (2)	0.035 (3)	0.035 (2)	0.0003 (19)	0.0148 (19)	0.000 (2)
C9	0.031 (2)	0.021 (2)	0.028 (2)	-0.0012 (19)	0.0081 (18)	-0.001 (2)

*Geometric parameters (Å, °) for (III)*

Br1—C1	1.901 (4)	C4—C5	1.404 (6)
Br2—C7	1.966 (5)	C5—C6	1.399 (6)
Br3—C9	1.971 (4)	C5—C9	1.488 (6)
O1—C4	1.387 (5)	C6—H6	0.9500
O1—C8	1.437 (5)	C7—H7A	0.9900
C1—C6	1.370 (6)	C7—H7B	0.9900
C1—C2	1.398 (6)	C8—H8A	0.9800
C2—C3	1.394 (6)	C8—H8B	0.9800
C2—H2	0.9500	C8—H8C	0.9800
C3—C4	1.387 (6)	C9—H9A	0.9900
C3—C7	1.510 (6)	C9—H9B	0.9900
C4—O1—C8	113.4 (3)	C3—C7—Br2	110.4 (3)
C6—C1—C2	121.0 (4)	C3—C7—H7A	109.6
C6—C1—Br1	120.2 (3)	Br2—C7—H7A	109.6
C2—C1—Br1	118.8 (3)	C3—C7—H7B	109.6
C3—C2—C1	119.3 (4)	Br2—C7—H7B	109.6
C3—C2—H2	120.3	H7A—C7—H7B	108.1
C1—C2—H2	120.3	O1—C8—H8A	109.5
C4—C3—C2	119.4 (4)	O1—C8—H8B	109.5
C4—C3—C7	121.2 (4)	H8A—C8—H8B	109.5
C2—C3—C7	119.3 (4)	O1—C8—H8C	109.5
C3—C4—O1	119.3 (3)	H8A—C8—H8C	109.5
C3—C4—C5	121.4 (4)	H8B—C8—H8C	109.5
O1—C4—C5	119.2 (4)	C5—C9—Br3	110.8 (3)
C6—C5—C4	118.1 (4)	C5—C9—H9A	109.5
C6—C5—C9	119.6 (4)	Br3—C9—H9A	109.5
C4—C5—C9	122.3 (4)	C5—C9—H9B	109.5
C1—C6—C5	120.7 (4)	Br3—C9—H9B	109.5
C1—C6—H6	119.6	H9A—C9—H9B	108.1
C5—C6—H6	119.6		
C6—C1—C2—C3	-0.1 (7)	O1—C4—C5—C6	176.9 (3)
Br1—C1—C2—C3	-179.1 (3)	C3—C4—C5—C9	-179.3 (4)
C1—C2—C3—C4	1.2 (6)	O1—C4—C5—C9	-2.4 (6)
C1—C2—C3—C7	180.0 (4)	C2—C1—C6—C5	-1.0 (6)

C2—C3—C4—O1	-178.0 (4)	Br1—C1—C6—C5	178.0 (3)
C7—C3—C4—O1	3.3 (6)	C4—C5—C6—C1	1.0 (6)
C2—C3—C4—C5	-1.2 (6)	C9—C5—C6—C1	-179.6 (4)
C7—C3—C4—C5	-179.9 (4)	C4—C3—C7—Br2	-105.0 (4)
C8—O1—C4—C3	-94.0 (4)	C2—C3—C7—Br2	76.3 (5)
C8—O1—C4—C5	89.1 (4)	C6—C5—C9—Br3	74.9 (4)
C3—C4—C5—C6	0.1 (6)	C4—C5—C9—Br3	-105.8 (4)

*Hydrogen-bond geometry (Å, °) for (III)*

<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>
C2—H2 $\cdots$ Br3 <sup>i</sup>	0.95	2.99	3.863 (5)	154
C7—H7A $\cdots$ Br2 <sup>ii</sup>	0.99	2.94	3.866 (5)	155

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