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1-[3,5-Bis(bromomethyl)-2,4,6-trimethoxybenzyl]-3,5-bis(bromomethyl)-2,4,6-trimethoxybenzene

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.073
Data-to-parameter ratio = 20.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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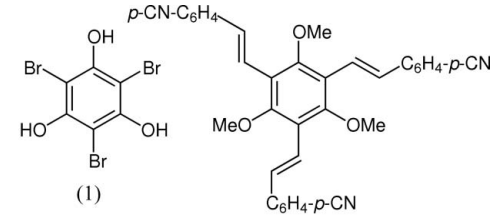
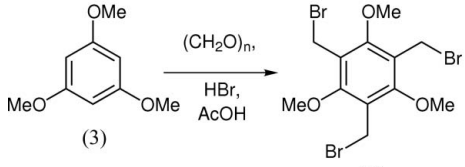
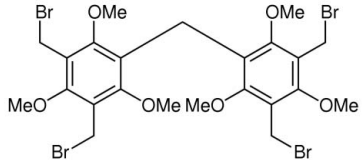
The crystal structure of the title compound, $C_{23}H_{28}Br_4O_6$, confirms that it consists of two hexasubstituted aromatic units linked by a central methylene group. The molecule lies on a crystallographic twofold axis that passes through the methylene bridging atom. Examination of the extended structure reveals the presence of ribbons of molecules held together by C—H···O and C—H···Br interactions.

Comment

The synthesis of hexasubstituted aromatic compounds has always been a particular challenge (Saito & Yamamoto, 2000; Gevorgyan & Yamamoto, 1999). Apart from being found as structural components of natural products, such as compound (1) (Blackman & Matthews, 1982), these types of compounds have also been used as candidates for nonlinear optical materials, for example compound (2) (Cho *et al.*, 2002).







Our research group has utilized polysubstituted aromatic rings in our synthetic endeavours (van Otterlo *et al.*, 2004; Michael *et al.*, 2001; de Koning *et al.*, 2000) and we wished to synthesize a number of hexasubstituted aromatic systems to use as potential molecular scaffolds. Towards this end, we repeated experimental work reported by Cho *et al.* (2002) and were able to isolate successfully 22% of the hexasubstituted product (4), by treating 1,3,5-trimethoxybenzene (3) with paraformaldehyde and hydrobromic acid (see scheme).

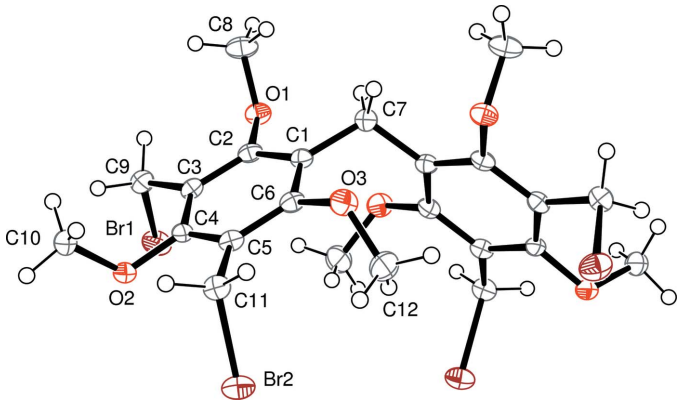


Figure 1
View of the molecule of (5), showing the atom-numbering scheme for the asymmetric unit. Unlabelled atoms are related to labelled atoms by ($-x$, y, $\frac{1}{2}-z$) with atom C7 sitting on the twofold axis. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown with an arbitrary radius.

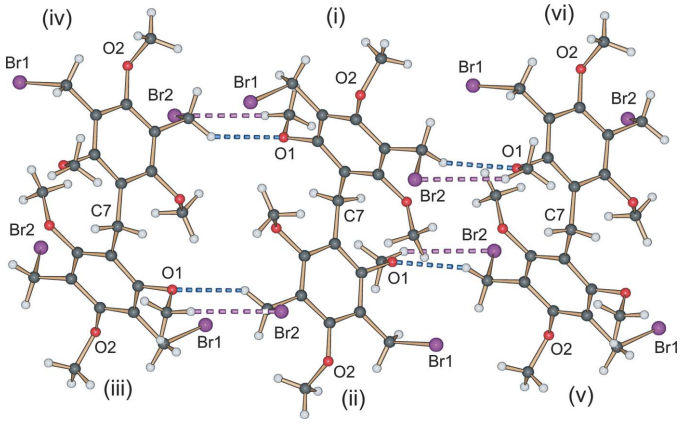


Figure 2
C—H···O and C—H···Br (see Table 1 for details) hydrogen bonding (dashed lines) in the title compound, forming a chain of molecules (or ribbon) running down the *c* axis. Each molecule is related to the next by a centre of inversion. Symmetry codes for the various molecules (and independent unit making up each molecule) are as follows: (i) x, y, z; (ii) $-x, y, -z+\frac{1}{2}$; (iii) $-x, -y, -z$; (iv) $x, -y, z-\frac{1}{2}$; (v) $-x, -y, -z+1$; (vi) $x, -y, z+\frac{1}{2}$.

However, another crystalline product was obtained in a yield of 6% after chromatography and recrystallization. NMR spectroscopic evidence suggested that the compound was a dimer and the structure of the title compound, (5), was confirmed by a single-crystal X-ray diffraction study. This compound is probably formed when the protonated hydroxymethyl intermediate is attacked in a nucleophilic manner by another aromatic molecule.

Compound (5) crystallizes in the space group *Pbcn* with one half-molecule in the asymmetric unit. The other half is related by a crystallographic twofold axis through the methylene (C2) bridging atom (Fig. 1). As a consequence, the molecule possesses C_2 point group symmetry. Although the molecule has two aryl rings, there are no C—H···π or π–π interactions. There are, however, intermolecular C—H···O and C—H···Br (Table 1) hydrogen bonds acting along the *c* axis, the interaction being between a benzyl bromide group and a methoxy group, to produce a ribbon of molecules running down the *c* axis (Fig. 2). Each molecule within the ribbon is related to the next by an inversion centre. These ribbons are further hydrogen-bonded to neighbouring ribbons related by *b* glide planes through C—H···O interactions and to ribbons related by translation along the *b* axis through C—H···Br interactions (Table 1 and Fig. 3).

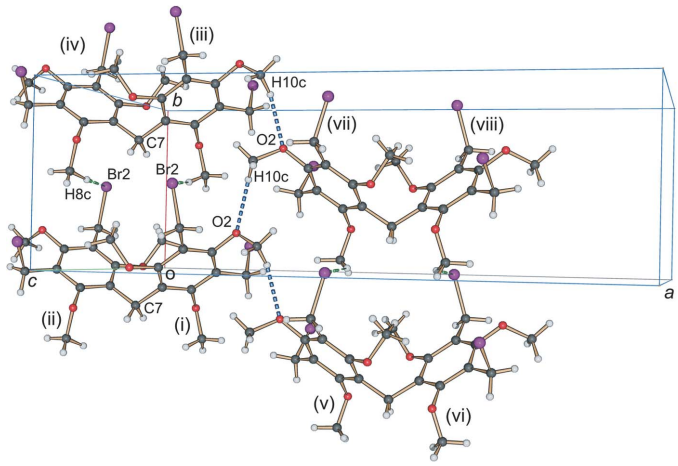


Figure 3
Each molecule in the ribbon described in Fig. 2 is C—H···O hydrogen-bonded to a neighbouring ribbon related by a *b* glide. In addition, molecules in ribbons related by translation along the *b* axis are involved in a C—H···Br interaction (see Table 1 for details). Symmetry codes for the various molecules (and independent unit making up each molecule) are as follows: (i) x, y, z; (ii) $-x, y, -z+\frac{1}{2}$; (iii) $x, y+1, z$; (iv) $-x, y+1, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (vi) $x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (viii) $x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Experimental

A thick-walled Carius tube (100 ml) was charged with 1,3,5-trimethoxybenzene (3.421 g, 20.34 mmol), dry glacial acetic acid (10 ml) and paraformaldehyde (2.016 g, 67.13 mmol). The mixture was shaken to dissolve the solids and then cooled to 273 K. HBr (30%) in glacial acetic acid (15 ml) was added and the contents of the tube were frozen in liquid N_2 and sealed. The tube was warmed to room temperature and then heated in an oil bath at 333 K for 3 h. After cooling to room temperature, the tube contents were poured into water (100 ml) and extracted once with ethyl acetate (200 ml). The organic phase was dried (magnesium sulfate), filtered and evaporated under reduced pressure to give a red residue. Silica-gel column chromatography with ethyl acetate:hexane (1:19) first afforded known compound (4) as a white powder (1.919 g, 4.29 mmol, 22%), followed by product (5) as a beige-coloured powder. Recrystallization of the latter powder from hexane:acetone (4:1) afforded pale-brown block crystals (0.823 g, 1.14 mmol, 6%, m.p. 350–352 K). Spectroscopic data: ^{1}H NMR (300 MHz, $CDCl_3$, δ, p.p.m.): 3.78 (12H, *s*, 4 × OCH_3), 4.08 (2H, *s*, CH_2), 4.11 (6H, *s*, 2 × OCH_3), 4.60 (8H, *s*, 4 × CH_2Br); ^{13}C NMR (75 MHz, $CDCl_3$, δ, p.p.m.): 20.0 (CH_2), 23.3 (4 × CH_2Br), 61.7 (4 × OCH_3), 62.5 (2 × OCH_3), 122.3 (4 × ArC), 124.5 (2 × ArC), 157.5 (2 × ArC—O), 159.7 (4 × ArC—O); ν_{max} (thin film, NaCl plate, cm^{-1}): 1578, 1457, 1414, 1324, 1265, 1216, 1195, 1152, 1102, 1002; *m/z*: 720.1 (M^+, 5%), 644.2 (9), 643.2 (36), 642.1 (25), 641.2 (100), 640.2 (26), 639.1 (99), 638.2 (9), 545.1 (16), 419.2 (6), 369.1 (9), 367.1 (18), 365.1 (9), 280.1 (9), 207.2 (15), 193.2 (11), 177.1 (10), 163.1 (9) 147.1 (9).

Crystal data

$C_{23}H_{28}Br_4O_6$
M_r = 720.09
Orthorhombic, *Pbcn*
a = 22.737 (7) Å
b = 7.280 (2) Å
c = 15.280 (4) Å
V = 2529.2 (13) Å^3
Z = 4
D_x = 1.891 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 863 reflections
θ = 2.7–28.1°
μ = 6.40 mm^{-1}
T = 173 (2) K
Block, pale brown
0.34 × 0.25 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: integration (*XPREP*; Bruker, 1999)
T_{min} = 0.220, T_{max} = 0.347
13104 measured reflections
3056 independent reflections
2374 reflections with $I > 2\sigma(I)$
R_{int} = 0.052
θ_{max} = 28.0°
$h = -30 \rightarrow 29$
$k = -9 \rightarrow 7$
$l = -19 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.073
S = 0.98
3056 reflections
153 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10*C*···O2^{i}	0.98	2.37	3.281 (3)	155
C11—H11*B*···O1^{ii}	0.99	2.49	3.287 (3)	138
C8—H8*B*···Br2^{iii}	0.98	3.04	3.874 (3)	143
C8—H8*C*···Br2^{iv}	0.98	3.06	3.860 (3)	140

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

H atoms were positioned geometrically and allowed to ride on their respective parent atoms, with C—H bond lengths of 0.99 (CH_2) or 0.98 Å (CH_3), and with U_{iso}(H) = 1.2 (CH_2) or 1.5 (CH_3) times U_{eq}(C).

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003) and *SCHAKAL97* (Keller, 1997); software used to prepare material for publication: *SHELXTL*.

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