4-Bromophenyl 2,3,4,5,6-pentabromophenyl ether

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean σ(C–C) = 0.015 Å

R factor = 0.065

wR factor = 0.092

Data-to-parameter ratio = 16.1

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

The title compound, $C_{12}H_4Br_6O$, belongs to a group of flame retardants known as polybrominated diphenyl ethers (PBDE). Intermolecular Br···Br contacts in the bc plane give a sheet-like character to the structure of the title compound.

Comment

Polybrominated diphenyl ethers (PBDE) are one of the most important groups of flame retardants. Most of the commercially available mixtures consist of highly brominated congeners, such as decabromodiphenyl ether (Eriksson *et al.*, 1999; Mrse *et al.*, 2000). The lower brominated PBDEs are, to a large extent, formed as decomposition products in the environment. Different decomposition pathways are presently being examined as part of a long-term project aimed at modelling the reactivity of different PBDEs often found deposited on soot particles *etc.* in the environment. Theoretical calculations require accurate geometries of the molecular species involved; thus the use of geometric data derived from crystallographic measurements is invaluable.


(I)
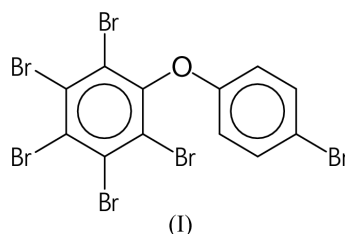
The monobrominated ring (C1–C6) of the title compound, (I), is planar, with an r.m.s. deviation of 0.017 Å; the O atom deviates by 0.055 (18) Å and Br1 by 0.042 (17) Å from the ring plane. The pentabrominated ring (C7–C12) is planar, with an r.m.s. deviation of 0.015 Å; the O deviates by 0.127 (16) Å, Br3 by 0.089 (16) Å, and Br4 by 0.070 (15) Å from the ring plane. The rest of the Br atoms, *viz.* Br2, Br5 and Br6, are coplanar with this ring. The dihedral angle between the two ring planes is 89.6 (3)°.

A view, along the b axis, of the arrangement of the molecules of the title compound, (I), is shown in Fig. 2, in which the three shortest intermolecular Br···Br contacts are marked. These contacts are: Br1···Br2[i] = 3.612 (2) Å, Br3···Br3[ii] = 3.604 (3) Å and Br4···Br5[iii] = 3.707 (2) Å [symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $-x, 2 - y, 2 - z$]. Inclusion of all Br···Br contacts less than or equal to 3.9 Å in Fig. 3 illustrates the extensive intermolecular Br···Br contacts present in the bc plane. As in the structure of 2,3,4,5,6-pentabromophenyl phenyl ether (Eriksson & Hu, 2002), in which there are no Br substituents on one of the rings, the title compound forms sheets defined by
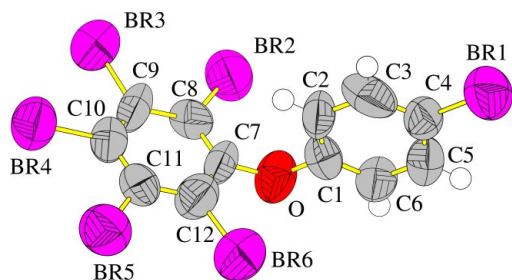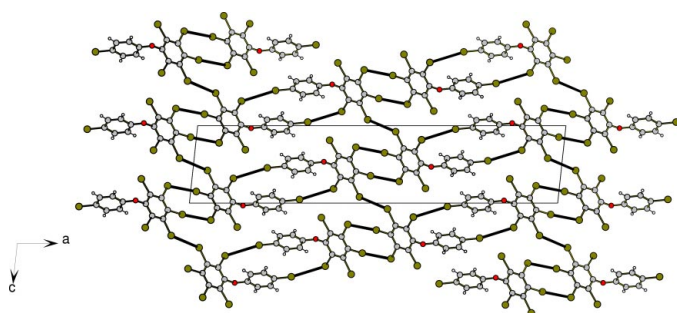
Figure 1
One molecule of the title compound with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

Figure 2
View of the packing, along the *b* direction, with the three shortest Br···Br contacts indicated by thick dashed bonds.

Figure 3
Stereoview of the packing, along the *b* direction, with all Br···Br contacts less than or equal to 3.9 Å indicated by thick dashed lines.

the Br···Br contacts, at $x \simeq 0.0$ and 0.5, with small cavities where the monobrominated ring of molecules from neighbouring layers may fit.
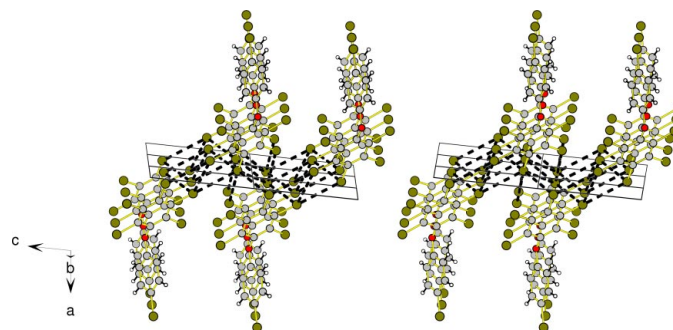
Experimental

The synthesis of the title PBDE was carried out by coupling of the decabromodiphenyl iodonium salt with a 4-bromophenylate (Beringer *et al.*, 1959; Ziegler & Marr, 1962; Hu, 1996, 1999). The product was recrystallized from methanol.

Crystal data

$C_{12}H_4Br_6O$	$D_x = 2.804$ Mg m^{-3}
$M_r = 643.61$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 46
$a = 37.325$ (6) Å	reflections
$b = 5.2140$ (6) Å	$\theta = 15.4–27.1°$
$c = 7.8782$ (10) Å	$\mu = 18.94$ mm^{-1}
$\beta = 96.073$ (13)°	$T = 293$ (2) K
$V = 1524.6$ (4) Å^3	Slab, colourless
$Z = 4$	$0.11 \times 0.06 \times 0.04$ mm

Data collection

Stoe AED-2 diffractometer	$R_{int} = 0.096$
ω–2θ scans	$\theta_{max} = 68.0°$
Absorption correction: numerical	$h = -44 \rightarrow 44$
(*XRED*; Stoe & Cie, 1997)	$k = -6 \rightarrow 6$
$T_{min} = 0.13$, $T_{max} = 0.48$	$l = -9 \rightarrow 9$
8595 measured reflections	4 standard reflections
2788 independent reflections	frequency: 90 min
1393 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
$wR(F^2) = 0.092$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} < 0.001$
2788 reflections	$\Delta\rho_{max} = 0.96$ e Å^{-3}
173 parameters	$\Delta\rho_{min} = -0.99$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.844 (11)	Br5—C11	1.883 (13)
Br2—C8	1.878 (10)	Br6—C12	1.845 (11)
Br3—C9	1.890 (11)	O—C7	1.391 (12)
Br4—C10	1.865 (10)	O—C1	1.414 (12)
C7—O—C1	116.7 (8)	C12—C7—C8	123.0 (10)
C2—C1—C6	121.7 (10)	C12—C7—O	119.4 (9)
C2—C1—O	122.4 (9)	C8—C7—O	117.1 (9)
C6—C1—O	115.7 (9)		
C8—C7—O—C1	104.2 (12)	C2—C1—O—C7	−15.7 (16)
C12—C7—O—C1	−83.3 (14)	C6—C1—O—C7	170.1 (10)

The rather high R_{int} value of 0.096 results from the large amount of weak insignificant reflections. With reflections fulfilling $I \geq 2\sigma(I)$, R_{int} is reduced to 0.0473.

Data collection: *DIF*4 (Stoe & Cie, 1988); cell refinement: *DIF*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

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