organic papers

4-Bromophenyl 2,4-dibromophenyl ether

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.006 Å
R factor = 0.035
wR factor = 0.044
Data-to-parameter ratio = 17.3

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

The title compound, $C_{12}H_7Br_3O$, belongs to a group of flame retardants known as polybrominated diphenyl ethers (PBDE). Salient features of the packing of the title compound are infinite intermolecular Br···Br contact chains along the b direction.

Comment

An important group of flame retardants are the polybrominated diphenyl ethers (PBDE). There are a total of 209 different PBDE's. The modelling of the reactivity of different PBDE's is a task that requires accurate geometries of the molecular species. Geometric data from crystallographic measurements on brominated diphenyl ethers with hetero substituents other than bromine are rather limited (Örn *et al.*, 1996; Eriksson *et al.*, 1999; Mrse *et al.*, 2000; Eriksson & Hu, 2001, 2002a,b). Furthermore, a partial structure of bis(4-bromophenyl) ether (Toussaint, 1946) has been published. In a search of the Cambridge Structural Database (Allen & Kennard, 1993) for hetero substituents other than bromine, a larger set of structures for use as model compounds were found, but still only in the order of 10–15 different structures.
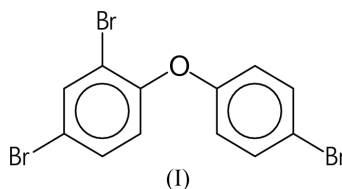

The monobrominated ring (C1–C6) of the title compound, (I), is planar within 0.005 (3) Å, with the O atom deviating by 0.018 (6) Å from the ring plane and atom Br1 residing within 0.005 Å of the ring plane. The dibrominated ring (C7–C12) of (I) is planar within 0.010 (3) Å, with the O atom deviating by 0.034 (5) Å, atom Br2 deviating by 0.044 (4) Å and atom Br3 deviating by 0.040 (5) Å from the ring plane. The molecular structure is shown in Fig. 1. The angle between the ring planes is 89.8 (1)°.

The fact that Br1 does not deviate from the plane of the ring to which it is connected is supported by the observation that Br1 is the bromine with the longest Br···Br contacts, and thus should be little affected by Br···Br intermolecular forces. No bromine on neighbouring molecules is closer than approximately 4.25 Å to Br1. The only close contacts for Br1 are to neighbouring aromatic ring systems of symmetry-related equivalents of the (C7–C12) ring; Br1···C10(1−x, −½+y, ½−z) = 3.641 (4) Å and Br1···C11(1−x, −½+y, ½−z) = 3.633 (4) Å. Furthermore, there are close contacts, and thus
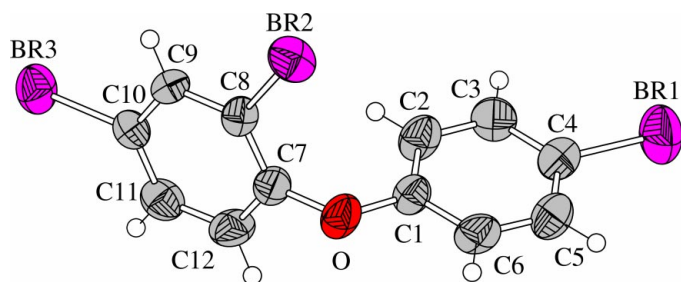
Figure 1
One molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as small circles of arbitrary radii.
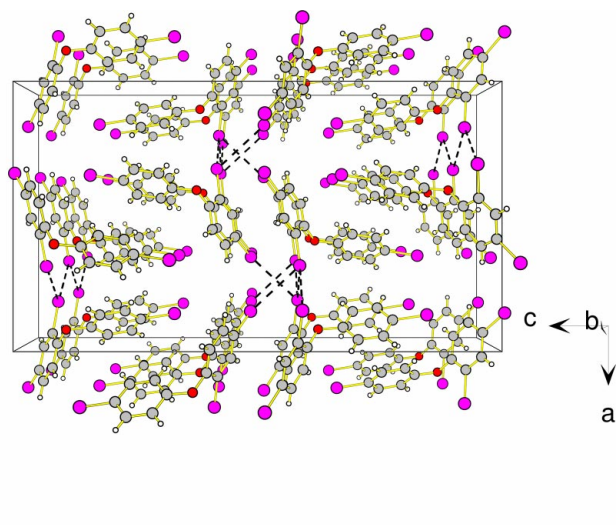
probably, interactions between symmetry-related equivalents of one of the rings (C1–C6) arranged in a herring-bone pattern (Desiraju, 1989). Atoms Br2 and Br3 are part of a network of short intermolecular Br···Br contacts along the b direction (Fig. 2). The two shortest unique intermolecular Br···Br contact distances are: Br2···Br2$(\frac{3}{2}-x, \frac{1}{2}+y, z)$ = 3.717 (1) Å and Br2···Br3$(\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$ = 3.763 (1) Å.

Experimental

The synthesis of (I) was carried out by coupling of the diphenyliodonium salt with a bromophenylate (Beringer *et al.*, 1959; Ziegler & Marr, 1962; Hu, 1996, 1999). The title compound was recrystallized from methanol.

Crystal data

$C_{12}H_7Br_3O$	Mo $K\alpha$ radiation
$M_r = 406.91$	Cell parameters from 1235
Orthorhombic, $Pbca$	reflections
$a = 15.480$ (3) Å	$\theta = 1.7$–$26.0°$
$b = 5.9692$ (9) Å	$\mu = 9.34$ mm^{-1}
$c = 27.962$ (5) Å	$T = 293$ (2) K
$V = 2583.7$ (8) Å^3	Irregular, colourless
$Z = 8$	$0.16 \times 0.07 \times 0.06$ mm
$D_x = 2.092$ Mg m^{-3}	

Data collection

Stoe IPDS area-detector diffractometer	2513 independent reflections
	1335 reflections with $I > 2\sigma(I)$
φ scans	$R_{int} = 0.103$
Absorption correction: numerical	$\theta_{max} = 26.0°$
(*XRED*; Stoe & Cie, 1997)	$h = -19 \rightarrow 19$
$T_{min} = 0.231$, $T_{max} = 0.574$	$k = -7 \rightarrow 7$
36351 measured reflections	$l = -34 \rightarrow 34$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.035$	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
$wR(F^2) = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2513 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.901 (4)	O—C7	1.380 (5)
Br2—C8	1.889 (4)	O—C1	1.385 (4)
Br3—C10	1.889 (4)		
C7—O—C1	117.9 (3)	C12—C7—O	119.3 (4)
C2—C1—C6	119.8 (4)	C12—C7—C8	119.0 (4)
C2—C1—O	124.9 (4)	O—C7—C8	121.5 (4)
C6—C1—O	115.3 (4)		
C7—O—C1—C2	8.5 (6)	C1—O—C7—C12	92.7 (5)
C7—O—C1—C6	−172.7 (4)	C1—O—C7—C8	−91.2 (5)

Two data sets were recorded with the Stoe IPDS system, with different settings of the crystal. The data sets were brought to a common scale by use of batch scale factors (BASF) determined with *SHELXL*97, and were merged. The high internal R value is a consequence of the large number of weak reflections. The internal R value calculated from reflections with $I \geq 2\sigma(I)$ is 0.041.

Data collection: *EXPOSE* in *IPDS* (Stoe, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS* and *X-RED* (Stoe, 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).

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Figure 2
Perspective view, along the b axis, of the packing of the molecules in the title compound. Note the close Br···Br contacts depicted as black dashed bonds.

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