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# 2,4-Dibromophenyl 2,6-dibromophenyl ether

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**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean σ(C–C) = 0.007 Å
*R* factor = 0.029
*wR* factor = 0.056
Data-to-parameter ratio = 17.4

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



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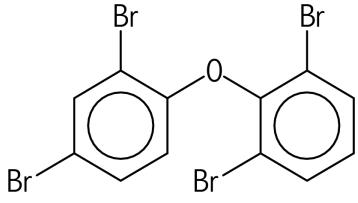
The title compound, $C_{12}H_6Br_4O$, is the fourth well characterized of a total of potentially 209 different brominated diphenyl ethers. Salient intermolecular interactions are between ether O and aromatic C atoms, and between a bromine substituent and the aromatic ring system.

## Comment

The title compound, (I), belongs to a class of compounds known as brominated diphenyl ethers (DE's) which are used as flame retardants. Commercially available mixtures mainly consist of highly brominated congeners, such as decabromodiphenyl ether (Eriksson *et al.*, 1999). The occurrence in the environment of less brominated congeners is dependent on both primary sources and decomposition from higher brominated DE's (Eriksson *et al.*, 2001). The crystal structures and packing patterns of these compounds are of fundamental importance in order to model the reaction mechanism in solid-state reaction, *e.g.* flame retardants adsorbed on soot particles.




(I)

Both aromatic rings of the title compound are planar within less than 0.01 Å. The deviation of the substituents from the ring plane of the first ring (C1–C6) are 0.050 (7) Å for O and 0.031 (8) Å for Br4, while Br3 is within the ring plane. The substituents of the second ring (C7–C12) all deviate significantly from the ring plane: O 0.016 (6) Å, Br1 0.110 (7) Å and Br2 0.053 (7) Å. The angle between the two ring planes is 89.1 (2)°.

Designating the aromatic rings of the molecule as ring1 = C1–C6 and ring2 = C7–C12, the structure can be described as a packing of molecules with close contacts between symmetry-equivalent ring1 systems (C1–C6)···(C1–C6)$^{i}$ *etc*. [symmetry code: (i) $-0.5-x$, $0.5+y$, $-0.5-z$]. Each of the neighbouring symmetry-equivalent ring1′s of the molecules are inclined at 37.9 (1)° to each other (Fig. 2). The two shortest intermolecular C···O contacts are O—C3$^{ii}$ and O···C4$^{ii}$, both of these distances being 3.33 (1) Å [symmetry code: (ii) $-x-0.5$, $y-0.5$, $-z+0.5$]. These intermolecular C···O distances are quite short compared to previously known structures containing the diphenyl ether moiety from the Cambridge

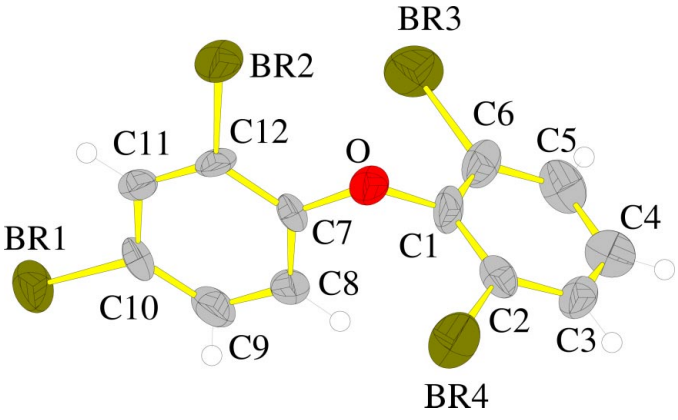



**Figure 1**
One molecule of the title compound, with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

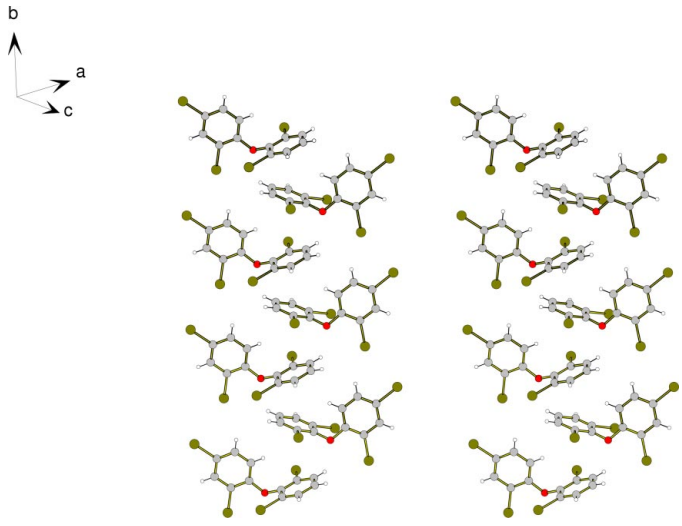



**Figure 2**
Stereoview of the molecular packing, with the close contacts between one of the two different aromatic rings (C1–C6) and symmetry equivalents.

Structural Database (CSD; Allen & Kennard, 1993). Another short intermolecular contact is due to ring2 packing with one parallel symmetry-equivalent copy of itself on one side together with a short Br···C interaction on the opposite side of ring2 [Br4···C11$^{iii}$ = 3.548 (5) Å; symmetry code: (iii) $x-1$, $y$, $z$]; this is the shortest intermolecular Br···C contact distance in the present structure.

Thus, the structure can be described as a packing of long chains held together by intermolecular interactions between ring1 of different molecules; ring2 then links different chains to each other. Intermolecular Br···Br contacts further stabilize the structure, with the shortest intermolecular Br···Br distance being Br3···Br4$^{iv}$ = 3.798 (1) Å [symmetry code: (iv) $x+1$, $y$, $z$]. This is not a specially short intermolecular distance compared to other bromine substituted aromatic compounds found in the CSD and is significantly longer than the short Br···Br contact in phenyl 2,4,6-tribromophenyl ether (Eriksson & Hu, 2001). Thus, one can speculate that the Br···Br contacts only contribute a small part of the lattice energy.

## Experimental

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

*Crystal data*

$C_{12}H_6Br_4O$
$M_r$ = 485.81
Monoclinic, $P2_1/n$
$a$ = 8.0274 (12) Å
$b$ = 8.389 (2) Å
$c$ = 20.562 (3) Å
$\beta$ = 90.606 (19)°
$V$ = 1384.5 (5) Å$^3$
$Z$ = 4
$D_x$ = 2.331 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1520 reflections
$\theta$ = 2.0–26.0°
$\mu$ = 11.61 mm$^{-1}$
$T$ = 293 (2) K
Prism, colourless
0.19 × 0.13 × 0.10 mm

*Data collection*

Stoe IPDS diffractometer
$\varphi$ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1998)
$T_{min}$ = 0.113, $T_{max}$ = 0.307
21426 measured reflections
2676 independent reflections
1625 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.049
$\theta_{max}$ = 26.0°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -25 \rightarrow 25$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.056
$S$ = 0.98
2676 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.73 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.48 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Br1—C10 | 1.895 (5) | Br4—C2 | 1.879 (5) |
| Br2—C12 | 1.902 (5) | O—C7 | 1.395 (5) |
| Br3—C6 | 1.885 (5) | O—C1 | 1.397 (5) |
| | | | |
| C7—O—C1 | 115.7 (4) | C8—C7—O | 123.3 (4) |
| C6—C1—O | 122.2 (4) | C12—C7—O | 116.9 (5) |
| O—C1—C2 | 118.8 (4) | | |
| C1—O—C7—C8 | 26.3 (6) | C1—O—C7—C12 | −154.2 (4) |
| C7—O—C1—C2 | −104.6 (5) | C7—O—C1—C6 | 78.0 (6) |

Two data sets were collected with the Stoe IPDS system (Stoe & Cie, 1997), and these were merged and scaled together. The applied scale factor between the two data sets was 0.989.

Data collection: *EXPOSE* (Stoe & Cie, 1997); cell refinement: *CELL* (Stoe & Cie, 1997); data reduction: *INTEGRATE* (Stoe & Cie, 1997) and *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).

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## References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-Straße 1, 53121 Bonn, Germany.
Beringer, F. M., Falk, R. A., Karniol, M., Lillien, G., Masullo, M., Mausner, M. & Sommer, E. (1959). *J. Am. Chem. Soc.* **81**, 342–351.
Eriksson, J., Eriksson, L. & Jakobsson, E. (1999). *Acta Cryst.* C**55**, 2169–2171.
Eriksson, J., Jakobsson, E., Marsh, G. & Bergman, Å. (2001). *Proceedings of the Second International Workshop on Brominated Flame Retardants*, May 14–16, 2001, Stockholm University.
Eriksson, L. & Hu, J. (2001). *Acta Cryst.* E**57**, o930–o932.
Hu, J. 1996). Licenciate Thesis, Department of Environmental Chemistry, Stockholm University, Sweden.
Hu, J. 1999). Doctorate Thesis (Research Report No. 73), Department of Chemistry, University of Jyväskylä, Finland.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Stoe & Cie (1997). *IPDS Software* (Version 2.87 of December 1997) and *X-RED* (Version 1.09). Stoe & Cie GmbH, Darmstadt, Germany.
Ziegler, H. & Marr, C. (1962). *J. Org. Chem.* **27**, 3335–3336.