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Key indicators

Single-crystal X-ray study
T = 293 K
 Mean σ (C–C) = 0.005 Å
R factor = 0.029
wR factor = 0.050
 Data-to-parameter ratio = 17.4

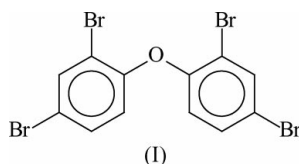
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis(2,4-dibromophenyl) ether

Packing effects are shown to be of minor importance in determining the molecular conformation of the title compound, C₁₂H₆Br₄O, by comparison with a conformational map calculated with semi-empirical (*AM1*) calculations.

Comment

The title compound, (I) (Fig. 1), crystallizes with two molecules in the asymmetric unit, a situation not occurring in the other brominated diphenyl ethers with known crystal structures. All four benzene rings are planar to within 0.01 (1) Å. No anomalous bond distances or angles are found (Table 1). The two rings of molecule 1, C1–C6 and C7–C12, are inclined at 67.5 (1)° to each other, and the two rings of molecule 2, C13–C18 and C19–C24, are inclined at 62.0 (1)° to each other.



The orientational relation between the two unique molecules, shown in Fig. 2, was computed using the program *ROTERA* (Norrestam, 2004; Diamond, 1988). The average deviation between the atoms in the two molecules, one of them rotated to a perfect overlap with the central O and neighbouring C atoms, is 0.22 Å. The similarity between the two molecules can also be deduced from the similar torsion angles involving the ether O atom in the two molecules (Table 1). The observed torsion angles defining the relative

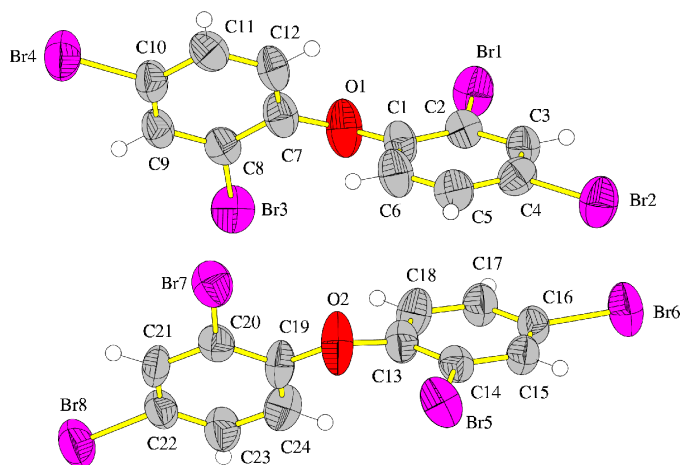


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

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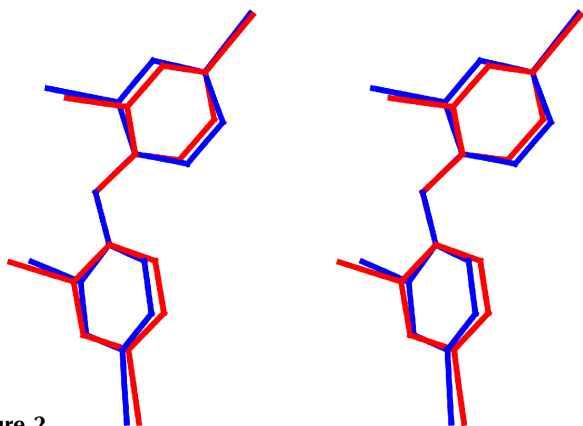


Figure 2

A stereoview of an overlay of the two unique molecules of (I), one of them rotated to a perfect overlap at the O and its two neighbouring C atoms.

orientation of the aromatic rings can be reproduced by semi-empirical calculations using the AM1 Hamiltonian with MOPAC-6 (Stewart, 1990), to an average discrepancy between observed and calculated torsion angles of 10° . Several broad shallow minima can be detected in the complete torsion map, shown in Fig. 3, computed with MOPAC-6 with 10° spacing for the two torsion angles defining the conformation over the ether O atom. Thus, one may draw the conclusion that packing effects are of minor importance in determining the conformations of the molecules comprising (I).

The two shortest intermolecular Br \cdots Br contacts are Br2 \cdots Br4ⁱ [3.808 (1) Å; symmetry code: (i) $1 - x, 1 - y, 1 - z$] and Br2 \cdots Br7ⁱ [3.779 (1) Å]. These intermolecular Br \cdots Br distances cannot be regarded as short in a comparison with similar intermolecular Br \cdots Br contacts for Br-substituted aromatic substances found in a search of the Cambridge Structural Database (CSD, Version 5.25 of November 2003; Allen, 2002; Orpen, 2002; Allen & Motherwell, 2002; Taylor, 2002). The intermolecular Br \cdots Br contacts in (I) shorter than 4.15 Å are mediating contacts between different molecules in the *a* direction. The cut-off distance of 4.15 Å should be considered long for Br \cdots Br interactions when compared with other Br \cdots Br contacts found in the CSD. Most of the intermolecular Br \cdots Br \cdots Br angles for the above-mentioned contacts shorter than 4.15 Å are close to 90° , and none is less than 55° .

Experimental

The synthesis of the title compound has been described earlier by Hu (1999). Crystals of (I) were obtained from a solution in ethanol.

Crystal data

$C_{12}H_6Br_4O$	$D_x = 2.343 \text{ Mg m}^{-3}$
$M_r = 485.81$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 962 reflections
$a = 8.5568 (14) \text{ \AA}$	$\theta = 3.3\text{--}52.0^\circ$
$b = 13.822 (2) \text{ \AA}$	$\mu = 11.67 \text{ mm}^{-1}$
$c = 23.295 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 90.842 (19)^\circ$	Prism, colourless
$V = 2754.9 (8) \text{ \AA}^3$	$0.26 \times 0.10 \times 0.08 \text{ mm}$
$Z = 8$	

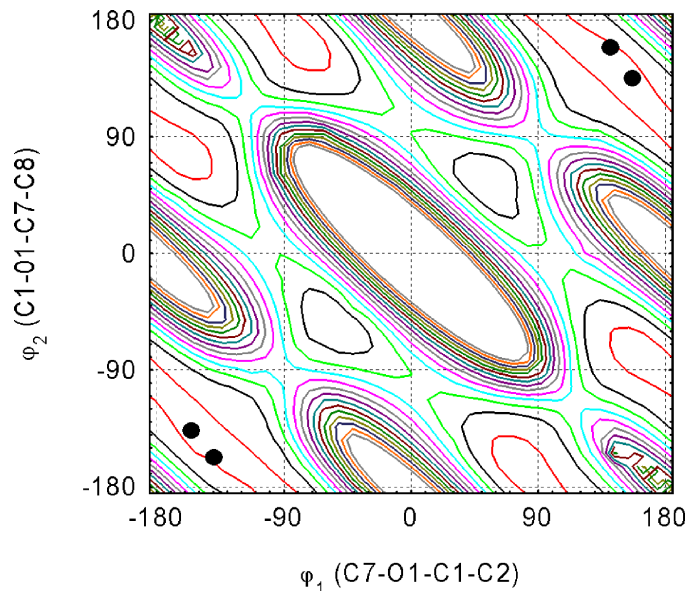


Figure 3

A conformational map of (I) with heat of formation as a function of the two torsion angles C2–C1–O1–C7 and C1–O1–C7–C8, or similar torsion angles in the second molecule. The contour levels are marked at 1 kcal mol^{-1} spacing from 51 to 64 kcal mol^{-1} ($1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$). The conformations of the two molecules are indicated with dots.

Data collection

Stoe IPDS area-detector diffractometer	5341 independent reflections
φ scans	3087 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (<i>X-RED</i> ; Stoe, 1997)	$R_{\text{int}} = 0.095$
$T_{\text{min}} = 0.047, T_{\text{max}} = 0.356$	$\theta_{\text{max}} = 26.0^\circ$
15 424 measured reflections	$h = -10 \rightarrow 10$
	$k = -16 \rightarrow 16$
	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.0151)^2]$
$wR(F^2) = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.86$	$(\Delta/\sigma)_{\text{max}} = 0.001$
5341 reflections	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
307 parameters	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Br1–C2	1.885 (3)	Br5–C14	1.885 (3)
Br2–C4	1.898 (3)	Br6–C16	1.895 (3)
Br3–C8	1.893 (4)	Br7–C20	1.896 (3)
Br4–C10	1.891 (3)	Br8–C22	1.909 (3)
C1–O1–C7	118.6 (3)	C13–O2–C19	120.1 (3)
C2–C1–O1	115.1 (3)	C18–C13–O2	123.6 (3)
O1–C1–C6	124.4 (3)	O2–C13–C14	116.3 (3)
C12–C7–O1	122.6 (3)	C20–C19–O2	115.3 (3)
C8–C7–O1	117.2 (3)	C24–C19–O2	124.4 (3)
C7–O1–C1–C2	–155.4 (3)	C19–O2–C13–C18	47.2 (5)
C7–O1–C1–C6	27.7 (5)	C19–O2–C13–C14	–139.8 (3)
C1–O1–C7–C12	50.0 (5)	C13–O2–C19–C20	–159.5 (3)
C1–O1–C7–C8	–135.7 (3)	C13–O2–C19–C24	25.2 (5)

The R_{int} value is rather high, due in large part to unobserved and/or weak reflections. Neglecting all reflections with negative observed intensity (none more significant than 3.5σ) decreases R_{int} to 0.073. Furthermore, if all reflections less significant than 3σ are omitted, R_{int} drops to 0.051. This shows clearly that a large number of weak reflections make large contributions to R_{int} . H atoms were placed in geometrical positions and refined as riding, with C–H distances of 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *EXPOSE* in *IPDS* (Stoe, 1997); cell refinement: *CELL* in *IPDS*; data reduction: *INTEGRATE* in *IPDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *EASYPLOT* (Karon, 1999)

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References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
Allen, F. H. & Motherwell, W. D. S. (2002). *Acta Cryst.* **B58**, 407–422.
Bergerhoff, G. (1996). *DIAMOND*. Gerhard-Domagk-str. 1, 53121 Bonn, Germany.
Diamond, R. (1988). *Acta Cryst.* **A44**, 211–216.
Hu, J. (1999). PhD thesis, University of Jyväskylä, Finland. ISBN 951-39-0524-1.
Karon, S. (1999). *EASYPLOT*. Spiral Software, 57 Baker Hill Road, Lyme, NH 03768, <http://www.spiralsoftware.com/ep/eplot.html>
Norrestam, R. (2004). *ROTERA*. Division of Structural Chemistry, Stockholm University, Sweden.
Orpen, A. G. (2002). *Acta Cryst.* **B58**, 398–406.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Stewart, J. J. P. (1990). *MOPAC-6 Manual*. Quantum Chemistry Program Exchange (QCPE-455), Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA. <http://qcpe.chem.indiana.edu/>
Stoe (1997). *IPDS* (Version 2.87) and *X-RED* (Version 1.09). Stoe & Cie, Darmstadt, Germany.
Taylor, R. (2002). *Acta Cryst.* **B58**, 879–888.