Synthesis and Characterization of Polybrominated Diphenyl Ethers – Unlabelled and Radiolabelled Tetra-, Penta- and Hexa-bromodiphenyl Ethers

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Diphenyl ether, 3-bromodiphenyl ether and 3,3'-dibromodiphenyl ether have been synthesized via coupling of the appropriate phenol and bromobenzene. Each of these compounds was subsequently brominated to (i) 2,2',4,4'-tetrabromodiphenyl ether, (ii) 2,2',3,4,4'-pentabromodiphenyl ether and 2,2',4,4',5-pentabromodiphenyl ether and (iii) 2,2',3,3',4,4'-hexabromodiphenyl ether, 2,2',3,4,4',5'-hexabromodiphenyl ether and 2,2',4,4',5,5'-hexabromodiphenyl ether, respectively. The tetrabromodiphenyl ether and two pentabromodiphenyl ethers were also prepared radiolabelled with ^{14}C. The compounds were characterized by ^{1}H NMR, melting points, mass spectrometry and UV. The structure of 2,2',3,4,4',5'-hexabromodiphenyl ether was unambigously determined by X-ray crystallography. Thereafter, the structure of the two pentabromodiphenyl ethers and remaining two hexabromodiphenyl ethers were assigned by comparison of their ^{1}H NMR spectra with that of the 2,2',3,4,4',5'-hexabromodiphenyl ether.

The use of flame retardants has increased over the last few decades with the increased production of synthetic polymers. A vast number of inorganic and organic substances are used as flame retardants; the compounds are either incorporated into the polymer during polymerization or added to the final product.[1,2] Several of the halogenated organic substances used as flame retardants have physicochemical properties in common with persistent, environmental pollutants, i.e., high hydrophobicity and low reactivity. Among these are the polybrominated diphenyl ethers (PBDE), which today are ubiquitous environmental contaminants.[3–6]

PBDE are used in large quantities in, e.g., electric devices, TV sets, computers, building materials and textiles.[4] There are several commercial PBDE products with varying degrees of bromination, but the product profile has changed with time and the main PBDE product on the market today consists almost entirely (ca. 97%) of decabromodiphenyl ether (decaBDE).[4] However, the most abundant PBDE in environmental samples are tetra-, penta- and hexa-brominated diphenyl ethers (tetraBDE, pentaBDE and hexaBDE). This may be due to the previous extensive use of lower brominated products (tetraBDE–hexaBDE), photochemical degradation

of decaBDE[7–9] or metabolic debromination in biota as indicated in rainbow trout dosed with decaBDE.[10]

The aim of the present study was to synthesize a number of tetraBDE, pentaBDE and hexaBDE to aid the identification and quantification of these substances in environmental samples, and to make them available for biological and toxicological studies. The most abundant PBDE found in environmental samples, 2,2',4,4'-tetraBDE[3,5,6] and two pentaBDE were also synthesized labelled with ^{14}C to allow their use in studies on their kinetics in mammals.

The bromination of diphenyl ether is fairly specific and substitution first occurs in the 4-positions relative to the ether oxygen[11] and then in the 2-position of each phenyl ring with the formation of 2,2',4,4'-tetraBDE.[12,13] Most preparations of PBDE reported are patents describing the bromination of diphenyl ether with bromine in the presence of a catalyst. The composition of commercial PBDE products has been determined and the major tetraBDE identified as 2,2',4,4'-tetraBDE[12] and the major pentaBDE as 2,2',4,4',5-pentaBDE.[12]

Few other PBDE have been described. A large number of polychlorinated diphenyl ethers and also some brominated diphenyl ethers have been synthesized via preparation of halogenated diphenyl iodonium salts and subsequent reaction with a halogenated phenol or via

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coupling of a phenolate and a halogenated benzene or nitrobenzene (see Ref. 14 for a summary).

Results and discussion

Diphenyl ether (1), 3-bromodiphenyl ether (3) and 3,3'-dibromodiphenyl ether (6) was prepared via the Ullman ether synthesis[15] and each of these compounds was subsequently brominated to yield one tetraBDE, two pentaBDE and three hexaBDE respectively, cf., Scheme 1. The tetraBDE was identified as 2,2',4,4'-tetraBDE (2), which is in accordance with previously reported findings.[13] The structure of the unsymmetrical hexaBDE (8) was unambigously determined by X-ray crystallography. Thereafter, the structure of the two pentaBDE and remaining two hexaBDE could be assigned by comparison of their ^{1}H NMR spectra with that of the hexaBDE (8). Hence, the two pentaBDE were identified as 2,2',3,4,4'-pentaBDE (4) and 2,2',4,4',5-pentaBDE (5) and the three hexaBDE as 2,2',3,3',4,4'-hexaBDE (7), 2,2',3,4,4',5'-hexaBDE (8) and 2,2',4,4',5,5'-hexaBDE (9). No PBDE congeners with bromine substituents in both the 2- and 6-positions in the same phenyl ring were observed.

Diphenyl ether and 3-bromodiphenyl ether were also prepared radiolabelled with ^{14}C and brominated to 2,2',4,4'-tetraBDE ([14]C-2) and 2,2',3,4,4'-pentaBDE ([14]C-4) and 2,2',4,4',5-pentaBDE ([14]C-5), respectively. The mass spectra of the synthesized PBDE did not indicate any structural specific fragmentation patterns. In addition to the characteristic peak clusters due to the natural abundance of [79]Br and [81]Br, the mass spectra showed losses of one and two bromine atoms and less abundant, doubly charged ions.

The UV spectra had absorbance maxima at 202–218 nm ($\log \varepsilon \approx 4.4$–5) and a second weak absorption at 270–300 nm (about 5% of the maximum absorption). It should be noted that at 254 nm, which is a commonly used wavelength for the detection of aromatic compounds by UV, the absorption of the brominated

diphenyl ethers was low. It is therefore recommended that another wavelength be used, e.g., 230 nm, when UV is used to detect these compounds, cf. the Experimental.

The phenyl ring defined by the atoms C1-C6 is planar to within 0.01(1) Å and the bromine atoms connected to the carbons are distorted from the plane by: Br1 (0.01 Å), Br3 (0.04 Å) and Br5 (−0.02 Å), thereby giving an approximate planar configuration, cf. Fig. 1. The other ring defined by C7–C12 is slightly less planar with an average deviation, for the C-atoms, of 0.02 Å from the ring plane. The bromine atoms connected to the carbons of this ring is distorted by: Br2 (−0.04 Å), Br4 (−0.14 Å) and Br6 (0.09 Å). This is as expected for a molecular structure with Br4 as the most sterically distorted bromine atom.

Two of the PBDE congeners synthesized, 2 and 5, have previously been identified in commercial PBDE products[12] and 2 and 5 have also been described in biological samples from the environment.[5,6] The synthesized PBDE will thus serve as useful analytical standards for a variety of purposes. The ^{14}C-labelled PBDE will be used for toxicological evaluation of these compounds.

Experimental

Chemicals. Uniformly labelled [*UL*-^{14}C]phenol (12.2 mCi mmol^{-1}) was purchased from Sigma Radio-chemicals, bromobenzene from BDH, 1,3-dibromo-benzene from Pfaltz & Bauer, 3-bromophenol and bromine from Aldrich and tris[2-(2-methoxyethoxy)-ethyl]amine from Fluka. Copper bronze was from Carlfors bruk, Sweden and sodium hydroxide from KEBO, Sweden. Iron powder, copper(I) chloride and solvents (all of analytical grade) were from Merck.

Thin-layer chromatography (TLC) was performed on silica gel plates (DC Fertigplatten, Kieselgel 60 F_{254}) and RP-18 plates (RP18 F_{254}S) from Merck. Liquid chromatography was performed on silica gel (Kieselgel 60, <0.063 mm), also from Merck. The scintillation
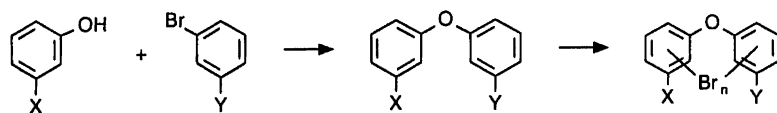
	Intermediate product	Final product
X = Y = H	Diphenyl ether (1)*	2,2',4,4'-Tetrabromodiphenyl ether (2)*
X = Br, Y = H	3-Bromodiphenyl ether (3)*	2,2',3,4,4'-Pentabromodiphenyl ether (4)* and 2,2',4,4',5-Pentabromodiphenyl ether (5)*
X = Y = Br	3,3'-Dibromodiphenyl ether (6)	2,2',3,3',4,4'-Hexabromodiphenyl ether (7), 2,2',3,4,4',5'-Hexabromodiphenyl ether (8) and 2,2',4,4',5,5'-Hexabromodiphenyl ether (9)

Scheme 1. * These compounds were also prepared as the corresponding ^{14}C-labelled compounds.
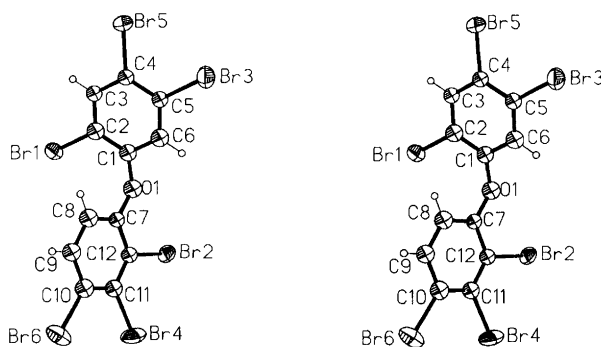
Fig. 1. Stereoscopic view of 2,2',3,4,4',5'-hexabromodiphenyl ether (**8**). Non-hydrogen atoms are shown as 50% probability ellipsoids.

measurements were made with the cocktail OptiScint HiSafe from Fison.

Instruments. Gas chromatography (GC) was performed on a Shimadzu GC-9AM gas chromatograph, equipped with a DB-5 fused silica capillary column, 30 m × 0.25 mm, 0.25 μm film thickness (J&W Scientific) and a flame ionization detector (FID). Nitrogen was used as the carrier gas. The injector temperature was 260 °C and the temperature program: 80 °C, 1 min; 30 °C min⁻¹, 200 °C; 10 °C min⁻¹, 280 °C, 10 min.

Gas chromatography–mass spectrometry (GC–MS) was performed on a Finnigan TSQ attached to a Varian 3400 gas chromatograph. Electron ionization (EI) was used as the ionization method with an ion source temperature of 150 °C The mass spectrometer was programmed to scan from 50 to 700 amu. Helium was used as the carrier gas. The GC parameters were identical with those described above.

¹H NMR spectra were recorded for samples in CDCl₃ solutions with a JEOL EX270 instrument at 270 MHz and at room temperature.

UV spectra were recorded using a Hitachi U-3200 Spectrophotometer. Radioactivity measurements were made with a Wallac 1409 liquid scintillation counter. The radiochemical purity of the labelled compounds was analysed by means of a radioactivity scanner from Raytest with the computer software RITA. Melting points were determinated with a Büchi 353 instrument. The crystallographic investigations were carried out on a Siemens STOE/AED4 diffractometer equipped with a graphite monochromator. SHELXTL-plus software was used to draw the stereographic picture in Fig. 1.[16]

2,2',4,4'-Tetrabromodiphenyl ether (**2**). The synthesis was performed by bromination of diphenyl ether as previously described.[13] Yield 1.74 g (3.6 mmol, 64%) of white crystals of 98% purity according to GC analysis. M.p. 82.0–82.5 °C. MS: m/z (rel. ab., %): 482 (15, M^+), 484 (62), 486 (100), 488 (70), 490 (15), 326 [78, $(M+2-2Br)^+$]. ¹H NMR (270 MHz, CDCl₃): δ 6.71 (d, $J_{H5,H5}$ 9 Hz, H6), 7.37 (dd, $J_{H5,H6}$ 9 Hz, $J_{H5,H3}$ 2 Hz, H5), 7.78 (d, $J_{H3,H5}$ 2 Hz, H3). UV [λ (log ε) in acetonitrile]: 204 nm (λ_{max}) (5.0), 230 nm (4.5).

3-Bromodiphenyl ether (**3**). Potassium phenolate (2.8 g, 21.3 mmol), 1,3-dibromobenzene (6 g, 25.4 mmol) and copper bronze (500 mg) were heated at 170 °C for 2 h. The residual 1,3-dibromobenzene was distilled off under reduced pressure and the product was purified on a silica gel column (3 × 35 cm) with hexane as the mobile phase. Yield 1.74 g (7.0 mmol, 33%) of a colourless oil of 98% purity according to GC analysis. MS: m/z (rel. ab., %): 248 (100, M^+), 250 (100), 169 [35, $(M-Br)^+$]. UV [λ (log ε) in acetonitrile]: 203 nm (λ_{max}) (4.4), 230 nm (3.9).

2,2',3,4,4'-Pentabromodiphenyl ether (**4**) *and* *2,2',4,4',5-pentabromodiphenyl ether* (**5**). Bromine (0.5 ml, 10 mmol) dissolved in tetrachloromethane (2 ml) was added slowly to a refluxing mixture of 3-bromodiphenyl ether (500 mg, 2.0 mmol, **2**) and iron powder (50 mg, 0.90 mmol) in tetrachloromethane (3 ml). After 2 h, the residual bromine was reduced by partitioning with sodium bisulphite in water (3 × 1 ml, 5% w/v). The organic phase was washed with water (3 × 2 ml) and dried with sodium sulphate and the solvent was evaporated off. The two pentaBDE isomers were separated on a silica gel column (3 × 35 cm) using hexane as the mobile phase.

2,2',3,4,4'-Pentabromodiphenyl ether (**4**): Yield 403 mg (0.7 mmol, 36%) of 98% purity according to GC. M.p. 123.3 °C. MS: m/z (rel. ab., %): 560 (8, M^+), 562 (47), 564 (85), 566 (79), 568 (31), 570 (7), 406 [100, $(M+4-2Br)^+$], 202 [19, $(M+2-2Br)^{2+}$]. NMR: ¹H (270 MHz, CDCl₃): δ 6.64 (d, $J_{H6',H5'}$ 9 Hz, H6'), 6.76 (d, $J_{H6,H5}$ 9 Hz, H6), 7.40 (dd, $J_{H5',H6'}$ 9 Hz, $J_{H5',H3'}$ 2 Hz, H5'), 7.54 (d, $J_{H5,H6}$ 8.8 Hz, H5), 7.79 (d, $J_{H3',H5'}$ 2.2 Hz, H3'). UV [λ (log ε) in hexane]: 216 nm (λ_{max}) (4.7), 230 nm (4.5).

2,2',4,4',5-Pentabromodiphenyl ether (**5**): Yield 617 mg (1.1 mmol, 54%) of 98% purity according to GC. M.p. 92.3 °C. MS: m/z (rel. ab., %): 560 (9, M^+), 562 (49), 564 (91), 566 (87), 568 (36), 570 (6), 406 [100, $(M+4-2Br)^+$], 202 [18, $(M+2-2Br)^{2+}$]. NMR: ¹H (270 MHz, CDCl₃): δ 6.80 (d, $J_{H6',H5'}$ 9 Hz, H6'), 6.99 (s, H6), 7.41 (dd, $J_{H5',H6'}$ 9 Hz, $J_{H5',H3'}$ 2 Hz, H5'), 7.79 (d, $J_{H3',H5'}$ 2 Hz, H3'), 7.87 (s, H3). UV [λ (log ε) in hexane]: 216 nm (λ_{max}) (4.7), 230 nm (4.5).

3,3′-Dibromodiphenyl ether (**6**). 3-Bromophenol (2.14 g, 12.4 mmol) was melted at 50 °C and potassium hydroxide (560 mg, 10 mmol) was added. The mixture was stirred for 10 min and 1,3-dibromobenzene (2.36 g, 10.0 mmol) and copper bronze (1.5 g) were added. The reaction was performed and the product purified as described above for the synthesis of **3**. Yield 1.0 g (3.2 mmol, 32%) of a colourless oil of 98% purity according to GC analysis. MS: m/z (rel. ab., %): 326 (60, M^+), 328 (100), 330 (60), 247 [8, $(M-Br)^+$]. UV [λ (log ε) in acetonitrile]: 202 nm (λ_{max}) (4.8), 230 nm (4.1).

2,2′,3,3′,4,4′-Hexabromodiphenyl ether (**7**), *2,2′,3,4,4′,5′-hexabromodiphenyl ether* (**8**) *and 2,2′,4,4′,5,5′-hexabromodiphenyl ether* (**9**). Bromine (600 μl, 11.9 mmol) in tetrachloromethane (5 ml) was added to a refluxing solution of 3,3′-dibromodiphenyl ether (780 mg, 2.38 mmol, **6**) and iron powder (200 mg, 3.58 mmol) in tetrachloromethane (10 ml). After 1 h, a second portion of bromine (200 μl, 3.97 mmol) in tetrachloromethane (1 ml) was added and the mixture was refluxed for another 2 h. The residual bromine was reduced with sodium bisulphite in water (3 × 2 ml, 5% w/v). The organic phase was washed with water (3 × 2 ml) and dried with sodium sulphate and the solvent was evaporated off. The isomers were purified and separated on silica gel with hexane–dichloromethane (9:1) as the mobile phase.

2,2′,3,3′,4,4′-Hexabromodiphenyl ether (**7**): Yield 184 mg (0.29 mmol, 12%) of 99% purity according to GC. M.p. 182.3–182.8 °C. MS: m/z (rel. ab., %): 638 (2, M^+), 640 (14), 642 (34), 644 (53), 646 (42), 648 (14), 650 (2), 484 [100, $(M+4-2Br)^+$], 242 [24, $(M+4-2Br)^{2+}$]. NMR: ^{1}H (270 MHz, CDCl₃): δ 6.70 (d, $J_{H6,H5}$ 8.8 Hz, H6) 7.60, (d, $J_{H5,H6}$ 8.8 Hz, H5). UV [λ (log ε) in hexane]: 217 nm (λ_{max}) (4.8), 230 nm (4.6).

2,2′,3,4,4′,5′-Hexabromodiphenyl ether (**8**): Yield 689 mg (1.07 mmol, 45%) of 99% purity according to GC. M.p. 134.2 °C. MS: m/z (rel. ab., %): 638 (3, M^+), 640 (24), 642 (55), 644 (70), 646 (48), 648 (18), 650 (3), 484 [100, $(M+4-2Br)^+$], 242 [31, $(M+2-2Br)^{2+}$]. NMR: ^{1}H (270 MHz, CDCl₃): δ 6.74 (d, $J_{H6,H5}$ 8.8 Hz, H6), 7.04 (s, H6′), 7.60 (d, $J_{H5,H6}$ 8.8 Hz, H5), 7.89 (s, H3′). UV [λ (log ε) in hexane]: 217 nm (λ_{max}) (4.9), 230 nm (4.8).

2,2′,4,4′,5,5′-Hexabromodiphenyl ether (**9**): Yield 490 mg (0.76 mmol, 32%) of 99% purity according to GC. M.p. 157.6 °C. MS: m/z (rel. ab., %): 638 (3, M^+), 640 (22), 642 (51), 644 (60), 646 (50), 648 (17), 650 (2). NMR: ^{1}H (270 MHz, CDCl₃): δ 7.26 (s, H6), 8.08 (s, H5). UV [λ (log ε) in hexane]: 218 nm (λ_{max}) (4.9), 230 nm (4.7).

General remarks on the synthesis of the radiolabelled compounds. The practical details for the synthesis and purification of radiolabelled compounds used in this laboratory have been described elsewhere.[17] The labelled

compounds synthesized were isolated by preparative TLC. The TLC bands were removed by vaccum, directly into small glass containers (60 mm, 10 mm ID), narrow at both ends and fitted with a glass-wool plug. The containers were kept in an upright position and the products were eluted from the gel with dichloromethane. The labelled products were all free of radiolabelled impurities according to TLC-analyses on both silica gel and reversed-phase plates.

[UL-^{14}C]Diphenyl ether (^{14}**C-1**). *[UL-^{14}C]*Phenol (1.0 mCi, 12.2 mCi mmol^{-1}, 82 μmol) was dissolved in an aqueous solution of potassium hydroxide (100 μl, 115 mg ml^{-1}, 200 μmol). Bromobenzene (100 μl, 950 μmol), tris[2-(2-methoxyethoxy)ethyl]amine (100 μl, 310 μmol) and copper(I) chloride (2 mg, 20 μmol) was added and the mixture was stirred at 170 °C for 2 h. The condenser and the fittings were carefully rinsed with hexane and the residual phenol was removed by partitioning with potassium hydroxide (5 × 1 ml, 1 M). The hexane phase was dried by passing the solution through a sodium sulphate column (3 × 20 mm). The solvent volume was reduced to 0.5 ml with a gentle stream of nitrogen. The product was purified on a silica gel column (1 × 10 cm) using hexane as the mobile phase. Yield 185 μCi (12.2 mCi mmol^{-1}, 15 μmol, 18.5%) of 99% purity according to GC analysis.

2,4,-Dibromo-[UL-^{14}C]phenyl 2′,4′-dibromophenyl ether (^{14}**C-2**). *[UL-^{14}C]*Diphenyl ether (185 μCi, 12.2 mCi mmol^{-1}, 15 μmol) was dissolved in tetrachloromethane (1 ml). Iron powder (20 mg, 360 μmol) and bromine (4 μl, 80 μmol) dissolved in tetrachloromethane (0.5 ml) were added and the mixture was refluxed. A second portion of bromine (2 μl, 40 μmol) dissolved in tetrachloromethane (0.2 ml) was added after 30 min and the mixture was refluxed for an additional 30 min and then allowed to reach room temperature. The solvent was reduced to 0.5 ml with a gentle stream of nitrogen. The product was purified by preparative TLC on silica gel plates using hexane–toluene (9:1) as the mobile phase. Yield 114 μCi (12.2 mCi mmol^{-1}, 9 μmol, 61.6%) of 95% purity according to GC analysis.

3-Bromophenyl [UL-^{14}C]phenyl ether (^{14}**C-3**). *[UL-^{14}C]*Phenol (910 μCi, 12.2 mCi mmol^{-1}, 75 μmol) was dissolved in an aqueous solution of potassium hydroxide (100 μl, 104.4 mg ml^{-1}, 190 μmol). 1,3-Dibromobenzene (200 μl, 166 μmol), tris[2-(2-methoxyethoxy)ethyl]-amine (100 μl, 310 μmol) and copper(I) chloride (2 mg, 20 μmol) were added. The reaction was performed and the product purified as described above for the synthesis of ^{14}**C-1**. Yield 206 μCi (12.2 mCi mmol^{-1}, 17 μmol, 22.6%) of 95% purity according to GC analysis.

2,3,4-Tribromophenyl 2′,4′-dibromo-[UL-^{14}C]phenyl ether (^{14}**C-4**) *and 2,4,5-tribromophenyl 2′,4′-dibromo-[UL-^{14}C]phenyl ether* (^{14}**C-5**). 3-Bromophenyl [*UL-*

[14C]phenyl ether (200 µCi, 12.2 mCi mmol⁻¹, 16 µmol, 14C-3) was dissolved in tetrachloromethane (1 ml). Iron powder (20 mg, 360 µmol) and bromine (5 µl, 100 µmol)

Table 1. Crystal data and data collection parameters.

Empirical formula	$C_{12}H_4Br_6O$
Formula weight	643.61
Cell weight	5148.90
Space group	$C2/c$ (15)
$\lambda/\text{Å}$	0.71060 (Mo Kα)
$a/\text{Å}$	26.07(4)
$b/\text{Å}$	8.848(18)
$c/\text{Å}$	20.62(3)
$\beta/°$	139.61(7)
$V/\text{Å}^3$	3082.5(92)
Z	8
$F(000)$	2352
μ/mm^{-1}	15.617
Transmission factor range, T_{min} and T_{max}	0.1976, 0.4214
Crystal dimensions/mm³	0.02 × 0.08 × 0.018
T/K	293(2)
Measured reflections	2999
Symmetry independent reflections	1449
Unique observed reflections [$I \geqslant 2\sigma(I)$]	843
Number of refined parameters	107
hkl-limits	(−24,−8,0)–(16,8,19)
2θ range/°	3.95–40.04
Calculated density/g cm⁻³	2.774
R(internal)	0.0912
Goodness of fit	1.0
Final R-indices [$I \geqslant 2\sigma(I)$][a]	$R1 = 0.0458$, $wR2 = 0.0827$
R-indices (all data)[a]	$R1 = 0.1147$, $wR2 = 0.1058$
Largest diff. peak and hole/e Å⁻³	0.658, −0.736

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$,
$wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{\frac{1}{2}}$.

dissolved in tetrachloromethane (0.5 ml) were added. The reaction was performed as described above for the synthesis of 14C-2 with a second addition of bromine (3 µl, 60 µmol) in tetrachloromethane (0.2 ml) after 30 min. The two products were purified and separated as described above for the synthesis of 14C-2.

2,3,4-Tribromophenyl 2′,4′-dibromo-[UL-14C]phenyl ether (14C-4): yield 70 µCi (12.2 mCi mmol⁻¹, 6 µmol, 3.2 mg, 34%) of 95% purity according to GC analysis. 2,4,5-Tribromophenyl 2′,4′-dibromo-[UL-14C]phenyl ether (14C-5): yield 101 µCi (12.2 mCi mmol⁻¹, 8 µmol, 4.7 mg, 49%) of 95% purity according to GC analysis.

Crystallography. Crystals of 2,2′,3,4,4′,5′-hexabromo-diphenyl ether were formed by recrystallization from hexane. Reflection conditions $hkl:h+k=2n$; $h0l:(h=2n,l=2n)$ and $0k0:k=2n$ indicated Cc and $C2/c$ as possible space groups. The structure was later successfully solved and refined in $C2/c$. Lattice parameters were refined from 2θ-angles of 18 selected reflections. The intensities were collected at room temperature. The intensities were corrected for Lorentz and polarization effects. Correction for absorption effects was made with empirical methods using ψ-scan data. Crystal data and data collection parameters are found in Table 1. The crystal structure was determined by direct methods using the program SHELXS[18] and refined by full-matrix least-squares calculations with the program SHELXL.[19] The coefficient for the scattering factor approximations of the neutral atoms were those included in SHELXL. All bromine atoms could be located in the first electron density map and the rest of the non-hydrogen atoms could easily be located in subsequent difference density maps. The hydrogens were placed by geometrical methods and were constrained in the least-squares calcu-

Table 2. Fractional atomic coordinates and U_{eq}/U_{iso}. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Estimated standard deviations are given in parentheses.

Atom	x	y	z	$U_{eq}./U_{iso}.$
Br(1)	0.84333(9)	0.0709(2)	0.73749(11)	0.0454(6)
Br(2)	0.73818(9)	−0.0223(2)	0.88556(12)	0.0437(5)
Br(3)	0.52470(10)	−0.3488(2)	0.40734(13)	0.0510(6)
Br(4)	0.88516(11)	−0.1990(2)	1.10452(12)	0.0646(7)
Br(5)	0.61083(9)	−0.2044(2)	0.35730(11)	0.0516(6)
Br(6)	1.01677(10)	−0.3938(2)	1.14339(13)	0.0614(7)
O(1)	0.7410(5)	−0.0801(11)	0.7494(7)	0.043(3)
C(1)	0.7164(8)	−0.1158(17)	0.6627(11)	0.036(4)
C(2)	0.7514(8)	−0.0516(18)	0.6425(11)	0.039(4)
C(3)	0.7194(8)	−0.0795(16)	0.5512(10)	0.031(4)
C(4)	0.6529(8)	−0.1684(16)	0.4816(10)	0.030(4)
C(5)	0.6165(8)	−0.2311(16)	0.5020(10)	0.032(4)
C(6)	0.6498(8)	−0.2031(17)	0.5938(10)	0.040(4)
C(7)	0.8028(8)	−0.1605(16)	0.8367(10)	0.028(4)
C(8)	0.8538(8)	−0.2516(16)	0.8520(11)	0.040(5)
C(9)	0.9165(8)	−0.3238(18)	0.9427(11)	0.038(4)
C(10)	0.9279(8)	−0.2979(19)	1.0206(11)	0.041(4)
C(11)	0.8751(8)	−0.2160(18)	1.0036(10)	0.034(4)
C(12)	0.8137(8)	−0.1436(17)	0.9139(11)	0.032(4)

Table 3. Selected bond distances (Å) with estimated standard deviations in parentheses.

Br(1)–C(2)	1.899(15)
Br(2)–C(12)	1.901(15)
Br(3)–C(5)	1.873(14)
Br(4)–C(11)	1.896(15)
Br(5)–C(4)	1.894(15)
Br(6)–C(10)	1.887(15)
O(1)–C(7)	1.387(15)
O(1)–C(1)	1.40(2)

Table 4. Selected bond angles (°) with estimated standard deviations in parentheses.

C(7)–O(1)–C(1)	119(1)
C(6)–C(1)–O(1)	116(1)
C(2)–C(1)–O(1)	122(1)
C(1)–C(2)–Br(1)	122(1)
C(3)–C(2)–Br(1)	119(1)
C(3)–C(4)–Br(5)	119(1)
C(5)–C(4)–Br(5)	121(1)
C(6)–C(5)–Br(3)	120(1)
C(4)–C(5)–Br(3)	122(1)
C(8)–C(7)–O(1)	124(1)
O(1)–C(7)–C(12)	117(1)
C(11)–C(10)–Br(6)	124(1)
C(9)–C(10)–Br(6)	116(1)
C(10)–C(11)–Br(4)	120(1)
C(12)–C(11)–Br(4)	119(1)
C(11)–C(12)–Br(2)	123(1)
C(7)–C(12)–Br(2)	116(1)

lations to ride on the carbons they were connected to, at a distance of 1.08 Å. The weighting scheme employed in the refinements was: $w = 1/[\sigma^2(F_o^2) + (0.0254P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. $\sigma(F_o^2)$ was determined from counting statistics. One reflection (-202) was omitted from the refinements due to severe secondary extinction effects. The bromine atoms were refined anisotropically and the rest of the atoms isotropically. The model was completely converged in the final least-squares cycle of the refinement. A stereographic picture of compound **8** is shown in Fig. 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2, bond distances in Table 3 and bond angles in Table 4. Additional material (anisotropic displacement factors and structure factor amplitudes) can be obtained on request for a period of one year after the publication of this article from one of the authors (L. Eriksson).

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