Synthesis of Fully Aromatic Cyclic Polyethers

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Ullmann-type condensation of 2,2'-oxydiphenol (2) with o-bromoanisole followed by treatment of the products with hydroiodic acid gave 2,2'-(o-phenylenedioxy)diphenol (4) and 2,2'-[oxydi-(o-phenylene)dioxy]diphenol (6). Similarly, compound (6) gave the homologous pentameric (8) and hexameric (10) diphenols. On condensation with o-dibromobenzene, the diphenol (8) gave hexabenzo-18-crown-6 (13), and the diphenol (10) gave hepta-benzo-21-crown-7 (14). Condensation of the trimer monomethyl ether with o-dibromobenzene gave the open-chain heptamer (12). Unlike their aliphatic or partly aliphatic analogues the fully aromatic cyclic polyethers (13) and (14) did not bind cations of alkali metals.
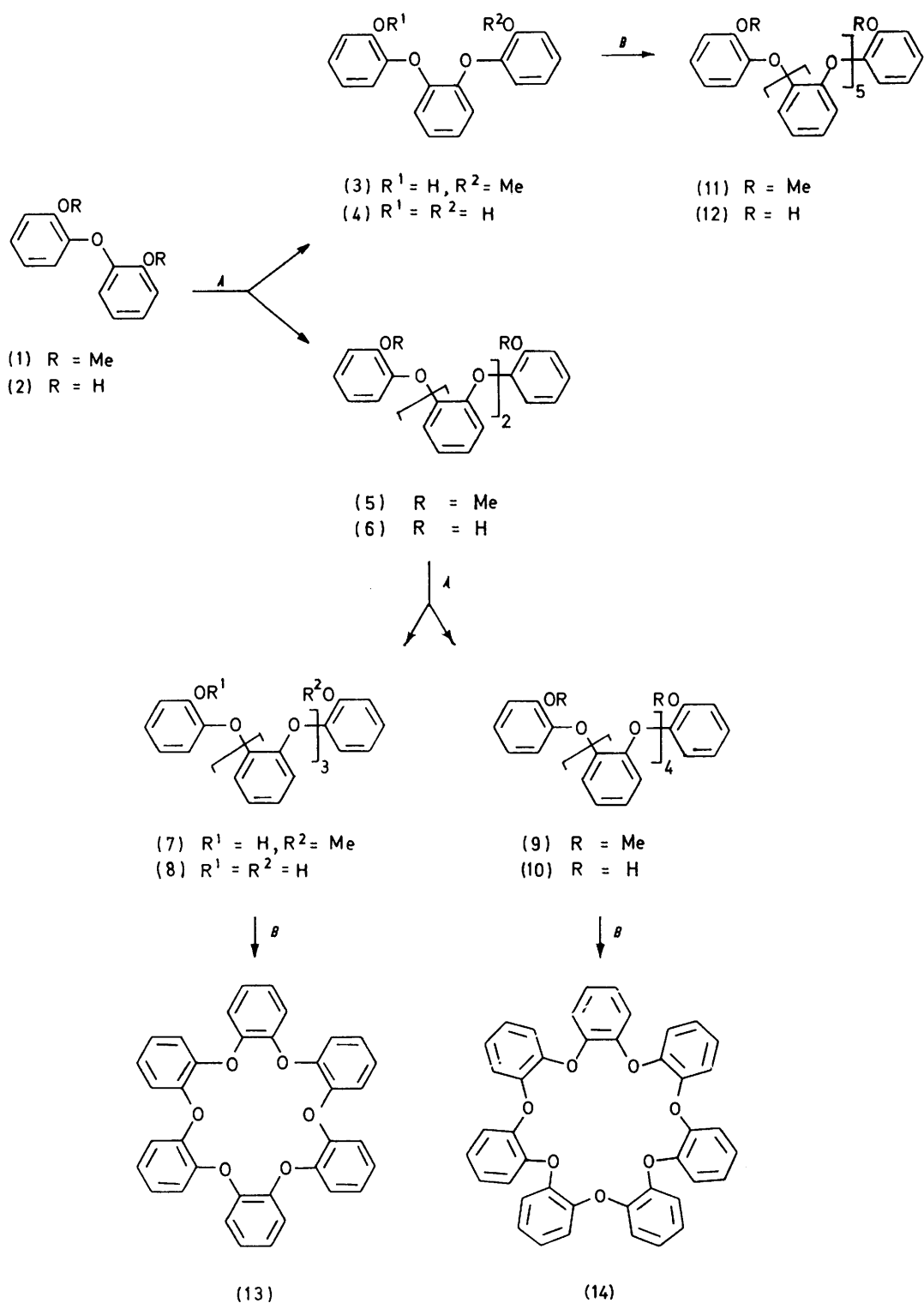
THE ability of cyclic polyethers ('crown' compounds; for references see Pedersen and Frensdorff [1]) to form stable complexes with cations depends on the basicity of the ethereal oxygen atoms in the macrocycle. Thus, dibenzo-18-crown-6 binds cations less readily than the corresponding perhydro- and analogous aliphatic compounds.[2] The selectivity of a ligand depends not only on the size of its crown cavity but also on its flexibility, which allows it to assume different conformations to suit the steric requirements of different cations.[3] The crown compounds so far synthesised are flexible structures of basic character because of the presence of aliphatic chains linking all or some of the oxygen atoms. Two other types of structure are of interest: (i) fully aromatic crown compounds (more rigid and less basic), and (ii) fully alicyclic crown compounds (more rigid but with essentially unchanged basicity). We now report the synthesis of hexabenzo[b,e,h,k,n,q][1,4,7,10,13,16]hexa-oxacyclo-octadecin (hexabenzo-18-crown-6) (13) and heptabenzo[b,e,h,k,n,q,t][1,4,7,10,13,16,19]heptaoxa-cycloheneicosin (heptabenzo-21-crown-7) (14), the first

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[2] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[3] N. S. Poonia and M. R. Truter, *J.C.S. Dalton*, 1973, 2062; N. S. Poonia, *J. Amer. Chem. Soc.*, 1974, **96**, 1012.

(3) R^1 = H, R^2 = Me
(4) R^1 = R^2 = H

(11) R = Me
(12) R = H

(1) R = Me
(2) R = H

(5) R = Me
(6) R = H

(7) R^1 = H, R^2 = Me
(8) R^1 = R^2 = H

(9) R = Me
(10) R = H

(13)

(14)

A, with *o*-bromoanisole; *B*, with *o*-dibromobenzene

examples of fully aromatic crown compounds and potential precursors of the corresponding fully alicyclic compounds.

2,2'-Oxydiphenol dimethyl ether (1) was first synthesised from guaiacol and o-bromoanisole by the classical Ullmann reaction.[4] This reaction, modified by the initial formation of the dry sodium salt of the phenol and the use of copper(I) chloride in pyridine as catalyst,[5] gave the ether (1) in greatly improved yield (46%). Subsequent treatment with hydroiodic acid gave 2,2'-oxydiphenol (2). Condensation of the diphenol (2) with o-bromoanisole gave 2,2'-(o-phenylenedioxy)diphenol monomethyl ether (3) in 12% yield and 2,2'-[oxydi-(o-phenylene)dioxy]diphenol dimethyl ether (5) in 40% yield. Cleavage of the methyl ethers gave the diphenols (4) and (6), respectively. Condensation of the tetrameric diphenol (6) with o-bromoanisole gave correspondingly 2,2'-[o-phenylenedioxydi-(o-phenylene)dioxy]diphenol monomethyl ether (7) in 3% yield and 2,2'-[oxydi-(o-phenylene)dioxydi-(o-phenylene)dioxy]diphenol dimethyl ether (9) in 19% yield. Cleavage of the methyl ethers gave the diphenols (8) and (10), respectively. Condensation of the trimeric diphenol monomethyl ether (3) with o-dibromobenzene gave 2,2'-[o-phenylenedioxydi-(o-phenylene)dioxydi-(o-phenylene)-dioxy]diphenol dimethyl ether (11) in 15% yield. The corresponding diphenol (12) was obtained in the usual way.

Structures of the diphenols (4), (6), (8), (10), and (12) and of the dimethyl ethers (5), (9), and (11) are assigned on the .basis of their elemental analyses and spectroscopic properties. The monomethyl ethers (3) and (7) were obtained as oils. The former was characterised spectroscopically; the latter was converted into the diphenol (8) without prior characterisation.

The synthetic route chosen for the preparation of cyclic polyethers consisted of condensation of the open-chain diphenols with o-dibromobenzene followed by separation of chromatographically non-polar products. The diphenols (2), (4), and (6) gave by this route unidentified bromine-containing products. However, the pentameric diphenol (8) gave a neutral bromine-free product of m.p. 282—283° in 5% yield. Its mass spectrum showed a molecular ion at m/e 552 and only a few minor fragments. Its n.m.r. spectrum showed only one peak, at τ 3.18, in sharp contrast to the complex spectra of all the open-chain polyethers. It is accordingly formulated as hexabenzo-18-crown-6 (13). Similarly, the hexameric diphenol (10) gave heptabenzo-21-crown-7 (14) (in 2% yield) with a molecular ion at m/e 644 and an n.m.r. singlet at τ 3.18.

The n.m.r. spectra of the macrocyclic ethers (13) and (14) closely resemble that of dibenzodioxin with its single peak at τ 3.15. This reference compound was prepared by self-condensation of sodium o-bromophen-

oxide in the presence of copper(I) chloride in pyridine. The yield (27%) of the product was substantially higher than that obtained by other methods.[6]

The mass spectra of the two cyclic ethers and of all the open-chain oligomers have in common one fragment of m/e 184 which, except for the case of the cyclic hexamer, is abundant. We attribute it to the stable [6] dibenzodioxin cation radical.

The i.r. spectra (in KBr) of the diphenols (2), (4), (6), (8), (10), and (12), of the dimethyl ethers (1), (5), (9), and (11), of the monomethyl ether (3), and of the cyclic ethers (13) and (14) all exhibit bands associated with aromatic C—C stretching (1 600—1 450 cm⁻¹), with C—O—C stretching (1 270—1 230 cm⁻¹), and with C—H out-of-plane deformation of 1,2-disubstituted benzene derivatives (750 cm⁻¹). The spectra of the diphenols in chloroform (10^{-1}—10^{-3}M-solutions) show striking differences in the 3 700—3 300 cm⁻¹ region. All exhibit a strong band between 3 540 and 3 550 cm⁻¹. For the trimer, this is a single symmetric band. The dimer shows a weak additional band at 3 430 cm⁻¹ and the tetramer a stronger one at the same frequency. The pentamer and the hexamer lack a discrete band at that frequency but have a shoulder on the main band, more pronounced in the case of the former than of the latter compound. The heptamer shows only a single band at 3 540 cm⁻¹, slightly broadened at its base. Being unaffected by concentration, the spectra are attributed to intramolecular hydrogen bonding. The frequency of the main band (3 550—3 540 cm⁻¹) is consistent with hydrogen bonding either to the vicinal ethereal oxygen atom as in guaiacol [7] or to the π-electrons of the neighbouring aromatic ring as in 2,2'-dihydroxybiphenyl; [8] the 3 430 cm⁻¹ band is consistent with hydrogen bonding between the terminal hydroxy-groups.[8] In the higher members of this homologous series, hydrogen bonding to more remote ethereal oxygen atoms or benzene rings cannot be ruled out.

Tested by Pedersen's method,[9] the crown compounds (13) and (14) did not form complexes with lithium, sodium, potassium, calcium, and ammonium cations.

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. I.r. spectra were taken for KBr discs with a Unicam SP 200 spectrophotometer and for solutions in chloroform with a Perkin-Elmer 180 spectrophotometer. U.v. spectra were recorded for solutions in ethanol and in ethanolic 0.1M-NaOH with a Unicam SP 8000 spectrophotometer, n.m.r. spectra for solution in [²H]chloroform with a Varian HA100 spectrometer, and mass spectra with an A.E.I. MS12 spectrometer. Preparative t.l.c. was performed on 1 mm-thick layers of silica gel (GF₂₅₄; Merck) in n-hexane-chloroform (2 : 1, 1 : 1, or 1 : 2 v/v). Unless otherwise stated the solvent for crystallisation was benzene–2,2,4-trimethylpentane.

Condensation of Phenols with o-*Bromoanisole and with* o-

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[6] H. J. Shine and L. R. Slade, *J. Heterocyclic Chem.*, 1974, **11**, 139.

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[8] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1947, 1260.

[9] C. J. Pedersen, *Fed. Proc.*, 1968, **27**, 1305.

Dibromobenzene. General Procedure.—The phenol in benzene (8—15 ml per g) and sodium methoxide (1.9 mol. equiv.) were mixed and the solvent was then evaporated off. The residue in boiling pyridine (8—15 ml per g) was treated under nitrogen with copper(I) chloride (0.5—1.0 mol. equiv.) and o-bromoanisole (4—5 mol. equiv.) or o-dibromobenzene (0.5 mol. equiv.) for 3 days. (Guaiacol was treated with half the quantities of sodium methoxide and o-bromoanisole for 1 day.) The cooled solution was poured into an excess of 2M-hydrochloric acid and the mixture then extracted with a suitable solvent. The extract was washed (1 × 2M-HCl; 1 × H₂O), dried (Na₂SO₄), and taken to dryness.

Cleavage of Methyl Ethers. General Procedure.—The ether in glacial acetic acid (15 ml per g) and an equal volume of 57% hydroiodic acid were refluxed overnight. The cooled solution was poured into water (3—4 volumes). The mixture, partially neutralised (K₂CO₃), was extracted with chloroform. The extract was washed (1 × dilute Na₂SO₃; 1 × H₂O), dried (Na₂SO₄), and taken to dryness.

2,2'-Oxydiphenol (2) and its Dimethyl Ether (1).—The acidified reaction mixture from the condensation of guaiacol (25 g) with o-bromoanisole was extracted with n-hexane. Evaporation [to remove solvent and then of o-bromoanisole (at 1 mmHg)] left a residue which from aqueous ethanol gave the pure dimethyl ether (1) (21 g), m.p. 77—79° (lit.,⁴ 78°), ν$_{max.}$ (KBr) 1 600, 1 580, 1 500, 1 460, 1 250, 760, and 740 cm⁻¹, λ$_{max.}$ 273 and 276 nm (ε 3 990 and 3 750), τ 2.97—3.19 (m, 8 aromatic H) and 4.0 (6 H, s, OMe), m/e 231 (38%), 230 (M⁺, 100), 215 (16), 185 (21), 184 (100), 121 (22), 92 (29), and 77 (34) (Found: C, 72.9; H, 6.4. Calc. for C₁₄H₁₄O₃: C, 73.0; H, 6.1%).

Cleavage of the dimethyl ether (3.3 g) by the general procedure followed by crystallisation of the crude product gave 2,2'-oxydiphenol (2.6 g), m.p. 122—123° (lit.,⁴ 121°), ν$_{max.}$ (CHCl₃) 3 550 and 3 430 cm⁻¹, ν$_{max.}$ (KBr) 1 600, 1 500, 1 465, 1 260, 1 250, 1 230, 1 210, and 760 cm⁻¹, λ$_{max.}$ 276 nm (ε 4 750), λ$_{max.}$ (NaOH) 297 nm (ε 7 500), τ 2.96—3.20 (m, 8 aromatic H) and 4.28 (s, 2 phenolic H), m/e 203 (15%) 202 (M⁺, 90), 109 (45), 94 (100), and 83 (40) (Found: C, 71.1; H, 5.2. Calc. for C₁₂H₁₀O₃: C, 71.3; H, 5.0%).

2,2'-[Oxydi-(o-phenylene)dioxy]diphenol (6) and its Dimethyl Ether (5).—The acidified reaction mixture from condensation of 2,2'-oxydiphenol (2) (14.5 g) with o-bromoanisole was extracted first with n-hexane and then with n-hexane–benzene (4 : 1 v/v). The first extract was discarded. The second extract was taken to dryness and the residue crystallised to furnish the *dimethyl ether* (5) (11.8 g), m.p. 123—124°, ν$_{max.}$ (KBr), 1 600, 1 582, 1 500, 1 455, 1 270, 1 255, and 745 cm⁻¹, λ$_{max.}$ 272 and 277 nm (ε 8 180 and 8 580), τ 3.00—3.25 (m, 16 aromatic H) and 6.18 (6 H, s, OMe), m/e 415 (30%), 414 (M⁺, 100), 198 (15), 185 (10), 184 (40), 85 (34), and 83 (46) (Found: C, 75.4; H, 5.6. C₂₆H₂₂O₅ requires C, 75.35; H, 5.35%). A second crop (1.2 g) of the dimethyl ether (5) was obtained from the mother liquors (see below).

Cleavage of the dimethyl ether (5) (1 g) followed by crystallisation of the crude product gave the *diphenol* (6) (670 mg), m.p. 129°, ν$_{max.}$ (CHCl₃) 3 550 and 3 440 cm⁻¹, ν$_{max.}$ (KBr) 1 595, 1 490, 1 455, 1 270, 1 250, 1 230, 755, and 750 cm⁻¹, λ$_{max.}$ 273 nm (ε 9 890), λ$_{max.}$ (NaOH) 282 and 294 nm (ε 10 070 and 10 790), τ 2.93—3.29 (m, 16 aromatic H) and 4.07 (s, 2 phenolic H), m/e 387 (18%), 386 (M⁺, 67), 185 (19), 184 (49), 85 (64), and 83 (100) (Found: C, 74.3; H, 4.7. C₂₄H₁₈O₅ requires C, 74.4; H, 4.7%).

2,2'-(o-Phenylenedioxy)diphenol (4) and its Monomethyl Ether (3).—The mother liquors from the crystallisation of the tetrameric dimethyl ether (5) were taken to dryness. The residue was partitioned between benzene and 3M-sodium hydroxide. The alkaline phase and the precipitate formed were acidified and the liberated acidic material was re-extracted with benzene. The partition step was repeated to give the monomethyl ether (3) (2.8 g) as an oil. By t.l.c., the material was estimated to contain less than 2% impurity. The impure monomethyl ether had ν$_{max.}$ (KBr) 3 500, 1 595, 1 497, 1 455, 1 260, and 745 cm⁻¹, λ$_{max.}$ 272.5 nm (ε 6 800), λ$_{max.}$ (NaOH) 280 and 290sh nm (ε 6 080 and 4 870), τ 3.01—3.15 (m, 12 aromatic H) and 6.25 (3 H, s, OMe), m/e 309 (17%), 308 (M⁺, 67), 216 (28), 185 (13), 184 (27), 170 (17), 108 (26), 85 (67), and 83 (100).

The neutral material (9 g) from the partition step consisted mainly of o-bromoanisole. This was evaporated *in vacuo* leaving a residue which on crystallisation gave a second crop (1.2 g) of the tetrameric dimethyl ether (5), m.p. 123—124°.

Cleavage of the monomethyl ether (3) (0.8 g) followed by crystallisation of the crude product gave the *trimeric diphenol* (4) (430 mg), m.p. 89°, ν$_{max.}$ (CHCl₃) 3 550 cm⁻¹, ν$_{max.}$ (KBr) 1 600, 1 590, 1 495, 1 450, 1 282, 1 261, 1 250, 750, and 740 cm⁻¹, λ$_{max.}$ 275 nm (ε 7 370), λ$_{max.}$ (NaOH) 295 nm (ε 10 150), τ 2.91—3.12 (m, 12 aromatic H) and 4.92 (broad, 2 phenolic H), m/e 295 (22%), 294 (M⁺, 100), 201 (21), 185 (46), 184 (46), 85 (33), and 83 (50) (Found: C, 73.9; H, 5.3. C₁₈H₁₄O₄ requires C, 73.5; H, 4.8%).

2,2'-[Oxydi-(o-phenylene)dioxydi-(o-phenylene)dioxy]diphenol (10) and its Dimethyl Ether (9).—The acidified reaction mixture from the condensation of the tetrameric diphenol (6) (11 g) with o-bromoanisole was extracted first with n-hexane and then with n-hexane–benzene (1 : 1 v/v). The crude product from the second extract was crystallised successively from benzene-2,2,4-trimethylpentane and benzene–ethanol to furnish the *dimethyl ether* (9) (3.2 g), m.p. 194—195°, ν$_{max.}$ 1 600, 1 580, 1 495, 1 455, 1 260, and 750 cm⁻¹, λ$_{max.}$ 271.5 and 277 nm (ε 13 540 and 12 220), τ 3.04—3.20 (m, 24 aromatic H) and 6.26 (6 H, s, OMe), m/e 599 (42%), 598 (M⁺, 100), 185 (15), 184 (76), 168 (13), 128 (20), and 77 (23) (Found: C, 76.5; H, 5.2. C₃₈H₃₀O₇ requires C, 76.2; H, 5.05%).

Crystallisation of the crude product of cleavage of the dimethyl ether (9) (3 g) gave the *diphenol* (10) (2.7 g), m.p. 152—153°, ν$_{max.}$ (CHCl₃) 3 540 cm⁻¹, ν$_{max.}$ (KBr) 1 600, 1 582, 1 500, 1 455, 1 261, 755, and 750 cm⁻¹, λ$_{max.}$ 272 and 276 nm (ε 10 560 and 10 135), λ$_{max.}$ (NaOH) 279 and 292sh nm (ε 9 560 and 8 279), τ 3.08—3.25 (m, 24 aromatic H) and 4.02 (s, 2 phenolic H), m/e 571 (43%), 570 (M⁺, 100), 185 (29), and 184 (67) (Found: C, 75.7; H, 4.8. C₃₆H₂₆O₇ requires C, 75.8; H, 4.6%).

2,2'-[o-Phenylenedioxydi-(o-phenylene)dioxy]diphenol (8).—The combined mother liquors from the crystallisation of the hexameric dimethyl ether (9) were freed from surplus o-bromoanisole on a silica column to give an oil (4.9 g) which was separated by t.l.c. into the hexameric dimethyl ether (9) (0.3 g), the tetrameric diphenol (6) (0.8 g), and (in the zone of intermediate mobility) the monomethyl ether (7) (1 g). The last fraction again submitted to t.l.c. gave an oil (0.42 g) which without further characterisation was treated with hydroiodic acid to give, after crystallisation, the *diphenol* (8) (380 mg), m.p. 69—70°, ν$_{max.}$ (CHCl₃) 3 545 cm⁻¹, ν$_{max.}$ (KBr) 1 590, 1 500, 1 460, 1 260, 1 230, 752, and 747 cm⁻¹, λ$_{max.}$ 272 and 276 nm (ε 10 480 and 10 300), λ$_{max.}$ (NaOH) 280 and 293 nm (ε 10 770 and 10 620), τ 2.98—3.20 (20 aromatic H) and 3.82 (s, 2 phenolic H), m/e 479 (39%),

478 (M^+, 100), 185 (31), 184 (63), 85 (21), and 83 (33) (Found: C, 75.0; H, 4.9. $C_{30}H_{22}O_6$ requires C, 75.3; H, 4.6%).

2,2'-[o-Phenylenedioxydi-(o-phenylene)dioxydi-(o-phenylene)dioxy]diphenol (12) *and its Dimethyl Ether* (11).—The acidified reaction mixture from the condensation of the trimeric monomethyl ether (3) (1.6 g) with o-dibromobenzene was extracted with benzene. Two crystallisations of the crude product gave the *dimethyl ether* (11) (270 mg), m.p. 217—218°, $\nu_{max.}$ (KBr) 1 595, 1 580, 1 490, 1 450, 1 260, and 750 cm^{-1}, $\lambda_{max.}$ 271.5 and 276.5 nm (ε 14 540 and 13 300), m/e 691 (10%), 690 (M^+, 19), 321 (14), 198 (13), 185 (25), 184 (100), 170 (91), 128 (17), 123 (18), 95 (20), and 77 (21) (Found: C, 76.9; H, 5.3. $C_{44}H_{34}O_8$ requires C, 76.5; H, 5.0%).

Cleavage of the dimethyl ether (220 mg) followed by two crystallisations of the crude product gave the *diphenol* (12) (70 mg), m.p. 91—93°, $\nu_{max.}$ (CHCl$_3$) 3 540 cm^{-1}, $\nu_{max.}$ (KBr) 1 595, 1 580, 1 490, 1 450, 1 250, and 750 cm^{-1}, $\lambda_{max.}$ 272 and 276.5 nm (ε 12 900 and 12 400), $\lambda_{max.}$ (NaOH) 272sh, 278.5, and 292sh nm (ε 12 400, 12 730, and 9 470), τ 3.07—3.24 (28 aromatic H) and 5.3 (m, 2 phenolic H), m/e 663 (42%), 662 (M^+, 85), 185 (50), and 184 (100) (Found: C, 76.4; H, 4.9. $C_{42}H_{30}O_8$ requires C, 76.1; H, 4.6%).

Hexabenzo[b,e,h,k,n,q][1,4,7,10,13,16]hexaoxacyclo-octadecin (13).—T.l.c. of the crude product from the reaction of the pentameric diphenol (8) (445 mg) with o-dibromobenzene gave two non-polar fractions. The more polar (96 mg) of them was twice crystallised to furnish *hexabenzo-18-crown-6* (13) (25 mg), m.p. 282—283°, $\nu_{max.}$ (KBr) 1 595, 1 579, 1 495, 1 450, 1 270, 1 240, and 752 cm^{-1}, $\lambda_{max.}$ 272 and 277.5 nm (ε 12 710 and 11 330), τ 3.18 (s, aromatic H), m/e 553 (39%), 552 (M^+, 100), 276 (7), 185 (2), and 184 (7) (Found: C, 77.9; H, 4.1. $C_{36}H_{24}O_6$ requires C, 78.2; H, 4.4%).

Heptabenzo[b,e,h,k,n,q,t][1,4,7,10,13,19]heptaoxacyclohen-eicosin (14).—T.l.c. of the crude product from the reaction of the hexameric diphenol (10) (860 mg) with o-dibromobenzene gave two non-polar fractions. The more polar (52 mg) was twice crystallised to furnish *heptabenzo-21-crown-7* (14) (16 mg), m.p. 198—200°, $\nu_{max.}$ (KBr) 1 581, 1 495, 1 450, 1 260, 1 230, and 735 cm^{-1}, $\lambda_{max.}$ 272 and 277 nm (ε 19 480 and 17 350), τ 3.18 (s, aromatic H), m/e 645 (52%), 644 (M^+, 100), 322 (27), 185 (16), 184 (52), and 124 (20) (Found: C, 77.8; H, 4.7. $C_{42}H_{28}O_7$ requires C, 78.2; H, 4.4%).

Dibenzodioxin.—The acidified reaction mixture from the copper(I) chloride–pyridine-catalysed self-condensation of o-bromophenol (1.5 g) was extracted with n-hexane. The crude product (330 mg) was crystallised to give dibenzodioxin (140 mg), m.p. 118.5° (lit.,[4] 119°), $\nu_{max.}$ (KBr) 1 590, 1 500, 1 300, 1 285, and 745 cm^{-1}, $\lambda_{max.}$ 289 nm (ε 3 841), τ 3.15 (s, aromatic H), m/e 185 (26%), 184 (M^+, 100), 155 (12), 154 (23), 128 (100), 127 (35), and 101 (47) (Found: C, 78.3; H, 4.55. Calc. for $C_{12}H_8O_2$; C, 78.25; H, 4.4%). A further 74 mg of pure dibenzodioxin was obtained by t.l.c. of the mother liquors.

Attempted Complex Formation of the Crown Compounds (13) *and* (14).—The crown compound in dichloromethane (7×10^{-5}M; 4.0 ml), aqueous picric acid (14×10^{-5}M; 2.0 ml), and an aqueous solution of the salt (0.2M; 2.0 ml) were mixed for 10 s with a vortex mixer and the phases were separated by centrifugation. The light absorption of the aqueous phase was measured at 353 nm, that of the organic phase at 359 nm. The salts used were LiCl, NaCl, KCl, CaCl$_2$, and (NH$_4$)$_2$SO$_4$. None formed a complex with either crown compound as judged by the absence of a light-absorbing entity in the organic phase.