

New Phenol-containing Bis(azacrown ether)s: Synthesis and Complexing Properties

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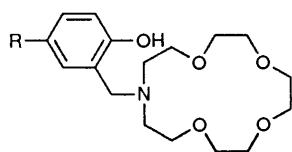
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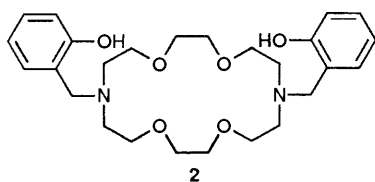
A simple synthesis of phenol-containing bis(azacrown ether)s by the treatment of *N*-methoxymethyl-substituted azacrowns with phenols has been elaborated. Temperature conditions have been found for selectively introducing into one phenolic ring both one and two monoazacrown ether substituents. New symmetric **14a–e** and asymmetric **15** phenol-bridged bis(azacrown ether)s exhibited strong complexation abilities towards both alkali and especially alkaline-earth metal cations. All measurements have been carried out using the pH-metric titration technique. Complexation constant values in neutral (K_1) and in alkaline (K_2) media are in the order: monocyclic **1b–d** < bicyclic ligands **14a–c**. In all cases, $K_2 > K_1$. These results show participation of phenolic ions in the complex formation process. In an alkaline medium, bis(azacrown ether)s **14b**, **14e** and **14d** showed high selectivity towards Li^+ , Ba^{+2} and Sr^{+2} , respectively.

Phenol-containing azacrown ethers are effective complexing agents for transfer of metal cations from an aqueous to an organic phase.^{1,2} In some cases, they also display high selectivity and can be used for spectrophotometric determinations of alkali and alkaline-earth metal cations.^{3–5}

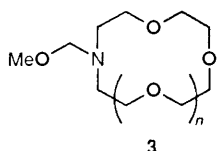
Earlier, we proposed a new method for the synthesis of the azacrown ethers **1a–d** and **2** bearing phenolic side-arms.⁶ The method is based on a special Mannich reaction using *N*-methoxymethylazacrown ethers **3b**, and **4** as reagents.



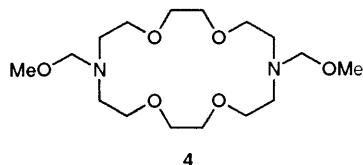
- 1**
 a R = H
 b R = Me
 c R = CHO
 d R = NO₂



2



- 3**
 a n = 1
 b n = 2
 c n = 3



4

It is known that bis(crown ether)s have different metal-ion complexation properties from their mononuclear analogues, often being more effective complexing agents.^{7,8} In this research, we used the aminomethylation of phenols for the synthesis of new bis(azacrown ether)s and studied their complexation abilities in relation to the medium, size of the

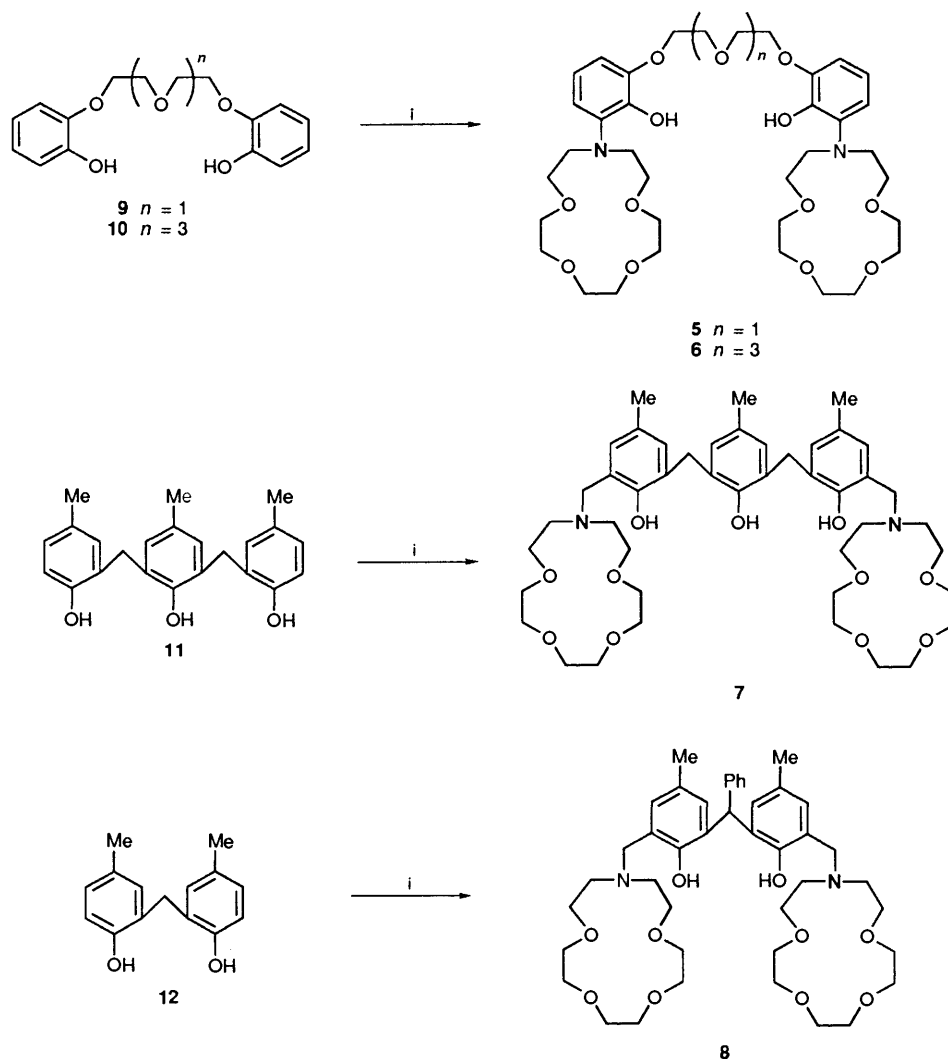
macrocyclic rings and type of substituent in the *para*-position of the phenol ring.

Results and Discussion

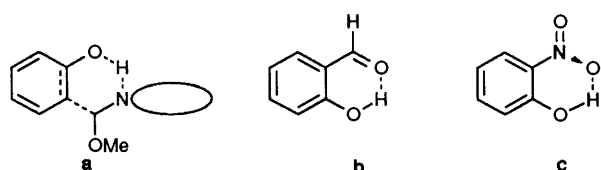
The bis(azacrown ether)s **5–8** were obtained by treatment of the appropriate phenols **9–12** with *N*-methoxymethylmonoaza-15-crown-5 **3b** (2 mol equiv.) in refluxing benzene as shown in Scheme 1. This method allows the preparation of bis(azacrown ether)s **5** and **6** without substituents in the *para*-position of the phenolic ring and with different species linking the azacrown units. The free *para*-position can be functionalized by chromophores.^{5,9} In our opinion, this is a good way for the synthesis of new extraction reagents containing chromogenic groups.

The preparation of *ortho*-aminomethylated phenols **5, 6** with free *para*-positions is typical of many described examples of the Mannich reaction.¹⁰ Evidently, a six-member transition state forms, **a** in most cases of aminomethylation of phenols. This *ortho*-attack is also typical for the preparation of polycyclic phenol-containing compounds.^{6,11} The necessity of phenolic proton participation in this reaction is supported by the inactivity of salicylaldehyde, **b**, and *o*-nitrophenol, **c**, toward aminomethylation with *N*-methoxymethylmorpholine or *N*-methoxymethylmonoaza-15-crown-5 in refluxing benzene. Probably, hydrogen bonding between the OH group and groups in the *ortho*-position of the last mentioned phenols prevents the aminomethyl substituents from being introduced because *p*-hydroxybenzaldehyde and *p*-nitrophenol give substitution products **1c** and **1d** in good yields.⁶

We failed to introduce two monoazacrown ether substituents on to one phenolic ring by aminomethylation of *para*-substituted phenols in benzene at 80 °C. However, symmetric bis(azacrown ether)s **14a–e** were prepared using refluxing xylene as the solvent (Scheme 2). Aminomethylation also allowed the preparation of asymmetric binuclear ligands by a two-step reaction of the appropriate phenol at 80 °C and then at 144 °C. The interaction of equivalent amounts of *p*-cresol with *N*-methoxymethyl-substituted azacrowns in CCl₄ at 80 °C gave monoaminomethylation products **17, 18**. Another aminomethyl substituent can be introduced into the phenolic ring at a higher temperature. The sequence of introducing substituents does not change the overall yield and purity of the final compounds. This

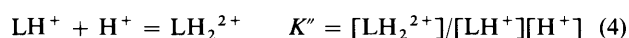
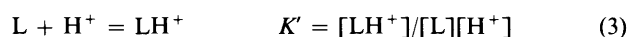
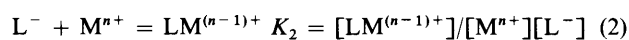
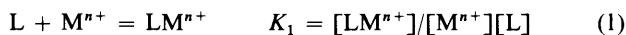


Scheme 1 Reagents and conditions: i, **3b**, C₆H₆, 80 °C, 14 h

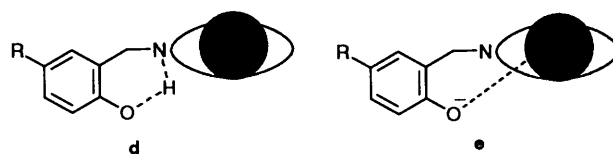


approach is convenient for the design of macrocyclic structures like **15** and **16a–b**. Alkylation of azacrown ethers by protected hydroxybenzyl halides allows only symmetric ligands.¹² More important, aminomethylation does not require protection for the phenolic OH group and allows the preparation of phenol-containing mono- and bis-(monoazacrown ether)s with different electron donor and electron acceptor substituents in the *para*-position of the connecting phenol.

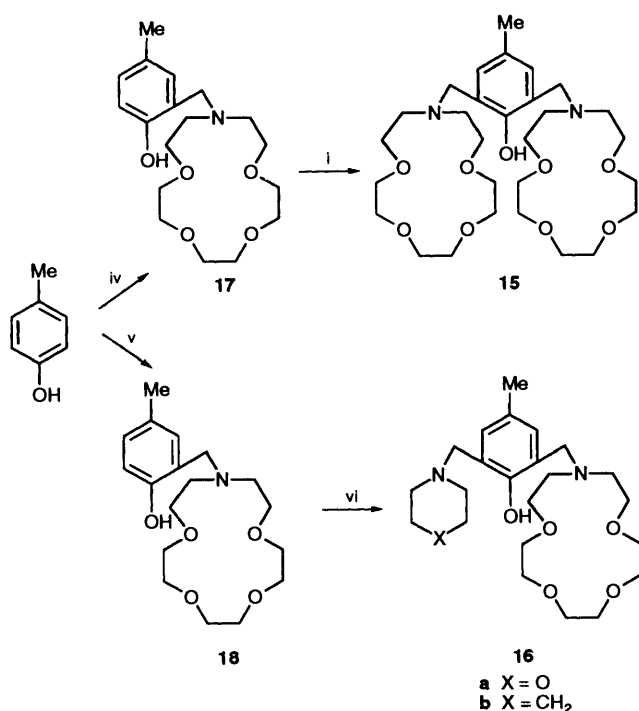
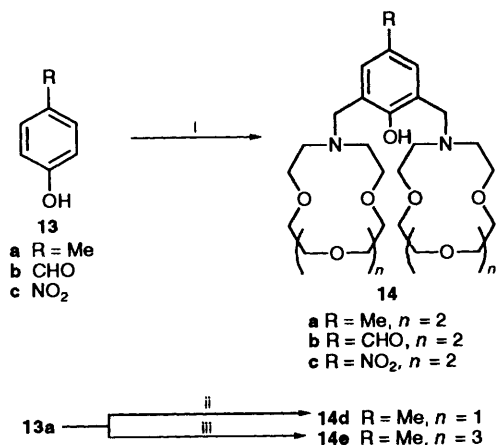
Complexing Properties.—We studied the complexing properties of monoazacrown ethers **1b–d** and **16a** and bis(azacrown ether)s **14a–e** and **15**. Determination of constants K_1 , K_2 , K' and K'' was carried out by the pH-metric titration technique in 95% aqueous methanol. Equations (1) and (2) describe complex formation in neutral and alkaline media, respectively. Protonation–deprotonation processes of the tested compounds are expressed by eqns. (3) and (4).



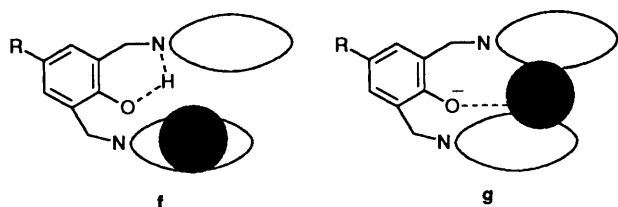
Evidently, the existence of monocyclic azacrown ethers **1b–d** in a betaine form,¹³ **d**, is the reason for the extremely low interaction of **1b–d** with alkali and alkaline-earth metal cations in a neutral medium. The [L⁻] forms of **1c** and **1d** form more stable complexes as compared with [L] and *N*-methylmonoaza-15-crown-5 (Table 1). This indicates the participation of phenolate ion, **e**, in the complexation process.



The [L] form of bis(azacrown ether)s **14a–e** and **15** has the azacrown ring in the betaine and the free form, **f**. Non-protonated azacrowns can interact with cations effectively, therefore, K_1 values of **14a–e** and **15** are considerably higher than the same values for **1b–d**. The conversion of **14a–e** and **15** from the [L] to the [L⁻] form in alkaline medium results in



Scheme 2 Reagents and conditions: i, **3b**, xylene, 144 °C, 12 h, N₂; ii, **3a**, xylene, 144 °C, 12 h, N₂; iii, **3c**, xylene, 144 °C, 12 h, N₂; iv, **3a**, CCl₄, 80 °C, 8 h; v, **3b**, CCl₄, 80 °C, 8 h; vi, MeOCH₂NCH₂CH₂XCH₂CH₂, 144 °C, 12 h, N₂



an increase in complex formation constants especially for the complexes of **14a–e** and **15** with the alkaline-earth metal cations. Moreover, K_2 for **14b** > K_2 for **1c** and K_2 for **14c** > K_2 for **1d**. Probably, these facts are connected with the complexation of a cation by two azacrown rings, **g**.

The nature of the substituent in the *para*-position of the phenol exerts an influence on the interaction of **14a–c** with the cations. The basicity of the nitrogen atoms and the acidity of the phenolic group changes depend on the type of substituent in the phenolic rings of **14a–c**. The divalent alkaline-earth cations, which are hard electrophiles, interact effectively with the

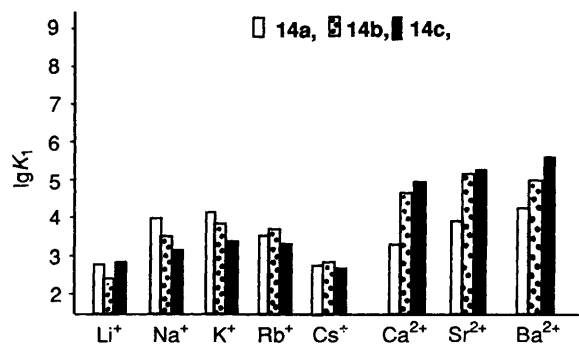


Fig. 1 The dependence of $\lg K_1$ values for the interaction of bis(azacrown ether)s with cations on the nature of the phenolic substituent in neutral medium (K_1 in dm³ mol⁻¹)

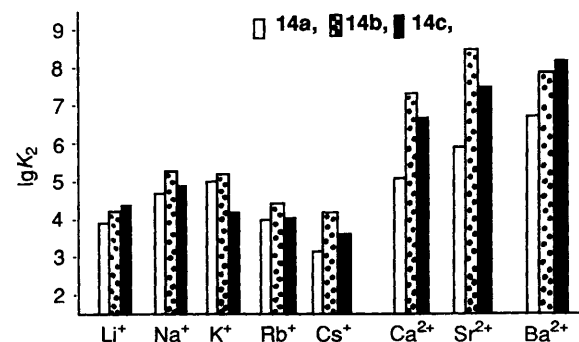


Fig. 2 The dependence of $\lg K_2$ values for the interaction of bis(azacrown ether)s with cations on the nature of the phenolic substituent in alkaline medium (K_2 in dm³ mol⁻¹)

phenolic OH group in neutral media. The more acidic phenolic group allows a greater interaction so that $K_1(\mathbf{14c}) > K_1(\mathbf{14b}) > K_1(\mathbf{14a})$ (see Fig. 1). It is assumed that the alkaline-earth cations deprotonate the phenolic group under the studied conditions.

For the mono charged cations, the basicity of the azacrown nitrogen atoms seems to play a major role in complexation. In this case, electron donor-substituted ligand **14a** forms stronger complexes. Thus, in general, for the alkali-metal ions, $K_1(\mathbf{14a}) > K_1(\mathbf{14b}) > K_1(\mathbf{14c})$ —the opposite order as compared to the alkaline-earth cations mentioned above (see Fig. 1).

The dependence of the K_2 values on the nature of the substituent also takes place. The values of K_2 are larger than those of K_1 for all tested ligands. This indicates the contribution to complexation by the phenolate ion. The increase of this contribution in basic media is especially demonstrated by the interactions of **14a–c** with the alkali metal cations (see Fig. 1 and Fig. 2). It is interesting that K_2 values for **14b** are larger than K_2 values for **14a** and **14c**. One might expect that **14a**, with the most electron-donating substituent, would always form the most stable complex in basic media. The fact that this is not the case may be due to strong solvent effects by the phenolate anion. The same order of the complexation abilities occurs for the phenol-containing monoazacrowns so $K_2(\mathbf{1c}) > K_2(\mathbf{1d})$ (Table 1).

The usual dependence of K_1 values on crown ring size is observed. Compounds **14d** and **14e** mainly interact with Li⁺ and K⁺, respectively (Table 1). In general, the same dependence is observed for the K_2 values. However, bis(azacrown ether) **14e** exhibits K⁺ > Rb⁺ selectivity in neutral media and Rb⁺ > K⁺ selectivity in an alkaline one. Compound **14d** formed strong complexes with Li⁺ in neutral or basic media and had considerable Li⁺ over Na⁺ selectivity. Ligands **14e** and **14b** in basic media formed strong complexes with Ba²⁺ and Sr²⁺, respectively.

Table 1 Protonation and stability constants (log K ; K in $\text{dm}^3 \text{mol}^{-1}$) for the complexation of alkali and alkaline earth metal cations by ligands **1b–d**, **14a–e**, **15**, **16a** in 95% methanol at 25 °C.

Ligand	K'	K''		Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
1b	8.00	—	K_1	<2	<2	<2	<2	<2	<2	<2	<2
			K_2	—	—	—	—	—	—	—	—
1c	7.20	—	K_1	<2	2.14	<2	<2	<2	<2	<2	<2
			K_2	3.94	4.65	4.17	3.62	4.02	6.84	7.47	6.90
1d	6.80	—	K_1	<2	<2	<2	<2	<2	<2	<2	<2
			K_2	1.94	3.67	3.88	3.46	—	6.18	6.20	6.23
14a	8.82	4.68	K_1	2.88	4.00	4.09	3.60	2.98	3.33	3.90	4.23
			K_2	3.99	4.60	4.82	4.10	3.20	5.02	5.90	6.69
14b	8.43	2.97	K_1	2.59	3.56	3.79	3.66	3.03	4.76	5.30	4.84
			K_2	4.40	5.29	5.15	4.33	4.19	7.38	8.54	7.95
14c	8.31	2.99	K_1	3.05	3.35	3.43	3.41	2.87	5.03	5.33	5.51
			K_2	4.44	4.74	4.19	4.09	3.66	6.71	7.67	8.23
14d	9.20	5.60	K_1	3.65	2.95	2.01	3.36	2.41	3.69	3.56	3.08
			K_2	4.77	2.81	2.00	3.35	2.90	5.72	5.64	6.47
14e	9.30	5.21	K_1	<2	3.15	4.45	3.99	2.94	3.96	5.25	5.39
			K_2	2.03	3.34	4.81	6.19	5.23	6.17	7.78	9.08
15	9.20	5.71	K_1	2.36	3.76	3.50	3.64	3.02	<2	4.29	4.60
			K_2	2.57	4.71	4.66	5.17	3.54	6.30	6.96	7.34
16a	8.55	7.05	K_1	<2	2.44	2.66	2.94	2.54	<2	4.11	4.43
			K_2	—	4.11	3.83	4.03	3.87	5.84	6.34	7.28
$\text{CH}_3\text{A15C5}^a$	—	—	K^*	<2	3.41	2.90	—	—	3.24	3.63	—

^a *N*-Methylmonoaza-15-crown-5. Data from ref. 14.

Experimental

The ^1H NMR spectra were recorded with Bruker AM 250 (250 MHz) and Tesla BS 497 (100 MHz) spectrometers in CDCl_3 with tetramethylsilane as an internal standard. Mass spectra were obtained on Varian MAT 112 and MX 1331 spectrometers with a direct-insertion probe at 70 and 12 eV. Elemental analyses were performed by the analytical laboratory of the A. V. Bogatsky Physico-Chemical Institute of the Ukrainian Academy of Sciences. The study of ligand complexation was carried out by the pH-metric titration method using the OP 208/1 (Radelkis) pH meter connected to a combined glass electrode OP0808P (Radelkis). Alkali and alkaline-earth metal chlorides of reagent grade were used. Measurement conditions and calculation techniques have been described.¹⁵ Starting materials and solvents were purchased from commercial sources where available. The phenols **9–12** were prepared by described procedures.^{16–19}

Preparation of *N*-Methoxyazacrown Ethers.—Compounds **3a** and **3c** were prepared in the same manner as reported for **3b**.²⁰

***N*-Methoxymethyl-1,7,10-trioxa-4-azacyclododecane 3a.** Oil (97%); δ_{H} 2.89 (4 H, t, J 6.1, CH_2N), 3.03 (3 H, s, OCH_3), 3.60 (12 H, m, CH_2O) and 4.07 (2 H, s, OCH_2N); m/z 219 (M^+) (Found: C, 54.7; H, 9.5; N, 6.4. $\text{C}_{10}\text{H}_{21}\text{NO}_4$ requires C, 54.79; H, 9.59; N, 6.39%).

***N*-Methoxymethyl-1,7,10,13,16-pentaoxa-4-azacyclooctadecane 3c.** Oil (98%); δ_{H} 2.90 (4 H, t, J 6.1, CH_2N), 3.03 (3 H, s, OCH_3), 3.61 (20 H, m, CH_2O) and 4.07 (2 H, s, OCH_2N); m/z 307 (M^+) (Found: C, 54.8; H, 9.7; N, 4.5. $\text{C}_{14}\text{H}_{29}\text{NO}_6$ requires C, 54.72; H, 9.55; N, 4.56%).

Synthesis of Monoazacrown Ethers.—Compounds **17** and **18**⁶ were obtained by the reported method.

1-Hydroxy-4-methyl-2-[(1',7',10'-trioxa-4'-azacyclododecan-4'-yl)methyl]benzene 17. Oil (79%); δ_{H} 2.02 (3 H, s, ArCH_3), 2.71 (4 H, t, J 5.5, NCH_2), 3.40–3.73 (14 H, m, CH_2O , NCH_2Ar) and 6.42–6.80 (3 H, m, ArH); m/z 295 (M^+) (Found: C, 65.1; H, 8.4; N, 4.7. $\text{C}_{16}\text{H}_{25}\text{NO}_4$ requires C, 65.08; H, 8.47; N, 4.75%).

General Procedure for the Preparation of Bis(monoazacrown ether)s 5–8.—A solution of *N*-methoxymethylmonoaza-15-crown-5 **3b** (2 mmol) in dry benzene (30 cm^3) was refluxed with

the appropriate phenol (1 mmol) for 14 h. After removing the benzene at reduced pressure from the reaction mixture, the final product was purified by column chromatography on neutral aluminium oxide using chloroform–benzene (1:2 v/v) and then chloroform–benzene (1:1 v/v).

1,7-Bis{2'-hydroxy-3'-[(1'',7'',10'',13''-tetraoxa-4''-azacyclo-pentadecan-4''-yl)methyl]phenyl}-1,4,7-trioxaheptane 5. Heavy oil (34%); δ_{H} 2.83 (8 H, t, J 5.8, NCH_2), 3.58–3.74 (32 H, m, CH_2O), 3.80 (4 H, s, ArCH_2N), 3.95 (4 H, t, J 6.4, CH_2O), 4.21 (4 H, t, J 5.7, ArOCH_2) and 6.60–6.91 (6 H, m, ArH); m/z 676 (M^+) (Found: C, 72.8; H, 8.9; N, 4.1. $\text{C}_{36}\text{H}_{60}\text{N}_2\text{O}_{13}$ requires C, 72.78; H, 8.87; N, 4.14%).

1,13-Bis{2'-hydroxy-3'-[(1'',7'',10'',13''-tetraoxa-4''-azacyclo-pentadecan-4''-yl)methyl]phenyl}-1,4,7,10,13-pentaoxatridecane 6. Heavy oil (32%); δ_{H} 2.83 (8 H, t, J 5.7, NCH_2), 3.60–3.76 (40 H, m, CH_2O), 3.81 (4 H, s, ArCH_2N), 3.89 (4 H, t, J 6.2, CH_2O), 4.19 (4 H, t, J 5.9, ArOCH_2) and 6.61–6.85 (6 H, m, ArH); m/z 764 (M^+) (Found: C, 62.8; H, 8.9; N, 3.7. $\text{C}_{40}\text{H}_{68}\text{N}_2\text{O}_{15}$ requires C, 62.83; H, 8.90; N, 3.66%).

2,6-Bis{2'-hydroxy-3'-[(1'',7'',10'',13''-tetraoxa-4''-azacyclo-pentadecan-4''-yl)methyl]-5'-methylbenzyl}-4-methylphenol 7. Heavy oil (75%); δ_{H} 1.93 (9 H, s, ArCH_3), 2.60 (8 H, t, J 5.8, NCH_2), 3.32–3.78 (40 H, m, ArCH_2N , ArCH_2Ar , CH_2O), 6.31–6.65 (6 H, m, ArH) and 6.65 (3 H, br s, OH); m/z 810 (M^+) (Found: C, 66.7; H, 8.1; N, 3.4. $\text{C}_{45}\text{H}_{66}\text{N}_2\text{O}_{11}$ requires C, 66.66; H, 8.14; N, 3.45%).

α -Bis{2'-hydroxy-3'-[(1'',7'',10'',13''-tetraoxa-4''-azacyclo-pentadecan-4''-yl)methyl]phenyl}toluene 8. Heavy oil (78%); δ_{H} 2.13 (6 H, s, ArCH_3), 2.78 (8 H, t, J 5.6, NCH_2), 3.42–3.80 (36 H, m, CH_2O , ArCH_2N), 6.19 (1 H, s, CHPh) and 6.48–7.27 (9 H, m, ArH); m/z 766 (M^+) (Found: C, 67.4; H, 8.1; N, 3.7. $\text{C}_{43}\text{H}_{62}\text{N}_2\text{O}_{10}$ requires C, 67.36; H, 8.09; N, 3.65%).

General Procedure for the Preparation of Symmetric Bis(monoazacrown ether)s 14a–e.—A solution of *N*-methoxymethylmonoazacrown ether (4 mmol) in dry xylene (30 cm^3) was refluxed with the appropriate *para*-substituted phenol (2 mmol) for 12 h under nitrogen. After removing the xylene at reduced pressure from the mixture, the final products were purified by column chromatography on neutral aluminium oxide using chloroform–benzene (1:1 v/v) and then chloroform–benzene (2:1 v/v).

2,6-Bis[(1',7',10',13'-tetraoxa-4'-azacyclopentadecan-4'-yl)methyl]-4-methylphenol **14a**. Oil (38%); δ_{H} 2.01 (3 H, s, CH₃Ar), 2.71 (8 H, t, *J* 5.5, NCH₂), 3.40–3.77 (36 H, m, CH₂O, ArCH₂N) and 6.67 (2 H, s, ArH); *m/z* 570 (M⁺) (Found: C, 61.0; H, 8.8; N, 4.9. C₂₉H₅₀N₂O₉ requires C, 61.05; H, 8.77; N, 4.91%).

2,6-Bis[(1',7',10',13'-tetraoxa-4'-azacyclopentadecan-4'-yl)methyl]-4-formylphenol **14b**. Oil (47.3%); δ_{H} 2.78 (8 H, t, *J* 5.8, NCH₂), 3.44–3.80 (36 H, m, CH₂O, ArCH₂), 7.46 (2 H, s, ArH) and 9.68 (1 H, s, HCO); *m/z* 584 (M⁺) (Found: C, 59.6; H, 8.3; N, 4.8. C₂₉H₄₈N₂O₁₀ requires C, 59.59; H, 8.2; N, 4.79%).

2,6-Bis[(1',7',10',13'-tetraoxa-4'-azacyclopentadecan-4'-yl)methyl]-4-nitrophenol **14c**. Oil (24%); δ_{H} 3.02 (8 H, t, *J* 6.2, NCH₂), 3.95–4.48 (36 H, m, CH₂O, ArCH₂), 8.61 (2 H, s, ArH) and 9.76 (1 H, br s, OH); *m/z* 601 (M⁺) (Found: C, 58.0; H, 7.8; N, 7.1. C₂₈H₄₇N₃O₁₁ requires C, 57.90; H, 7.82; N, 6.99%).

2,6-Bis[(1',7',10',13'-trioxa-4'-azacyclododecan-4'-yl)methyl]-4-methylphenol **14d**. Oil (57%); δ_{H} 2.03 (3 H, s, CH₃Ar), 2.69 (8 H, t, *J* 5.6, NCH₂), 3.42–3.75 (28 H, m, CH₂O, ArCH₂N) and 6.70 (2 H, s, ArH); *m/z* 482 (M⁺) (Found: C, 62.15; H, 8.7; N, 5.7. C₂₅H₄₂N₂O₇ requires C, 62.24; H, 8.71; N, 5.81%).

2,6-Bis[(1',7',10',13',16'-pentaoxa-4'-azacyclooctadecan-4'-yl)methyl]-4-methylphenol **14e**. Oil (31%); δ_{H} 2.01 (3 H, s, CH₃Ar), 2.79 (8 H, t, *J* 5.7, NCH₂), 3.45–3.81 (44 H, m, CH₂O, ArCH₂N) and 6.80 (2 H, s, ArH); *m/z* 658 (M⁺) (Found: C, 60.3; H, 8.8; N, 4.2. C₃₃H₅₈N₂O₁₁ requires C, 60.18; H, 8.81; N, 4.26%).

General Procedure for the Preparation of Asymmetric Ligands 15, 16a, b.—Compounds **17** or **18** (2 mmol) were refluxed in dry xylene (30 cm³) with the appropriate *N*-methoxymethylamine (2 mmol) for 12 h under nitrogen. The final products were purified as described above for **14a–e**.

4-Methyl-2-[(1',7',10',13'-tetraoxa-4'-azacyclopentadecan-4'-yl)methyl]-6-[(1',7',10'-trioxa-4'-azacyclododecan-4'-yl)methyl]phenol **15**. Oil (69%); δ_{H} 2.01 (3 H, s, CH₃Ar), 2.70 (8 H, t, *J* 5.6, NCH₂), 3.43–3.72 (32 H, m, CH₂O, ArCH₂N) and 6.68 (2 H, s, ArH); *m/z* 526 (M⁺) (Found: C, 61.7; H, 8.8; N, 5.4. C₂₇H₄₆N₂O₈ requires C, 61.60; H, 8.85; N, 5.32%).

4-Methyl-2-(morpholinomethyl)-6-[(1',7',10',13'-tetraoxa-4'-azacyclopentadecan-4'-yl)methyl]phenol **16a**. Oil (52%); δ_{H} 2.03 (3 H, s, ArCH₃), 2.27–2.47 (4 H, m, CH₂N), 2.70 (4 H, t, *J* 5.6, CH₂N), 3.40–3.76 (24 H, m, CH₂O, CH₂NAr), 6.62 (1 H, s, ArH) and 6.73 (1 H, s, ArH); *m/z* 438 (M⁺) (Found: C, 63.1; H, 8.7; N, 6.4. C₂₃H₃₈N₂O₆ requires C, 63.01; H, 8.68; N, 6.39%).

4-Methyl-2-(piperidinomethyl)-6-[(1',7',10',13'-tetraoxa-4'-azacyclopentadecan-4'-yl)methyl]phenol **16b**. Oil (64%); δ_{H}

1.08–1.68 (6 H, m, CH₂), 2.08 (3 H, s, ArCH₃), 2.36–2.49 (4 H, m, CH₂N), 2.73 (4 H, t, *J* 5.6, CH₂N), 3.48–3.71 (20 H, m, CH₂O, NCH₂Ar), 6.74 (1 H, s, ArH) and 6.78 (1 H, s, ArH); *m/z* 436 (M⁺) (Found: C, 66.1; H, 9.3; N, 6.4. C₂₄H₄₀N₂O₅ requires C, 66.06; H, 9.17; N, 6.42%).

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