Two Series of Aza Macrocycles containing the Phenyldinaphthomethane Subunit (a three bladed propeller); Crystal Structures and Dynamic NMR Spectroscopy

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Two new series of azapropeller crowns have been synthesised and investigated. The aza-propeller crowns 7,10-ditosylaza-1,4,13,16-tetraoxacyclooctadecane, (**9a**) and 4,7,10-tritosylaza-1,13-dioxacyclopentadecane, (**11**) have been shown by X-ray structure determination to have the propeller conformation matching that of the common isomer found previously in the polyether propeller crowns **1**. The *N*-tosyl substituents, used as a probe of the movement of attached ring segments on the macrocyclic ring, rendered observable (in ^1H NMR studies) the flipping of these segments, for which the calculated free energy of activation was typical of that for an unsubstituted propeller, $\Delta G^{\ddagger}_{217} = 10.54$ kcal mol^{-1}† at the coalescence temperature for **9a**, $\Delta G^{\ddagger}_{215} = 10.74$ kcal mol^{-1} for the analogous ring compound **10** with one additional methylene residue, and $\Delta G^{\ddagger} = 12.5 \pm 0.4$ kcal mol^{-1} (at 230–240 K) for the tritosyl compound **11**. These results and other NMR data show that the relatively slow switch of the propeller is the movement which mainly controls the observable process. Successful detosylation of **9a** is reported. Two examples of a second series of propeller crowns having amide links in the macrocyclic ring have been prepared by two routes. Their selectivity for transport of silver and lead cations is described.

The propeller crowns, **1**, with suitable NMR labels, have proved useful as reporters of the fluxional state of crown ethers, giving detailed insight into the fluxionality of the free ligand,[1] its role in complexation–decomplexation reactions, and the kinetic origin of selectivity.[2] Earlier studies of a range of simple propeller crowns in which each end of a polyether strand was attached to one blade of a molecular propeller (a triarylmethane) ensured that the relatively slow switch of the propeller moiety controlled the movement of the ether ring. The crowns were divided arbitrarily into two categories, locked and mobile, depending on whether the room temperature configuration exhibited (on the NMR timescale) rapid symmetrisation of the two halves of the molecule, to right and left of the propeller methine (mobile propellers), or exhibited distinguishable spectra for the two sides of the polyether ring (locked propellers); the process by which the two halves of the ring became equivalent (symmetrisation) could readily be investigated by NMR methods. Appropriate substitution of the aryl rings rendered propeller crown ethers rigid (locked) on the NMR timescale at room temperature, while unsubstituted ones were mobile (symmetrised). The crown ether derivatives of the locked propellers were found to be more selective for alkali cations in transport and ISE measurements, than those of the mobile propellers.[3,4] As part of a programme to produce an expanded range of propeller-containing macrocycles, and exploit their reporting value in complexes with anions, and the transition and other metals which prefer nitrogen to oxygen as a donor, we report here two series of aza-propeller crowns. The first series was obtained with tosylated nitrogens following the route shown in Scheme 1 (or appropriate modifications) and analysed by X-ray structure determination and/or NMR methods. Detosylation to produce the free azacrowns in this series was also achieved. The second series, synthesised as in Schemes 2 and 3, incorporated amide links, and was investigated in three-phase transport studies of alkali, lead and silver cations.

Experimental

Tosylated polyamines **2–4** were prepared by the general method used by Hay and Norman.[5] Characterising details are shown in Tables 1 and 2. NMR spectra were obtained on a Bruker WP200, Bruker WM300WB, and Bruker AMX500 as specified later. *J*-Values are given in Hz. Mass spectra were obtained on a Kratos MS80.

Method A.—General preparation of polyamines with an hydroxyalkyl sidearm. Reaction of *N*,*N*′-ditosylethylenediamine **2** with 2-(2′-chloroethoxy)ethanol. A mixture of *N*,*N*′-ditosylethylenediamine (31.3 g, 0.085 mol) and potassium carbonate (23.6 g, 0.17 mol) in dry dimethylformamide (DMF) (750 cm^3) was left stirring at room temperature overnight. To this was added dropwise 2-(2′-chloroethoxy)ethanol (22.4 g, 0.17 mol) and the reaction mixture heated at 100 °C for 48 h. After cooling to room temperature the mixture was filtered and the DMF evaporated. The residue was dissolved in $CHCl_3$ (100 cm^3), washed with H_2O (2 × 100 cm^3), dried over $MgSO_4$ and evaporated to afford 46.9 g of crude product. Column chromatography (silica gel, ethyl acetate) afforded colourless crystals of **5a**, m.p. 92–93 °C (Found: C, 53.0; H, 6.6; N, 5.15; MH$^+$ 545; $C_{24}H_{36}N_2O_8S_2$ requires C, 52.9; H, 6.7; N, 5.1%; *M*, 544.1913). By this method, compounds **6a** and **7a** were also made. Characterising details are shown in Tables 1 and 2.

Amines with a single arm. The partially substituted derivatives **5c–7c** were always obtained in Method A, and were automatically separated during the chromatography, eluting in advance of the required double-armed ligand. Characterising details are shown in Tables 1 and 2 (compounds **5c**, **6c** and **7c** respectively).

Method B.—General method of tosylating hydroxyalkyl sidearms. Reaction of **5a** with toluene-*p*-sulfonyl chloride. To **5a** (4.97 g, 0.0058 mol) in ice-cold dry pyridine (400 cm^3) was added tosyl chloride (3.52 g, 0.018 mol) in small portions ensuring the reaction mixture temperature did not exceed 5 °C. This solution was kept stirring in a cold room for 36 h. To the mixture was added 100 cm^3 of ice with 70 cm^3 concentrated

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† 1 cal. = 4.184 J.

Table 1 Analytical data for intermediates

Compound formula	M.p./°C	Mass spec observed	Observed (%)			Calculated (%)			Calculated mass
			C	H	N	C	H	N	
2 $C_{16}H_{20}N_2O_4S_2$	161–163	369, MH^+	52.1	5.4	7.5	52.2	5.5	7.6	368.0861
3 $C_{17}H_{22}N_2O_4S_2$	150–152	383, MH^+	53.6	5.8	7.3	53.4	5.8	7.3	382.1021
4 $C_{25}H_{31}N_3O_6S_3$	177–179	566, MH^+	53.7	5.25	6.9	53.1	5.5	7.4	565.1375
5a $C_{24}H_{36}N_2O_8S_2$	92–93	545, MH^+	53.0	6.6	5.15	52.9	6.7	5.1	544.1913
5c $C_{20}H_{28}N_2O_6S_2$	95–99	457, MH^+	52.6	6.1	6.1	52.6	6.2	6.1	456.139
6a $C_{25}H_{38}N_2O_8S_2$	oil	559, MH^+							558.2069
6c $C_{21}H_{30}N_2O_6S_2$	63–67	471, MH^+	53.6	6.45	5.9	53.6	6.4	5.95	470.1545
7a $C_{29}H_{39}N_3O_8S_3$	116–118	654, MH^+	53.3	6.0	6.4	53.3	6.0	6.4	653.1899
7c $C_{27}H_{35}N_3O_7S_3$	102–104	610, MH^+	53.3	5.75	6.9	53.2	5.8	6.9	609.1637
5b $C_{38}H_{48}N_2O_{12}S_4$	73–80	853, MH^+	53.7	5.6	3.4	53.5	5.7	3.3	852.2090
6b $C_{39}H_{50}N_2O_{12}S_4$	oil	867, MH^+							866.2247
7b $C_{43}H_{51}N_3O_{12}S_5$	159–161	962, MH^+	54.0	5.4	4.4	53.7	5.3	4.4	961.2076

HCl. The resulting mixture was then extracted into chloroform, dried over magnesium sulfate and evaporated to afford 5.37 g of crude product. Column chromatography (silica gel, eluent ethyl acetate–petroleum ether 7 : 3) afforded the desired product **5b** as colourless crystals, m.p. 73–80 °C (Found: C, 53.7; H, 5.6; N, 3.35; MH^+ 853. $C_{38}H_{48}N_2O_{12}S_4$ requires C, 53.5; H, 5.7; N, 3.3%; *M*, 852.2090).

Method C.—General method of synthesis of propeller azacrowns. Synthesis of azacrown **9a**. To a solution of benzylidine binaphthol, **8** (1.62 g, 0.0042 mol) in dry nitrogen-purged tetrahydrofuran (THF) (400 cm^3) was added NaH (0.36 g, 0.015 mol). This mixture was kept at gentle reflux for 2 h, after which a solution of toluene-*p*-sulfonate **5b** (3.61 g, 0.0042 mol) in THF (100 cm^3) was added dropwise. The solution was refluxed gently for 48 h, and left stirring cold for a further 48 h. The reaction mixture was then filtered and the THF stripped off affording 5.41 g of crude product. Column chromatography (silica gel, ethyl acetate–petroleum ether; gradient elution) afforded the desired product as a white crystalline powder **9a** (the best yield was 0.84 g, 50%), m.p. 202–206 °C (Found: C, 69.3; H, 5.8; N, 3.1%; MH^+, 885. $C_{51}H_{52}N_2O_8S_2$ requires C, 69.2; H, 5.9; N, 3.2%; *M*, 884.3165); $\delta_H(CDCl_3)$ 7.78–6.91 (26 H, m, aromatic and methine), 3.29–3.50 (4 H, m, 2 × $ArOCH_2CH_2O$), [3.15–3.27 (8 H, m), 3.10–3.13 (4 H, m), 3.00–3.06 (2 H, m), all macrocycle CH_2] 2.68–2.99 (2 H, m) $CH_2CH_2OCH_2CH_2N$) and 2.35 (6 H, s, 2 × $ArCH_3$).

Synthesis of Crown **10**.—By a similar route, crown **10** was obtained (eluted from silica gel, with ethyl acetate–petroleum ether 6 : 4) as a pale yellow powder, yield 15%, m.p. 209–211 °C (Found: C, 68.4; H, 6.1; N, 2.85%; MH^+, 899. $C_{52}H_{54}N_2O_8S_2$ requires C, 69.5; H, 6.05; N, 3.1%; *M*, 898.3322); $\delta_H(CDCl_3)$ 1.71–1.74 (q, 2 H, $CH_2CH_2CH_2$), 2.38 (s, 6 H, 2 × $ArCH_3$), [2.75–2.91 (br, 2 H), 2.93–3.16 (2 × m, 10 H), 3.20–3.23 (m, 4 H), all macrocycle CH_2], 3.48–3.62 (br, 4 H, $ArOCH_2CH_2O$) and 6.96–7.77 (m, 26 H, aromatic + methine).

Preparation of Crown **11**.—A mixture of benzylidine binaphthol **8** (1.95 g, 0.0052 mol) and sodium hydride (0.57 g, 0.024 mol of an 80% oil suspension, washed in dry petroleum ether) in dry nitrogen-purged tetrahydrofuran (500 cm^3) was left stirring at gentle reflux for 2 h. It was necessary to give the hydride and binaphthol time to react to form a salt before the toluene-*p*-sulfonate was added in this reaction, otherwise a competing elimination reaction of the toluene-*p*-sulfonate (described below) occurred as well as the desired condensation. To the cooled mixture a solution of *O,O′,N,N′,N″*-pentatosyl *N,N″*-bis(hydroxyethyl) diethylenetriamine **7b** (5.0 g, 0.0052 mol) in THF (200 cm^3) was added dropwise, and the reaction carried out as in Method C, to give 5.61 g of crude product. The white crystalline crown **11** was isolated from a yellow oily chromatographic fraction, by treatment with acetone–dichloromethane. Yield 1.55 g, 30%, m.p. 191–193 °C (Found: C, 67.2; H, 5.5; N, 4.1%; MH^+, 994. $C_{56}H_{55}N_3O_8S_3$ requires C, 67.65; H, 5.6; N, 4.2%; *M*, 993.3151); $\delta_H(CDCl_3)$ 2.23 (s, 3 H, $ArCH_3$), 2.44 (s, 6 H, $ArCH_3$), 2.74–3.65 (br, 16 H, $OCH_2CH_2NCH_2CH_2N$) and 6.79–7.81 (m, 30 H, aromatic + methine).

Elimination Product **12** *Obtained during the Synthesis of* **11**.—During the work-up from one reaction, a second chromatographic fraction was obtained, which crystallised to a white powder, m.p. 140–141 °C (Found: C, 56.5; H, 5.7; N, 6.6%; MH^+, 618. $C_{29}H_{35}N_3O_6S_3$ requires C, 56.4; H, 5.7; N, 6.8%; *M*, 617.1688); $\delta_H(CDCl_3)$ 2.39 (s, 9 H, $ArCH_3$), [(3.22–3.29, m, 4 H) and 3.47–3.55 (m, 4 H) all NCH_2CH_2N], 4.30–4.50 (m, 4 H, $CH{=}CH_2$), 6.77–6.89 (m, 2 H, $CH{=}CH_2$) and 7.23–7.69 (m, 12 H, ArH).

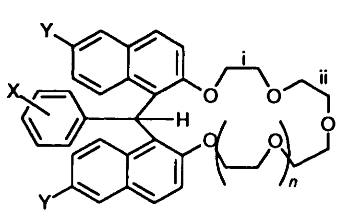
Detosylation[6] *of the Nitrogen Propellers*.—To a freshly prepared slurry of sodium amalgam (96 g Hg, 1.92 g Na) was added a mixture of dry acetonitrile and methanol (800 cm^3, 6 : 2) and the tosylated crown **9a** (2.0 g). No phosphate buffer was used in this reaction. The mixture was heated at gentle reflux under nitrogen for 24 h, with rapid stirring. At this stage a TLC run (10% methanol in dichloromethane) showed detosylation had occurred. Since several earlier attempts had also appeared successful at this stage, a fresh 2% amalgam was prepared and the reaction repeated at reflux for a further 24 h. After this second period, the mixture was cooled, and decanted from the excess mercury into water, the product was extracted into chloroform (4 × 30 cm^3); the chloroform extract was then dried

Table 2 NMR data for intermediates

Compound formula	Shifts/ppm (description of integral assignment)
2 $C_{16}H_{20}N_2O_4S_2$	2.30 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 2.71 (s, 4 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 7.34–7.60 (m, 8 H, $\mathrm{Ar}H$)
3 $C_{17}H_{22}N_2O_4S_2$	1.63–1.79 (q, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.41 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 2.93–3.04 (m, 4 H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$), 6.43 (br, 2 H, 2 × $\mathrm{N}H$), 7.41–7.80 (m, 8 H, $\mathrm{Ar}H$)
4 $C_{25}H_{31}N_3O_6S_3$	2.56 (s, 9 H, 3 × $\mathrm{ArC}H_3$), 3.18–3.22 (m, 4 H, 2 × $\mathrm{TsNCH_2C}H_2\mathrm{HNTs}$), 3.28–3.35 (m, 4 H, 2 × $\mathrm{TsNHCH_2C}H_2\mathrm{NTs}$), 6.74–6.77 (t, 2 H, 2 × $\mathrm{N}H$), 7.50–7.92 (m, 12 H, $\mathrm{Ar}H$)
5a $C_{24}H_{36}N_2O_8S_2$	2.44 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 3.00–3.05 (t, 2 H, 2 × $\mathrm{O}H$), 3.32–3.37 (t, 4 H, 2 × $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.46 (s, 4 H, 2 × $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.49–3.52 (t, 4 H, 2 × $\mathrm{OC}H_2\mathrm{CH_2N}$), 3.54–3.60 (t, 4 H, 2 × $\mathrm{OC}H_2\mathrm{CH_2OH}$), 3.61–3.67 (m, 4 H, 2 × $\mathrm{OCH_2C}H_2\mathrm{OH}$), 7.24–7.74 (m, 8 H, ArH)
5c $C_{20}H_{28}N_2O_6S_2$	2.39 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 2.92 (br, 1 H, $\mathrm{O}H$), 3.14–3.17 (m, 4 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.18–3.24 (t, 2 H, $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.54–3.58 (m, 2 H, $\mathrm{OC}H_2\mathrm{CH_2N}$), 3.65–3.70 (t, 2 H, $\mathrm{OC}H_2\mathrm{CH_2OH}$), 3.73–3.77 (m, 2 H, $\mathrm{OCH_2C}H_2\mathrm{OH}$), 7.24–7.74 (m, 8 H, $\mathrm{Ar}H$)
6a $C_{25}H_{38}N_2O_8S_2$	1.81–1.95 (q, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.34 (s, 6 H, 2 × $\mathrm{ArCH_3}$), 3.08–3.15 (t, 4 H, 2 × $\mathrm{TsNC}H_2\mathrm{CH_2CH_2}$), 3.20–3.25 (t, 4 H, 2 × $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.41–3.43 (t, 4 H, 2 × $\mathrm{OC}H_2\mathrm{CH_2N}$), 3.50–3.60 (m, 4 H, 2 × $\mathrm{OC}H_2\mathrm{CH_2OH}$), 3.60–3.76 (m, 4 H, 2 × $\mathrm{OCH_2C}H_2\mathrm{OH}$), 7.21–7.66 (m, 8 H, $\mathrm{Ar}H$)
6c $C_{21}H_{30}N_2O_6S_2$	1.65–1.77 (q, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.32 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 2.85–2.94 (m, 2 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{NTs}$), 3.03–3.10 (t, 2 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2NTs}$), 3.12–3.18 (t, 2 H, $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.36–3.39 (t, 2 H, $\mathrm{OC}H_2\mathrm{CH_2N}$), 3.41–3.50 (t, 2 H, $\mathrm{HOCH_2C}H_2\mathrm{O}$), 3.58–3.60 (m, 2 H, $\mathrm{HOC}H_2\mathrm{CH_2O}$), 5.87–5.93 (t, 1 H, $\mathrm{N}H$), 7.18–7.68 (m, 8 H, $\mathrm{Ar}H$)
7a $C_{29}H_{39}N_3O_8S_3$	2.39 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 2.40 (s, 3 H, $\mathrm{ArC}H_3$), 2.40–2.47 (t, 2 H, 2 × $\mathrm{O}H$), 3.18–3.23 (t, 4 H, 2 × $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.30–3.51 (m, 8 H, 2 × $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.72–3.81 (m, 4 H, 2 × $\mathrm{OC}H_2\mathrm{CH_2N}$), 7.25–7.77 (m, 12 H, $\mathrm{Ar}H$)
7c $C_{27}H_{35}N_3O_7S_3$	2.37 (s, 3 H, $\mathrm{ArC}H_3$), 2.39 (s, 3 H, $\mathrm{ArC}H_3$), 2.40 (s, 3 H, $\mathrm{ArC}H_3$), 2.76 (br, 1 H, $\mathrm{O}H$), 3.15–3.23 (m, 6 H, $\mathrm{TsNC}H_2\mathrm{C}H_2\mathrm{N}$ + $\mathrm{OHCH_2C}H_2\mathrm{N}$), 3.31 (s, 4 H, $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.73–3.78 (m, 2 H, $\mathrm{OHC}H_2\mathrm{CH_2N}$), 5.67 (br, 1 H, $\mathrm{N}H$), 7.23–7.73 (m, 12 H, $\mathrm{Ar}H$)
5b $C_{38}H_{48}N_2O_{12}S_4$	2.43 (s, 12 H, 4 × $\mathrm{ArC}H_3$), 3.26–3.36 (t, 4 H, 2 × $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.37 (s, 4 H, 2 × $\mathrm{NC}H_2\mathrm{C}H_2\mathrm{N}$), 3.52–3.61 (m, 8 H, 2 × $\mathrm{C}H_2\mathrm{OC}H_2$), 4.07–4.12 (t, 4 H, 2 × $\mathrm{TsOC}H_2\mathrm{CH_2}$), 7.26–7.78 (m, 16 H, $\mathrm{Ar}H$)
6b $C_{39}H_{50}N_2O_{12}S_4$	1.79–1.98 (q, 2 H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.36 (s, 12 H, 4 × $\mathrm{ArC}H_3$), 3.10–3.29 (m, 8 H, 2 × $\mathrm{TsNC}H_2\mathrm{CH_2CH_2}$ + 2 × $\mathrm{OCH_2C}H_2\mathrm{N}$), 3.42–3.64 (m, 8 H, 2 × $\mathrm{C}H_2\mathrm{OC}H_2$), 4.01–4.05 (t, 2 H, $\mathrm{TsOC}H_2\mathrm{CH_2}$), 4.10–4.15 (t, 2 H, $\mathrm{TsOC}H_2\mathrm{CH_2}$), 7.22–7.76 (m, 16 H, $\mathrm{Ar}H$)
7b $C_{43}H_{51}N_3O_{12}S_5$	2.40 (s, 9 H, 3 × $\mathrm{ArC}H_3$), 2.44 (s, 6 H, 2 × $\mathrm{ArC}H_3$), 3.22 (s, 8 H, 4 × $\mathrm{TsNC}H_2$), 3.32–3.36 (t, 4 H, 2 × $\mathrm{TsOCH_2C}H_2\mathrm{N}$), 4.07–4.11 (t, 4 H, 2 × $\mathrm{TsOC}H_2\mathrm{CH_2N}$), 7.29–7.73 (m, 20 H, $\mathrm{Ar}H$)

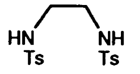
over $MgSO_4$, filtered and the chloroform removed *in vacuo* to yield a pale yellow oil. The oil was then dissolved in a small amount of dichloromethane and put in a crystallisation pot through which diethyl ether was allowed to diffuse slowly. After several days, white shell crystals of **9b** had started to form on the side of the tube, m.p. 189–191 °C (Found: C, 69.4; H, 6.7; N, 4.4%; MH^+, 576. $C_{37}H_{40}N_2O_4\cdot CH_2Cl_2$ requires C, 69.0; H, 6.4; N, 4.2%; *M*, 576.2988 without solvate); $\delta_H(\mathrm{CDCl_3})$ 7.78–7.75 (6 H, d, aromatic), 7.3–7.03 (12 H, m, aromatic), 5.4 (4 H, bs, –NH and CH_2Cl_2), 3.88 (2 H, bm, $\mathrm{ArOC}H_2\mathrm{CH_2}$), 3.60 (2 H, bm, $\mathrm{ArOC}H_2\mathrm{CH_2}$), 3.43–3.09 (6 H, 2 m, $\mathrm{C}H_2\mathrm{O}$) and 2.66–2.46 (10 H, several m, $\mathrm{C}H_2\mathrm{N}$); $\delta_C(\mathrm{CD_2Cl_2})$ 156.349, 145.701, 134.836, 130.679, 129.719, 129.325, 128.911, 126.731, 126.475, 126.408, 125.871, 124.034, 117.135 (aromatic), 70.605, 69.027, 68.395 ($\mathrm{O}C\mathrm{H_2}$), 47.980, 45.853 ($\mathrm{NH}C\mathrm{H_2}$) and 44.339 (methine *C*H).

Mass Spectra of the Tosylated Azacrowns.—In general, the



1

Ligand	X	Y	n
1a	3,4,5-(MeO)$_3$	H	1
1b	3,4,5-(MeO)$_3$	H	2



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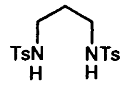

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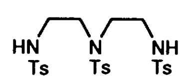

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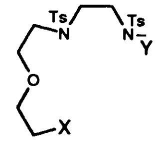

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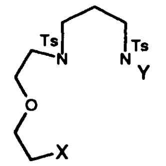

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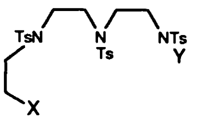
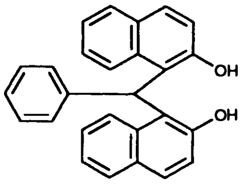


7

a, X = OH, Y = $CH_2CH_2OCH_2CH_2OH$
b, X = OTs, Y = $CH_2CH_2OCH_2CH_2OTs$
c, X = OH, Y = H



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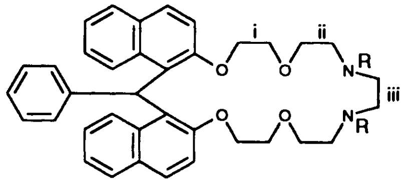
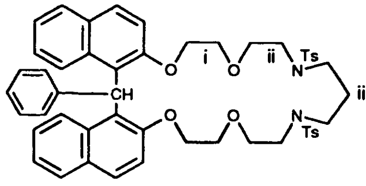


9

a, R = Ts; b, R = H



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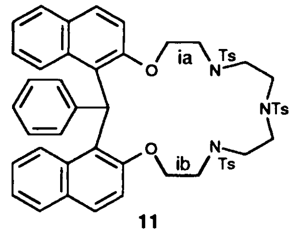

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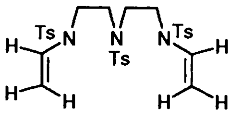
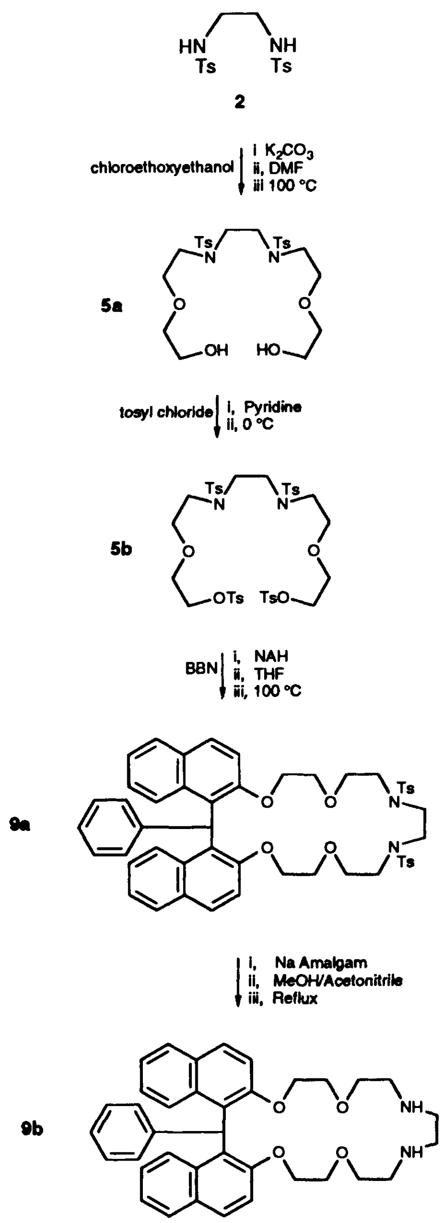


12

azacrowns showed both the $(M + 1)^+$ ion, and a parent ion of very low abundance. Most of the fragment ions were low mass toluene-*p*-sulfonate fragment ions. Major breakdown products appeared to be from loss of tosyl groups, and the fragments earlier[7] suggested to be xanthenium ions (m/z 356) and (m/z 281) were also abundant. The ratio of the two xanthenium ions 281/356 in the mass spectra obtained was > 1 for EI spectra, but < 1 for FAB. The simple loss of m/z 44 units, typical of crown ethers, was not generally observed.

2,2'-*Bis*(*ethoxycarbonylmethoxy*)-1,1'-*benzylidenedinaphthalene* (**13**) *and* 2-*Ethoxycarbonylmethoxy*-2'-*hydroxy*-1,1'-*benzylidenedinaphthalene* (**14**).—To a stirred solution of benzylidene binaphthol **8** (3.76 g, 0.01 mol) in nitrogen-purged tetrahydrofuran (150 cm^3) was added sodium hydride (80% mineral oil dispersion, 700 mg, 0.023 mol). After approximately 1 h, hydrogen evolution had ceased and a bottle green colour had developed in the solution. To this green solution was added dropwise with stirring a solution of ethyl bromoacetate (3.68 g, 0.022 mol) in dry tetrahydrofuran (50 cm^3). The reaction mixture was then heated to reflux and stirred at this elevated temperature for 16 h. Excess hydride was destroyed at room temperature by the careful addition of distilled water (0.5 cm^3) and the precipitated sodium bromide removed by filtration. The filtrate was concentrated *in vacuo* to give a heavy yellow syrup which was then redissolved in ethanol, dried ($MgSO_4$), filtered and reduced in volume on the evaporator. The addition of ethyl acetate, followed by cooling to 0 °C, initiated the crystallisation of the diester **13**, a colourless chunky solid (3.84 g, 70%), m.p. 119.5–121.5 °C (Found: C, 76.4; H, 5.7%; M$^+$, 548. $C_{35}H_{32}O_6$ requires: C, 76.4; H, 5.8%; *M*, 548); δ_H(200 MHz, $CDCl_3$), 8.01–7.07 (18 H, m, aromatic and methine), 4.02 (4 H, m, 2 × ArO–CH_2), 4.01 (4 H, q, *J* 7.14, 2 × CO_2CH_2) and 1.16 (6 H, t, *J* 7.13, 2 × CH_3).

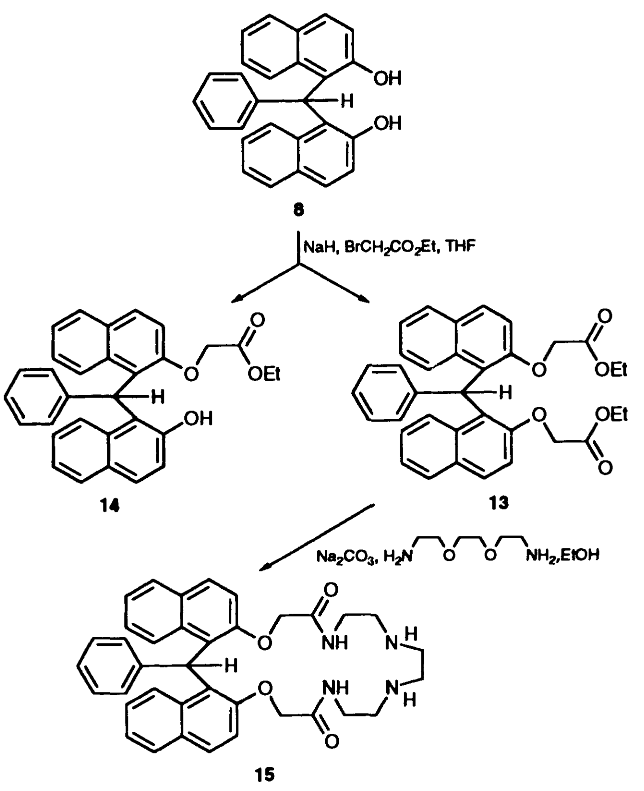
The diester was the only product isolated using the conditions above. However, when larger reactions were attempted, a second compound, the monoester, was isolated in sufficient quantities to be identified. Separation of the two reaction products was achieved using silica gel chromatography. Crystallisation from ethanol–dichloromethane afforded the *monoester* **14**, as a fine white powder, m.p. 174–175 °C (Found: C, 80.3; H, 5.6%; M$^+$,462. $C_{31}H_{26}O_4$ requires: C, 80.5; H, 5.7%;



Scheme 1

M, 462); δ_H(200 MHz, CDCl$_3$) 8.04–7.07 (18 H, m, aromatic and hydroxy), 6.66 (1 H, s, methine), 4.30–3.88 (4 H, m, $-CH_2-CO_2-CH_2-$) and 1.18 (3 H, t, J 7.14, $-CH_3$).

Preparation of 2,2′-*Bis*(*carboxymethoxy*)-1,1′-*benzylidenedinaphthalene* **16**.—To a solution of the diester **13** (1.00 g, 1.82 × 10^{-3} mol) in hot ethanol (200 cm^3) was added a saturated solution of potassium carbonate (50 cm^3). After this mixture had been heated at reflux for five days the two layers which had formed were separated. The ethanolic layer was reduced in volume on the evaporator and a precipitated pink/white solid (900 mg) was removed by filtration. This solid was then suspended in dichloromethane (150 cm^3) and treated with concentrated hydrochloric acid (5 cm^3), the suspension was stirred overnight, and the two layers were filtered prior to separation. The organic phase was washed with distilled water (20 cm^3), dried (MgSO$_4$), decolourised (charcoal), filtered and concentrated *in vacuo* to yield a white foam (700 mg). Recrystallisation of the foam from diethyl ether afforded the diacid **16** as a colourless powder (500 mg, 57%), m.p. 145–146 °C (Found: C, 75.4; H, 5.1%; M$^+$, 492. $C_{31}H_{24}O_6$ requires C, 75.6; H, 4.9%; M, 492).



Scheme 2

Preparation of Macrocyclic Amides.—The macrocyclic amides were prepared under normal condensation conditions (see Schemes 2 and 3) either directly[8] from the diester **13** or from the diacid **16** *via* the diacid chloride **17**[9] which was not isolated. An example of each procedure is given.

Synthesis of propeller diamide **18**.* To a solution of the diacid **16** (492 mg, 1.0 × 10^{-3} mol) in dichloromethane (250 cm^3) was added dropwise with stirring thionyl chloride (1.0 g). The reaction mixture was heated at reflux for 4 h, cooled and concentrated *in vacuo*. The resultant purple tar containing the acid chloride **17** was used without further purification. The tar and 1,8-diamino-3,6-dioxaoctane (160 mg, 1.08 × 10^{-3} mol) were separately dissolved in toluene (100 cm^3). These two solutions were added dropwise with vigorous stirring at an identical rate to a solution of triethylamine (1 cm^3) in dry toluene (300 cm^3). The reaction mixture was then stirred for a further four days whereupon the precipitated triethylamine hydrochloride was removed by filtration. The orange filtrates were concentrated *in vacuo* to afford a light orange foam (800 mg). The foam was dissolved in dichloromethane prior to the separation of its components on preparatory Merck silica TLC plates (4 glass plates, 20 × 20 cm, thickness 2 mm) using an ethyl acetate–light petroleum (3 : 7) solvent system. Desorption of the silica gel using hot ethyl acetate (Soxhlet) followed by concentration afforded crude solid amide **18** (400 mg, 66%). Recrystallisation from ethyl acetate–light petroleum gave **18** as colourless feathery needles, m.p. 171–173 °C (Found: C, 72.7; H, 5.8; N, 4.5%; M$^+$, 604. $C_{37}H_{36}N_2O_6{\cdot}0.25\ H_2O$ requires C, 72.9; H, 6.1; N, 4.6%; M, 604); δ_H(200 MHz, CDCl$_3$) 7.86–7.77 (6 H, m, aromatic), 7.40–7.09 (12 H, m, aromatic and methine), 6.32 (2 H, broad singlet, 2 × NH), 3.93 (4 H, s, 2 × ArO–CH$_2$), 3.45–3.31 (8 H, m, 4 × O–CH$_2$–) and 3.27–3.14 (4 H, m, 2 × –CH$_2$–NH).

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* 29-Phenyl-10,11,12,13,14,15,16,17,18,19-decahydro-29*H*-dinaphtho-[2,1-q;1,2-t](1,7,10,16,4,13)-tetraoxadiazaheneicosin-9(8*H*),20(21*H*)-dione.

Table 3 Crystallographic data

Compound	**9a**	**11**
Formula	$C_{51}H_{52}N_2O_8S_2{\cdot}C_3H_6O$	$C_{56}H_{66}N_3O_8S_3{\cdot}CHCl_3$
M	943.1	1113.6
Crystal system	orthorhombic	monoclinic
Space group	*Pbca*	$P2_1/c$
a/Å	47.058(11)	28.524(17)
b/Å	16.194(5)	17.342(9)
c/Å	12.944(5)	11.243(11)
β/°		99.88(4)
U/Å^3	9864.1	5479.0
Z	8	4
D_c/g cm^{-3}	1.270	1.350
Radiation, λ/Å	CuKα, 1.541 84	MoKα, 0.710 73
μ/mm^{-1}	1.37	0.34
F(000)	4000	2328
Crystal size/mm	0.16 × 0.28 × 0.36	0.16 × 0.27 × 0.68
$2\theta_{max}$/°	110	45
Reflections measured	5936	7989
Unique reflections	5936	7180
Observed reflections	2961	4565
R_{int}		0.083
No. of refined parameters	605	668
R	0.070	0.054
$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.056	0.062
Goodness of fit	0.92	1.07
Mean, max. shift/esd	0.018, 0.071	0.004, 0.016
Max., min. el. density/e Å^{-3}	0.42, −0.25	0.72, −0.79

Table 4 Torsion angles (°) for the macrocycle ring of **9a**

C(21)–O(1)–C(2)–C(3)	170.8(5)	O(1)–C(2)–C(3)–O(4)	84.0(6)
C(2)–C(3)–O(4)–C(5)	−77.3(6)	C(3)–O(4)–C(5)–C(6)	−178.3(5)
O(4)–C(5)–C(6)–N(7)	177.4(4)	C(5)–C(6)–N(7)–C(8)	82.0(6)
C(6)–N(7)–C(8)–C(9)	79.7(6)	N(7)–C(8)–C(9)–N(10)	−178.1(4)
C(8)–C(9)–N(10)–C(11)	112.8(5)	C(9)–N(10)–C(11)–C(12)	−94.0(6)
N(10)–C(11)–C(12)–O(13)	67.1(6)	C(11)–C(12)–O(13)–C(14)	178.1(5)
C(12)–O(13)–C(14)–C(15)	81.1(6)	O(13)–C(14)–C(15)–O(16)	69.0(7)
C(14)–C(15)–O(16)–C(17)	−160.2(5)	C(15)–O(16)–C(17)–C(18)	−116.3(6)
O(16)–C(17)–C(18)–C(19)	4.5(8)	C(17)–C(18)–C(19)–C(20)	35.6(7)
C(18)–C(19)–C(20)–C(21)	−100.5(6)	C(19)–C(20)–C(21)–O(1)	3.0(8)
C(20)–C(21)–O(1)–C(2)	−163.6(5)		

Table 5 Torsion angles (°) for the macrocycle ring of **11a**

C(18)–O(1)–C(2)–C(3)	−165.8(4)	O(1)–C(2)–C(3)–N(4)	69.8(5)
C(2)–C(3)–N(4)–C(5)	−127.1(4)	C(3)–N(4)–C(5)–C(6)	88.1(5)
N(4)–C(5)–C(6)–N(7)	−169.4(4)	C(5)–C(6)–N(7)–C(8)	72.3(5)
C(6)–N(7)–C(8)–C(9)	96.7(5)	N(7)–C(8)–C(9)–N(10)	−168.8(4)
C(8)–C(9)–N(10)–C(11)	129.1(4)	C(9)–N(10)–C(11)–C(12)	−92.1(5)
N(10)–C(11)–C(12)–O(13)	76.9(6)	C(11)–C(12)–O(13)–C(14)	166.1(4)
C(12)–O(13)–C(14)–C(15)	−123.3(5)	O(13)–C(14)–C(15)–C(16)	1.4(6)
C(14)–C(15)–C(16)–C(17)	−113.6(5)	C(15)–C(16)–C(17)–C(18)	37.3(5)
C(16)–C(17)–C(18)–O(1)	8.5(6)	C(17)–C(18)–O(1)–C(2)	−124.6(4)

Synthesis of propeller diamide **15**.* To a solution of the diester **13** (1.096 g, 2.0 × 10^{-3} mol) in dry ethanol (400 cm^3) was added triethylene tetramine (293 mg, 2.0 × 10^{-3} mol) and sodium carbonate (424 mg, 4.0 × 10^{-3} mol). The reaction mixture was heated at reflux under nitrogen for 18 days. TLC at this stage indicated no remaining diester. The reaction mixture was cooled and concentrated in the presence of Celite prior to purification *via* flash chromatography (silica gel Merck TLC grade) using ethyl acetate–light petroleum (1:1 v/v) followed by methanol–dichloromethane (3:17 v/v) as eluents. The colourless syrup (740 mg) so obtained crystallised from acetone–dichloromethane (1:1 v/v) as a colourless powder **15** (420 mg, 35%), m.p. 170–172 °C (Found: C, 71.3; H, 6.1; N, 8.2%; [M + 1]$^+$, 603. $C_{37}H_{38}N_4O_4{\cdot}H_2O{\cdot}0.5\,CH_3COCH_3$ requires C, 71.6; H, 6.5; N, 8.5%; [M + 1], 603); δ_H(60 MHz, CDCl$_3$) 8.02–6.98 (18 H, m, aromatic and methine), 6.15 (2 H, broad singlet, D$_2$O exchangeable, 2 × CONH), 3.98 (4 H, s, 2 × Ar–O–CH$_2$–), 3.50–3.00 (4 H, broad singlet, 2 × CONH–CH$_2$–), 2.65 (4 H, s, 2 × NH–CH$_2$–), 2.25 (4 H, s, 2 × NH–CH$_2$–) and 1.98 (2 H, s, D$_2$O exchangeable, 2 × NH).

Copper Complex of the Diamide Macrocycle **15**.—This was prepared by mixing a colourless solution of the ligand (60.2 mg, 1.0 × 10^{-4} mol) in methanol (10 cm^3) with a yellow/orange solution of copper(II) bromide (22.4 mg, 1.0 × 10^{-4} mol) in methanol (3 cm^3). The green precipitate which formed was redissolved with the aid of an ultrasonic bath and allowed to crystallise over several days. The greenish-brown solid copper complex of **15** was filtered off (Found: C, 52.3; H, 4.7; N, 6.4. $C_{37}H_{38}Br_2CuN_4O_4{\cdot}H_2O$ requires C, 52.6; H, 4.7; N, 6.6%).

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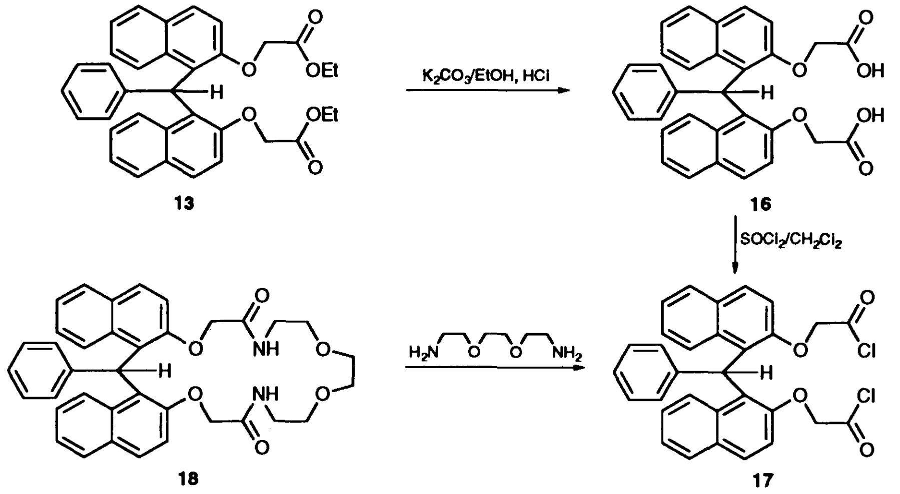
* 29-Phenyl-10,11,12,13,14,15,16,17,18,19-decahydro-29*H*-dinaphtho-[2,1-q;1,2-t] (1,16,4,7,10,13)-dioxatetraazaheneicosin-9(8*H*),20(21*H*)-dione.



Scheme 3

X-Ray Crystallography.—The crystal data for **9a** and **11a** are shown in Table 3, together with other information on data collection and structure determination. Measurements were made on a Stoe-Siemens diffractometer at room temperature. Intensities were collected by an on-line profile-fitting procedure;[10] no absorption corrections were applied. The structures were solved by direct methods.[11] Reflections with $F > 3\sigma(F)$ for **9a** and with $F > 4\sigma(F)$ for **11**, were used in blocked-cascade least-squares refinement,[11] with anisotropic thermal parameters for non-H atoms and with constrained isotropic H atoms. The weighting scheme was $w = 1/\sigma^2(F)$ with contributions from both counting statistics and an analysis of variance.[12] Atomic scattering factors were taken from ref. 13. Refined atomic coordinates and selected geometrical results are given in Tables 4 and 5, bond lengths, angles and torsion angles have been deposited at CCDC.*

Three-phase Transport.—Three-phase transport results were obtained for amide crowns **15**, **18** and some propeller ether and other crowns available from earlier work **19**–**24**, using the apparatus described below;[3,14] results are tabulated in Table 6. All experiments were repeated in triplicate. A chloroform layer (20 cm^3) saturated with distilled deionised water and containing 1.0×10^{-3} mol dm^{-3} carrier was pipetted into the bottom of the three-phase cell. Suspended above the bottom of the cell (below the chloroform surface) was a glass cylinder open at both ends which separated outer and inner areas. On top of the outer layer of chloroform was carefully pipetted 20 cm^3 of distilled deionised water saturated with chloroform. Inside the cylinder, on top of the chloroform layer was added 4 cm^3 of a metal salt solution (1 mol dm^{-3}, saturated with chloroform). The chloroform phase was agitated by a stirring bar located at the bottom of the cell. A Rank Brothers Ltd synchronous motor provided constant reproducible stirring. Specially designed miniature overhead mechanical stirrers were included in the receiving phase, primarily to guard against concentration gradients and assist in the faster attainment of a constant flux of metal ions. The cells were maintained at 25 °C ± 1 by sharing common thermostatting (Tecam TD-7 Tempette), from a water bath. Each cell had a glass cavity around its outer wall which was in turn connected to the next cell, through which the water could be pumped. Samples of 2 cm^3 were extracted from the outer receiving phase by Teflon syringe after 2.5 h and analysed for cation content on a Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer, at the most sensitive wavelengths. The results are subject to errors of ±25%. The results cannot be compared directly with those of Izatt *et al.*[15] as their equipment is not identical to ours. However, data for transport of Pb^{2+} and Ag^+ by the crown ligands **23**, **24** previously established by Izatt and co-workers[15,16] were compared to data for the same experiments carried out in this study. To allow comparison of the results contained in this study with those of Izatt and co-workers, our results should be multiplied by 1.14.

Ligands **15**, **18** were also tested for their ability to transport alkali picrates (as in ref. 3), but transport was negligible over periods of 24 h.

Results and Discussion

The *N*-tosyl-substituted azapropeller crowns **9a**, **10** and **11** were prepared by the route shown for compound **9a** in Scheme 1, and in one instance the tosyl groups were successfully removed to give the free azacrown **9b**. In the synthetic route chosen, tosylated amines **2**–**4** were first derivatised with appropriate hydroxyalkyl side-arms to give compounds (**5a**, **6a**, **7a**), which were then tosylated at the hydroxy group, to give the intermediates **5b**, **6b**, **7b**. These were used directly in the condensation for the crown synthesis. Analytical data for intermediates **2**, **3**, **4**, **5a**, **6a**, **7a**, **5b**, **6b**, **7b** are in Table 1, and corresponding NMR data in Table 2. Some one-armed polyamines (**5c**, **6c**, **7c**) which are useful synthons, were produced during the syntheses of **5a**, **6a** and **7a** and details for these are also provided in Tables 1 and 2. Analytical details for the crowns are given in the Experimental section. Much effort was expended in attempts to detosylate the resulting tosyl crowns. There is a comprehensive review[6] of known methods for removal of tosyl groups from *N*-tosylated materials. The best known method uses hot concentrated sulfuric acid, and a second valuable method, used where diethyl ethers are present, is the hydrogen bromide–acetic acid treatment in the presence of phenols. These and other methods involving acids were unsuitable in this work because of the acid-sensitive triarylmethyl segment of the propellers, but most of the known alternative methods[6] were attempted. Success was achieved with the sodium amalgam method. Crown **9b** was obtained as its methylene chloride adduct. Partial detosylation using the sodium amalgam method was achieved for most of the other tosylated propellers, but the resultant crown was not obtained analytically pure, and could be characterised only by mass spectroscopic and NMR data. It seems probable that the reactions are sluggish in the presence of the propeller moiety. The ligands themselves are expected to

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* Details of the deposition scheme are available in 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

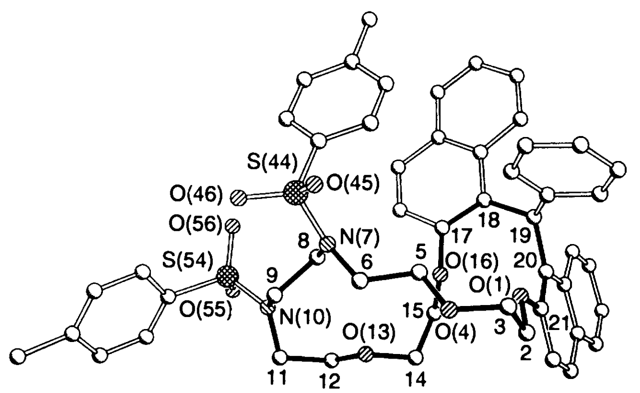


Fig. 1 Structure of **9a**, with the labelling of the macrocycle and heteroatoms. Carbon atoms are labelled by number only. Hydrogen atoms are omitted. Bonds in the polyether strand are shown filled, others hollow.

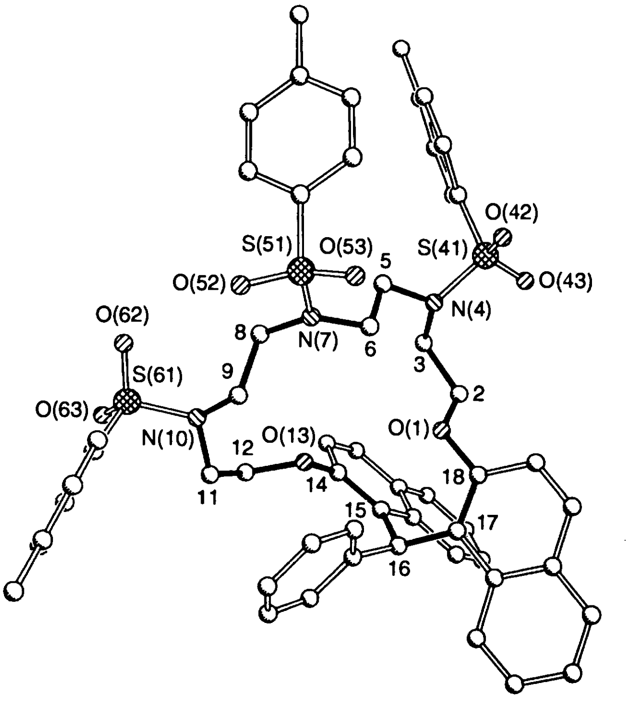


Fig. 2 Structure of **11**, with the labelling of the macrocycle and heteroatoms. Carbon atoms are labelled by number only. Hydrogen atoms are omitted. Bonds in the polyether strand are shown filled, others hollow.

be suitable hosts for a wide range of materials, including water and other small polar molecules, metal ions, and even anions, so that adventitious inclusion of one or more of these entities may have complicated the resulting analyses. In the synthesis of crown **11** an elimination reaction afforded the novel intermediate **12**, characterised in the experimental section.

The *N*-tosyl crowns were further characterised by X-ray crystal structure analysis and/or NMR spectroscopy; their mass spectra were also distinctively different from those of the ether crowns.

Crystal Structure Determination of **9a**.—Torsion angles for the macrocycle are shown in Table 4. Fig. 1 shows the structure of ligand **9a**; the view shows the propeller section, which has the common isomer (B in ref. 17) for this part of the skeleton. The *N*-tosyl groups are on the same side of the macrocyclic ring, but are not equivalent in the crystal. The torsion angles about the C–C bonds in the segments are *anti* for segment iii, *i.e.* the segment between the two nitrogens. It is possible that the steric interaction of the bulky S=O residues forces this segment *anti*. One adjacent N–C–C–O segment iii is also *anti*, but otherwise the segments have *gauche* torsion angles. This is an unusual conformation for a crown ring, and is clearly due to the presence of the bulky tosyl groups and their interaction with the propeller section. Specific stacking interactions were not found between aryl rings within one molecule.

Crystal Structure Determination of **11**.—The structure of **11** is shown in Fig. 2. Torsion angles for the macrocycle are shown in Table 5. The three tosyl groups are clearly differentiated in the crystal; once more there are no obvious stacking interactions between the aromatic rings. The torsion angles of the macrocyclic ring are again distinctive. There are two *anti* N–C–C–N torsions, but the O–C–C–N torsions are *gauche*. It seems unlikely that two bulky sulfonyl groups would be stable in a *gauche* conformation on an N–C–C–N segment. Despite the dominance of the propeller in the NMR behaviour of these crowns, the macrocycle conformation in the crystal bears no resemblance to those observed for the simple ether crowns, and is clearly dominated by the presence of the bulky tosyl substituents.

NMR Determination for Propeller Crowns.—Tosyl derivatives. Propeller crowns were designed to allow NMR probing of ring mobility. In **1**, the propeller flip has earlier[1] been correlated with the movement of ether segment i (see in formula **1**). With **9a**, we have added the further probe of the tosyl groups, with which we can monitor the movement of segment iii (see **9a**). In CD_2Cl_2 at room temperature, this isomer gives a ^1H spectrum which is clearly averaged, and reflects a structure effectively symmetrised on this NMR timescale. The signals for methyl groups on the tosyls broaden at lower temperatures, and decoalesce at 217 K. The magnitude of the free energy of activation for this process ($\Delta G^{\ddagger}_{217}$ = 10.54 kcal mol^{-1}) is close to that found for the mobile propellers (*cf.* **1a**, $\Delta G^{\ddagger}_{210}$ = 10.9 kcal mol^{-1}) in earlier work.[1] The observed process involving segment iii on crown **9a** can thus confidently be correlated with movement of the propeller. The corresponding compound in which segment iii consists of three instead of two methylene groups (**10**) has also been examined by the NMR method, and provides a convincing corroboration of this hypothesis, since its free energy of activation for the rendering equivalent of the two tosyl groups was almost identical, $\Delta G^{\ddagger}_{215}$ = 10.73 kcal mol^{-1} at coalescence. The rings of **9a** and **10** differ in size, and would be expected to move at different rates. Since the observed activation energies are almost identical, this confirms a process in which the 'averaged' structure observed for the (still mobile) oxaza chain reflects the environment induced by the slow switching process we have called the locking or unlocking of the propeller, rather than intrinsic movement of the macrocycle ring, which is clearly too fast to be accessed by our measurements. These much faster averaging processes of the whole oxaza strand are evident in the low temperature NMR spectra, but observable detail is inadequate for analysis. Very fast conformational changes in crown ethers have been discovered using the ultrasonic absorption technique for the kinetic determination[18] although it is not clear how the processes may be identified in chemical terms. Additionally, the basic torsional movements of the ring, simulable with MD methods, suggest the ring torsions may be on a picosecond timescale, much faster than anything measurable with NMR spectroscopy, which is a relatively slow technique. In the search for molecular switches, for use in materials, these faster processes will be a more profitable study.

For the triaza crown **11**, the crystal structure shows for the single isomer isolated, that there are three non-equivalent tosyl groups, but the NMR shows two sets, in the ratio 2:1 at room

Table 6 Transport data for various macrocycles

Ligand	J_mAgNO$_3$	J_mPb(NO$_3$)$_2$[a,b]
19	99	16
20	17	168
21	110	0
22	—	89
15[c]	0.9	11
18	32	75
23[d]	223	118
24[d]	34	—

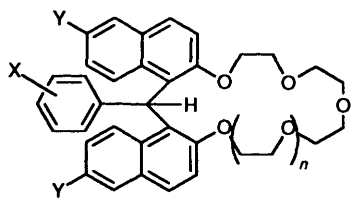
[a] J_m = no. moles salt transported per 24 h. [b] Results shown are from this work, except for the last two rows. To compare directly with the work from refs. 15 and 16, the J values in the first six rows should be multiplied by f = 1.14. [c] In competitive experiments, the relative J_m values for Ag and Pb salts were 1 and 8. [d] Data from refs. 15 and 16.

temperature. The structure is thus deduced to be mobile, undergoing a rapid symmetrisation process at room temperature on the NMR timescale, which makes two of the tosyl groups equivalent. The unique tosyl must be that on the central N of the -N-C-C-N-C-C-N- string. On cooling, the larger signal (which must appertain to the tosyls on the outer N of the string) decoalesces at 230–240 K, giving two signals of equal intensity, with a separation of 5.65 Hz at 220 K, each equal in intensity to the remaining tosyl methyl singlet. The free activation energy observed for this process is $\Delta G^{\ddagger}$ = 12.5 ± 0.4 kcal mol^{-1}, at 230–240 K. The process is thus of a similar rate to that described in the last paragraph, and is consistent with the hypothesis that the process of which the kinetics are being observed is actually the 'locking' of the propeller at low temperatures. Since this reaction is actually slightly slower than that for the compounds **9a** and **10**, it may indicate that the steric bulk of three adjacent tosyl groups is a factor in the flipping observed. The aliphatic NMR signals of this crown were almost undetectable at room temperature, appearing as a very broad shallow peak, but at low temperatures (230 K in CD$_2$Cl$_2$) the signals separated into sets reminiscent of those of the simple propeller crown ethers. Five multiplets of intensity corresponding to one proton were clearly resolved; these were assigned to the individual protons of the ABCD segments labelled ia and ib on structure **11** on the basis of 2D COSY experiments, using the starting assumption that one ArOCH signal of each segment i was the aliphatic multiplet observed furthest downfield, as was demonstrated for every propeller crown studied heretofore.[1,2,17] However, the quality (of the 1D spectra, even at high resolution) was never adequate for the detailed assignment of couplings, so the detailed solution conformation of the -CH$_2$CH$_2$- links of the macrocycle could not be ascertained. There was one methine signal observable, and five distinctive aromatic multiplets (each of the intensity for one single proton) were clearly resolved in 1D spectra. The 1D ^{13}C spectra of this crown showed several instances of the conformation freezing out on cooling. The ring carbons adjacent to ether oxygen appeared as one singlet at room temperature, while those next to nitrogen appeared as one sharp and one wide line. At 230 K, the OC appeared as two lines, and the NC had split to six lines, while the methine carbon appeared as just a single line, all as expected for a single locked propeller conformation. Comparison of the ^{13}C spectra at room temperature and at 230 K is tabulated and has been deposited at CCDC. In summary, the ^{1}H and ^{13}C NMR spectra are convincing proof that there is only one time-averaged structure present at 230 K, and that it has a 'locked' propeller conformation, rendering all three tosyl groups distinctive.

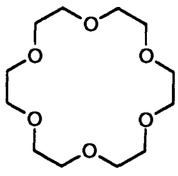
The spectrum of the detosylated azacrown **9b** was examined in CD$_2$Cl$_2$ using variable temperature techniques. At room temperature, in CD$_2$Cl$_2$, the ^{1}H spectrum was typically that of a symmetrised propeller crown, showing a broad signal for the NH protons; the ArOCH$_2$CH$_2$ segment protons were not sufficiently well resolved for analysis in detail. A COSY and a HETCOR study enabled assignment of certain signals as indicated in the Experimental section. Disappointingly, in a variable temperature ^{1}H study down to 180 K all proton signals did not separate cleanly so that no interpretation of the decoalescence was possible.

A second method of incorporating nitrogen donors into the ether ring involved the synthesis of propeller amides **15**, **18**, by the Kimura cyclisation[8] route shown in Scheme 2 and by the modified Schotten–Baumann technique[9] (outlined in Scheme 3). The Kimura cyclisation was very sluggish, as are most of the syntheses involving these propellers. Cleaner products were obtained by the second route, with no evidence of sensitivity of the triarylmethine to acid attack. Characterisation of the ligands and a copper bromide chelate of **15** were described in the Experimental section. Attempts to reduce these amide links using a considerable range of techniques were unsuccessful; again, the reductions were very sluggish, and did not go to completion. This does not seem to be a promising route to the nitrogen-containing propellers; such propellers would be desirable synthons for propeller cryptands, which if attainable, would have valuable reporter properties in metal ion complexation.

The amides **15** and **18** were tested in three-phase transport for their ability to transport lead and silver, and also alkali cations. There was no evidence for the transport of alkali cations under the conditions which succeeded for simple propellers **1**. The crown ethers **19**–**24** were also tested for their ability to transport Pb and Ag. The transport results are shown in Table 6. It would seem that propeller crown-5 ligands transport silver more favourably than lead, while the reverse occurs for the propeller-crown-6 ligands. The hypothesis of Hancock and co-workers[19] that the Pb^{2+} ionic radius is expanded when the only donor groups are ether oxygens, but contracted when at least three of the donors are nitrogen, may account for this, since the radii quoted for Pb^{2+} and Ag$^+$ (1.18 and 1.15 Å) are only marginally different. The locked propellers appeared to transport both cations marginally less well, but decomposition of the dichloro compound **22** in the presence of silver ions marred this study. From previous studies[3] it had been concluded that the locked propellers (*i.e.* those offering a more rigid coordination environment) were more effective ligands for alkali cations, due to more favourable rates of dissociation at the 'in' interface allowing cations to be loaded. Also, it has been shown that the



Ligand	X	Y	n
19	3,4,5-(MeO)$_3$	Bu^t	1
20	3,4,5-(MeO)$_3$	Bu^t	2
21	2,6-Cl$_2$	Bu^t	1
22	2,6-Cl$_2$	Bu^t	2



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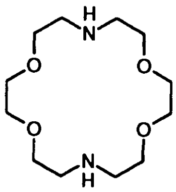

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locked propellers present a partially organised environment for the cations, reducing the conformational options, as proposed by Cram and Lein.[20]

Molecular mechanics calculations (using the program COSMIC[21] and the Drew method[22]) showed that the best cavity size of a propeller crown ether for metals with radii 1.15–1.18 Å should be somewhere between that of a crown-5 (which in this series is an 18-membered ring) and a crown-6 (which is a 21-membered ring). Such a cavity size could be achieved by using sulfur donors to increase the size, or nitrogens to decrease the size; this latter would, on the Hancock theory, also effectively shrink the lead cation size.[19] The first propeller crown with sulfur donors has been reported recently.[23]

Summarising, the synthesis of the new *N*-tosylated propellers has enabled more information on the conformational processes in the crown ethers in general to be obtained from NMR spectroscopy; crystallographic data were also obtained on two of these crowns. The detosylated azapropeller crown **9b** is fluxional at room temperature. The new amide crowns **15**, **18** were tested for their ability to transport metal ions (silver or lead nitrate) either separately or in competition. Comparison with the results for the simple propeller crowns, shows that silver is transported best by 5-donor crowns, and lead by 6-donor crowns.

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