Macroheterocycles. Part 44.[1] Facile Synthesis of Azacrown Ethers and Cryptands in a Two-Phase System

Nikolai G. Lukyanenko,* Stepan S. Basok, and Lyubov K. Filonova
A. V. Bogatsky Physico-Chemical Institute, Academy of Sciences of the Ukrainian SSR, 86 Chernomorskaya doroga, 270080, Odessa, U.S.S.R.

A facile procedure is proposed for the preparation of azacrown ethers and cryptands by condensation of dibromides or ethylene glycol bis(toluene-*p*-sulphonate)s with acyclic bis(sulphonamide)s or with bis[2-(*p*-tolylsulphonylamino)ethyl]diazacrown ethers, respectively. The reaction was carried out in a two-phase system of aqueous alkali–toluene (benzene) in the presence of quaternary ammonium salts as phase transfer catalysts. The catalytic activity decreased in the sequence: $Bu_4NI \approx Bu_4NBr > Bu_4NCl > Bu_4NHSO_4 > Et_3NCH_2C_6H_5NCl$. Maximum yields of twelve-membered azacrown ethers are obtained when lithium hydroxide is used, while crown ethers of larger size are observed in the presence of sodium or potassium hydroxides; this may be due to a template effect.

Known procedures for the synthesis of azacrown ethers and cryptands require the use of large amounts of dry solvents and hydrides or alcoholates of alkali metals as the base which, in combination with rather moderate yields of the products, makes them unsuitable for wide-scale usage.[2–6] In previous communications we have shown that azacrown ethers and cryptands may be prepared *via* interaction of bis(sulphonamide)s with dibromides under interphase catalysis.[6,7] In the present work we extend this method to the synthesis of di- and poly-azacrown ethers (**24**)—(**44**) and cryptands (**48**)—(**64**) differing in cycle size, and the number and position of nitrogen atoms.

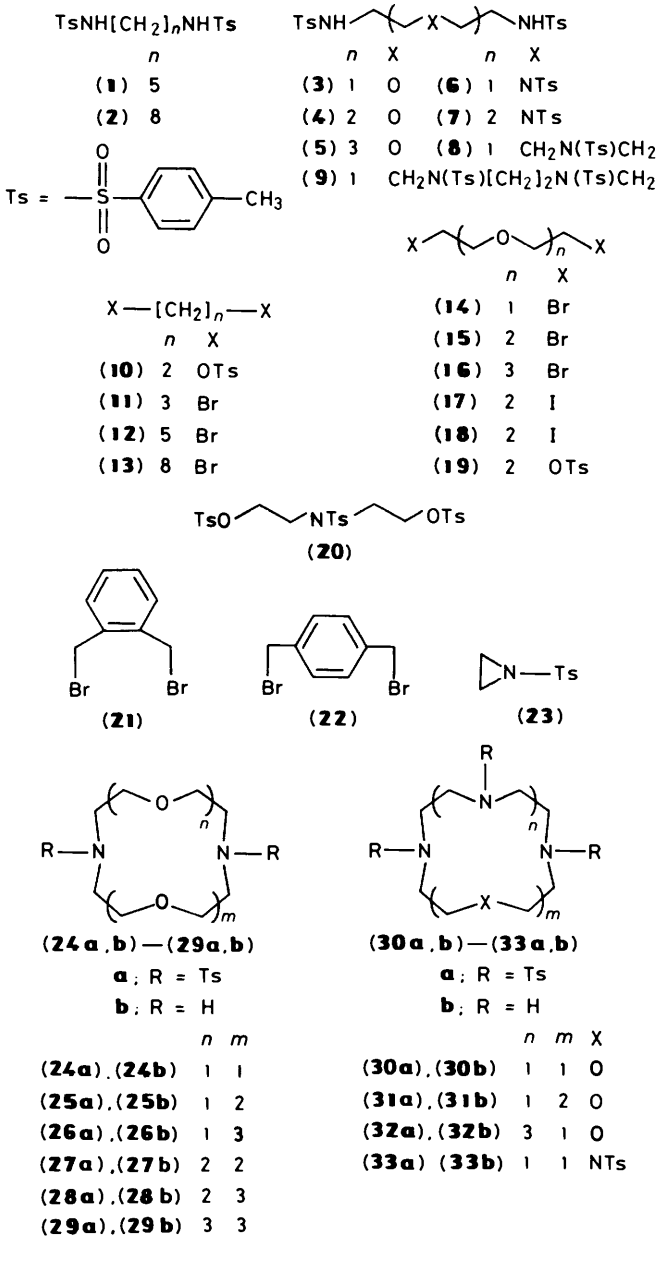
Results and Discussion

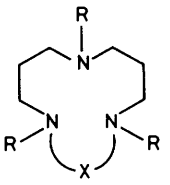
N-Tosylated azacrown ethers (**24**)—(**44**) were formed in good yields (50—94%) from the reaction of bis(sulphonamide)s (**1**)—(**9**) with dibromides (**11**)—(**16**) or ethylene glycol bis-(toluene-*p*-sulphonate)s (**10**), (**19**), and (**20**) in aqueous alkali–toluene (benzene) in the presence of quaternary ammonium salts as phase transfer catalyst. The reaction was carried out at the boiling point of the organic solvent for 8—10 h.

In most cases, the yield of the azacrown ethers (**24a**)—(**44**) was 5—15% higher when the reaction was performed in toluene rather than benzene. The yield of compounds (**24a**)—(**29a**) and (**42**)—(**44**) did not depend on the alkali concentration within the range 2.5—50%. However, for tri- and tetra-azacrown ethers (**30a**)—(**41a**) 50% alkali solutions were preferable. A decrease in alkali concentration reduced the yield of these compounds by 10—20%. The optimum concentration interval for bis(sulphonamide)s and alkylating agents is 0.017—0.1 mol l^{-1}.

Good yields of azacrown ethers (**25a**) and (**26a**) resulted from alkylation of the bis(sulphonamide) (**3**) with dibromides (**15**) and (**16**). An alternative method of synthesis of these compounds *via* alkylation of bis(sulphonamide)s (**4**) and (**5**) with dibromide (**14**) is unsatisfactory due to the preferable formation of morpholinic salts.[8]

It is commonly known that the yield of crown ethers in the Williamson reaction depends on the template effect of the metal cation.[2] However, literature on the occurrence of the template effect during the synthesis of azacrown ethers is ambiguous and in some cases contradictory.[3] We have therefore studied the effect of alkali metal cations on the yield of azacrown ethers (**24a**), (**25a**), (**27a**), (**29a**)—(**31a**), and (**42**)—(**44**) (Table 1). Like that of the crown ethers,[2] the yield of twelve-membered azacrown ethers (**24a**) and (**30a**) was highest in the presence of lithium hydroxide, and that of fifteen-membered compounds





(**34a**,**b**)—(**37a**,**b**)

a; R = Ts

b; R = H

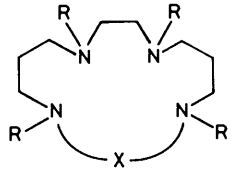
X

(**34a**),(**34b**) $[CH_2]_3$

(**35a**),(**35b**) $CH_2CH_2OCH_2CH_2$

(**36a**),(**36b**) $CH_2[CH_2OCH_2]_2CH_2$

(**37a**),(**37b**) $CH_2[CH_2OCH_2]_3CH_2$



(**38a**,**b**)—(**41a**,**b**)

a; R = Ts

b; R = H

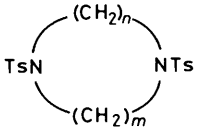
X

(**38a**),(**38b**) $[CH_2]_3$

(**39a**),(**39b**) $CH_2CH_2OCH_2CH_2$

(**40a**),(**40b**) $CH_2[CH_2OCH_2]_2CH_2$

(**41a**),(**41b**) $CH_2[CH_2OCH_2]_3CH_2$



	n	*m*
(**42**)	5	5
(**43**)	5	8
(**44**)	8	8

(**25a**) and (**31a**) in the presence of sodium hydroxide. The yield of *N*,*N*′-bis(*p*-tolylsulphonyl)diaza-18-crown-6 (**27a**) and *N*,*N*′-bis(*p*-tolylsulphonyl)diaza-24-crown-8 (**29a**) was minimal in the presence of lithium hydroxide and practically the same when sodium or potassium hydroxide was used. The yields are not dependent on either the concentration or other properties

Table 1. Dependence of yield of azacrown ethers on the nature of hydroxide used

Compound	Yield (%) LiOH	NaOH	KOH
(**24a**)	86	74	67
(**30a**)	88	65	65
(**25a**)	67	77	47
(**31a**)	51	80	57
(**27a**)	50	74	72
(**29a**)	23	50	46
(**42**)	69	69	67
(**43**)	73	75	73
(**44**)	66	68	69

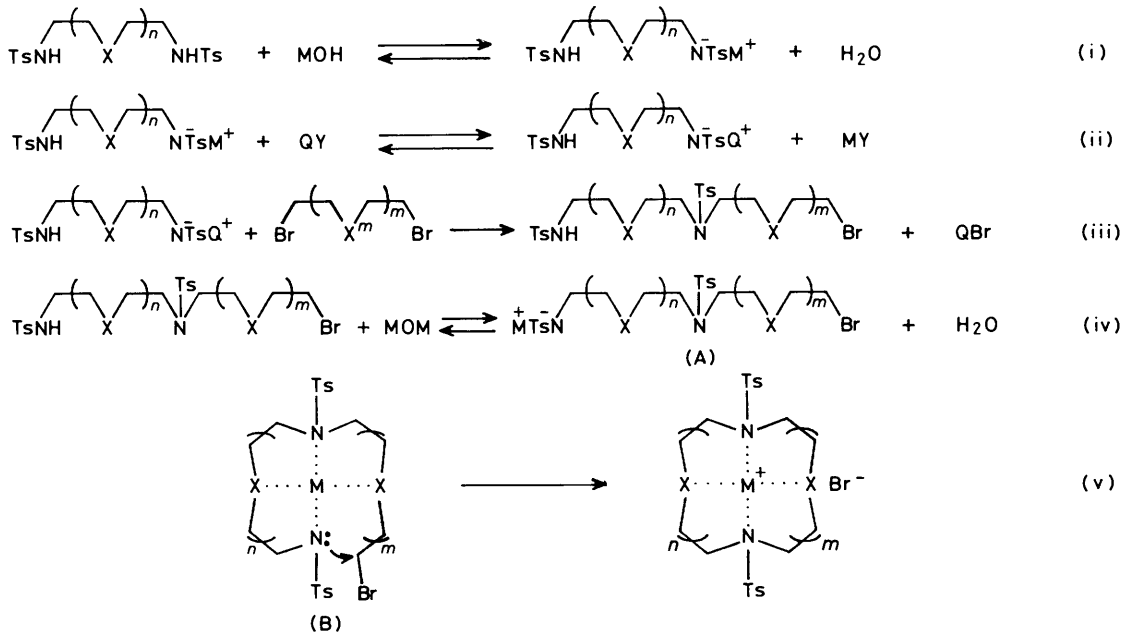
of the aqueous base,[9,10] since the yield of aliphatic cyclic *N*-*p*-tolylsulphonylamines (**42**)—(**44**) which are not able to form complexes with alkaline metal cations, does not depend on the nature of the alkali used. This suggests that a template effect is occurring. Additional evidence for this effect was given in the decrease of the yield of compound (**24a**) to 41% in the presence of tetrabutylammonium hydroxide; complexation is impossible here for steric reasons.

The twelve-membered azacrown ethers (**24a**) and (**30a**) were, therefore, synthesized in the presence of lithium hydroxide, while sodium hydroxide was used for the others.

The studied quaternary ammonium salts are arranged in the following sequence of catalytic activity: $Bu_4NI \geqslant Bu_4NBr > Bu_4NCl > Bu_4NHSO_4 > Et_3NCH_2C_6H_5NCl$. The high catalytic activity of tetrabutylammonium iodide and tetrabutylammonium bromide is probably due to their thermal stability in an alkaline medium.[11]

The yield of azacrown ethers increased with an increase in the molar ratio of catalyst:substrate from 5 to 25%. Further increase in catalyst concentration had no marked effect on the yield of the product.

Taking into account the experimental results and the general trends of interphase reactions[10,12] the formation of azacrown ethers may be presented by the following scheme:



Deprotonation of sulphonamide groups with alkali probably occurs successively (reactions i and iv). In the absence of the catalyst (QY), no alkylation of sulphonamide is observed after deprotonation of the first sulphonamide group (reaction i), however, exchange (reaction ii) takes place when a catalyst is present. The ionic pair formed undergoes alkylation in the organic phase (reaction iii). Deprotonation of the alkylated product results in the formation of the highly-lipophilic anion A (reaction iv) which is able to solvate alkaline metal cations forming a cation-associated precursor of the crown ether (B), which is probably responsible for the effect of base on the yield of the azacrown ether. Intramolecular alkylation (v) completes the process.

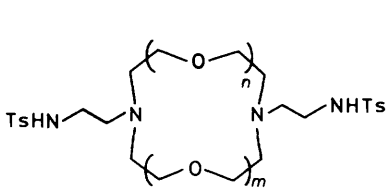
Synthesis of *N,N'*-bis(*p*-tolylsulphonyl)diaza-18-crown-6 (**27a**) *via* interaction of bis(sulphonamide) (**4**) with dichloride (**17**), dibromide (**15**), di-iodide (**18**) and bis(toluene-*p*-sulphonate) (**19**) showed that in concentrated solutions of sodium hydroxide (50%) the above alkylating agents are arranged in the sequence: Br ≥ OTs > I ≫ Cl. In diluted alkaline solutions (2.5%) inversion of the alkylating ability of di-iodides and bis(toluene-*p*-sulphonate)s is observed: Br > I > OTs ≫ Cl, which is probably due to the greater activity of water in such solutions[10] and the acceleration of the bis(toluene-*p*-sulphonate)s hydrolysis rate.

Synthesis of *N*-tosylated cryptands (**48**)—(**64**) was carried out under the conditions optimized for azacrown ethers by the reaction of ethylene glycol bis(toluene-*p*-sulphonate) (**10**), *N*-(*p*-tolylsulphonyl)diethanolamine bis(toluene-*p*-sulphonate) (**20**) or dibromides (**14**), (**15**), (**21**), and (**22**) with bis[2-(*p*-tolylsulphonylamino)ethyl]diazacrown ethers (**45**)—(**47**). The latter are formed in excellent yields from the interaction of the corresponding diazacrown ethers with *N*-(*p*-tolylsulphonyl)-aziridine (**23**).

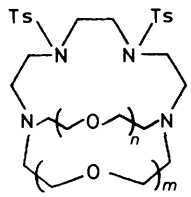
Azacrown ethers (**24b**)—(**29b**) were prepared from compounds (**24a**)—(**29a**) by the action of lithium aluminium hydride in tetrahydrofuran (THF). In the case of azacrown ethers (**30a**)—(**41a**) and cryptands (**51a**)—(**53a**), (**55a**), and (**56a**) better yields of compounds (**30b**)—(**41b**), (**51b**)—(**53b**), (**55b**), and (**56b**) were achieved with HBr in glacial acetic acid.

Physical properties and analytical results for obtained compounds are summarized in Table 2.

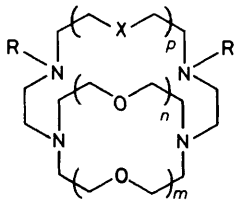
The simplicity of this synthesis and the good yields obtained make this method suitable for large-scale preparations of azacrown ethers and cryptands.



	n	*m*
(**45**)	1	1
(**46**)	1	2
(**47**)	2	2

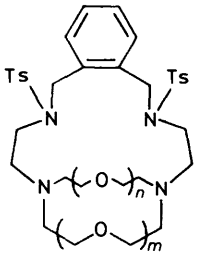


	n	*m*
(**48**)	1	1
(**49**)	1	2
(**50**)	2	2

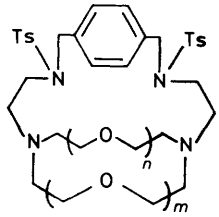


(**51a**,**b**)—(**58a**,**b**)
a; R = Ts
b; R = H

	n	*m*	*p*	X
(**51a**),(**51b**)	1	1	1	O
(**52a**),(**52b**)	2	1	1	O
(**53a**),(**53b**)	2	2	1	O
(**54a**)	1	1	2	O
(**55a**),(**55b**)	1	2	2	O
(**56a**),(**56b**)	2	2	2	O
(**57a**)	2	1	1	NTs
(**58a**)	2	2	1	NTs



	m	*n*
(**59**)	1	1
(**60**)	1	2
(**61**)	2	2



	m	*n*
(**62**)	1	1
(**63**)	1	2
(**64**)	2	2

Experimental

All m.p.s are uncorrected. ^{1}H N.m.r. (60 MHz) were recorded on a Tesla BS-467 spectrometer in deuteriochloroform using HMDS as an internal standard. Mass spectra were recorded on a Varian MAT 112 instrument using electron impact ionization (at 70 eV). The purity of all the compounds was controlled by chromatography. T.l.c. was carried out on glass plates coated with neutral alumina L5/40 (Chemapol, Czechoslovakia) and on pre-coated silica gel plates 'Sulifol 254' (Chemapol, Czechoslovakia). Column chromatography was performed over neutral alumina L40/250 (Chemapol, Czechoslovakia).

Bis(sulphonamide)s (**1**)—(**3**) and (**6**)—(**9**) were prepared by the reaction of toluene-*p*-sulphonyl chloride with diamines as previously described in ref. 13. Bis(toluene-*p*-sulphonate)s (**10**), (**19**), and (**20**) were obtained by standard procedure.[14,15] *N*-*p*-Tolylsulphonylaziridine (**23**) was prepared by the published method.[16] Commercially available dihalides (**11**)—(**18**) and (**21**) and (**22**) were used.

1,8-*Bis*(p-*tolylsulphonylamino*)-3,6-*dioxaoctane* (**4**).—*p*-Tolylsulphonylamine (37.6 g, 0.22 mol) was added to a hot saturated solution of anhydrous sodium carbonate (42.4 g, 0.4 mol) in water (50 ml) and the solution heated for 2 h. 1,8-Dibromo-3,6-dioxaoctane (27.6 g, 0.1 mol) was added, the mixture was stirred under reflux for 4 h, poured into water (500 ml), and the oil formed was separated. The oil was successively boiled with saturated aqueous sodium carbonate (100 ml) and water (200 ml). The organic layer was separated and dissolved in $CHCl_3$, then dried (Na_2SO_4), and evaporated under reduced pressure to yield a colourless oil which slowly solidified to give compound (**4**) (43.7 g, 96%) as a white powder, m.p. 102 °C (lit.,[17] 102 °C); δ_H 2.3 (6 H, s, Me), 3.00 (4 H, t, *J* 5 Hz, NCH_2), 3.40 (8 H, t, *J* 5 Hz, OCH_2), 5.55 (2 H, m, NH), and 7.40 (8 H, m, ArH) (Found: C, 58.7; H, 6.2; N, 6.1. $C_{20}H_{28}N_2O_6S_2$ requires C, 52.63; H, 6.14; N, 6.14%).

1,11-*Bis*(p-*tolylsulphonylamino*)-3,6,9-*trioxaundecane* (**5**).—This compound was similarly obtained by the above procedure as a white powder (43.5 g, 87%), m.p. 98 °C; δ_H 2.23 (6 H, s, Me), 3.00 (4 H, t, *J* 5 Hz, NCH_2), 3.35 (12 H, t, *J* 5 Hz, OCH_2), 5.56 (2 H, m, NH), and 7.40 (8 H, m, ArH) (Found: C, 53.0; H, 6.3; N, 5.7. $C_{22}H_{32}N_2O_7S_2$ requires C, 52.78; H, 6.44; N, 5.60%).

4,10-*Bis*(p-*tolylsulphonyl*)-1,7-*dioxa*-4,10-*diazacyclododecane* (**24a**).—1,5-Bis(*p*-tolylsulphonylamino)-3-oxapentane (**3**) (4.12 g, 0.01 mol) and 1,5-dibromo-3-oxapentane (**14**) (2.32 g, 0.01 mol) in toluene (benzene) (400 ml) were added to a refluxing

Table 2. Analytical data for azacrown ethers (**24**)—(**47**) and cryptands (**48**)—(**64**)

Compound (Formula)	Yield (%)	M.p. (°C) (Lit,)	Found (%) (Required) C	H	N
(24a)	90	203—204	54.5	6.45	6.0
$(C_{22}H_{30}N_2O_6S_2)$		(203—204)[a]	(54.75)	(6.27)	(5.80)
(24b)	76	82—84	55.0	10.35	16.4
$(C_8H_{18}N_2O_2)$		(83—84)[b]	(55.14)	(10.41)	(16.08)
(25a)	80	127—128	54.9	6.6	5.0
$(C_{24}H_{34}N_2O_7S_2)$			(54.73)	(6.50)	(5.32)
(25b)	88	86—89	55.4	10.45	12.65
$(C_{10}H_{22}N_2O_3)$		(89—90)[b]	(55.02)	(10.16)	(12.83)
(26a)	86	102—104	54.8	6.5	5.05
$(C_{26}H_{38}N_2O_8S_2)$			(54.71)	(6.71)	(4.91)
(26b)	68	96—98	54.75	9.8	10.4
$(C_{12}H_{26}N_2O_4)$		(syrup)[c]	(54.93)	(9.99)	(10.68)
(27a)	79	163—165	54.75	6.4	5.25
$(C_{26}H_{38}N_2O_8S_2)$		(163—164)[a]	(54.71)	(6.71)	(4.91)
(27b)	94	115—116	54.9	9.75	10.35
$(C_{12}H_{26}N_2O_4)$		(115—116)[b,d]	(54.93)	(9.99)	(10.68)
(28a)	82	Oil	55.0	6.7	4.8
$(C_{28}H_{42}N_2O_9S_2)$			(54.70)	(6.89)	(4.56)
(28b)	45	Oil	55.0	10.0	9.2
$(C_{14}H_{30}N_2O_5)$		(15)[b]	(54.88)	(9.87)	(9.14)
(29a)	50	100—102	54.45	7.2	4.05
$(C_{30}H_{46}N_2O_{10}S_2)$		(104)[e]	(54.69)	(7.04)	(4.25)
(29b)	47	Oil	55.05	9.85	8.1
$(C_{16}H_{34}N_2O_6)$		(oil)[e]	(54.83)	(9.78)	(7.99)
(30a)	90	200—202	54.6	6.0	6.3
$(C_{28}H_{37}N_3O_7S_3)$		(200—204)[f]	(54.78)	(5.87)	(6.61)
(30b)	62	84.5—85	55.3	11.1	24.5
$(C_8H_{19}N_3O)$		(83.85)[g,h]	(55.45)	(11.05)	(24.25)
(31a)	90	198—199	54.85	6.4	6.45
$(C_{31}H_{41}N_3O_8S_3)$		(198—199)[f]	(54.76)	(6.08)	(6.18)
(31b)	64	Oil	55.35	10.5	19.15
$(C_{10}H_{23}N_3O_2)$		(oil)[g,h]	(55.27)	(10.67)	(19.34)
(32a)	60	134—135	56.0	6.5	6.05
$(C_{33}H_{45}N_3O_9S_3)$			(54.75)	(6.27)	(5.80)
(32b)	50	Oil	55.3	10.2	16.3
$(C_{12}H_{27}N_3O_3)$			(55.14)	(10.41)	(16.08)
(33a)	90	288—290	54.91	5.9	7.15
$(C_{36}H_{44}N_4O_8S_4)$		(292)[i]	(54.80)	(5.62)	(7.20)
(33b)	70	33—34	55.8	11.7	32.7
$(C_8H_{20}N_4)$		(34—35)[j]	(55.77)	(11.70)	(32.52)
(34a)	90	170—171	56.95	6.1	6.85
$(C_{30}H_{39}N_3O_6S_3)$		(172)[i]	(56.84)	(6.20)	(6.63)
(34b)	63	Oil	63.25	12.2	24.55
$(C_9H_{21}N_3)$			(63.11)	(12.36)	(24.54)
(35a)	86	192—195	55.85	6.05	6.5
$(C_{31}H_{41}N_3O_7S_3)$			(56.08)	(6.22)	(6.33)
(35b)	65	Oil	59.95	11.8	21.05
$(C_{10}H_{23}N_3O)$			(59.66)	(11.51)	(20.87)
(36a)	96	102—104	56.2	6.25	5.95
$(C_{33}H_{45}N_3O_8S_3)$		(102—104)[f]	(55.99)	(6.41)	(5.94)
(36b)	30	Oil	59.05	11.2	17.0
$(C_{12}H_{27}N_3O_2)$			(58.74)	(11.09)	(17.13)
(37a)	54	Glass	56.05	6.85	5.7
$(C_{35}H_{49}N_3O_9S_3)$		(glass)[f]	(55.90)	(6.57)	(5.59)
(37b)	25	Oil	58.05	10.85	14.7
$(C_{14}H_{31}N_3O_3)$		(oil)[f]	(58.10)	(10.80)	(14.52)
(38a)	85	284—285	56.5	6.25	6.65
$(C_{39}H_{50}N_4O_8S_4)$			(56.36)	(6.06)	(6.74)
(38b)	60	98—100	61.75	12.4	26.35
$(C_{11}H_{26}N_4)$			(61.63)	(12.23)	(26.14)
(39a)	94	220—222	55.7	6.0	6.7
$(C_{40}H_{52}N_4O_9S_4)$			(55.79)	(6.09)	(6.51)
(39b)	45	Oil	58.75	11.85	23.15
$(C_{12}H_{28}N_4O)$			(58.98)	(11.55)	(22.93)
(40a)	88	Glass	55.85	6.4	6.25
$(C_{42}H_{56}N_4O_{10}S_4)$			(55.73)	(6.24)	(6.19)
(40b)	37	Oil	58.55	11.2	19.6
$(C_{14}H_{32}N_4O_2)$			(58.30)	(11.18)	(19.43)
(41a)	54	Glass	55.9	6.1	6.15
$(C_{44}H_{60}N_4O_{11}S_4)$			(55.67)	(6.37)	(5.90)
(41b)	35	Oil	57.85	11.0	16.7
$(C_{16}H_{36}N_4O_3)$			(57.80)	(10.91)	(16.85)
(42)	69	240	60.3	7.1	6.1
$(C_{24}H_{34}N_2O_4S_2)$		(242—244)[k]	(60.22)	(7.16)	(5.85)
(43)	75	160—165	62.45	7.55	5.3
$(C_{27}H_{40}N_2O_4S_2)$			(62.27)	(7.74)	(5.38)
(44)	68	195—198	64.15	8.05	5.2
$(C_{30}H_{46}N_2O_4S_2)$			(64.02)	(8.24)	(4.98)
(45)	92	165—167	54.85	7.25	9.8
$(C_{26}H_{40}N_4O_6S_2)$			(54.90)	(7.09)	(9.85)
(46)	96	66—67	54.95	7.1	9.25
$(C_{28}H_{44}N_4O_7S_2)$			(54.88)	(7.24)	(9.14)
(47)	98	112—115	54.75	7.25	8.45
$(C_{30}H_{48}N_4O_8S_2)$			(54.85)	(7.36)	(8.53)
(48)	76	185—186	55.7	7.3	9.5
$(C_{28}H_{42}N_4O_6S_2)$		(191)[l]	(56.54)	(7.12)	(9.42)
(49)	70	165	56.55	7.25	9.0
$(C_{30}H_{46}N_4O_7S_2)$			(56.40)	(7.26)	(8.71)
(50)	50	83—84	56.4	7.3	8.2
$(C_{32}H_{50}N_4O_8S_2)$		(83—84)[l]	(56.28)	(7.38)	(8.20)
(51a)	81	60—63	56.65	7.35	8.7
$(C_{30}H_{46}N_4O_7S_2)$			(56.40)	(7.26)	(8.77)
(51b)	60	Oil	58.4	10.65	16.85
$(C_{16}H_{34}N_4O_3)$			(58.14)	(10.97)	(16.95)
(52a)	87	Oil	56.5	7.45	8.3
$(C_{32}H_{50}N_4O_8S_2)$			(56.28)	(7.38)	(8.20)
(52b)	30	Oil	58.0	10.1	15.05
$(C_{18}H_{38}N_4O_4)$			(57.72)	(10.23)	(14.96)
(53a)	87	Oil	56.45	7.45	7.65
$(C_{34}H_{54}N_4O_9S_2)$			(56.17)	(7.49)	(7.71)
(53b)	65	Oil	57.3	10.15	13.4
$(C_{20}H_{42}N_4O_5)$			(57.39)	(10.11)	(13.39)
(54a)	73	Oil	56.5	7.5	8.3
$(C_{32}H_{50}N_4O_8S_2)$			(56.28)	(7.38)	(8.20)
(55a)	83	Oil	56.1	7.55	7.7
$(C_{34}H_{54}N_4O_9S_2)$			(56.17)	(7.49)	(7.71)
(55b)	55	Oil	57.35	10.25	13.35
$(C_{20}H_{42}N_4O_5)$			(57.39)	(10.11)	(13.39)
(56a)	84	48—50	55.95	7.65	7.35
$(C_{36}H_{58}N_4O_{10}S_2)$			(56.08)	(7.58)	(7.27)
(56b)	52	Oil	57.15	10.2	12.15
$(C_{22}H_{46}N_4O_6)$			(57.11)	(10.02)	(12.11)
(57a)	62	Oil	56.1	6.75	8.1
$(C_{39}H_{57}N_5O_9S_3)$			(56.02)	(6.87)	(8.58)
(58a)	57	Oil	56.2	7.0	7.85
$(C_{41}H_{61}N_5O_{10}S_3)$			(55.94)	(6.97)	(7.95)
(59)	71	Glass	60.65	6.95	8.2
$(C_{34}H_{46}N_4O_6S_2)$			(60.87)	(6.91)	(8.35)
(60)	76	Glass	60.6	7.2	7.7
$(C_{36}H_{50}N_4O_7S_2)$			(60.48)	(7.05)	(7.83)
(61)	68	Glass	60.3	7.25	7.55
$(C_{38}H_{54}N_4O_8S_2)$			(60.13)	(7.17)	(7.38)
(62)	56	196	60.7	7.0	8.3
$(C_{34}H_{46}N_4O_6S_2)$			(60.87)	(6.91)	(8.35)
(63)	56	157—160	60.4	6.9	8.0
$(C_{36}H_{50}N_4O_7S_2)$			(60.48)	(7.05)	(7.83)
(64)	68	93—96	60.2	7.3	7.5
$(C_{38}H_{54}N_4O_8S_2)$			(60.13)	(7.17)	(7.38)

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mixture of tetrabutylammonium iodide (25% mol), 2.5% aqueous lithium hydroxide (100 ml) and toluene or benzene (200 ml). The vigorously stirred mixture was heated under reflux for 8—10 h, the organic layer was separated and dried (Na_2SO_4), and the solvent was evaporated off under reduced pressure. The solid was washed with methanol, filtered, and purified by recrystallization from ethanol to give compound (**24a**) as a white powder, δ_H 2.37 (6 H, s, Me), 3.20 (8 H, t, *J* 5 Hz, NCH_2), 3.68 (8 H, t, *J* 5 Hz, OCH_2), and 7.42 (8 H, m, ArH); *m/z* 327 ($M - Ts^+$).

4,7,10-*Tris*(p-*tolylsulphonyl*)-1-oxa-4,7,10-*triazacyclododecane* (**30a**) was prepared as above, δ 2.20 (9 H, s, Me), 3.07 (12 H, t, *J* 5 Hz, NCH_2), 3.43 (4 H, t, *J* 5 Hz, OCH_2), and 7.30 (12 H, m, ArH); *m/z* 480 ($M - Ts^+$).

7,13-*Bis*(p-*tolylsulphonyl*)-1,4,10-*trioxa*-7,13-*diazacyclopentadecane* (**25a**).—This was prepared in a similar way to (**24a**) *via* 1,5-bis(*p*-tolylsulphonylamino)-3-oxapentane (4.12 g, 0.01 mol) and 1,8-dibromo-3,6-dioxaoctane (2.76 g, 0.01 mol) in the presence of 50% aqueous sodium hydroxide (70 ml), δ 2.33 (6 H, s, Me), 3.25 (8 H, t, *J* 5 Hz, NCH_2), 3.50 (12 H, m, OCH_2), and 7.40 (8 H, m, ArH); *m/z* 371 ($M - Ts^+$). By this method the following compounds were prepared.

10,16-*Bis*(p-*tolylsulphonyl*)-1,4,7,13-*tetraoxa*-10,16-*diazacyclo-octadecane* (**26a**), δ 2.43 (6 H, s, Me), 3.33 (8 H, t, *J* 5 Hz, NCH_2), 3.76 (16 H, m, OCH_2), and 7.50 (8 H, m, ArH); *m/z* 415 ($M - Ts^+$).

7,16-*Bis*(p-*tolylsulphonyl*)-1,4,10,13-*tetraoxa*-7,16-*diazacyclo-octadecane* (**27a**), δ 2.33 (6 H, s, Me), 3.50 (24 H, m, OCH_2, NCH_2), and 7.40 (8 H, m, ArH); *m/z* 415 ($M - Ts^+$).

10,19-*Bis*(p-*tolylsulphonyl*)-1,4,7,13,16-*pentaoxa*-10,19-*diazacyclohenicosane* (**28a**), δ 2.30 (6 H, s, Me), 3.43 (28 H, m, OCH_2, NCH_2), and 7.50 (8 H, m, ArH); *m/z* 459 ($M - Ts^+$).

10,22-*Bis*(p-*tolylsulphonyl*)-1,4,7,13,16,19-*hexaoxa*-10,22-*diazacyclotetracosane* (**29a**), δ 2.08 (6 H, s, Me), 3.43 (32 H, m, OCH_2, NCH_2), and 7.60 (8 H, m, ArH); *m/z* 503 ($M - Ts^+$).

7,10,13-*Tris*(p-*tolylsulphonyl*)-1,4-*dioxa*-7,10,13-*triazacyclopentadecane* (**31a**), δ 2.27 (9 H, s, Me), 3.30 (20 H, m, OCH_2, NCH_2), and 7.30 (12 H, m, ArH); *m/z* 524 ($M - Ts^+$).

10,13,16-*Tris*(p-*tolylsulphonyl*)-1,4,7-*trioxa*-10,13,16-*triazacyclo-octadecane* (**32a**), 2.43 (9 H, s, Me), 3.41 (24 H, m, OCH_2, NCH_2), and 7.40 (12 H, m, ArH); *m/z* 568 ($M - Ts^+$).

1,4,7,10-*Tetrakis*(p-*tolylsulphonyl*)-1,4,7,10-*tetra-azacyclododecane* (**33a**), δ 2.35 (12 H, s, Me), 3.30 (16 H, s, NCH_2), and 7.50 (16 H, m, ArH); *m/z* 621 ($M - Ts^+$).

1,5,9-*Tris*(p-*tolylsulphonyl*)-1,5,9-*triazacyclododecane* (**34a**), δ 1.86 (6 H, m, CH_2), 2.30 (9 H, s, Me), 3.13 (12 H, t, *J* 5 Hz, NCH_2), and 7.36 (12 H, m, ArH); *m/z* 478 ($M - Ts^+$).

4,8,12-*Tris*(p-*tolylsulphonyl*)-1-*oxa*-4,8,12-*triazacyclotetradecane* (**35a**), δ 2.05 (4 H, m, CH_2), 2.41 (9 H, s, Me), 3.21 (12 H, m, NCH_2), 3.60 (4 H, m, OCH_2), and 7.40 (12 H, m, ArH); *m/z* 508 ($M - Ts^+$).

7,11,15-*Tris*(p-*tolylsulphonyl*)-1,4-*dioxa*-7,11,15-*triazacycloheptadecane* (**36a**), δ 2.03 (2 H, m, CH_2), 2.40 (9 H, s, Me), 3.21 (12 H, m, NCH_2). 3.55 (8 H, m, OCH_2), and 7.50 (12 H, m, ArH); *m/z* 552 ($M - Ts^+$).

10,14,18-*Tris*(p-*tolylsulphonyl*)-1,4,7-*trioxa*-10,14,18-*triazacycloicosane* (**37a**), δ 1.92 (4 H, m, CH_2), 2.40 (9 H, s, Me), 3.21 (12 H, m, NCH_2), 3.55 (12 H, m, OCH_2), and 7.48 (12 H, m, ArH); *m/z* 596 ($M - Ts^+$).

1,4,8,12-*Tetrakis*(p-*tolylsulphonyl*)-1,4,8,12-*tetra-azacyclopentadecane* (**38a**), δ 1.90 (6 H, m, CH_2), 2.40 (12 H, s, Me), 3.16 (16 H, m, NCH_2), and 7.40 (16 H, m, ArH); *m/z* 663 ($M - Ts^+$).

4,8,11,15-*Tetrakis*(p-*tolylsulphonyl*)-1-*oxa*-4,8,11,15-*tetra-azacycloheptadecane* (**39a**), δ 1.95 (4 H, m, CH_2), 2.41 (12 H, s, Me), 3.20 (16 H, m, NCH_2), 3.58 (4 H, m, OCH_2), and 7.33 (16 H, m, ArH); *m/z* 706 ($M - Ts^+$).

7,11,14,18-*Tetrakis*(p-*tolylsulphonyl*)-1,4,-*dioxa*-7,11,14,18-*tetra-azacycloicosane* (**40a**), δ 1.95 (4 H, m, CH_2), 2.41 (12 H, s, Me), 3.20 (16 H, m, NCH_2), 3.53 (8 H, m, OCH_2), and 7.50 (16 H, m, ArH); *m/z* 750 ($M - Ts^+$).

10,14,17,21-*Tetrakis*(p-*tolylsulphonyl*)-1,4,7-*trioxa*-10,14,17,21-*tetra-azacyclotricosane* (**41a**), δ 1.92 (4 H, m, CH_2), 2.38 (12 H, s, Me), 3.28 (16 H, m, NCH_2), 3.50 (12 H, m, OCH_2), and 7.40 (16 H, m, ArH); *m/z* 794 ($M - Ts^+$).

1,7-*Bis*(p-*tolylsulphonyl*)-1,7-*diazacyclododecane* (**42**), δ 1.28 (12 H, m, CH_2), 2.33 (6 H, s, Me), 2.93 (8 H, m, NCH_2), and 7.45 (8 H, m, ArH); *m/z* 323 ($M - Ts^+$).

1,7-*Bis*(p-*tolylsulphonyl*)-1,7-*diazacyclopentadecane* (**43**), δ 1.16 (16 H, m, CH_2), 2.33 (6 H, s, Me), 2.90 (8 H, m, NCH_2), and 7.50 (8 H, m, ArH); *m/z* 365 ($M - Ts^+$).

1,10-*Bis*(p-*tolylsulphonyl*)-1,10-*diazacyclo-octadecane* (**44**), δ 1.16 (24 H, m, CH_2), 2.10 (6 H, s, Me), 2.90 (8 H, m, NCH_2), and 7.50 (8 H, m, ArH); *m/z* 407 ($M - Ts^+$).

4,10-*Bis*[2-(p-*tolylsulphonylamino*)*ethyl*]-1,7-*dioxa*-4,10-*diazacyclododecane* (**45**).—*N*-Tosylaziridine (**23**) (9.85 g, 0.05 mol) in dry acetonitrile (120 ml) was added dropwise over 1 h to a refluxing solution of diazacrown ether (**24b**) (4.35 g, 0.025 mol) in acetonitrile (120 ml) under nitrogen. Evaporation of the solvent under reduced pressure and recrystallization of the residue from ethanol gave compound (**45**) as white crystals, δ 2.31 (6 H, s, Me), 2.50 (12 H, m, NCH_2), 2.80 (4 H, m, CH_2NTs), 3.55 (8 H, t, *J* 5 Hz, OCH_2), 6.75 (2 H, m, NH), and 7.40 (8 H, m, ArH); *m/z* 568 (M^+). In a similar way the following compounds were obtained.

7,13-*Bis*[2-(p-*tolylsulphonylamino*)*ethyl*]-1,4,10-*trioxa*-7,13-*diazacyclopentadecane* (**46**), δ 2.2 (6 H, s, Me), 2.43 (12 H, m, NCH_2), 2.70 (4 H, m, CH_2NTs), 3.35 (12 H, m, OCH_2), 5.70 (2 H, m, NH), and 7.33 (8 H, m, ArH); *m/z* 612 (M^+).

7,16-*Bis*[2-(p-*tolylsulphonylamino*)*ethyl*]-1,4,10,13-*tetraoxa*-7,16-*diazacyclo-octadecane* (**47**), δ 2.30 (6 H, s, Me), 2.50 (12 H, m, NCH_2), 2.80 (4 H, m, CH_2NTs), 3.41 (16 H, m, OCH_2), 5.87 (12 H, m, NH), and 7.41 (8 H, m, ArH); *m/z* 656 (M^+).

4,7-*Bis*(p-*tolylsulphonyl*)-13,18-*dioxa*-1,4,7,10-*tetra-azabicyclo*[8.5.5]*icosane* (**48**).—Crown ether (**45**) (5.68 g, 0.01 mol) and ethylene glycol bis(toluene-*p*-sulphonate) (**10**) (3.7 g, 0.01 mol) in toluene (400 ml) were added to a refluxing mixture of tetrabutylammonium iodide (1 g), 50% aqueous sodium hydroxide (100 ml), and toluene (200 ml) and the mixture was heated under reflux for 12—16 h. The organic layer was separated, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by column chromatography on neutral alumina (eluant benzene–chloroform–isopropyl alcohol 8:5:0.1), to give cryptand (**48**) as colourless crystals, δ 2.30 (6 H, s, Me), 3.68 (16 H, m, OCH_2, CH_2NTs), 2.50 (12 H, m, NCH_2), and 7.30 (8 H, m, ArH); *m/z* 594 (M^+). By this method the following compounds were prepared.

4,7-*Bis*(p-*tolylsulphonyl*)-13,16,21-*trioxa*-1,4,7,10-*tetra-azabicyclo*[8.8.5]*tricosane* (**49**), δ 2.32 (6 H, s, Me), 3.60 (20 H, m, OCH_2, CH_2NTs), 2.55 (12 H, m, NCH_2), and 7.43 (8 H, m, ArH); *m/z* 638 (M^+).

13,16-*Bis*(p-*tolylsulphonyl*)-4,7,21,24-*tetraoxa*-1,10,13,16-*tetra-azabicyclo*[8.8.8]*hexacosane* (**50**), δ 2.37 (6 H, s, Me), 3.67 (24 H, m, OCH_2, NCH_2Ts), 2.56 (12 H, m, NCH_2), 7.40 (8 H, m, ArH); *m/z* 682 (M^+).

4,10-*Bis*(p-*tolylsulphonyl*)-7,16,21-*trioxa*-1,4,10,13-*tetra-azabicyclo*[11.5.5]*tricosane* (**51a**), δ 2.33 (6 H, s, Me), 2.40 (12 H, m, NCH_2), 3.31 (20 H, m, OCH_2, CH_2NTs), and 7.00 (8 H, m, ArH); *m/z* 638 (M^+).

4,10-*Bis*(p-*tolylsulphonyl*)-7,16,19,24-*tetraoxa*-1,4,10,13-*tetra-azabicyclo*[11.8.5]*hexacosane* (**52a**), δ 2.33 (6 H, s, Me), 2.63 (12 H, m, NCH_2), 3.40 (24 H, m, OCH_2, CH_2NTs), and 7.40 (8 H, m, ArH); *m/z* 682 (M^+).

4,10-*Bis*(p-*tolylsulphonyl*)-7,16,19,24,27-*pentaoxa*-1,4,10,13-

tetra-azabicyclo[11.8.8]*nonacosane* (**53a**), δ 2.33 (6 H, s, Me), 2.60 (12 H, m, NCH_2), 3.40 (28 H, m, OCH_2, CH_2NTs), and 7.33 (8 H, m, ArH); *m/z* 726 (M^+).

4,13-*Bis*(p-*tolylsulphonyl*)-7,10,19,24-*tetraoxa*-1,4,13,16-*tetra-azabicyclo*[14.5.5]*hexacosane* (**54a**), δ 2.33 (6 H, s, Me), 2.43 (12 H, m, NCH_2), 3.33 (24 H, m, OCH_2, CH_2NTs), and 7.00 (8 H, m, ArH); *m/z* 682 (M^+).

4,13-*Bis*(p-*tolylsulphonyl*)-7,10,19,22,27-*pentaoxa*-1,4,13,16-*tetra-azabicyclo*[14.8.5]*nonacosane* (**55a**), δ 2.30 (6 H, s, Me), 2.67 (12 H, m, NCH_2), 3.45 (28 H, m, OCH_2, CH_2NTs), and 7.43 (8 H, m, ArH); *m/z* 726 (M^+).

4,13-*Bis*(p-*tolylsulphonyl*)-7,10,19,22,27,30-*hexaoxa*-1,4,13,16-*tetra-aza*[14.8.8]*dotriacontane* (**56a**), δ 2.37 (6 H, s, Me), 2.67 (12 H, m, NCH_2), 3.67 (32 H, m, OCH_2, CH_2NTs), and 7.35 (8 H, m, ArH); *m/z* 770 (M^+).

4,7,10-*Tris*(p-*tolylsulphonyl*)-16,19,24-*trioxa*-1,4,7,10,13-*penta-azabicyclo*[11.8.5]*hexacosane* (**57a**), δ 2.33 (9 H, s, Me), 2.45 (12 H, m, NCH_2), 2.66 (12 H, m, CH_2NTs), 3.38 (12 H, m, OCH_2), and 7.40 (12 H, m, ArH); *m/z* 681 ($M - Ts^+$).

4,7,10-*Tris*-(p-*tolylsulphonyl*)-16,19,24,27-*tetraoxa*-1,4,7,10,13-*penta-azabicyclo*[11.8.8]*nonacosane* (**58a**), δ 2.23 (9 H, s, Me), 2.43 (12 H, m, NCH_2), 2.66 (12 H, m, CH_2 NTs), 3.33 (16 H, m, OCH_2), and 7.30 (12 H, m, ArH); *m/z* 725 ($M - Ts^+$).

4,9-*Bis*(p-*tolylsulphonyl*)*benz*[f]-15,20-*dioxa*-1,4,9,12-*tetra-azabicyclo*[10.5.5]*docosane* (**59**), δ 2.30 (6 H, m, Me), 2.60 (12 H, m, NCH_2), 2.76 (4 H, m, CH_2NTs), 3.43 (8 H, m, OCH_2), 4.37 (4 H, s, $PhCH_2N$), 7.01 (4 H, s, Ph), and 7.50 (8 H, m, ArH); *m/z* 670 (M^+).

4,9-*Bis*(p-*tolylsulphonyl*)*benz*[f]-15,18,23-*trioxa*-1,4,9,12-*tetra-azabicyclo*[10.8.5]*pentacosane* (**60**), δ 2.32 (6 H, s, Me), 2.50 (12 H, m, NCH_2), 2.92 (4 H, m, NCH_2Ts), 3.57 (8 H, m, OCH_2), 3.55 (4 H, s, OCH_2CH_2O), 4.50 (4 H, s, $PhCH_2N$), 7.25 (4 H, s, Ph), and 7.49 (8 H, m, ArH); *m/z* 715 (M^+).

4,9-*Bis*(p-*tolylsulphonyl*)*benz*[f]-15,18,23,26-*tetraoxa*-1,4,9,12-*tetra-azabicyclo*[10.8.8]*octacosane* (**61**), δ 2.37 (6 H, s, Me), 2.50 (12 H, m, NCH_2), 3.07 (4 H, m, CH_2NTs), 3.20 (8 H, m, OCH_2), 3.37 (8 H, s, OCH_2CH_2O), 4.50 (4 H, s, $PhCH_2N$), 7.25 (4 H, s, Ph), and 7.50 (8 H, m, ArH); *m/z* 756 (M^+).

4,11-*Bis*(p-*tolylsulphonyl*)-6,9-*etheno*-17,22-*dioxa*-1,4,11,14-*tetra-azabicyclo*[12.5.5]*tetracosa*-6,8-*diene* (**62**), δ 2.33 (6 H, s, Me), 2.43 (12 H, m, NCH_2), 2.83 (4 H, m, CH_2NTs), 3.23 (8 H, t, *J* 5 Hz, OCH_2), 4.10 (4 H, s, $PhCH_2N$), 7.01 (4 H, s, Ph), and 7.50 (8 H, m, ArH); *m/z* 670 (M^+).

4,11-*Bis*(p-*tolylsulphonyl*)-6,9-*etheno*-17,20,25-*trioxa*-1,4,11,14-*tetra-azabicyclo*[12.8.5]*heptacosa*-6,8-*diene* (**63**), δ 2.25 (6 H, s, Me), 2.50 (12 H, m, NCH_2), 3.50—3.12 (16 H, m, OCH_2, CH_2NTs), 4.13 (4 H, s, $PhCH_2N$), 7.30 (4 H, s, Ph), and 7.40 (8 H, m, ArH); *m/z* 715 (M^+).

4,11-*Bis*(p-*tolylsulphonyl*)-6,9-*etheno*-17,20,25,28-*tetraoxa*-1,4,11,14-*tetra-azabicyclo*[12.8.8]*triaconta*-6,8-*diene* (**64**), δ 2.33 (6 H, s, Me), 2.43 (12 H, m, NCH_2), 2.83 (4 H, m, CH_2NTs), 3.20 (8 H, m, OCH_2), 3.37 (8 H, s, OCH_2CH_2O), 4.10 (4 H, s, $PhCH_2N$), 7.20 (4 H, s, Ph), and 7.50 (8 H, m, ArH); *m/z* 756 (M^+).

1,7-*Dioxa*-4,10-*diazacyclododecane* (**24b**).—A solution of crown ether (**24a**) (9.6 g, 0.02 mol) in dry THF was added to a boiling suspension of $LiAlH_4$ (7.6 g, 0.2 mol) in dry THF (100 ml) and the mixture heated under reflux for 20 h. The excess of $LiAlH_4$ was decomposed under cooling by the action of ethyl acetate and water. The precipitate formed was filtered and washed many times with ethyl acetate and chloroform. The combined extracts were dried ($MgSO_4$), and the residue was boiled with hexane. Evaporation of the solvent resulted in compound (**24b**) as white needles, δ 2.40 (2 H, s, NH), 2.80 (8 H, t, *J* 4.8 Hz, NCH_2), and 3.66 (8 H, t, *J* 5 Hz, OCH_2); *m/z* 174 (M^+). By this method the following compounds were prepared.

1,4,10-*Trioxa*-7,13-*diazacyclopentadecane* (**25b**), δ 2.20 (2 H, s, NH), 2.75 (8 H, t, *J* 4.9 Hz, NCH_2), and 3.60 (12 H, t, *J* 5 Hz, OCH_2); *m/z* 218 (M^+).

1,4,7,13-*Tetraoxa*-10,16-*diazacyclo-octadecane* (**26b**), δ 2.10 (2 H, s, NH), 2.70 (8 H, t, *J* 4.9 Hz, NCH_2), and 3.55 (16 H, m, OCH_2); *m/z* 262 (M^+).

1,4,10,13-*Tetraoxa*-7,16-*diazacyclo-octadecane* (**27b**), δ 2.30 (2 H, s, NH), 2.70 (8 H, t, *J* 4.9 Hz), and 3.60 (16 H, m, OCH_2); *m/z* 262 (M^+).

1,4,7,13,16-*Pentaoxa*-10,19-*diazacyclohenicosane* (**28b**), δ 1.88 (2 H, s, NH), 2.57 (8 H, t, *J* 5 Hz, NCH_2), and 3.48 (20 H, m, OCH_2); *m/z* 306 (M^+).

1,4,7,13,16,19-*Hexaoxa*-10,22-*diazacyclotetracosane* (**29b**), δ 2.07 (2 H, s, NH), 2.72 (8 H, t, *J* 5 Hz, NCH_2), and 3.48 (24 H, m, OCH_2); *m/z* 350 (M^+).

1-*Oxa*-4,7,10-*triazacyclododecane* (**30b**).—A mixture of the azacrown ether (**30a**) (1.7 g, 0.005 mol) and phenol (2 g) in a 30% solution of HBr in glacial acetic acid (25 g) was stirred at 50 °C for 12—14 h. The solution was poured into dry diethyl ether (700 ml) and the hydrobromide formed filtered off, basified with sodium hydroxide (pH 11), and the product extracted with chloroform (5 × 50 ml). The combined extracts were dried ($MgSO_4$), and the residue was heated under reflux with hexane. Evaporation of the solvent yielded the azacrown ether (**50b**) as white crystals, δ 2.00 (3 H, s, NH), 2.73 (12 H, t, *J* 5 Hz, NCH_2), and 3.57 (4 H, t, *J* 5 Hz, OCH_2); *m/z* 173 (M^+). By this method the following compounds were prepared.

1,4-*Dioxa*-7,10,13-*triazacyclopentadecane* (**31b**), δ 2.17 (3 H, s, NH), 2.77 (12 H, t, *J* 5.5 Hz, NCH_2), and 3.63 (8 H, t, *J* 5 Hz, OCH_2); *m/z* 217 (M^+).

1,4,7-*Trioxa*-10,13,16-*triazacyclo-octadecane* (**32b**), δ 2.10 (3 H, s, NH), 2.78 (12 H, m, NCH_2), and 3.60 (12 H, m, OCH_2); *m/z* 261 (M^+).

1,4,7,10-*Tetra-azacyclododecane* (**33b**), δ 2.50 (4 H, s, NH) and 2.80 (16 H, s, NCH_2); *m/z* 172 (M^+).

1,5,9-*Triazacyclododecane* (**34b**), δ 1.61 (6 H, m, CH_2), 2.60 (3 H, s, NH), and 2.80 (12 H, t, *J* 8 Hz, NCH_2); *m/z* 171 (M^+).

1-*Oxa*-4,8,12-*triazacyclotetradecane* (**35b**), δ 1.37 (4 H, m, CH_2), 2.03 (3 H, s, NH), 2.50 (12 H, t, *J* 5.5 Hz, NCH_2), and 3.30 (4 H, t, *J* 5 Hz, OCH_2); *m/z* 201 (M^+).

1,4-*Dioxa*-7,11,15-*triazacycloheptadecane* (**36b**), δ 1.37 (4 H, m, CH_2), 2.03 (3 H, s, NH), 2.63 (12 H, t, *J* 4.9 Hz, NCH_2), and 3.35 (8 H, m, OCH_2); *m/z* 245 (M^+).

1,4,7-*Trioxa*-10,14,18-*triazacycloicosane* (**37b**), δ 1.48 (4 H, m, CH_2), 2.05 (3 H, s, NH), 2.48 (12 H, t, *J* 5 Hz, NCH_2), and 3.40 (12 H, t, *J* 5 Hz, OCH_2); *m/z* 289 (M^+).

1,4,8,12-*Tetra-azacyclopentadecane* (**38b**), δ 1.63 (6 H, m, CH_2), 2.21 (4 H, s, NH), and 2.67 (16 H, t, *J* 5 Hz, NCH_2); *m/z* 215 (M^+).

1-*Oxa*-4,8,11,15-*tetra-azacycloheptadecane* (**39b**), δ 1.63 (4 H, m, CH_2), 1.88 (4 H, s, NH), 2.63 (16 H, m, NCH_2), and 3.53 (4 H, t, *J* 5 Hz, OCH_2); *m/z* 244 (M^+).

1,4-*Dioxa*-7,11,14,18-*tetra-azacycloicosane* (**40b**), δ 1.65 (4 H, m, CH_2), 1.90 (4 H, s, NH), 2.65 (16 H, m, NCH_2), and 3.53 (8 H, m, OCH_2); *m/z* 288 (M^+).

1,4,7-*Trioxa*-10,14,17,21-*tetra-azacyclotricosane* (**41b**), δ 1.60 (4 H, m, CH_2), 1.90 (4 H, s, NH), 2.65 (16 H, m, NCH_2), and 3.55 (12 H, m, OCH_2); *m/z* 332 (M^+).

7,16,21-*Trioxa*-1,4,10,13-*tetra-azabicyclo*[11.5.5]*tricosane* (**51b**), δ 2.20 (2 H, s, NH), 2.75 (20 H, m, NCH_2), and 3.41 (12 H, m, OCH_2); *m/z* 330 (M^+).

7,16,19,24-*Tetraoxa*-1,4,10,13-*tetra-azabicyclo*[11.8.5]*hexacosane* (**52b**), δ 2.33 (2 H, s, NH), 2.61 (20 H, m, NCH_2), and 3.47 (16 H, m, OCH_2); *m/z* 374 (M^+).

7,16,19,24,27-*Pentaoxa*-1,4,10,13-*tetra-azabicyclo*[11.8.8]-

nonacosane (**53b**), δ 2.30 (2 H, s, NH), 2.60 (20 H, m, NCH_2), and 3.47 (16 H, m, OCH_2); *m/z* 418 (M^+).

7,10,19,22,27-*Pentaoxa*-1,4,13,16-*tetra-azabicyclo*[14.8.5]-*hexacosane* (**55b**), δ 2.53 (20 H, m, CH_2) and 3.50 (22 H, m, OCH_2, NH); *m/z* 418 (M^+).

7,10,19,22,27-*Hexaoxa*-1,4,13,16-*tetra-azabicyclo*[14.8.8]-*dotriacontane* (**56b**), δ 2.31 (2 H, s, NH), 2.68 (20 H, m, NCH_2), and 3.48 (24 H, m, OCH_2); *m/z* 462 (M^+).

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