# Formation of Complexes between Aza Derivatives of Crown Ethers and Primary Alkylammonium Salts. Part 8.[1] 12-Crown-4, 15-Crown-5, 21-Crown-7, and 24-Crown-8 Derivatives

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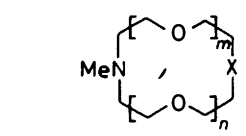
The monoaza-crown ethers (**3**), (**4**), and (**5**) and the diaza-crown ethers (**6**), (**7**), (**10**), and (**11**) form complexes with primary alkylammonium thiocyanates in organic solvents. The diaza-15-crown-5 system (**11**) forms well defined 1 : 1 complexes with the *cis*-,*cis*-stereochemistry shown in (**16**) but the diaza-24-crown-8 derivative (**7**) forms a 2 : 1 complex (G : H ratio) with benzylammonium thiocyanate having the *cis,cis,trans,trans*-stereochemistry (**17a**). The diaza-24-crown-6 derivative (**10**) forms weak 1 : 1 complexes which apparently adopt the double nesting conformation (**18**).

In previous papers of this series[1] we have discussed complex formation between a variety of aza-crown ethers and alkylammonium cations in organic solvents such as chloroform and methylene dichloride. Most of the complexes of this type that have been described[2] have been formed by host macrocycles having a ring size of 15—22 atoms and the complexes of 18-membered rings have been investigated particularly extensively. Smaller ring systems have also been used and, in particular, the diaza-12-crown-4 derivative (**1**) has been shown to form complexes[3] with both primary and secondary alkylammonium salts. Larger ring systems, such as 30-crown-10, form complexes with metal cations and primary alkylammonium salts[2,4] and, in general, large rings are expected to form complexes provided that they can adopt an appropriate conformation. In principle, the multiple binding sites of the larger rings might permit them to act as hosts for two guest alkylammonium cations, as has been reported,[5] for example, for the complex of 24-crown-8 with potassium ions. Although no example of a 2 : 1 complex between guest organic cations and a monocyclic host had been recognised at the time that this work was commenced[6] the formation of 1 : 1 : 1 complexes between the 30-crown-10 system (**2**), a guest primary alkylammonium cation, and water or a primary amine has recently been reported.[7]

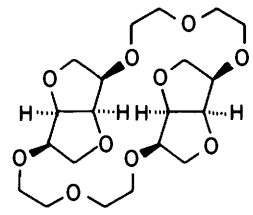
Large ring systems of the crown ether type can also act as hosts for guests other than alkylammonium cations. For example, 27-crown-9 has been shown[8,9] to be an efficient host for the guanidinium and imidazolium cations, dibenzo-30-crown-10 forms complexes with the diquat dication,[10] and other dibenzo-crown ethers form complexes with metal ammines.[11] Other large ring systems may even complex, and stabilize, transition states for ester aminolysis.[12] It was therefore of interest to examine complex formation involving alkylammonium cations and aza analogues of 21-crown-7 and 24-crown-8.

The required monoaza systems (**3**), (**4**), and (**5**) were readily synthesized by the reaction of the dianion from *N*-(*p*-tolylsulphonyl)diethanolamine with the appropriate polyethylene glycol bis(toluene-*p*-sulphonate) using a procedure analogous to that used previously[13] for the synthesis of monoaza-15-crown-5 and monoaza-18-crown-6. The corresponding diaza systems (**6**) and (**7**) may be prepared either by the methods used by J. M. Lehn and co-workers[14] for the synthesis of cryptands or by suitable adaptation of the methods that we have reported[15] in this series of papers. The reaction of the dianion from *N*-(*p*-tolylsulphonyl)diethanolamine with diethyleneglycol bis(toluene-*p*-sulphonate) gave a mixture of the 12-crown-4 derivative (**8**) (6% yield), used for the synthesis of the *N*-methyl derivative (**3**), and the 24-crown-8 derivative (**9**) (10% yield) which could be used to provide an alternative route to the *NN'*-dimethyldiaza-24-crown-8 (**7**). Finally, the reaction between α,α'-dibromo-*m*-xylene and the dianion from *N*-methyldiethanolamine gave a low, but acceptable, yield (11%) of the 24-crown-6 derivative (**10**).

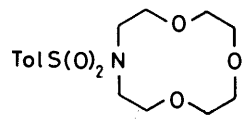
The formation of complexes by the aza-crown ethers (**3**)—(**7**) and (**10**) has been investigated and in addition we report details of complex formation by the diaza-15-crown-5 derivative (**11**).



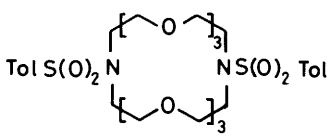
(**1**) X = NMe, *m* = *n* = 1
(**3**) X = O, *m* = *n* = 1
(**4**) X = O, *m* = 2, *n* = 3
(**5**) X = O, *m* = *n* = 3
(**6**) X = NMe, *m* = 2, *n* = 3
(**7**) X = NMe, *m* = *n* = 3
(**11**) X = NMe, *m* = 1, *n* = 2



(**2**)

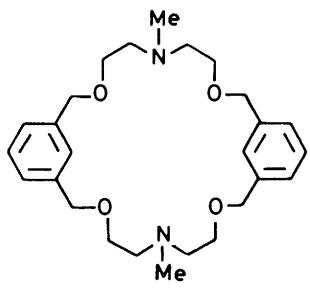


(**8**)



(**9**)

Tol = *p*-$CH_3C_6H_4$



(**10**)

**Table 1.** $^1$H N.m.r. spectra (220 MHz) of complexes of monoaza-crown ethers (**3**), (**4**), and (**5**) with primary alkylammonium thiocyanates[a]

| Host | Guest cation | Ratio G:H | Temp. °C | Host spectrum: $NCH_2$ | Host spectrum: NMe | Guest spectrum: $CH_2$ | Guest spectrum: CH[b] | Guest spectrum: Me[b] | Guest spectrum: $\overset{+}{N}H_3$ |
|---|---|---|---|---|---|---|---|---|---|
| (3) | — | — | 26 | 2.64[c] | 2.33 | | | | |
| (3) | $PhCH_2\overset{+}{N}H_3NCS^-$ | 1:1 | 26 | 2.99[c] (AB) | 2.47 | 3.98 | | | |
| | | | −70 | 2.38 (A), 2.78 (B) | 1.91 | | | | 8.4 (br) |
| | | 2:1 | −70 | 2.5br (A), 2.85br (B) | 1.95(br) | 3.96 | | | 7.9 (br) |
| | | | −110 | | | | | | 7.5 (F), 8.4 (C) |
| (3) | $PhCHMe\overset{+}{N}H_3NCS^-$ | 1:1 | 26 | 2.88 (m, ABCD) | 2.30 | | 4.23 | 1.52 | |
| | | | −70 | 2.30 (B + D), 2.53 (A) 2.80 (C) | 1.67 | | 4.26 | 1.57 | 8.2 (br) |
| (3) | $Ph_2CH\overset{+}{N}H_3NCS^-$ | 1:1 | 26 | 3.17[c] (AB) | 2.63 | | | | |
| | | | −70 | 2.56 (A), 2.87 (B) | 1.83,[g] 2.27[h] | | | | |
| (4) | — | — | 26 | 2.69[c] | 2.33 | | | | |
| (4) | $PhCH_2\overset{+}{N}H_3NCS^-$ | 1:1 | 26 | 2.57[c] | 2.13 | 4.13 | | | |
| | | | −95 | *ca.* 2.2,[d] 2.82[d] | 2.17,[d] 1.34[e] | 4.07,[d] 4.20 | | | 7.73,[d] 7.90[e] |
| (5) | — | — | 26 | 2.67[c] | 2.32 | | | | |
| (5) | $PhCH_2\overset{+}{N}H_3NCS^-$ | 1:1 | 26 | 2.46[c] | 2.11 | 4.24 | | | |
| | | | −110 | 1.61br,[f] 2.25br,[f] 2.54br[f] | 1.96,[f] 2.10[f] | | | | *ca.* 7.5,[f] 8.6[f] |

[a] All spectra run for *ca.* 0.15M solutions in $CD_2Cl_2$, chemical shifts recorded in p.p.m. (δ) relative to tetramethylsilane. The descriptions (AB) and (ABCD) refer to time-averaged signals from sites (A) and (B) and sites (A), (B), (C), and (D) respectively. The descriptions (F) and (C) refer to signals from the free and complexed guest species respectively. [b] $AX_3$ System, $J_{AX}$ 7 Hz for guest $PhCHCH_3\overset{+}{N}H_3$. [c] $NCH_2$ (t, *J* 5 Hz at 26 °C) for all cases. [d] Major isomer. [e] Minor isomer. [f] Signals from two complexes in *ca.* 1:1 ratio. [g] Broadens and sharpens on further cooling, s 1.36 at −110 °C. [h] Probably assignable to free host.

## Formation of Complexes by Aza-crown Ether Derivatives

*Monoaza-crown Ethers.*—*N*-Methyl monoaza-12-crown-4 (**3**) in $CD_2Cl_2$ shows changes in its $^1$H n.m.r. spectrum, on the addition of one molar equivalent of benzylammonium thiocyanate, that are consistent with the formation of a 1:1 complex (Table 1). When the solution is cooled the triplet signal for the $NCH_2$ group broadens and separates into two broad signals at low temperatures (< −75 °C) indicating that face-to-face exchange of the guest cation is slow (process E + I).[13] The spectrum of a solution containing an excess of the guest salt (guest:host ratio 2:1) shows similar temperature dependence of the host signals and at very low temperatures (< −90 °C) two broad $\overset{+}{N}H_3$ signals are observable which may be assigned to free (δ 7.5) and complexed (δ 8.4) cations. The free-energy barriers for guest exchange, derived* from these line-shape changes, are somewhat lower ($\triangle G^{\ddagger}$ 10.5 kcal mol$^{-1}$ for a 1:1 guest:host ratio and $\triangle G^{\ddagger}$ 11.5 kcal mol$^{-1}$ for a 2:1 guest:host ratio) than the energy barriers for similar processes[3] in complexes of *NN'*-dimethyldiaza-12-crown-4 (**1**) and there is no clear evidence for hindered conformational changes in the complex (**3**)·$PhCH_2\overset{+}{N}H_3NCS^-$. Similar phenomena are observable in the n.m.r. spectrum of the complex of the host (**3**) with (*R*)-1-phenylethylammonium thiocyanate, but in this case, because the guest cation is chiral,[13,15] two overlapping pairs of $NCH_2$ signals (Table 1, A + B and C + D) are observable at low temperatures due to the lack of symmetry in the complex. There are also further poorly defined changes in the n.m.r. spectrum in the range −90 to −110 °C which may be associated with hindered conformational changes of the host macrocycle (*cf.* ref. 3). There is no evidence that the monoaza-12-crown-4 system (**3**) forms more than one type of complex with each of these two guests and, in view of the high-field shifts observed for the host NMe signal at low temperatures, it appears likely that these complexes both have the *cis*-stereochemistry (**12**), similar to that noted[13] for analogous complexes (**13**) of *N*-methylaza-15-crown-5. The host (**3**) also forms a complex with benzhydrylammonium thiocyanate, but in this case there are two NMe signals at low temperatures (Table 1, δ1.83 and δ 2.27) corresponding to either a mixture of *cis*- and *trans*-complex or a mixture of the *cis*-complex and some free host. On the basis of these results the monoaza-12-crown-4 system is evidently a less satisfactory host macrocycle for primary alkylammonium cations than is the monoaza-15-crown-5 system which has one additional heteroatom to participate in guest–host binding.

The monoaza-21-crown-7 (**4**) and monoaza-24-crown-8 (**5**) derivatives also form complexes with primary alkylammonium salts (Table 1) but the temperature dependence of the n.m.r. spectra of these complexes is, in both cases, complex and rather poorly defined. At low temperature the $NCH_2$ triplet broadens and separates into two or more broad signals indicating that the process E + I becomes slow. In the case of the 21-membered host (**4**) the NMe signals indicate a major (δ 2.17) and a minor (δ 1.34) species of complex at −95 °C, and in the case of the 24-membered host (**5**) there are two NMe signals (δ 1.96 and δ 2.10) at −110 °C, of approximately equal intensity. In both cases, the addition of an excess of the guest cation does not lead to the formation of a 2:1 complex, in contrast with the complexing properties of the diaza-24-crown-8 system (**7**).

*Diaza-crown Ethers.*—The diaza-15-crown-5 derivative (**14**) has been shown[16] to form 1:1 complexes with primary alkylammonium cations. These complexes had well defined $^1$H n.m.r. spectra which provided evidence for the formation of a single type of complex, presumed to have the *cis,cis*-stereochemistry shown in (**15**). It was therefore of interest to examine the complexes of the structurally simpler diaza-15-crown-5 derivative (**11**). The diaza crown ether (**11**) readily formed complexes with primary alkylammonium salts and the $^1$H n.m.r. spectra of the complexes in $CD_2Cl_2$ showed well defined sets of multiplets at low temperatures for the $NCH_AH_B$ protons of the

* Free energies of activation, as in earlier papers in this series,[13,15,16] are based upon the rate of the exchange process at the temperature where the separate n.m.r. signals observable at lower temperatures just coalesce to a broad singlet.

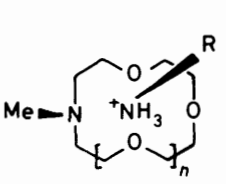
**Table 2.** $^1$H N.m.r. spectra (220 MHz) of complexes of diaza-crown ethers (**6**), (**7**), and (**11**) with primary alkylammonium thiocyanates[a] and diaza-crown ether (**11**) with hydronium thiocyanate

| | | | | Host spectrum | | Guest spectrum | | | |
|---|---|---|---|---|---|---|---|---|---|
| Host | Guest cation | Ratio G:H | Temp./°C | $NCH_2$ | NMe | $CH_2$ | CH[e] | Me[e] | $\overset{+}{N}H_3$ |
| (**11**) | — | — | 26 | 2.57,[b] 2.59[b] | 2.24 | | | | |
| (**11**) | $PhCH_2\overset{+}{N}H_3$ | 1:1 | 30 | 2.46[b] (AB1 + AB2) | 2.02 | 3.93 | | | 8.29 |
| | | | −50 | 2.06,[c] 2.31[c] (B1 + B2) | 1.90 | | | | 8.64 |
| | | | | 2.54,[d] 2.87[d] (A1 + A2) | | | | | |
| | | 2:1 | −80 | 2.02,[c] 2.26[c] (B1 + B2) | 1.84 | 3.84 (C) | | | 7.7 (br, F) |
| | | | | 2.51,[d] 2.84[d] (A1 + A2) | | 3.93 (F) | | | 8.61 (C) |
| (**11**) | (R)-$PhCHCH_3$ \| $^+NH_3$ | 1:1 | 26 | 2.3—2.5 (m, AB1234) | 1.92 | | 4.27 | 1.57 | |
| | | | −50 | 1.84,[c] 1.94,[c] 2.07[c] | (Me 12) | | | | |
| | | | | 2.40[c] | 1.16 | | | | |
| | | | | (B1 + B2 + B3 + B4) | (Me 1), 2.44 (Me 2) | | | | |
| | | | | 2.24,[d] 2.83,[d] 2.84,[d] 2.97[d] (A1 + A2 + A3 + A4) | | | | | |
| | | 2:1 | −70 | 1.85,[c] 2.00,[c] 2.09,[c] 2.40[c] | 1.12 | | 4.1—4.4 | 1.57 (C) | 8.44 (C) |
| | | | | (B1 + B2 + B3 + B4) | (Me 1) | | (br, C + F) | | |
| | | | | | 2.41 (Me 2) | | | 1.66 (F) | 7.5 (br, F) |
| | | | | 2.27,[d] 2.84,[d] 2.84,[d] 2.97[d] (A1 + A2 + A3 + A4) | | | | | |
| (**11**) | $H_3O^+$ | 1:1 | 26 | 2.59[b] (AB12) | 2.37 | | | | |
| | | | −68 | 2.33[c] (B1), 2.81[d] (A1) | 2.40 | | | | |
| | | | | 2.61 (m, A2 + B2) | | | | | |
| (**6**) | — | — | 26 | 2.59[b] | 2.27 | | | | |
| (**6**) | $PhCH_2\overset{+}{N}H_3$ | 1:1 | 26 | 2.52,[b] 2.54[b] | 2.13 | 4.08 | | | |
| | | | −90 | 2.6 (A1), 2.55 (B1) | 2.20 | | | | 7.94 |
| | | | | 2.89 (A2), 2.55 (B2) | | | | | |
| (**6**) | (*R*)-$PhCHCH_3\overset{+}{N}H_3$ | 1:1 | 26 | 2.4—2.7 (m) | 2.17 (Me 12) | | 4.42 | 1.54 | |
| | | | −110 | | 2.04 (Me 1), 2.16 (Me 2) | | 4.5 (br) | 1.5 (br) | |
| (**7**) | — | — | | 2.68[b] | 2.32 | | | | |
| (**7**) | $PhCH_2\overset{+}{N}H_3$ | 1:1 | 26 | 2.51[b] | 2.14 | 4.13 | | | |
| | | 2:1 | 26 | 2.56[b] | 2.17 | 4.05 ($CH_2$ 12) | | | |
| | | | −93[f] | 2.84[d] (A1), 2.56[c] (B1) | 1.95 | 3.85 ($CH_2$ 2), | | | |
| | | | | 2.61[d] (A2), 2.25[c] (B2) | | 3.93 ($CH_2$ 1) | | | |
| | | 4:1 | −70 | | 2.10 | 3.98 (br) | | | 8.19 (C) 7.75 (br, F) |
| (**7**) | (*R,S*)-*PhCHMe*$\overset{+}{N}H_3$ | 2:1 | 26[f] | 2.70[b] | 2.25 | | 4.35 | 1.57 | |
| (**7**) | (*R*)-$PhCHMe\overset{+}{N}H_3$ | 2:1 | 26[f] | 2.67[g] (A), 2.72 (B)[g] | 2.28 | | 4.35 | 1.58 | |

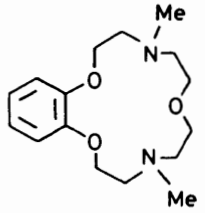
[a] All spectra run for *ca.* 0.15M solutions in $CD_2Cl_2$, chemical shifts recorded in p.p.m. (δ) relative to tetramethylsilane. [b] $NCH_2$ (t, *J* 5 Hz). [c] $NCH_B$ (d, *J* *ca.* 12 Hz). [d] $NCH_A$ (t, *J* *ca.* 12 Hz). [e] $AX_3$ spectrum, $J_{AX}$ 7 Hz for $PhCHCH_3\overset{+}{N}H_3$. [f] Spectrum run at 400 MHz. [g] $NCH_A$ (dt, *J* 13 and 5 Hz); $NCH_B$ (dt, *J* 13 and 5 Hz).

$NCH_2CH_2O$ units. The vicinal coupling constants derived from these multiplets* (Table 2) are consistent with the expected *gauche* conformation about the NC–CO bonds of the macrocycle and a slow rate for the process E + I. These multiplets collapsed as a result of rapid face-to-face guest exchange at temperatures above *ca.* 0 °C, corresponding to relatively high energy barriers ($\Delta G^{\ddagger}$ *ca.* 13 kcal mol$^{-1}$) for this process. The $NCH_2$ and NMe signals for the complex (**16**; R = $CH_2Ph$) show shifts to high field relative to the corresponding signals for the free host (**11**) (Table 2); this suggests that the complex has the *cis,cis*-stereochemistry shown. This stereochemistry is also consistent with the $^1$H n.m.r. spectrum of the complex (**16**; R = PhCHMe) which shows the expected[15,16] pair of NMe signals at low temperatures, one of which shows a considerable shift to high field (δ 1.16) as compared with the other (δ 2.44). At very low temperatures (< 90 °C) the spectrum shows additional changes, probably as a result of the slow interconversion of two enantiomeric conformations of the 15-membered ring, a result that is analogous to the behaviour[3] of the complexes of the diaza-12-crown-4 system (**1**). There are no additional signals detectable in the $^1$H n.m.r. spectra of either of the complexes (**16**; R = $CH_2Ph$) or (**16**; R = CHMePh) which might be associated

* Owing to the line widths of the signals at low temperatures only large coupling constants are resolved (*J* *ca.* 10—14 Hz); these are typically associated with geminal coupling in $CH_2$ groups and vicinal coupling for protons attached to C–H bonds having an antiperiplanar relationship.



(12) $n = 1$
(13) $n = 2$



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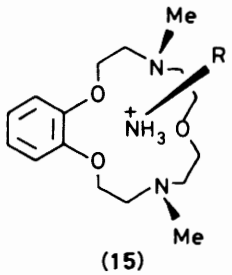

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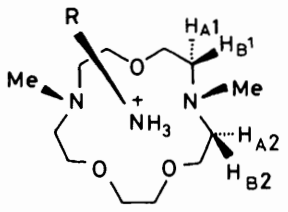


(16)

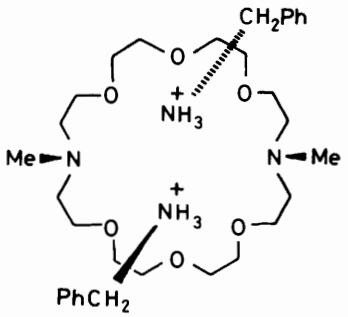
with another diastereoisomeric complex as noted[15] for the complexes of diaza-18-crown-6 systems. The host (**11**) also forms a hydronium ion complex[17] which shows similar spectroscopic behaviour to that of the ammonium salt complexes (**16**) in that the $NCH_2$ protons are observable as AB systems at low temperatures (Table 2), but neither the $NCH_2$ nor the NMe signals show the shifts to high field reported for the complexes (**16**). The energy barrier, derivable from the spectra, for face-to-face exchange of the guest hydronium cation ($\Delta G^{\ddagger}$ 13.8 kcal $mol^{-1}$) is too high to associate with a simple intramolecular proton exchange and is consistent with an $H_3O^+$ complex structurally analogous to the $R\overset{+}{N}H_3$ complexes.

The diaza-21-crown-7 derivative (**6**) forms rather poorly defined 1:1 complexes in $CD_2Cl_2$ with benzylammonium thiocyanate and 1-phenylethylammonium thiocyanate. The $^1H$ n.m.r. spectra of these complexes show changes associated with slow face-to-face guest exchange at very low temperatures (< −70 °C; $\Delta G^{\ddagger}$ 9.0 kcal $mol^{-1}$ for process E + I). The signal multiplicity at low temperatures suggests that more than one species of complex is present in the solution but the spectra are not sufficiently well resolved to allow us to comment on signal assignments. The diaza-24-crown-8 derivative (**7**) also gives a rather poorly defined, weakly bound complex with benzylammonium thiocyanate in a guest:host ratio of 1:1. However, the spectrum of a solution containing a 2:1 ratio of guest:host was more informative (Table 2) and at low temperatures (< −70 °C) the spectrum was well defined and could be associated with the formation of a 2:1 complex. Further evidence for the formation of a 2:1 complex was provided by the addition of further guest salt (4:1 guest:host ratio) which resulted in the observation of separate signals for the $\overset{+}{N}H_3$ protons of free and complexed guest at −70 °C whereas the spectrum of the $\overset{+}{N}H_3$ group in a solution containing a 2:1 guest:host ratio remained as a singlet down to −93 °C. The $NCH_2$ protons of the host in the 2:1 complex were shown, by decoupling experiments, to give the $H_A$ and $H_B$ signals of two different $NCH_AH_BCH_CH_DO$ systems at −93 °C. The resolvable vicinal coupling constants (*ca.* 12 Hz, see Table 2) are consistent with a *gauche* conformation for each $NCH_2$–$CH_2O$ system. The host NMe signal remained a singlet at all temperatures but the guest $\overset{+}{N}CH_2$ signal was observable as two singlets at −93 °C. There are five possible geometries (**17a**—**e**)* for a 2:1 complex but these signal multiplicities are only consistent with a complex having the *cis,cis,trans,trans*-stereochemistry (**17a**) (see Table 3 which shows the expected $NCH_2$, N*Me*, and $PhCH_2\overset{+}{N}$ multiplicities for all five complexes) in which guest–host dissociation and recombination is slow at low temperatures.

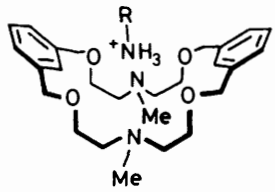
**Table 3.** Expected multiplicities[a] for $^1H$ n.m.r. spectra of $NCH_2$, $NCH_3$, and $PhCH_2$ groups in the complexes (**17a**—**e**)

| Complex | $PhCH_2$ | $NCH_2$ | $NCH_3$ | Stereochemistry[b] |
|---|---|---|---|---|
| (**17a**) | 2 × s | 2 × AB | 1 × s | *trans,trans*; *cis,cis* |
| (**17b**) | 1 × s | 1 × AB | 1 × s | *cis,cis*; *cis,cis* |
| (**17c**) | 1 × s | 1 × AB | 1 × s | *trans,trans*; *trans,trans* |
| (**17d**) | 1 × s | 2 × AB | 2 × s | *cis,trans*; *cis,trans* |
| (**17e**) | 1 × s | 2 × AB | 1 × s | *trans,cis*; *cis,trans* |

[a] s refers to a singlet signal, AB refers to the A and B signals of an ABCD system. [b] The first pair of stereochemical relationships refer to the first molecule of guest salt and its relationship to the two NMe groups of the host, the second pair refer similarly to the second molecule of guest salt and the two NMe groups taken in the *same* sequence.



(17a)



(18)

The stereoselectivity observed for the formation of the 2:1 complex (**17a**) is similar for that found[5] in the 2:1 complexes formed between sodium and potassium cations and 24-crown-8. The energy barriers for face-to-face guest exchange and site exchange of the guest molecules are of the same order ($\Delta G^{\ddagger}$ *ca.* 10—11 kcal $mol^{-1}$) and only a little lower than those found for similar processes in the 1:1 complexes formed between alkylammonium cations and aza-15-crown-5 and aza-18-crown-6 systems.[13,15,16] This suggests that all of the macrocycle heteroatoms are involved in binding the two guest cations but, in the absence of more precise structural information, it is not possible to speculate on the distribution of the hydrogen bonding that is involved. The 2:1 complex between methylammonium thiocyanate and the diaza-24-crown-8 (**7**) gives an n.m.r. spectrum that is less well resolved but spectral changes below −100 °C are not inconsistent with the formation of a complex analogous to (**17a**). The 2:1 complex formed between (*R,S*)-phenylethylammonium thiocyanate and the host (**7**) could consist of the two diastereoisomeric species (**7**)·(*R*)-$PhCHMe\overset{+}{N}H_3NCS^-$·(*S*)-$PhCHMe\overset{+}{N}H_3NCS^-$ and (**7**)·(*R*)-$PhCHMe\overset{+}{N}H_3NCS^-$·(*R*)-$PhCHMe\overset{+}{N}H_3NCS^-$ (and its enantiomer); on the other hand the 2:1 complexes of either (*R*)- or (*S*)-phenylethylammonium thiocyanate would consist of the second diastereoisomer only. The n.m.r. spectrum of (**7**)·[(*R,S*)-$PhCHMe\overset{+}{N}H_3$-

* One stereoisomer (**17a**) is shown; the other four possibilities are listed in Table 3.

**Table 4.** $^1$H N.m.r. spectra (220 MHz) of guest primary alkylammonium salts in complexes with the diaza-24-crown-6 derivative (**10**)

| | N.m.r. spectrum of guest salt[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $-CH-\overset{+}{N}H_3$ | | | | $-CH-C-\overset{+}{N}H_3$ | | | | $CH-C-C-\overset{+}{N}H_3$ |
| Temp./ °C | $CH_2Ph$ | $CH_3$ | $CH_2Me$ | $CH_2Et$ | $CHMe_2$ | $CH_2Me$ | $CH_2CHMe$ | $CHMe_2$ | $CMe_3$ | $CH_2CH_2Me$ |
| +26 | 3.23 | 1.60 (2.07)[b] | 1.86 | 2.13 | 2.65 | 0.75 | 1.30 | 0.88 | 1.11 | 0.76 |
| −30 | 2.51 | 0.94 (1.84)[b] | 0.89 | 1.13 | 1.92 | 0.55 | 1.03 | 0.72 | 0.91 | 0.69 |
| −70 | 2.03 | 0.66 (1.75)[b] | 0.45 | 0.40 | 1.46 | 0.52 | 0.90 | 0.45 | 0.77 | 0.50 |
| −100 | 1.33[c] | 0.49 | | | | 0.53 | 0.90 | 0.36 | 0.71 | 0.48 |

[a] Unless stated otherwise data refer to 1:1 ratios of guest thiocyanate salts and host (**10**), *ca.* 0.15M in $CD_2Cl_2$. Guest cations include $PhCH_2\overset{+}{N}H_3$, $Me\overset{+}{N}H_3$, $Et\overset{+}{N}H_3$, $Pr\overset{+}{N}H_3$, $Pr^i\overset{+}{N}H_3$, and $Bu^t\overset{+}{N}H_3$. Chemical shifts are given in p.p.m. (δ) relative to $SiMe_4$. [b] Values in parentheses refer to a G:H ratio of 2:1. [c] An additional signal assignable to a minor species appears at δ 1.60.

$NCS^-]_2$ differed from the spectrum of (**7**)·[(*R*)-$PhCHMe\overset{+}{N}H_3$-$NCS^-]_2$ over the temperature range +26 to −100 °C; at low temperatures the spectra were complex and definite assignments to $NCH_2$ and $NCH_3$ groups could not be made, nevertheless it is evident from the differences that there is no preference for the formation of either of the two diastereoisomeric complexes when the (*R*,*S*)-guest salt is used.

The diaza-24-crown-6 derivative (**10**) has fewer binding sites than the diaza-24-crown-8 derivative (**7**) and although it forms[6] a crystalline 2:1 (G:H ratio) complex with benzylammonium thiocyanate it is clear that the crystal structure of this complex is not related to the structure of complexes formed in solution. Thus the host (**10**) forms 1:1 complexes with a variety of primary alkylammonium thiocyanates and in all cases the n.m.r. spectrum of the $NCH_2$ protons of the macrocycle are observable as a triplet at 26 °C which collapses and changes to a very broad AB system ($\delta_A$ *ca.* 2.85, $\delta_B$ *ca.* 2.4) for samples at very low temperatures (< −100 °C) with a low energy barrier for the process E + I ($\Delta G^{\ddagger}$ *ca.* 9 kcal mol$^{-1}$). The most interesting feature of the n.m.r. spectra of these complexes is the high-field chemical shift for the $CH-\overset{+}{N}H_3$ signal of the guest cation which moves to higher field as the solution of the complex is cooled (Table 4). This high-field chemical shift is consistent with a double 'nesting' conformation (**18**) for the complex[18] and, as expected for such a structure, the high-field shift is still evident but decreased in magnitude for the $CH-C-\overset{+}{N}H_3$ signals. The spectra at low temperatures are not sufficiently well resolved to define the relative stereochemistry of the guest cation and the NMe groups (*cf.* ref. 15) but since the NMe signal does not show the shift to high field for a guest benzylammonium cation that is expected for a *cis,cis*-complex, such as (**16**), it is probable that the 1:1 complexes of the host (**10**) have *trans,trans*- or *cis,trans*-stereochemistry. The n.m.r. spectra of solutions of the guest cations and the host (**10**) in a 2:1 ratio show guest signals at a chemical shift intermediate between that of the free guest salt and the guest salt in a 1:1 complex and there is no evidence from these spectra for the formation of a 2:1 complex.

We conclude, from the results described in this paper, that 12-, 15-, and 18-membered aza-crown ethers form stronger complexes with guest primary alkylammonium cations than the analogous 21- and 24-membered hosts. Nevertheless hosts such as the diaza-24-crown-8 (**7**) and the diaza-24-crown-6 (**10**) may be of interest as components of macropolycyclic host systems because of their predictable stereochemistry of complexation.

## Experimental

$^1$H N.m.r. spectra were recorded in $CDCl_3$, unless otherwise stated, using either a Perkin-Elmer R34 (220 MHz) CW spectrometer or by the S.E.R.C. High Field n.m.r. service at Sheffield using a Bruker WH 400 FT spectrometer. Chemical shifts are given in p.p.m. (δ) relative to tetramethylsilane as internal reference. Sample temperatures were measured using either a methanol standard or a calibrated thermocouple. High-resolution mass spectra were recorded using an AE1 MS902 instrument. Columns for chromatography were prepared using Hopkin and Williams or Whatman silica gel (100—250 mesh) or Fluka neutral or basic alumina. Products were eluted using chloroform or methylene dichloride with increasing amounts of ethanol for the more polar products. M.p.s were determined using a Kofler hot-stage apparatus and are not corrected. Tetrahydrofuran (THF) was dried by heating under reflux with sodium in the presence of benzophenone under nitrogen until a blue solution was obtained, followed by distillation. Distillation of products was carried out using a Büchi Kügelrohr apparatus. Sodium hydride was obtained as a 50% dispersion in oil, the oil was removed by washing with dry pentane or hexane, and the quantities quoted refer to the reagent after the removal of the oil.

NN′-*Dimethyl*-2,8,17,23-*tetraoxa*-5,20-*diaza*[9.9]*metacyclophane* (**10**).—Half of a solution of α,α′-dibromo-*m*-xylene (7.92 g) in dry THF (50 ml) was added dropwise during 1 h to a gently boiling solution prepared from *N*-methyldiethanolamine (1.785 g) and sodium hydride (2.18 g) in dry THF (500 ml) under $N_2$. The remainder of the solution of the dibromide and *N*-methyldiethanolamine (1.785 g) in dry THF (25 ml) was added dropwise and simultaneously to the heated reaction mixture during 1 h and the reaction mixture was then heated under reflux and stirred for a further 6 h. The solution was cooled, water (200 ml) was added cautiously, and the THF was removed by evaporation. The products were extracted into chloroform (2 × 300 ml) and the combined extracts were washed with water, dried ($Na_2SO_4$), and evaporated. The residual oil was purified by column chromatography [alumina; ether and ether–ethanol (98:2)] to give the metacyclophane (**10**) (0.729 g, 11%) as a viscous oil which could be further purified by short-path distillation, b.p. 215 °C at 0.01 Torr (Found: $M^+$, 442.2829. $C_{26}H_{38}N_2O_4$ requires *M*, 442.2831); δ 7.15—7.40 (m, 8 × ArH), 4.50 (s, 4 × $ArCH_2O$), 3.53 (t, *J* 5 Hz, 4 × $OCH_2$), 2.66 (t, *J* 5 Hz, 4 × $NCH_2$), and 2.31 (s, 2 × $NCH_3$).

N-*Methyl*-1,4,7,10,13,16-*hexaoxa*-19-*azacyclohenicosane* (**4**).—A solution of *N*-(*p*-tolylsulphonyl)diethanolamine (12.95 g) in dry THF (75 ml) was added dropwise during 1 h to a stirred suspension of sodium hydride (3.60 g) in dry THF (300 ml) and the mixture was stirred for a further 2 h at room temperature. A solution of pentaethylene glycol bis(toluene-*p*-sulphonate) (27.3 g) in dry THF (75 ml) was added during 1 h to the solution of the dianion and the reaction mixture was stirred for a further 48 h at room temperature. Water (200 ml) was

added cautiously and the THF was removed by evaporation. The products were extracted into chloroform (4 × 200 ml) and purified by column chromatography on silica gel to give N-(p-*tolylsulphonyl*)-1,4,7,10,13,16-*hexaoxa*-19-*azacyclohenicosane* as a viscous oil (5.39 g, 23%) (Found: $M^+$ 461.2088. $C_{21}H_{35}NO_8S$ requires *M*, 461.2083); δ (AA′BB′ system) $\delta_A$ 7.70, $\delta_B$ 7.28 ($J_{AB} = J_{A'B}$ = 8 Hz, 4 × ArH), 3.4—3.8 (m, 2 × $NCH_2$ + 12 × $OCH_2$), and 2.39 (s, Ar$CH_3$). A solution of the *N*-(toluene-*p*-sulphonyl) derivative (850 mg) in THF (60 ml) containing lithium aluminium hydride (600 mg) was heated under reflux for 24 h. The suspension was cooled and excess of hydride was destroyed by the dropwise addition of cold water. The precipitated alumina was removed by filtration and washed with chloroform (50 ml) containing a little ethanol. The combined filtrate and washings were evaporated and the residual oil was purified by column chromatography on alumina to give 1,4,7,10,13,16-*hexaoxa*-19-*azacyclohenicosane* as an oil (428 mg, 77%) (Found: $M^+$, 307.1967. $C_{14}H_{29}NO_6$ requires *M*, 307.1995); $\nu_{max.}$ 3 340 $cm^{-1}$; δ 3.6—3.8 (m, 12 × $OCH_2$), 2.82 (t, *J* 5 Hz, 2 × $NCH_2$), and 2.59 (br s, NH). The above secondary amine (370 mg) was heated at 100 °C for 20 h with formic acid (1.2 ml) and formaldehyde (1.2 ml; 37% aqueous solution). Hydrochloric acid was added (2 ml; 11M) and the solution was evaporated to dryness. The residue was treated with excess of aqueous potassium hydroxide and the product was extracted into chloroform (3 × 35 ml). The extracts were washed with water and evaporated to give N-*methyl*-1,4,7,10,13,16-*hexaoxa*-19-*azacyclohenicosane* (**4**) as an oil (Found: $M^+$, 321.2152. $C_{15}H_{31}NO_6$ requires *M*, 321.2151); δ ($CD_2Cl_2$) 3.63 (m, 12 × $OCH_2$), 2.69 (t, *J* 5 Hz, 2 × $NCH_2$), and 2.33 (s, $NCH_3$).

N-*Methyl*-1,4,7,10,13,16,19-*heptaoxa*-22-*azacyclotetracosane* (**5**) was prepared by a similar reaction sequence. Addition of hexaethylene glycol bis(toluene-*p*-sulphonate) (29.5 g) to *N*-(*p*-tolylsulphonyl)diethanolamine (12.95 g) and sodium hydride (3.60 g) in THF (500 ml) gave N-(p-*tolylsulphonyl*)-1,4,7,10,13,16,19-*heptaoxa*-22-*azacyclotetracosane* as a viscous oil (4.25 g, 17%) (Found: $M^+$, 505.2345. $C_{23}H_{39}NO_9S$ requires *M*, 505.2385); δ (AA′BB system) $\delta_A$ 7.71, $\delta_B$ 7.29 ($J_{AB} = J_{A'B'}$ = 8 Hz, 4 × ArH), 3.4—3.8 (m, 2 × $NCH_2$ + 14 × $OCH_2$), and 2.40 (s, Ar$CH_3$). Treatment of the *N*-(toluene-*p*-sulphonyl) derivative (1.10 g) with lithium aluminium hydride (600 mg) in refluxing THF (50 ml) gave 1,4,7,10,13,16,19-*heptaoxa*-22-*azacyclotetracosane* as an oil (506 mg, 66%) [Found: $(M - 1)^+$, 350.2213. $C_{16}H_{33}NO_7$ requires $(M - 1)$, 350.2179]; $\nu_{max.}$ 3 330 $cm^{-1}$; δ 3.64 (t, *J* 5 Hz, 2 × $OCH_2$), 3.5—3.8 (m, 12 × $OCH_2$), 2.81 (t, *J* 5 Hz, 2 × $NCH_2$), and 2.56 (br s, NH). The secondary amine (380 mg) was methylated using formic acid (1.2 ml) and formaldehyde (1.2 ml; 37% aqueous solution) to give N-*methyl*-1,4,7,10,13,16,19-*heptaoxa*-22-*cyclotetracosane* (**5**) as an oil (365 mg, 93%) (Found: $M^+$, 365.2389. $C_{17}H_{35}NO_7$ requires *M*, 365.2413); δ($CD_2Cl_2$) 3.64 (t, *J* 5 Hz, 2 × $OCH_2$), 3.55—3.75 (m, 12 × $OCH_2$), 2.67 (t, *J* 5 Hz, 2 × $NCH_2$), and 2.32 (s, $NCH_3$).

NN′-*Bis*(*benzyloxycarbonyl*)-1,4,10,13,16-*pentaoxa*-7,19-*diazacyclohenicosane*.—A solution of *NN*′-bis(benzyloxycarbonyl)-1,8-diamino-3,6-dioxaoctane (4.16 g) in dry dimethyl sulphoxide (DMSO) (40 ml) was added during 15 min to a stirred suspension of sodium hydride (0.72 g) in DMSO (125 ml) under $N_2$. The mixture was stirred for a further 2 h and then a solution of tetraethylene glycol bis(toluene-*p*-sulphonate) (5.02 g) in DMSO (50 ml) was added dropwise during 30 min. The reaction mixture was stirred for a further 20 h, water (100 ml) and hydrochloric acid (125 ml; 2M) were added cautiously, and the products were extracted into chloroform (3 × 300 ml). The combined extracts were washed with water, dried ($Na_2SO_4$), and evaporated and the residual oil was purified by column chromatography on silica gel to give the required *macrocycle* as a viscous oil (1.92 g, 34%) (Found: C, 62.5; H, 7.4; N, 4.6%; $M^+$, 574. $C_{30}H_{42}N_2O_9$ requires C, 62.7; H, 7.3; N, 4.9%; *M*, 574); $\nu_{max.}$ 1 700 $cm^{-1}$; δ 7.25—7.50 (m, 2 × $C_6H_5$), 5.10 (s, 2 × $CH_2$Ar), 3.40 —3.75 (m, 4 × $NCH_2$ + 10 × $OCH_2$).

NN′-*Dimethyl*-1,4,7,13,16-*pentaoxa*-1,10-*diazacyclohenicosane* (**6**).—Treatment of the above macrocyclic dicarbamate (500 mg) with lithium aluminium hydride (600 mg) in refluxing THF (35 ml) for 8 h gave the *title product* (**6**) as an oil (170 mg, 58%) after purification by column chromatography on alumina (Found: $M^+$, 334.2461. $C_{16}H_{34}N_2O_5$ requires *M*, 334.2468); δ($CD_2Cl_2$) 3.40—3.65 (m, 10 × $OCH_2$), 2.59 (t, *J* 5 Hz, 4 × $NCH_2$), and 2.27 (s, 2 × $NCH_3$).

*Reaction of* N-(p-*Tolylsulphonyl*)*diethanolamine with Diethyleneglycol Bis*(*toluene*-p-*sulphonate*). *Formation of* N-(p-*Tolylsulphonyl*)-1,4,7-*trioxa*-10-*azacyclododecane* (**8**) *and* NN′-*Bis*-(p-*Tolylsulphonyl*)-1,4,7,13,16,19-*hexaoxa*-10,22-*diazacyclotetracosane* (**9**).—A solution of diethylene glycol bis(toluene-*p*-sulphonate) (41.4 g) in THF (150 ml) was added during 1 h to a solution prepared from *N*-(*p*-tolylsulphonyl)diethanolamine (25.9 g) and sodium hydride (7.20 g) in THF (150 ml). The reaction mixture was stirred for 48 h under $N_2$, water (400 ml) was added cautiously, and the THF was removed by evaporation. The products were extracted into chloroform (4 × 400 ml), the combined extracts were dried ($Na_2SO_4$) and evaporated, and the residual oil was purified by chromatography on silica gel to give two products. N-(p-*Tolylsulphonyl*)-1,4,7-*trioxa*-10-*azacyclododecane* (**8**) (1.85 g, 6% yield) was obtained as a solid, m.p. 55—62 °C (Found: $M^+$, 329.1305. $C_{15}H_{23}NO_5S$ requires *M*, 329.1297); δ(AA′BB′ system) $\delta_A$ 7.68, $\delta_B$ 7.28 ($J_{AB'} = J_{A'B'}$ = 8 Hz, 4 ArH), 3.78 (t, *J* 5 Hz, 2 × $OCH_2$), 3.60 (m, 4 × $OCH_2$), 3.29 (t, *J* 5 Hz, 2 × $OCH_2$), and 2.37 (s, Ar$CH_3$). NN′-*Bis*-(*p*-*tolylsulphonyl*)-1,4,7,13,16,19-*hexaoxa*-10,22-*diazacyclotetracosane* (**9**) (3.40 g, 10%) was obtained as needles from ether–ethanol, m.p. 104 °C (Found: C, 54.4; H, 7.0; N, 4.3%; $M^+$, 658. $C_{30}H_{46}N_2O_{10}S_2$ requires C, 54.7; H, 7.0; N, 4.3%; *M*, 658); δ (AA′BB′ system) $\delta_A$ 7.69, $\delta_B$ 7.28 ($J_{AB} = J_{A'B'}$ = 8 Hz, 8 ArH), 3.56 (s, 4 × $OCH_2CH_2O$), 3.55—3.65 (m, 4 × $OCH_2CH_2N$), and 2.40 (s, 2 × Ar$CH_3$).

1,4,7-*Trioxa*-10-*azacyclododecane*.—Lithium aluminium hydride (660 mg) was added in portions to a stirred solution of *N*-(*p*-tolylsulphonyl) monoaza-12-crown-4 (**8**) (1.00 g) in THF (50 ml). The reaction mixture was heated under reflux for 24 h, cooled, and excess of hydride was destroyed by the cautious addition of water. The precipitated alumina was removed by filtration and washed with chloroform (50 ml) containing a little ethanol. The combined filtrate and washings were evaporated and the residual oil was purified by column chromatography on alumina to give the monoaza-crown ether (224 mg, 42%) as a waxy solid, m.p. 44—46 °C (Found: $M^+$, 175.1196. $C_8H_{17}NO_3$ requires *M*, 175.1208); δ 3.72 (t, *J* 5 Hz, 2 × $OCH_2$), 3.55—3.70 (m, 2 × $OCH_2CH_2O$), 3.18 (br, s, NH), and 2.76 (t, *J* 5 Hz, 2 × $NCH_2$). The N-*methyl derivative* (**3**) (Eschweiler–Clark, 92% yield) was obtained as an oil, b.p. 88—90 °C at 0.005 Torr (Found: C, 56.5; H, 9.8; N, 6.0%; $M^+$, 233.1624. $C_{11}H_{23}NO_4$ requires C, 56.6; H, 9.9; N, 6.0%; $M^+$, 233.1627); δ 3.55—3.75 (m, 8 × $OCH_2$), 2.56 (t, *J* 5 Hz, 2 × $NCH_2$), and 2.24 (s, $NCH_3$).

NN′-*Dimethyl*-1,4,7,13,16,19-*hexaoxa*-10,22-*diazacyclotetracosane* (**7**).—Lithium aluminium hydride (800 mg) was added in portions to a solution of the 24-crown-8 derivative (**9**) (1.82 g) in THF (50 ml). The reaction mixture was heated under reflux for 50 h, cooled, and excess of hydride was destroyed by the cautious addition of water. The precipitated alumina was removed by filtration and washed with chloroform containing

a little ethanol. The combined filtrate and washings were evaporated and the residual oil was purified by column chromatography on alumina to give 1,4,7,13,16,19-hexaoxa-10,22-diazacyclotetracosane (270 mg, 42%), identical with a sample prepared by the published procedure.[14] The NN'-*dimethyl derivative* (**7**) (Eschweiler–Clark, 92% yield) was obtained as an oil (Found: $M^+$, 378.2746. $C_{18}H_{38}N_2O_6$ requires $M$, 378.2730); δ ($CD_2Cl_2$) 3.5—3.8 (m, 4 × $OCH_2CH_2O$), 3.62 (t, $J$ 5 Hz, 4 × $OCH_2$), 2.68 (t, $J$ 5 Hz, 4 × $NCH_2$), and 2.32 (s, 2 × $NCH_3$).

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