

Ion Selectivity Control in Ester- and Amide-armed Diaza-crown Ethers: Side-arm Effects in Co-operative Binding and Specific Transport

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A variety of double-armed diaza-18-crown-6 derivatives were prepared, in which ester-, amide-, and ether-functionalized arms were attached as secondary donor sites. Their cation-binding behaviour was largely dependent on the nature of the donor groups on the flexible arms. Typically, an amide-armed diaza-18-crown-6 derivative enveloped Zn^{2+} ion in a cryptand-like cavity, while an ester-armed one formed an encapsulated complex with Na^+ ion. This type of armed crown ether exhibited characteristic guest-selectivity and high binding dynamics, and provided efficient cation-transport phenomena.

Double-armed crown ethers and related macrocyclic host molecules are designed to mimic biological ion-carriers,¹ which are characterized by a parent macrocyclic ligand skeleton and functionalized donor-arms. In this class of compounds, the guest cation can be wrapped in such a way that the donor group on the flexible arm would provide further co-ordination to the guest cation trapped in the parent macro-ring. Their cation-binding structures are closely similar to those of bicyclic cryptand compounds, but high mobility of the ligating arm attached to the macro-ring may permit stable and dynamic complexation.

Previously, we have prepared a series of furan- and thiophene-armed crown ether, cyclam, and thia-crown ether derivatives.^{2,3} They provided excellent cation-transport abilities and high catalytic activities in phase-transfer reactions. Since cation-binding and related functions of armed macrocycles were determined by the combination of parent macrocycle and donor-arm group, further structural modification should offer the possibility in design of new host molecules showing interesting cation-binding and subsequent chemical functions.

We therefore prepared a series of diaza-18-crown-6 derivatives having a variety of donor groups on their side-arms. As new cation-ligating arm groups, we chose ester and amide groups which are frequently found in biological ion-carriers

such as valinomycin and nonactin. The purpose of this study was to understand the effect of ester- or amide-functionalized arms on the cation-binding and transport functions of the crown ether system. Recently, many kinds of lariat ethers and related macrocycles have been reported,⁴ but most of them have ether-oxygen atoms on the ligating side-arms. We found that ester- and amide-armed crown ethers formed characteristic host-guest complexes and exhibited interesting cation-transport properties.^{5,6}

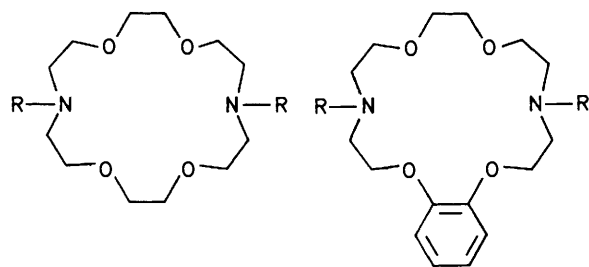
Results and Discussion

Cation-binding Properties of Double-armed Crown Ethers.—

The cation-binding behaviour of the armed crown ether derivatives was investigated by means of ^{13}C n.m.r. spectroscopy. Figure 1 illustrates Na^+ - and Zn^{2+} -induced changes in ^{13}C n.m.r. chemical shifts of carbonyl and crown ring (OCH_2) carbons of the armed crown ethers (**1a**) and (**4a**). For example, the addition of $NaClO_4$ to the ester-armed crown ether (**1a**) solution caused significant shifts of the signals both for arm- and for crown ring-carbons upon complexation, while only slight changes were observed in the presence of Zn^{2+} ion. This suggests that the ester group on the flexible arm selectively co-ordinates to the guest Na^+ ion trapped in the crown ring. Since the titration curves of ester-armed crown ether (**1a**) show sharper bends with Na^+ ion than with Zn^{2+} ion, it formed a more stable complex with the former ion.

Amide-armed crown ether (**4a**) showed largely different cation-binding profiles. Zn^{2+} ion induced remarkable shifts for the signals of amide carbons, while no change in the chemical shift of the amide carbons was observed on addition of Na^+ ion. Therefore, the amide-armed crown ether (**4a**) effected circular recognition for Na^+ ion, but acted as a cryptand-like ligand for Zn^{2+} ion. Although Zn^{2+} ion has a much smaller ionic size than the cavity size of the diaza-18-crown-6 ring, the flexible molecular structure may envelop the small Zn^{2+} ion in a three-dimensional sense. The pyridine-armed crown ethers have been reported to bind similarly with some transition metal cations.⁷ Probably, pronounced conformational changes easily occurred in the flexible crown ring skeleton. Figure 1 also indicates that amide-armed crown ether (**4a**) has a higher stability constant for Zn^{2+} ion than for Na^+ ion. Hence, the nature of the introduced arm-donor group is an essential factor in determining guest-selectivity and the structure of the resulting complex for an armed crown ether.

Table 1 summarizes the results of ^{13}C n.m.r. binding studies for the ester-, amide-, and ether-armed crown ethers, (**1a**), (**4a**),



R = CH_2CO_2Et	(1a)	(1b)
R = $[CH_2]_2CO_2Et$	(2a)	(2b)
R = $[CH_2]_3CO_2Et$	(3a)	(3b)
R = CH_2CONEt_2	(4a)	(4b)
R = $[CH_2]_2OMe$	(5a)	(5b)
R = $[CH_2]_9Me$	(6)	
R = H	(7)	
RR = $[CH_2]_2O[CH_2]_2O[CH_2]_2$	(8)*	

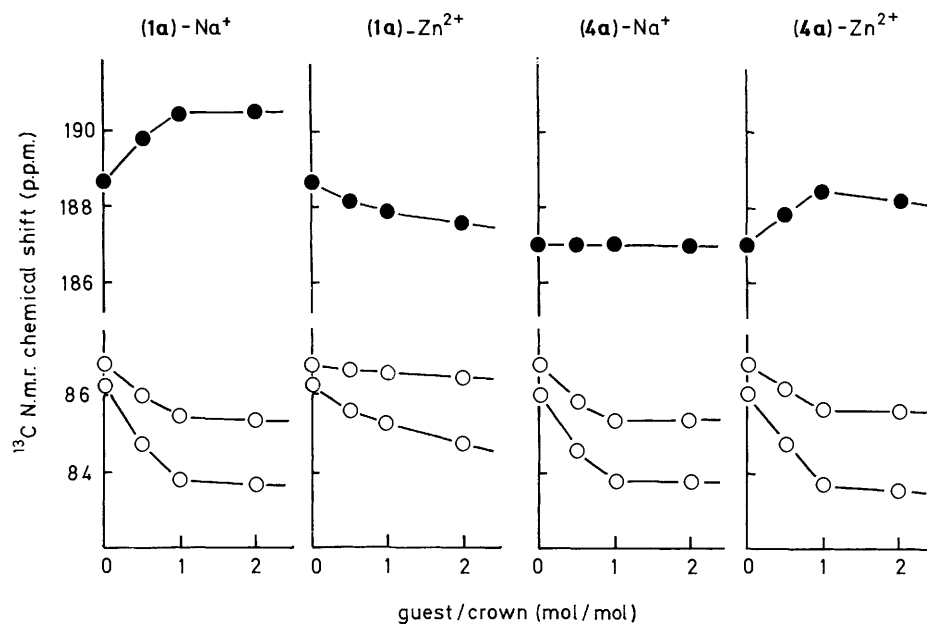


Figure 1. Guest-induced changes in ^{13}C n.m.r. chemical shifts of armed crown ethers (**1a**) and (**4a**) in DMF- D_2O (4:1). —●—: $-\text{CO}-$, —○—: $-\text{OCH}_2\text{CH}_2-$. The chemical shift indicated was determined by using the peak of the DMF carbonyl carbon (δ_{c} 180.00) as reference

Table 1. Guest-induced changes in ^{13}C n.m.r. chemical shifts of armed crown ethers^a

Crown	Carbon	Induced chemical shift (p.p.m.) ^b				
		Li^+	Na^+	K^+	Pb^{2+}	Zn^{2+}
 (1a)	a	-0.1	-1.4	-0.3	-1.0	-0.2
	b	-0.2	+1.2	-0.9	0	-0.9
	c	-0.1	+0.4	+1.1	+2.4	0
 (4a)	a	-0.2	-1.5	-0.3	-1.4	-1.2
	b	-0.1	-2.3	-1.7	-1.9	-2.4
	c	+0.7	+0.3	+0.6	+0.4	-2.1
 (5a)	a	-0.1	-1.7	-0.4	-1.1	-0.3
	b	-0.1	-2.1	-1.4	-1.1	-3.8
	c	-0.1	-0.9	-1.4	-2.9	-0.1
 (7)	a	-0.1	+0.4	-0.9	-2.6	-2.6
	b	-0.1	-1.1	+0.4	-0.9	-2.6
	c	-0.1	-1.2	-1.0	-1.7	-3.6
 (7)	a	0	-0.2	0	-0.6	-0.5
	b	0	-0.1	+0.2	+0.4	-4.0
 (7)	a	0	-0.1	+0.2	-0.5	-1.2
	b	0	-0.1	+0.2	-0.5	-1.2

^a Conditions: crown (0.050 mmol), guest perchlorate (0.050 mmol), DMF- D_2O (4:1; 1.0 ml). ^b Positive shift is downfield.

and (5a), and indicates that they form cryptand-like complexes with some guest cations in which arm-donor groups and the parent crown ring effectively co-operate. Typically, ester-armed crown ether (1a) was confirmed to envelop the K^+ and Pb^{2+} ions in its pseudo-cavity as well as Na^+ ion. Interestingly, the shifted values for arm-carbonyl carbons were dependent on the nature of the guest cations, moving 0.6 p.p.m. downfield in the K^+ complex; 4.4 p.p.m. downfield in the Pb^{2+} complex; and 0.8 p.p.m. upfield in the Zn^{2+} complex. As reported for ester-armed crown ether complexes,⁸ this type of armed crown ether has a sufficiently flexible molecular skeleton such that it can adjust the co-ordination geometries for the binding of various guest cations. Gatto and Gokel have observed that ester- and ether-armed crown ethers (1a) and (5a) showed higher stability constants for Na^+ and K^+ cations than did unsubstituted crown ether (7);⁶ $\log K$ in MeOH; for (1a), 5.51 (Na^+) and 5.78 (K^+); for (5a), 4.75 (Na^+) and 5.46 (K^+); for (7), 1.5 (Na^+) and 1.8 (K^+). Hence, our spectroscopic observations clearly support the concept that co-operative binding of ligating arm and parent crown ring leads to three-dimensional complexes having enhanced stability constants.

In order to examine the effects of arm donor position on the cation complexation, we examined a series of crown ethers (1a)—(3a) having ester groups at various positions on the side-arms. Figure 2 illustrates the guest-induced changes in ^{13}C

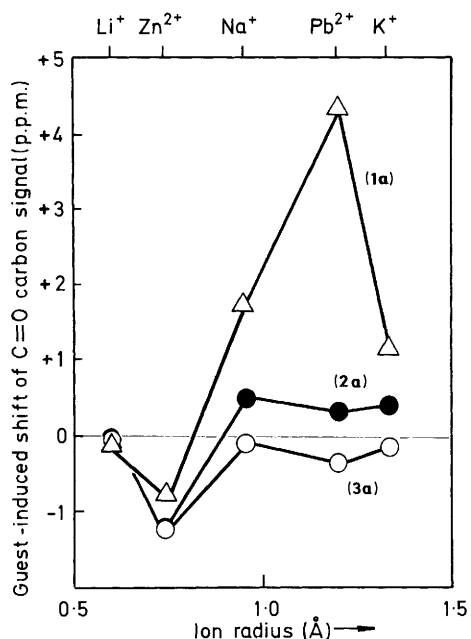


Figure 2. Guest-induced changes in ^{13}C n.m.r. chemical shifts for C=O carbons of ester-armed crown ethers (1a)—(3a). Guest:crown 1:1. Other conditions were the same as those shown in Table 1

n.m.r. chemical shifts of carbonyl carbons in armed crown ether systems. Their shifted values clearly depended on the position of the carbonyl group as well as the size of the guest cation. Co-operative binding of crown ring and arm donor group was realized when the ester group was sterically disposed to permit co-ordination to the guest cation trapped in the crown ring. Among the examined ester-armed crown ethers, crown ether (1a) has its carbonyl donor groups in the best position to interact effectively with guest Na^+ , Pb^{2+} , and K^+ ions. Other crown ethers (2a) and (3a) were thought to bind these guest cations in the same way as do simple crown ethers.

Table 2. Cation-transport properties of double-armed diaza-18-crown-6 derivatives^a

Guest cation	Transport rate $\times 10^6$ (mol h ⁻¹)						
	(1a)	(2a)	(3a)	(4a)	(5a)	(6)	(8)
Li ⁺	*	*	*	1.5	*	*	0.8
Na ⁺	9.0	0.4	*	4.3	4.8	*	6.5
K ⁺	9.1	3.9	2.0	7.0	11.0	2.2	1.2
Cs ⁺	0.8	*	*	2.2	0.9	0.4	1.4
Ag ⁺	1.0	2.4	2.3	*	1.0	*	2.0
Mg ²⁺	*	*	*	*	*	*	*
Ca ²⁺	*	*	*	1.9	*	*	0.4
Ba ²⁺	5.6	1.4	1.3	0.6	5.5	1.7	3.7
Pb ²⁺	2.5	2.1	3.4	1.4	1.0	0.4	0.8
Cu ²⁺	*	*	*	1.2	*	*	*
Ni ²⁺	*	*	*	0.7	*	*	*
Co ²⁺	*	*	*	3.4	*	*	*
Zn ²⁺	*	*	*	5.6	*	*	*

^a Conditions: see Experimental section.

* Below limit of detection ($<0.3 \times 10^{-6}$ mol h⁻¹).

Table 3. Cation-transport properties of double-armed benzodiaza-18-crown-6 derivatives^a

Guest cation	Transport rate $\times 10^6$ (mol h ⁻¹)				
	(1b)	(2b)	(3b)	(4b)	(5b)
Li ⁺	*	*	*	*	*
Na ⁺	8.2	*	*	3.5	1.6
K ⁺	6.0	0.8	0.5	9.5	5.6
Cs ⁺	0.4	*	*	0.6	*
Ag ⁺	0.8	2.9	1.5	0.4	0.8
Mg ²⁺	*	*	*	*	*
Ca ²⁺	*	*	*	2.0	*
Ba ²⁺	4.4	*	*	2.7	1.5
Pb ²⁺	5.7	2.2	2.0	1.5	2.8
Cu ²⁺	*	*	*	1.6	*
Ni ²⁺	*	*	*	*	*
Co ²⁺	*	*	*	2.0	*
Zn ²⁺	*	*	*	6.1	*

^a Conditions: see Experimental section.

* Below limit of detection.

Cation-transport Properties of Double-armed Crown Ethers.—By using double-armed crown ethers as synthetic ion-carriers, transport experiments were performed in a chloroform liquid membrane system.⁹ As shown in Table 2, arm functionalizations successfully modified transport efficiency and selectivity of diaza-18-crown-6. Typically, ester-armed crown ether (1a) transported Na^+ , K^+ , Ba^{2+} , and Pb^{2+} ions much more effectively than did simple crown ether (6) and cryptand (8). On the other hand, crown ethers (2a) and (3a) having ester groups at remote positions on the side-arms showed almost identical transport efficiencies to that of the simple crown ether (6). Their transport profiles were almost parallel to those of the cation-binding experiments described above. Hence, co-operative binding of the ester-functionalized arm group and the diaza-crown ring produced a stable and dynamic complex and enhanced transport efficiency.

Introduction of amide-functionalized arms remarkably changed transport selectivity of the parent diaza-18-crown-6. Thus, amide-armed crown ether (4a) provided efficient transport of transition metal cations such as Zn^{2+} and Co^{2+} ions as well as some alkali metal cations. Since these transition metal cations were very poorly transported by other crown

ethers, the nature of the introduced donor atoms in the side-arms is an essential factor in determining transport functions. Many kinds of synthetic ligands are known to bind strongly with transition metal cations, but most of them form very static complexes and have not been employed as ion carriers.¹⁰ In contrast, the present type of armed crown ether has several advantages and acts as an effective ion carrier for transition metal cations. Arm functionalization clearly provides unique cation-binding and transport functions.

Table 3 summarizes the transport rates of benzo-crown ether derivatives (1b)–(5b). Attachment of a benzene ring to the diaza-crown ring skeleton was expected to increase lipophilicity of the crown compound and decrease the donor ability of ether-oxygen atoms for hard guest cations. However, their transport profiles were almost parallel to those of the corresponding diaza-18-crown-6 derivatives (1a)–(5a). Structural modification of the crown skeleton had only a slight influence on cation-binding and transport functions of armed crown ethers.

Figure 3 shows the relationship between binding constants

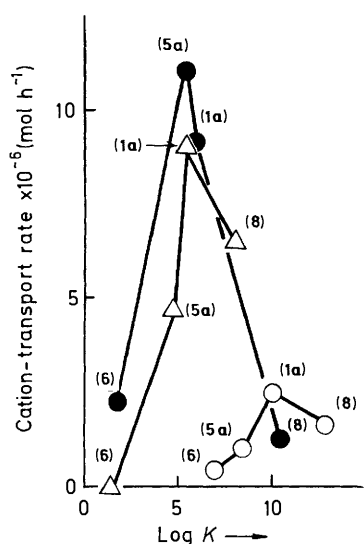


Figure 3. Plot of cation transport rate vs. stability constant ($\log K$). —●—: K^+ , —△—: Na^+ , —○—: Pb^{2+} . Since the stability constants of crown ether (6) could not be determined in the examined solvents, $\log K$ values for crown ether (7) are indicated for comparison

reported previously and transport rates measured here for Na^+ , K^+ , and Pb^{2+} ions. Although the binding constants have been measured in different solvent systems,* these plots have distinct maxima. As frequently reported for synthetic ion-carrier systems,¹¹ the guest cation which was complexed moderately with the carrier was effectively transported. The double-armed crown ethers have intermediate stability constants, between those of the parent crown ether and the bicyclic cryptand, but they showed the highest transport rates for several guest cations. Their flexible structures accommodate the guest cations in a three-dimensional manner and exhibit suitable binding dynamics, which are effective in promoting membrane transport. Therefore, further combination of potential donor-arms and a powerful macrocyclic ligand may offer excellent binding and transport phenomena for a new series of guest cations.

* The indicated stability constants have been measured in MeOH (Na^+ and K^+ ions) and water (Pb^{2+} ion); R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271; H. Tsukube, K. Takagi, T. Higashiyama, T. Iwachido, and N. Hayama, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 293.

In conclusion, we have developed a new series of double-armed crown ethers which selectively enveloped the guest cations in a three-dimensional sense, and which exhibited suitable binding dynamics. Since their cation-binding and transport functions were clearly controlled by the nature of the ligating side-arm groups, the present study provides a new guideline for the design of a guest-specific host molecule having a crown ether skeleton.

Experimental

I.r. spectra were run on neat films, except where stated otherwise, on a Hitachi 260-10 spectrophotometer; 1H n.m.r. spectra were run in $CDCl_3$ solution, containing $SiMe_4$ internal standard, with a JEOL 90 MHz spectrometer.

Materials.—The crown ethers (6) and (7) and cryptand (8) were purchased from Merck and employed as received. Other crown ether derivatives were prepared according to the modified literature methods.⁵ Typically, ester-armed crown ether (1a) was synthesized from unsubstituted diaza-18-crown-6 (7) (2.6 g), ethyl chloroacetate (4.0 g), and triethylamine (10.0 g) in ethanol (20 ml), was refluxed for 18 h, and then was poured into water and extracted with chloroform. The extract was evaporated and the residue was chromatographed (alumina; chloroform); the eluate was evaporated and the residue dried *in vacuo*. The same conditions were applied for synthesis of other crown ethers. They have been fully characterized spectroscopically and have correct elemental compositions determined by high-resolution mass spectrometry. Selected data of the newly obtained materials are summarized below.

N,N'-Bis(2-ethoxycarbonyl)ethyl)diaza-18-crown-6 (2a) (70%), an oil; δ_H 1.25 (6 H, 2 × Me), 2.43 (4 H, 2 × CH_2CO), 2.76 + 2.87 (12 H, 6 × NCH_2), 3.60 (16 H, 8 × OCH_2 , ring), and 4.12 (4 H, 2 × CO_2CH_2); ν_{max} 1 730 (ester) and 1 120 cm^{-1} (ether) (Found: M^+ , 462.294. $C_{22}H_{42}N_2O_8$ requires M , 462.294).

N,N'-Bis(3-ethoxycarbonyl)propyl)diaza-18-crown-6 (3a) (65%), a yellowish oil; δ_H 1.27 (6 H, 2 × Me), 1.78 (4 H, 2 × $CH_2CH_2CH_2$), 2.34 (4 H, 2 × CH_2CO), 2.59 (4 H, 2 × NCH_2 , arm), 2.81 (8 H, 4 × NCH_2 , ring), 3.59 (16 H, 8 × OCH_2 , ring), and 4.11 (4 H, 2 × CO_2CH_2); ν_{max} 1 715 (ester) and 1 120 cm^{-1} (ether) (Found: M^+ , 490.326. $C_{24}H_{46}N_2O_8$ requires M , 490.325).

N,N'-Bis(diethylcarbamoylmethyl)diaza-18-crown-6 (4a) (60%), white crystals from Et_2O , m.p. 50–53 °C; δ_H 1.10 + 1.15 (12 H, 4 × Me), 2.89 (8 H, 4 × NCH_2CH_2), 3.35 (8 H, 4 × NCH_2Me), 3.38 (4 H, 2 × NCH_2CO), and 3.58 (16 H, 8 × OCH_2); ν_{max} (Nujol) 1 640 (amide) and 1 110 cm^{-1} (ether) (Found: M^+ , 488.358. $C_{24}H_{48}N_4O_6$ requires M , 488.357).

Benzo-substituted crown ethers (1b)–(5b) were also prepared from benzodiaza-18-crown-6.¹²

N,N'-Bis(ethoxycarbonylmethyl)benzodiaza-18-crown-6 (1b) (80%), an oil; δ_H 1.24 (6 H, 2 × Me), 3.03 + 3.20 (8 H, 4 × NCH_2 ring), 3.54 + 3.62 (12 H, 4 × OCH_2 , ring + 2 × CH_2CO), 4.06 + 4.11 (8 H, 2 × CH_2OAr + 2 × CO_2CH_2), 6.81 (4 H, ArH); ν_{max} 1 730 (ester), 1 590 (benzene), and 1 125 cm^{-1} (ether) (Found: M^+ , 482.263. $C_{24}H_{38}N_2O_8$ requires M , 482.263).

N,N'-Bis(2-ethoxycarbonyl)ethyl)benzodiaza-18-crown-6 (2b) (60%), an oil; δ_H 1.24 (6 H, 2 × Me), 2.45 (4 H, 2 × CH_2CO), 2.89 + 2.91 + 3.06 (12 H, 6 × NCH_2), 3.54 + 3.59 (8 H, 4 × OCH_2), 4.03 + 4.10 (8 H, 2 × CH_2OAr + 2 × CO_2CH_2), and 6.85 (4 H, ArH); ν_{max} 1 730 (ester), 1 590 (benzene), and 1 140 cm^{-1} (ether) (Found: M^+ , 510.294. $C_{26}H_{42}N_2O_8$ requires M , 510.294).

N,N'-Bis(3-ethoxycarbonylpropyl)benzodiazia-18-crown-6 (**3b**) (60%), an oil; δ_{H} 1.24 (6 H, 2 \times Me), 1.76 (4 H, 2 \times CH₂CH₂CH₂), 2.34 (4 H, 2 \times CH₂CO), 2.59 (4 H, 2 \times NCH₂, arm), 2.88 (4 H, 2 \times NCH₂, ring), 3.06 (4 H, 2 \times NCH₂, ring), 3.57 + 3.60 (8 H, 4 \times OCH₂, ring), 4.05 + 4.07 (8 H, 2 \times CH₂OAr + 2 \times CO₂CH₂), and 6.87 + 6.88 (4 H, ArH); ν_{max} . 1 715 (ester), 1 598 (benzene), and 1 130 cm⁻¹ (ether) (Found: M^+ , 538.325. C₂₈H₄₆N₂O₈ requires M , 538.325).

N,N'-Bis(diethylcarbamoylmethyl)benzodiazia-18-crown-6 (**4b**) (60%), an oil; δ_{H} 1.10 + 1.15 (12 H, 4 \times Me), 3.01 (4 H, 2 \times NCH₂ ring), 3.19 (4 H, 2 \times NCH₂ ring), 3.39 (8 H, 4 \times NCH₂Me), 3.48 (4 H, 2 \times NCH₂CO), 3.59 (8 H, 4 \times OCH₂), 4.11 (4 H, 2 \times CH₂OAr), and 6.86 (4 H, ArH); ν_{max} . 1 635 (amide), 1 595 (benzene), and 1 130 cm⁻¹ (ether) (Found: M^+ , 536.357. C₂₈H₄₈N₄O₆ requires M , 563.357).

N,N'-Bis(2-methoxyethyl)benzodiazia-18-crown-6 (**5b**) (45%), an oil; δ_{H} 2.87 + 2.97 + 3.14 (12 H, 6 \times NCH₂), 3.33 (6 H, 2 \times OMe), 3.46 + 3.57 + 3.63 (12 H, 6 \times OCH₂), 4.08 (4 H, 2 \times CH₂OAr), and 6.86 (4 H, ArH); ν_{max} . 1 595 (benzene) and 1 120 cm⁻¹ (ether) (Found: M^+ , 426.273. C₂₂H₃₈N₂O₆ requires M , 426.273).

¹³C N.m.r. Studies.—¹³C N.m.r. studies were carried out at a frequency of 25.12 MHz with a JEOL 90A spectrometer. The crown ether was normally at a concentration of 5.0 \times 10⁻² M. Solvent systems employed are indicated in Table 1.

Transport Experiments.—Transport experiments were performed at room temperature (ca. 16 °C) in a U-tube glass cell (2.0 cm i.d.). The macrocycle, dissolved in chloroform (0.0372 mmol/12 ml), was placed in the base of the U-tube, and two aqueous phases [Aq. 1: MClO₄ (0.500 mmol) in water (5 ml); Aq. 2: water (5 ml)] were placed in the arms of the U-tube, floating on the chloroform membrane phase. The membrane phase was constantly stirred with a magnetic stirrer. The transport rates were calculated from the initial rates of appearance of guest cation and co-transported ClO₄⁻ anion into Aq. 2 phase, which were determined by means of atomic absorption and flame spectroscopic methods and ion-selective electrode techniques. Reproducibilities were confirmed as 15% or better.

Acknowledgements

We are grateful to Professors M. Kimura and K. Satake of Okayama university for helpful discussions. We also thank Professor K. Maruyama and Mr. H. Sohmiya of Kyoto university for the mass spectrometric measurements. This research was supported in part by a Grant-In-Aid from the Ministry of Education, Culture, and Science, Japan.

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Received 23rd May 1988; Paper 8/02042F