Photoresponsive Crown Ethers. Part 3.[1] Photocontrol of Ion Extraction and Ion Transport by Several Photofunctional Bis(Crown Ethers)

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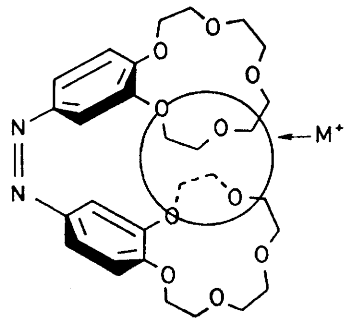
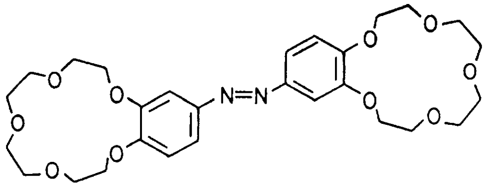
Three photoresponsive bis(crown ethers) with an azo-linkage (2)—(4) were synthesised for the purpose of controlling ion extraction and ion transport by an on-off light switch. The compound *trans*-(2), in which azobenzene is linked with two monoaza-15-crown-5 compounds *via* an amide linkage, extracted K^+ and Rb^+ in 6.7% and 0.5%, respectively, whereas the extractive abilities (ex%) of photoisomerised *cis*-(2) were higher (16.7% and 8.0%, respectively). Similarly, the ex% of *cis*-(3) (methylene linkage between azobenzene and two monoaza-15-crown-5 compounds) was greater than that of *trans*-(3). The results suggest that in the photoisomerised *cis*-forms alkali-metal cations are extracted as intramolecular 1 : 2 cation–crown complexes. On the other hand, the ex% of compound (4), which has an unsymmetrical structure was scarcely affected by photoirradiation. The rate of ion transport across a liquid (*o*-dichlorobenzene) membrane with compounds (2) and (3) as ion carriers was accelerated by u.v. irradiation, but retarded by u.v. and visible irradiation. This implies that ion transport is accelerated by the photoconversion of the *trans*- to the *cis*-forms in the membrane phase. The difference in the ex% and the ion-transport ability is discussed in relation to the crown structure.

PHOTORESPONSIVE systems are ubiquitous in nature and light is frequently the trigger for subsequent life processes. To model natural photoresponsive systems, one has to combine a photoantenna (to capture a photon) with a functional group (to mediate some subsequent event). As an example of artificial photofunctional systems, we have reported [1] that ion extraction and ion transport through a liquid membrane can be controlled with an on-off light switch by the use of the photoresponsive azobis(benzo-15-crown-5) compound (1) which contains within the molecule both a photoantenna (azobenzene) and a functional group (crown ether). The photocontrol stems from the light-mediated reversible *cis-trans* interconversion of the azobenzene moiety, in which the photoisomerised *cis*-form exhibits greater binding abilities toward large alkali-metal cations than the *trans*-form due to the formation of intramolecular, sandwich-type 1 : 2 cation–crown complexes. Several azobenzene-containing crown ethers have been reported [2,3] and Yamashita *et al.*[4] have adopted the photodimerisation of anthracene to the formation of crown ethers. Similarly, azobenzene derivatives have been utilised as a light trigger to control chemical and physical functions of β-cyclodextrin,[5] membranes,[6] micelles,[7] and microemulsions.[8]

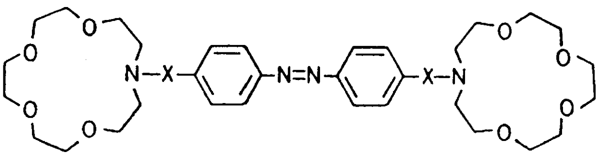


cis-(1)—M^+ complex

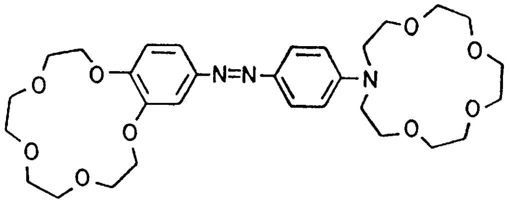
The high ion selectivity is one of the most noticeable characteristics of crown ether family. In a previous paper,[1] we reported that the most stable, intramolecular 1 : 2 cation–crown complex formed by *cis*-(1) is with Rb^+ ions, a result of the spacial cavity between two crown ethers of *cis*-(1), being of a similar size to Rb^+. The size of this spacial cavity may be adjusted by changing the distance between the photoisomerisable N=N bond and the crown ether. We have, therefore, synthesised three new photoresponsive bis(crown ethers) (2)—(4) and assessed the correlation between the ion selectivity and the bis(crown ether) structure by an investigation of the ion extraction and ion transport capabilities of the compounds across a liquid membrane.



trans-(1)



trans-(2) X = CO
trans-(3) X = CH_2



trans-(4)

RESULTS AND DISCUSSION

Photoisomerisation.—The spectroscopic properties of the crown ethers (2)—(4) are summarised in Table 1. Since the π–π^* band of the *trans*-forms and the n–π^* band of the *cis*-forms of compounds (2) and (3) are clearly separated, one may expect that *trans*-to-*cis* and *cis*-to-*trans* isomerisations are controlled by irradiation with u.v. and visible light, respectively. Compounds (2) and (3) were photoisomerised to give the corresponding *cis*-forms by irradiation with a high-pressure Hg-lamp through a visible filter; the *cis* concentration at the photostationary state was 50% and 79%, respectively.* Compound (4) has its absorption maximum in the visible region and was isomerised by irradiation with the same Hg-lamp through a u.v. filter; the *cis* concentration at the photostationary state was 47%.

TABLE 1

Spectroscopic properties of azobis(crown ethers) [a]

Crown ether	$\lambda_{max.}$ (nm) π–π^*	$\lambda_{max.}$ (nm) n–π^*	$\epsilon_{max.}$ (π–π^*)	*cis* : *trans* ratio [b]
(2)	334	442	20 600	50 : 50 [c]
(3)	337	445	23 600	79 : 21 [d]
(4)	418		35 500	47 : 53 [e]

[a] At 30 °C in *o*-dichlorobenzene. [b] At photostationary state. [c] Visible filter, 5 min to reach photostationary state. [d] Visible filter, 2 min to reach photostationary state. [e] U.v. filter, 4 min to reach photostationary state.

Thermal cis-*to*-trans *Isomerisation.*—It has been reported that for the thermal *cis*-to-*trans* isomerisation of azobenzene derivatives the plot of log(rate constant) *vs.* Hammett's σ is V-shaped [9,10] which suggests that the thermal isomerisation is facilitated by the resonance stabilisation of both electron-withdrawing and electron-donating substituents. In the azobis(crown ethers) (2)—(4), the order of the thermal isomerisation rate (Table 1) was (4) > (2) > (3), a trend which is explicable in terms of resonance stabilisation.

The rate of *cis*-to-*trans* isomerisation was also facilitated by irradiation with visible light. When a solution which contained the *cis*-isomers was irradiated with a 200-W tungsten-lamp for 15 s at intervals of 10 min, the rates of isomerisation were enhanced 23-fold for compound (2) and 41-fold for compound (3).

It has been established in host–guest chemistry that alkali-metal cations which exactly fit the cavity of crown ethers form 1 : 1 complexes, whereas those which have larger ion radii form 1 : 2 cation–crown complexes.[11-13] For example, 15-crown-5 and its analogues form a 1 : 1 cation–crown complex with Na^+, whereas they form a 1 : 2 cation–crown complex with K^+ and other alkali-metal cations larger than K^+.[14,15] In fact, *cis*-(1) forms the most stable intramolecular 1 : 2 cation–crown complex with Rb^+ and the rate of the thermal *cis*-to-*trans* isomerisation of *cis*-(1) is markedly suppressed by added Rb^+. The novel behaviour may be because additional free energy of activation is required for the thermal *cis*-to-*trans* isomerisation process in order to disrupt the interaction between the cation and the crown ethers. In the present system (Table 2), however, the rates of the thermal isomerisation for compounds (2)—(4) were scarcely affected by added alkali-metal cations. Although the thermal isomerisation of *cis*-(2) was inhibited to a smaller extent, that of *cis*-(3) was slightly enhanced (*ca.* 2-fold). The slight increase in the rate constants caused by added salts is common and is attributed to a salt effect: the rate of the thermal isomerisation increases in polar solvents and added salts usually enhance the polarity of solvents which results in the apparent rate acceleration.[16]

TABLE 2

Influence of added alkali-metal cations on the *cis*-to-*trans* thermal isomerization [a]

Crown ether	M^+	$[M^+][\text{crown ether}]^{-1}$	$k \times 10^5/s^{-1}$
cis-(2)	None	0	0.988
	None [b]	0	23.1
	Na^+	20	0.943
	K^+	20	0.838
	Rb^+	20	0.750
	Cs^+	20	0.813
cis-(3)	None	0	0.440
	None [b]	0	17.9
	Na^+	6	1.10
	K^+	6	1.09
	Rb^+	10	1.01
	Cs^+	10	0.911
cis-(4)	None	0	105
	Na^+	10	107
	K^+	10	115
	Rb^+	10	104
	Cs^+	10	114

[a] At 30 °C in *o*-dichlorobenzene–Bu^nOH (86.8 : 13.2 v/v); [(2)] = [(3)] = 2.36×10^{-5} M, [(4)] = 2.03×10^{-5} M. [b] Visible irradiation (200 W tungsten-lamp) for 15s at intervals of 10 min.

The contrasting behaviour of compound (1) and compounds (2)—(4) may be rationalised in terms of the difference in the 'rotational freedom' of the crown ether groups. Compound (1) employs benzo-15-crown-5 as an ion-binding group, so that the geometrical change induced by the isomerisation of the N=N bond would be readily transmitted to the crown ethers (in particular, to the distance between them). On the other hand, compounds (2)—(4) have one or two free-rotating single bonds between the crown ether and the azobenzene, which may act as an absorber of the geometrical change which occurs at the N=N bond. As a result, the isomerisation of the N=N bond may start without disruption of the interaction between the cation and crown ethers. The small, but significant, inhibitory effect observed for compound (2) may thus be because the free rotation of the amide group of (2) is more restricted than that of the methylene group of compound (3).

These considerations suggest that free rotation of the crown ether moiety is disadvantageous to the formation of a stable and selective 1 : 2 cation–crown complex.

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* The *cis* percentage was calculated from the optical density (OD) at the absorption maxima, assuming that the OD of the *cis*-forms at these wavelengths is negligible in comparison with that of the *trans*-forms.

Further, no inhibitory effect for compound (4) is associated with another important factor, molecular symmetry. This will be described below.

Photocontrolled Ion-extraction.—Solvent extraction of alkali-metal cations was conducted between water and *o*-dichlorobenzene by using either Methyl Orange or picrate as the counter-anion (Table 3). The compound *trans*-(3) showed the selectivity order of $Na^+ > K^+ > Rb^+ > Cs^+$, which is in accord with the magnitude of the stability constants of the 15-crown-5 family.[11-13] Probably, the two crown ether moieties of *trans*-(3) act independently as the extractant. On the other hand, *trans*-(2) showed a maximum extractive ability (ex%) for K^+. Since the crown ether ring of *trans*-(2) involves one amide nitrogen, the extractive ability is somewhat weaker than that of *trans*-(3) (see extraction conditions under Table 3). Hence, one may consider some co-operative extraction mechanism for *trans*-(2) (*e.g.* intermolecular 1 : 2 cation–crown complex) and, as a result, K^+ may become the most extractable cation.

TABLE 3

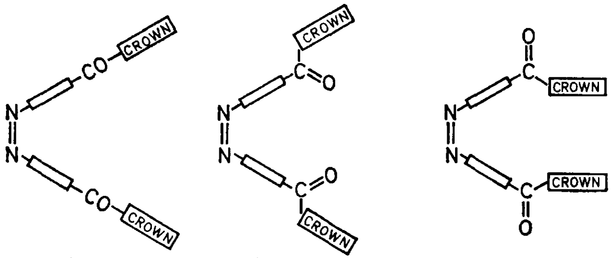
Extraction of alkali-metal salts

Crown ether	Anion	Anion extracted to *o*-dichlorobenzene phase (ex%)			
		Na^+	K^+	Rb^+	Cs^+
trans-(2) [c]	MO [a]	1.8	6.7	0.5	1.3
photoirradiated (2)	MO	2.7	11.7	4.0	3.2
cis-(2) [d]	MO	3.6	16.7	8.0	5.1
trans-(2) [e]	Pic [b]			0	
photoirradiated (2)	Pic			4.8	
cis-(2)	Pic			9.6	
trans-(3) [f]	Pic	62.8	11.9	6.5	6.3
photoirradiated (3)	Pic	68.9	15.1	7.9	11.5
cis-(3) [g]	Pic	69.8	15.8	8.2	12.6
trans-(4) [h]	Pic	4.3	17.8	6.9	2.3
photoirradiated (4)	Pic	6.4	18.8	8.4	4.0
cis-(4) [i]	Pic	8.7	19.7	9.4	4.9

[a] Methyl Orange. [b] Picrate. [c] Extraction conditions: aqueous phase, [MO] 8.10×10^{-6} M, [MOH] 0.01 M, [MCl] 0.04 M; *o*-dichlorobenzene phase, [*trans*-(2)] 7.50×10^{-3} M. [d] Calculated by the equation $ex_{cis-(2)} = [ex_{\text{photoirradiated (2)}} - 0.5ex_{trans-(2)}]/0.5$. [e] [*trans*-(2)] 1.50×10^{-3} M, [Pic] 5.00×10^{-5} M. Other extraction conditions are identical to those given in footnote *c*. [f] [*trans*-(3)] 1.50×10^{-3} M, [Pic] 5.00×10^{-5} M. Other extraction conditions are identical to those given in footnote *c*. [g] Calculated by the equation $ex_{cis-(3)} = [ex_{\text{photoirradiated (3)}} - 0.21ex_{trans-(2)}]/0.79$. [h] [*trans*-(4)] 3.00×10^{-4} M, [Pic] 5.00×10^{-5} M. Other extraction conditions are identical to those given in footnote *c*. [i] Calculated by the equation $ex_{cis-(4)} = [ex_{\text{photoirradiated (4)}} - 0.53ex_{trans-(2)}/0.47$.

All the ex% of compounds (2) and (3) were enhanced by photoinduced isomerisation which suggests the formation of intramolecular 1 : 2 cation–crown complexes as extraction species. We previously reported that *cis*-(1) has an outstanding selectivity for Rb^+ [1] which was attributed to the similarity of the ion size of Rb^+ and the cavity size between the two benzo-15-crown-5 moieties. Such a sharp selectivity was not found for *cis*-(3), however. The loss of selectivity is also attributed to the ' rotational freedom ' of the crown ether groups: that is, the fluctuating crown ethers are able to fit various sizes of alkali-metal cations as required. On the other hand, *cis*-(2) exhibited relatively good ion selectivity, which may be derived from a partially inhibited rotation of the crown ether groups. As shown in Table 3, the most oustanding ex% difference between *trans*-(2) and *cis*-(2) was observed for Rb^+ (0.5 ⟶ 8.0% for Methyl Orange and 0 ⟶ 9.6% for picrate).

The most stable complex formed by *cis*-(2) is with K^+, the ion radius of which is smaller than that of Rb^+; the latter is most strongly bound to *cis*-(1). Conceivably, the distance between the two crown ether moieties of *cis*-(2) is smaller than that of *cis*-(1). If the amide linkage in the *cis*-(2)–K^+ complex enjoys coplanarity with both *N*-alkyl groups and the aromatic ring, the distance between two crown ether groups has to be greater than that of *cis*-(1). If two amide oxygens are directed inside the aromatic rings [*cis*-(2)-*endo*], the distance becomes much greater. Hence, these two conformations are incompatible with the observed ion selectivity. Conceivably, two amide oxygens are directed (at least partially) outside the aromatic rings [*cis*-(2)-*exo*] which enables the compound to capture cations in a 1 : 2 complex. Only this conformation is compatible with the fact that the sandwich-type cavity of *cis*-(2) is smaller than that of *cis*-(1) (see Figure 1).



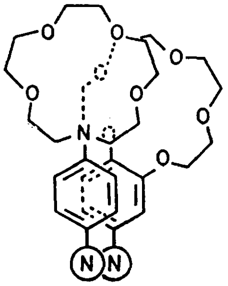
cis-(2) *cis*-(2)-*endo* *cis*-(2)-*exo*

FIGURE 1

When compared with compounds (2) and (3), the ex% of compound (4) was scarcely changed by photoirradiation. The trend is in line with the loss of the inhibitory effect of added metal cations on the thermal isomerisation. The most essential difference between compound (4) and other bis(crown ethers) is that (4) has an unsymmetrical structure. When the symmetrical compounds (1)—(3) are isomerised to the *cis*-forms, the two crown rings can overlap in a face-to-face orientation. This orientation would provide a favourable binding site for alkali-metal cations. As shown by a Newman-type projection (Figure 2), however, the two crown ether groups of *cis*-(4) cannot overlap. In view of this a sandwich-type extraction is not effective. Probably, the two crown ether groups of *cis*-(4) act independently even in the *cis*-form.

The foregoing results show that the stability of intramolecular 1 : 2 cation–crown complexes is governed by two important factors: the rotational freedom and the molecular symmetry of the crown ether groups.

Although unsymmetrical bis(crown ethers) may not bind ' symmetrical ' alkali-metal cations efficiently in a 1 : 2 complex, they may become good receptors for unsymmetrical cations such as amino-acids [$RCH(NH_3^+)CO_2^-M^+$] and dicationic ammonium salts.[17,18] The possibility is currently under investigation in this laboratory.



cis-(4)

FIGURE 2

Light-driven Ion-transport across a Liquid Membrane.—Various kinds of chemical phenomena have been used to increase the rate of ion transport through membranes.[19-22] We have considered that light would be one of the most convenient sources to control the rate of ion transport. In a liquid membrane system, Kobuke *et al.*[23] and Kirch and Lehn [24] independently established that the best carrier for ion transport is a ligand that gives a moderately, rather than a very, stable complex, which suggests that the very stable complex cannot release the ion efficiently to the OUT aqueous phase. In the K^+ transport with compound (1), we found that the rate with picrate as the counter-anion was rather retarded by u.v. irradiation, whereas that with 2-nitrodiphenylamine-4-sulphonate as the counter-anion was increased.[1] The result suggests that when a hydrophobic anion is used as the counter-anion, the photoisomerised *cis*-(1) efficiently extracts K^+ from the IN aqueous phase to the membrane phase, but the complex releases K^+ to the OUT aqueous phase very slowly. We thus expected that if the conversion of *cis*-(1) into *trans*-(1) in the membrane phase is accelerated by visible light, the ion-release step would no longer be rate-limiting and the overall rate of the K^+ transport would be significantly enhanced. Unfortunately, we could not find any useful wavelength to mediate photoisomerisation of *cis*-(1) to *trans*-(1).[1] This is probably due to the overlap of π–π* band with *n*–π* band. Since the regeneration of *trans*-(2) and *trans*-(3) is mediated by visible light, we assessed the influence of visible light, as well as that of u.v. light, on the rate of the ion transport across a liquid (*o*-dichlorobenzene) membrane.

The photoisomerisation of *trans*-(4) to *cis*-(4) was attained by irradiation with visible light. As expected from the solvent extraction result, irradiation with visible light had almost no effect on the rate of ion (K^+ and Cs^+) transport (Table 4). Interestingly, we found that ion transport with compounds (2) and (3) was significantly accelerated by u.v. irradiation which isomerises the *trans*-forms to the *cis*-forms. When u.v. and visible irradiation were used alternately, the interconversion between *cis*- and *trans*-forms should have occurred rapidly. However, the rates of the ion transport were smaller than those under u.v. irradiation. These results indicate that the ion-release to the OUT aqueous phase is not involved in the rate-limiting step and that the light-driven ion transport is solely attributed to the enhanced binding ability of the *cis*-forms which extract cations from the IN aqueous phase to the liquid membrane phase. In other words, the rate enhancement observed for compounds (2) and (3) is simply correlated to the enhancement of the *cis* concentration in the liquid membrane phase. Probably, the complexes with *cis*-(2) and *cis*-(3) are not stable enough to render ion-release to the rate-limiting step. In order to utilise visible light as a source of the ion transport accelerator a bis(crown ether) has to be synthesised, the *cis*-form of which forms a stable complex with alkali-metal cations and is converted into the *trans*-form by visible light.

TABLE 4

Photocontrol of ion-transport across a liquid (*o*-dichlorobenzene) membrane (30 °C)

Crown ether	Cation	Rate of ion-transport × 10^2 (μmol/25 ml per h) Dark	Hg-lamp with visible-filter [d]	Hg-lamp with u.v.-filter [d]	Hg-lamp with visible-filter + W lamp [e]
(2) [a]	Rb^+	2.3	6.6		2.6
(3) [b]	K^+	11.5	17.2		16.3
(3) [b]	Cs^+	4.7	6.5		5.9
(4) [c]	K^+	74.8		78.7	
(4) [c]	Cs^+	44.4		40.5	

[a] IN aqueous phase, [MOH] 0.01 M, [MCl] 0.08 M, [Picrate] 4.00×10^{-4} M; *o*-dichlorobenzene phase, [(2)] 1.00×10^{-3} M. [b] IN aqueous phase, [MOH] 0.01 M, [MCl] 0.08 M, [Picrate] = 4.00×10^{-4} M; *o*-dichlorobenzene phase, [(3)] 1.00×10^{-3} M. [c] IN aqueous phase, [MOH] 6.00×10^{-3} M, [MCl] 0.02 M, [Picrate] 4.00×10^{-3} M; *o*-dichlorobenzene phase, [(4)] 5.00×10^{-4} M. [d] 5 Min irradiation at intervals of 30 min. [e] 5 Min irradiation at intervals of 60 min.

Conclusions.—We have demonstrated that ion extraction and ion transport can be photocontrolled by the use of photoresponsive azobis(crown ethers) and have found that molecular symmetry and rotational freedom of crown ether groups are significantly associated with the stability and selectivity of intramolecular 1 : 2 cation–crown complexes. Although further improvement is required to enhance the efficiency of light-driven ion transport (in particular with visible light), the principal concept reported herein may lead to more interesting systems controlled by switching the light source on and off.

EXPERIMENTAL

Materials.—4,4′-*Bis*-(1,4,7,10-*tetraoxa*-13-*azacyclopentadec*-13-*ylcarbonyl*)*azobenzene* (2). 4,4′-Bis(chlorocarbonyl)-azobenzene (0.414 g, 1.3 mmol) in benzene (50 ml) was added as drops to a stirred solution of benzene (50 ml) which contained the 1,4,7,10-tetraoxa-13-azacyclopentadecane (0.59 g, 2.7 mmol) and triethylamine (3 ml) and the mixture was left overnight at room temperature. The solution was washed with water to remove triethylamine hydrochloride and the benzene layer was evaporated to dryness under reduced pressure. The residue (an oil), dissolved in hot benzene, was crystallised by pouring the solution into cold diethyl ether to give the *azobenzene* (2) (72%), m.p. 99—101 °C; M^+, 672 (Found: C, 60.1; H, 7.3; N, 8.2. Calc. for $C_{34}H_{48}N_4O_{10}\cdot 0.5H_2O$: C, 59.90; H, 7.24; N, 8.22%.

4,4′-*Bis*-(1,4,7,10-*tetraoxa*-13-*azacyclopentadec*-13-*yl-methyl*)*azobenzene* (3). 4,4′-Bis(hydroxymethyl)azobenzene, m.p. 225—228 °C, prepared from *p*-nitrobenzyl alcohol by reductive coupling in the presence of zinc as for *trans*-(1),[1] was chlorinated with thionyl chloride to give 4,4′-bis-(chloromethyl)azobenzene, m.p. 175—178 °C. 4,4′-Bis-(chloromethyl)azobenzene (2.0 g, 6.4 mmol) in acetonitrile (50 ml) was added as drops to a stirred acetonitrile solution (50 ml) which contained 1,4,7,10-tetraoxa-13-azacyclopentadecane (3.0 g, 13.7 mmol) and powdered potassium carbonate (1.9 g, 14.0 mmol). The solution was refluxed for 3 h and, after cooling, potassium carbonate and potassium chloride were filtered off. The filtrate was concentrated under reduced pressure to give a residue (an oil) which was crystallised by pouring a hot benzene solution of it into cold n-hexane. The precipitated solid was recrystallised from benzene–diethyl ether to give the *azobenzene* (3) (36%), m.p. 74—76 °C; M^+, 644; δ ($CDCl_3$) 2.90 (t, NCH_2 of crown ring), 3.70—3.90 (m, NCH_2Ar and OCH_2), 7.68 (d, 3,3′-ArH), and 8.05 (d, 2,2′-ArH) (Found: C, 63.35; H, 8.15; N, 8.5. Calc. for $C_{34}H_{52}N_4O_8$: C, 63.33; H, 8.13; N, 8.69%).

2,3,5,6,8,9,11,12-*Octahydro*-1,4,7,10,13-*benzopentaoxa-pentadecin*-15-*azo*-[4′-(1,4,7,10-*tetraoxa*-13-*azapentadecan*-13-*yl*)*benzene*] (4). 4′-Aminobenzo-15-crown-5, prepared from 4′-nitrobenzo-15-crown-5 (3.0 g, 6.4 mmol) by catalytic hydrogenation with Pd on charcoal was dissolved in water (50 ml) which contained concentrated HCl (3 ml). Aqueous sodium nitrite (0.43 g, 6.5 mmol) was then added as drops at 0 °C. *N*-Phenyl-1,4-7,10-tetraoxa-13-azacyclopentadecane [25] (2.6 g, 8.8 mmol), dissolved in concentrated HCl (5 ml), and water (50 ml) were added and, to promote the diazo-coupling, urea (5.0 g) was also added.[26] After 36 h, the reaction mixture was adjusted to pH 10 and extracted with chloroform. Evaporation of the chloroform layer under reduced pressure gave an oily product, which was developed by preparative thin layer chromatography [silica gel, chloroform–methanol (10 : 1 v/v)]. The azo-compound (4) was collected, extracted with methanol, and the methanol solution was evaporated to dryness. The residue was recrystallised from benzene–diethyl ether to give the pure *azo-compound* (4) (13%), m.p. 126—127 °C; M^+, 589 (Found: C, 61.1; H, 7.4; N, 7.1%. Calc. for $C_{30}H_{43}N_3O_9$: C, 61.10; H, 7.35; N, 7.13%).

Kinetic Measurements, Solvent Extraction, and Ion Transport.—The rate of the thermal *cis*-to-*trans* isomerisation was monitored by the appearance of *trans*-isomers (detected spectrophotometrically). To obviate photoisomerisation (*trans* $\longrightarrow$ *cis*) by light from the spectrophotometer, we measured the absorbance for a few seconds per minute; the detail of the method has been described previously as has the method of solvent extraction.[1,16]

Transport of alkali-metal cations across an *o*-dichlorobenzene liquid membrane was examined within a U-tube immersed in a thermostatted water-bath and, when required, irradiated by either a 500-W high pressure Hg-lamp or a 200-W tungsten lamp at a distance of 12.5 cm. The filter was a Toshiba UV-D34 ($\lambda < 400$ nm) and the visible light filter was a Toshiba L-42 ($\lambda < 390$ nm). Further details are described in ref. 1.

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