Photoresponsive Crown Ethers. Part 14.† Photoregulated Crown–Metal Complexation by Competitive Intramolecular Tail(Ammonium)-biting‡

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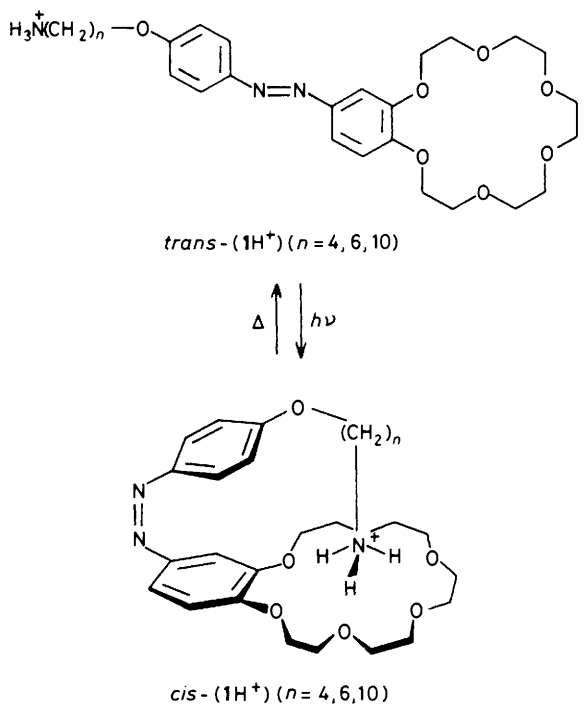
New photoresponsive crown ethers ($1H^+$) having a crown ether ring and an ammoniumalkyl [H_3N^+-$(CH_2)_n$, n = 4,6,10] group attached to the two sides of an azobenzene have been synthesized. These photoresponsive 'tail-biting' crown ethers have been designed so that intramolecular 'biting' of the ammonium group to the crown can only occur upon photoisomerisation to the *cis*-forms. In the thermal *cis–trans* isomerisation, the first-order rate constants for *cis*-($1H^+$) were smaller by 1.6—2.2-fold than those for (**1**) (the analogous free amines). Moreover, this rate increased with increasing added K^+ concentration. This suggests that the ammonium tail is intramolecularly bound to the crown ether ring in *cis*-($1H^+$). This intramolecular 'biting' is further reflected in the relative affinities of ($1H^+$) for alkali-metal cations. The affinities were markedly reduced by u.v.-light irradiation and in particular, *cis*-($1H^+$)(n = 6) and *cis*-($1H^+$)(n = 10) showed almost no metal-binding ability. This marked difference in the metal-binding ability was used to generate the light-controlled systems for the passive or active ion-transport of ions across a liquid membrane.

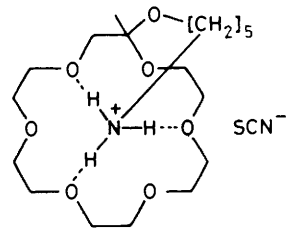
Cations are known to be transported through membranes by synthetic macrocyclic polyethers as well as by antibiotics.[1–4] In particular, some polyether antibiotics such as nigericin and monensin display an interconversion between cyclic and acyclic forms in the membrane phase, a feature which is believed to be crucial for their ability to transport certain ions rapidly through membranes. This phenomenon suggests that a rapid, reversible interconversion between two states could lead to highly efficient artificial carrier molecules. A prominent feature of azobenzene is a photoinduced, reversible *cis–trans* isomerism. The geometrical change is so large that it has frequently been employed as a photoantenna to photocontrol functionalised molecules such as crown ethers,[5–9] cyclodextrins,[10] polymers,[11,12] *etc.* Recently, Nakatsuji *et al.*[13] reported a new synthetic ionophore (**2**) having an intramolecularly complexable crown ring and ammonium ion. Here, we wish to report new photoresponsive crown ethers ($1H^+$) bearing a covalently appended ammonium tail. These photoresponsive 'tail-biting' crown ethers are designed so that the crown ring can bind intramolecularly the ammonium group only upon photoisomerisation to the *cis*-forms. Examination of Corey–Pauling–Koltun models suggests that the hexamethylene group is required to optimise the interaction between the ammonium tail and the crown ring in *cis*-($1H^+$). In this paper, we describe (i) the influence of photoirradiation on the ion-affinity of ($1H^+$) and (**1**) (free amine analogues), (ii) the rates of thermal *cis–trans* isomerisation and the effect of $[K^+]$ on these rates, and (iii) light-driven, passive and active ion-transport across a liquid membrane mediated by ($1H^+$) and (**1**).



Scheme 1.

Results and Discussion

Metal Effects on Photo and Thermal Isomerisation.—The spectroscopic properties of the crown ethers are summarised in Table 1. Usually, *trans*-azobenzene derivatives show a π–π^* absorption band at *ca.* 330 nm and an n–π^* absorption band at *ca.* 440 nm. In *trans*-(**1**), however, the n–π^* band could not be clearly detected because of a red shift of the π–π^* band ($\lambda_{max.}$ 362—370 nm). The photoisomerisation was carried out using a



(**2**)

500 W high-pressure mercury lamp equipped with a coloured glass filter (330 < λ < 380 nm). In *o*-dichlorobenzene–butan-1-

† Part 13, S. Shinkai, K. Shigematsu, Y. Honda, and O. Manabe, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2879.
‡ Preliminary communication, S. Shinkai, M. Ishihara, K. Ueda, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1984, 727.

Table 1. Spectroscopic properties[a]

Crown ether	$\lambda_{max.}$/nm	$\varepsilon_{max.}$	*cis*:*trans* ratio
trans-(**1**)(n = 4)	366	18 600	63:37
trans-(**1**)(n = 6)	370	22 500	72:28
trans-(**1**)(n = 10)	366	19 100	61:39
trans-(**1**H$^+$)(n = 4)	362	18 800	77:23
trans-(**1**H$^+$)(n = 6)	368	23 200	80:20
trans-(**1**H$^+$)(n = 10)	364	18 800	63:37

[a] *o*-Dichlorobenzene:butan-1-ol 80:20 v/v.

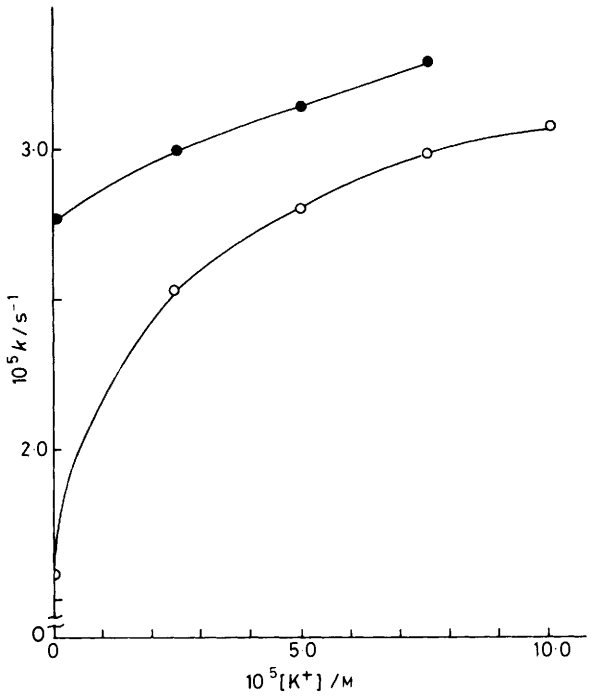


Figure 1. First-order rate constants (k) for the thermal *cis–trans* isomerisation plotted against the K^+ concentration; 30 °C, Bu^{n}OH: *o*-dichlorobenzene = 2:8 v/v, [crown] 1.14 × 10^{-5}M: ● *cis*-(**1**)(n = 6); ○ *cis*-(**1**H$^+$)(n = 6)

ol (80:20 v/v) the isomerisation reached a photostationary state after 30 s, the *cis–trans* ratio being recorded in Table 1. The initial spectra of the *trans*-forms were quantitatively regenerated thermally or by irradiation with a 200 W tungsten lamp.

We previously investigated the metal effect on the photoresponsive behaviours of azobis(benzocrown ethers).[7,14,15] It has been found that in the presence of metal ions which can form intramolecular 1:2 metal–crown sandwich-type complexes with the *cis*-forms, the *cis*-percentage at the photostationary state is markedly enhanced and the rate of the thermal *cis–trans* isomerisation is suppressed. This novel behaviour is attributed to the 'lock-in' effect of metal ions flanked by two crown rings. That is, an additional free energy of activation is required for the *cis–trans* isomerisation process, which reflects the need to disrupt favourable interactions between the metal ion and the crown ethers. Examination of Table 1 reveals that the percentages of *cis*-(**1**H$^+$)(n = 4) and (**1**H$^+$)(n = 6) in the photostationary state are somewhat greater than those of (**1**)(n = 4) and (**1**)(n = 6). This may be due to the binding of the ammonium tail to the crown ring. On the other hand, the *cis*% of (**1**H$^+$)(n = 10) is almost equal to that of (**1**)(n = 10). The difference is easily rationalised in terms of the greater

Table 2. First-order rate constants (k) for thermal *cis–trans* isomerisation[a]

	$10^5k/s^{-1}$	
Crown ether	No metal	Excess of K^+[b]
cis-(**1**)(n = 4)	10.2	10.5
cis-(**1**)(n = 6)	2.77	3.4
cis-(**1**)(n = 10)	9.85	9.6
cis-(**1**H$^+$)(n = 4)	4.68	10.0
cis-(**1**H$^+$)(n = 6)	1.59	3.3
cis-(**1**H$^+$)(n = 10)	6.08	9.3

[a] *o*-Dichlorobenzene:butan-1-ol = 80:20 v/v. [b] $[C_{11}H_{23}CO_2K]$ 1.2 × 10^{-4}M.

conformational freedom of the decamethylene group in (**1**H$^+$) (n = 10).[14]

More direct evidence for the intramolecular ammonium-tail 'biting' was found in the thermal *cis–trans* isomerisation (Figure 1). The first-order rate constants (k) for this process were determined in *o*-dichlorobenzene:butan-1-ol = 80:20 (v/v) at 30 °C: k for *cis*-(**1**H$^+$)(n = 6) = 1.59 × 10^{-5} s^{-1}. The rate increased with increasing K^+ ion concentration (as potassium dodecanoate). Similar rate increases were also seen for *cis*-(**1**H$^+$) (n = 4) and *cis*-(**1**H$^+$)(n = 10). Use of potassium perchlorate instead of potassium dodecanoate afforded essentially the same result. It is known that the thermal isomerisation is suppressed when the interaction between the two azo-substituents exists.[7,15] The smaller k for *cis*-(**1**H$^+$)(n = 6) relative to *cis*-(**1**)-(n = 6) is thus attributed to intramolecular binding between the ammonium tail and the crown ring. The K^+-dependent rate acceleration is due to competitive complexation of K^+ to the crown ring which inhibits such intramolecular interactions.

The rates reach maximum values at $[K^+]$ *ca.* 10^{-4}M. In Table 2, the k values in the absence of K^+ and the maximum k values at $[K^+]$ 1.2 × 10^{-4}M are summarised. The data in Table 2 reveal that the maximum k values are enhanced by 2.1-fold in *cis*-(**1**H$^+$)(n = 4) and *cis*-(**1**H$^+$)(n = 6) and by 1.5-fold in *cis*-(**1**H$^+$)(n = 10). The smaller rate augmentation in *cis*-(**1**H$^+$)(n = 10) may again reflect the greater conformational freedom of the decamethylene group. Interestingly, k for *cis*-(**1**)(n = 6) [but not for *cis*-(**1**)(n = 4) and *cis*-(**1**)(n = 10)] also increased, although to a smaller extent, with increasing K^+ concentration. This result suggests that the amino group in *cis*-(**1**)(n = 6) also interacts with the crown ether ring. There is much precedent for amino groups forming complexes with 18-crown-6 and its analogues.[16] The interaction, however, should be much weaker than that with ammonium groups. In fact, it seems reasonable to expect that the most significant crown–amino interaction should be observed for the system which displays the best-fit geometry for intramolecular interaction [*i.e.*, *cis*-(**1**)(n = 6)]. Furthermore, it is interesting to note that at high K^+ concentration, the k values for *cis*-(**1**H$^+$) are almost equal to those for corresponding *cis*-(**1**). Conceivably, all intramolecular stabilisation has been destroyed.

Solvent Extraction of Alkali-metal Cations.—The photoresponsive ionophoric properties of (**1**) were evaluated through two-phase extraction of alkali toluene-*p*-sulphonates from water to *o*-dichlorobenzene:butan-1-ol = 45:55 (v/v). This particular organic solvent was selected in order to prevent relatively hydrophilic (**1**H$^+$) from leaking into the aqueous phase. Previously, we confirmed ion extraction by the spectroscopic measurement of the counteranion (A^-). This method was, however, unsuitable for the present system because A^- could be extracted not only as M^+A^- but also as (**1**H$^+$)A^-. We therefore measured the concentration of M^+ in the organic

Table 3. Extraction of alkali toluene-*p*-sulphonate (M^+Ts^-) with photoresponsive crown ethers[a]

Crown ether	Metal	$10^4[M^+]$/M in the organic phase			
		trans-($1H^+$)	*cis*-($1H^+$)[c]	*trans*-(**1**)[b]	*cis*-(**1**)[b,c]
(**1**)(n = 4)	K^+	0.15	0.32	0.45	0.43
(**1**)(n = 6)	Li^+	0.09	0.01	0.12	0.03
	K^+	0.22	0.04	1.16	0.39
	Rb^+	0.30	0.17	0.66	0.43
	Cs^+	0.38	0.24	0.60	0.63
(**1**)(n = 10)	K^+	0.29	0.02	0.81	0.49

[a] Aqueous phase (3 ml): $[M^+Ts^-]$ = 0.0102M, pH 4.7 with 10mM-phosphate. Organic phase (*o*-dichlorobenzene:butan-1-ol 45:55 v/v; 3 ml): [(**1**) or ($1H^+$)] 1.88 × 10^{-4}M. [b] Aqueous phase: $[M^+Ts^-]$ 0.0102M, [MOH] 10mM. [c] Contents of the *cis*-forms are recorded in Table 1.

phase by atomic absorption spectroscopy. While this method (see Experimental section) has an advantage in that the metal concentrations are obtained directly, it is experimentally somewhat inconvenient and the Na^+ concentration could not be determined because of slight changes in the Na^+ background. We could not stabilise the background to a satisfactory level even when we effected solvent extraction in quartz vessels. We thus carried out solvent extraction only for Li^+, K^+, Rb^+, and Cs^+. The results are summarised in Table 3 and Figures 2 and 3. In Table 3, corrections for M^+ extracted into the organic phase in the absence of (**1**) or ($1H^+$) have been made.

Examination of Figure 2 reveals the following facts: (i) *trans*-(**1**)(n = 6) exhibits the highest affinity for K^+, (ii) the extracted ion concentrations decrease, except for Li^+, in the following sequence: *trans*-(**1**)(n = 6) > *cis*-(**1**)(n = 6) > *trans*-($1H^+$)(n = 6) > *cis*-($1H^+$)(n = 6), and (iii) the most conspicuous extractability change is seen for K^+ ion and *cis*-($1H^+$)(n = 6) shows very small K^+ ion affinity. It has been established that 18-crown-6 and its analogues show the highest selectivity towards K^+ ion among the various alkali-related cations.[17–20] As expected, *trans*-(**1**)(n = 6) exhibited the highest affinity for K^+. To account for the extractability order, *trans*-(**1**)(n = 6) > *cis*-(**1**)(n = 6), two different explanations are possible. These are considered in turn. First, it is known that *cis*-azobenzene is more hydrophilic than *trans*-azobenzene because the two dipole moments are orientated in the same direction across the azo-linkage.[21] Since the extraction performance of crown ethers is substantially improved by lipophilic substituents,[22–24] the lower extractability of *cis*-(**1**)(n = 6) relative to *trans*-(**1**)(n = 6) might be ascribed to the increased hydrophilic nature of *cis*-(**1**)(n = 6). We consider, however, that this is probably not the case in the present system, because this phenomenon should be ion dependent. In fact, the difference between *trans*- and *cis*-(**1**)(n = 6) is not seen for Cs^+. Clearly, the difference in extractability does depend upon the metal ion. We therefore rather favour an alternative explanation in which a crown–amino interaction is responsible for this decrease in extractability. K^+ (most favourable fit for 18-crown-6) nests in the benzo-18-crown-6 ring whilst the larger Cs^+ perches on its edge.[25] Therefore, Cs^+ on the crown edge is expected to be less affected by interaction with the terminal amino group of *cis*-(**1**)(n = 6) which most probably binds to the opposite side of the crown ether ring. The difference between *trans*- and *cis*-isomers is not seen for (**1**)(n = 4) in which such a crown–amino interaction is not likely to occur, further supporting the suggestion that the difference in extractability be attributed to a crown–amino interaction but not to changes in hydrophilicity.

The extractabilities of *trans*-($1H^+$) are generally lower than those of *trans*-(**1**) for three crown ethers having different

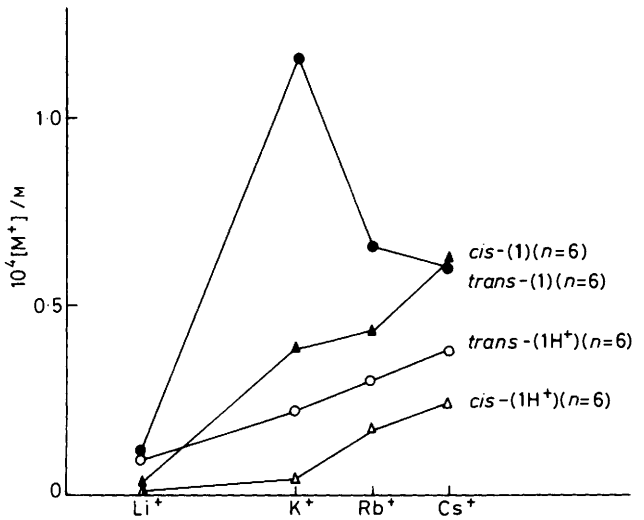


Figure 2. Concentrations of alkali-metal ions extracted to the organic phase. The data in Table 3 are plotted

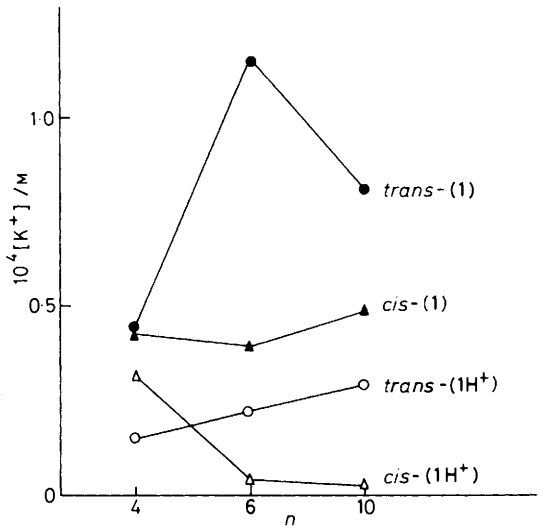


Figure 3. Effect of the methylene group on $[K^+]$. The data in Table 3 are plotted

methylene groups. This lowering can be attributed to the intermolecular binding between the ammonium group and the crown ether ring. It is well known that, in addition to alkali-metal cations, primary ammonium cations also fit into the 18-crown-6 ring and form stable complexes.[17–20] One may suppose, therefore, that the *trans*-($1H^+$) compounds would exist as cyclic dimers or polymers. On the other hand, the further decrease observed in *cis*-($1H^+$)(n = 6) relative to *trans*-($1H^+$)(n = 6) can be rationalised in terms of intramolecular complexation of the ammonium tail by the crown ether ring. In other words, intramolecular complexation of the ammonium-group tail in the *cis*-configuration displaces K^+ ion from the crown ether ring. Again as expected, a large decrease in extractibility is seen for K^+ and a relatively small decrease is observed for Cs^+.

Figure 3 shows two-phase extraction of K^+ ion with three different crown ethers. The extractabilities for *trans*-($1H^+$) vary only slightly as a function of the methylene group. This is quite reasonable because they are subjected primarily to the intermolecular complexation which should be nearly independent

Table 4. Ion-transport across a liquid membrane at 30 °C[a]

Entry	Membrane phase	OUT aqueous phase	$10^7 v$/mol h^{-1}
1	(**1**)(n = 10) Dark	[Me_4NOH] 0.10M	144
2	(**1**)(n = 10) Dark	[HCl] 0.50M	14.6
3	(**1**)(n = 10) Photoirradiated[b]	[HCl] 0.50M	30.5
4	(**1**)(n = 10) Dark	pH 3.0 with H_3PO_4 (0.02M)–Me_4NOH	37.2
5	(**1**)(n = 10) Dark	pH 3.0 with H_3PO_4 (0.02M)–Me_4NOH [Pic] 1.00mM[c]	44.6
6	(**1**)(n = 10) Photoirradiated[b]	pH 3.0 with H_3PO_4 (0.02M)–Me_4NOH [Pic] 1.00mM[c]	78.4
7[d]	(**1**)(n = 6) Dark	[KSCN] = [HCl] = 30mM	2.6
8[d]	(**1**)(n = 6) Photoirradiated[b]	[KSCN] = [HCl] = 30mM	2.7
9[e]	(**1**)(n = 10) Dark	[KSCN] = [HCl] = 30mM	0.66
10[e]	(**1**)(n = 10) Photoirradiated[b]	[KSCN] = [HCl] = 30mM	1.4

[a] IN aqueous phase: [KSCN] = 0.50M, [Me_4NOH] = 0.10M. Membrane phase (Bu^nOH:*o*-dichlorobenzene 55:45 v/v): [(**1**)(n = 10)] = 1.00×10^{-4}M. [b] 10 min irradiation per 4 h. [c] Pic = picric acid. [d] [(**1**)(n = 6)] = 1.00×10^{-3}M, IN aqueous phase: [KSCN] = [Me_4NOH] = 30mM. [e] [(**1**)(n = 10)] = 1.00×10^{-4}M, IN aqueous phase: [KSCN] = [Me_4NOH] = 30mM.

of spacer length. In contrast, the extractibility order *cis*-($1H^+$)-(n = 4) > *cis*-($1H^+$)(n = 6) ≧ *cis*-($1H^+$)(n = 10) clearly reflects a dependence on spacer length. Corey–Pauling–Koltun molecular models suggest that the hexamethylene chain is the shortest one for which optimal interaction between the terminal ammonium group and the crown ether ring in *cis*-($1H^+$) can occur. In the case of *cis*-($1H^+$)(n = 10), the extra conformational freedom of the decamethylene group should allow for the formation of a very stable intramolecular complex. By contrast, the shorter length of the tetramethylene chain in *cis*-($1H^+$)(n = 4) should preclude the formation of such a stable intramolecular complex.

Passive and Active Ion-transport across a Liquid Membrane.— It is well known that in ion-transport from an IN aqueous phase to an OUT aqueous phase across a liquid membrane, there exist two possible rate-determining steps: ion-extraction from the IN aqueous phase to the membrane phase (step I) and ion-release from the membrane phase to the OUT aqueous phase (step II). Previous investigations on liquid-membrane-transport established that step II becomes rate determining at $K_s > 10^6$ l mol^{-1}, resulting in a rate maximum at K_s *ca.* 10^6 l mol^{-1}.[26–28] This phenomenon occurs because very stable complexes do not release the ion efficiently into the OUT aqueous phase. The use of an enforced ion-release mechanism may be useful to obviate the problems associated with rate-determining step II;[29] that is, it may be advantageous selectively to reduce K_s at the ion-release site by utilising some transport condition. In the present study utilising photoresponsive crown ethers, we thought that photoinduced specific, intramolecular complexation to an ammonium tail could be used to trigger an accelerated ion-release into the OUT aqueous phase. We thus carried out a detailed study of the effect of irradiation on the ability of ($1H^+$) to transport K^+.

In the passive ion-transport studies (entries 1—6 in Table 4), we used an IN aqueous phase with a high KSCN concentration (0.50M) in order to facilitate step I. In a separate study, we confirmed that the membrane phase contained 60% *cis*-form immediately after 10 min photoirradiation. Figure 4 shows that a steady state giving straight lines against transport time has been attained after 5 h. The rate of K^+ transport (Table 4) was determined from the slopes of these lines.

Examination of entries 1—3 in Table 4 indicates that (i) *trans*-(**1**)(n = 10) can transport K^+ more efficiently than interconvertible systems such as those recorded in entry 2 [*trans*-(**1**)(n = 10)⇌*trans*-($1H^+$)(n = 10)] and entry 3 [*trans*-(**1**)(n = 10)⇌*cis*-

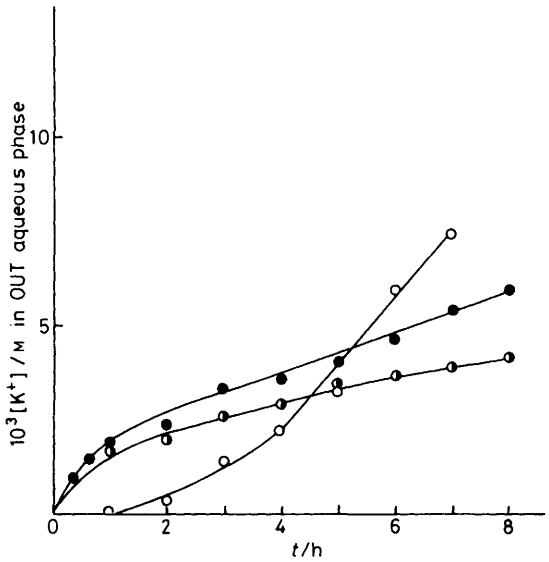


Figure 4. Transport of K^+ across a liquid membrane at 30 °C: ○ entry 1, ◑ entry 2, ● entry 3 in Table 4. The [K^+] determinations were continued for 28 h, which provided good straight lines about those after 5 h

($1H^+$)(n = 10)] and (ii) photoirradiation can enhance the rate by 2.1-fold. Result (ii) implies that the photoinduced ammonium-'biting' is useful as a tool to facilitate step II: therefore, step II is involved (at least partly) in the rate-determining step. This explanation however seems incompatible with (i) where *trans*-(**1**)(n = 10), which exhibited the highest extractability, serves as the most effective carrier. Detailed examination of Figure 4 may provide a reasonable rationalisation for this apparent contradiction. In entries 2 and 3, K^+ in the OUT aqueous phase increased rapidly during the initial stage but the subsequent increase after steady state was achieved was rather low. In entry 1, on the other hand, [K^+] in OUT did not increase during the initial 5 h but the increase during the steady-state region is relatively high. The contrasting behaviour implies that the membrane phase containing *trans*-(**1**)(n = 10) can solubilise a high concentration of K^+. A long induction period, therefore, results. We considered it possible that the interconvertible systems (entries 2 and 3) could have the latent capability to transport K^+ but *trans*-($1H^+$)(n = 10) and *cis*-($1H^+$)(n = 10)

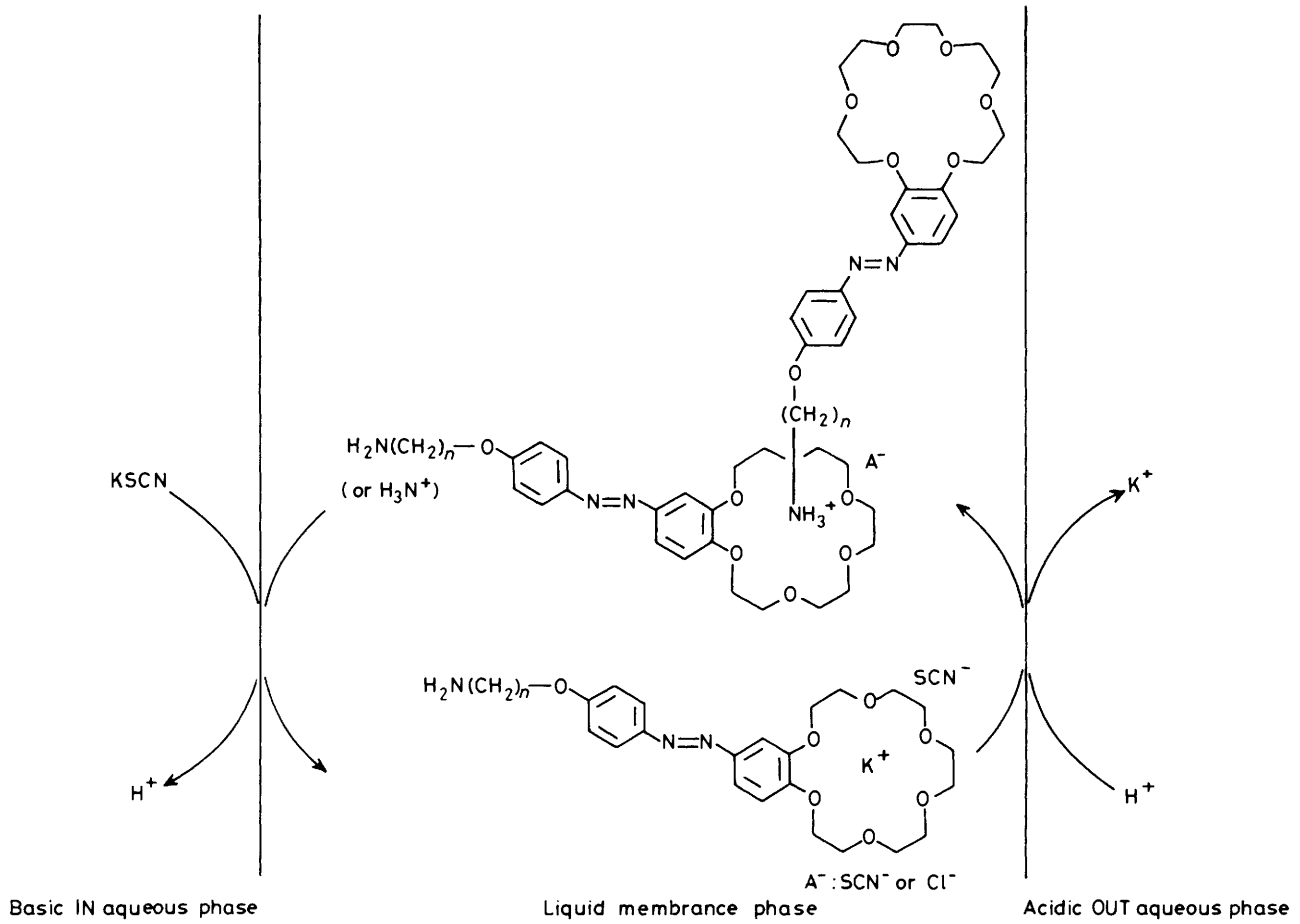


Figure 5. Schematic representation of K^+ transport at the high carrier concentration where the ion-release occurs mainly due to intermolecular complexation

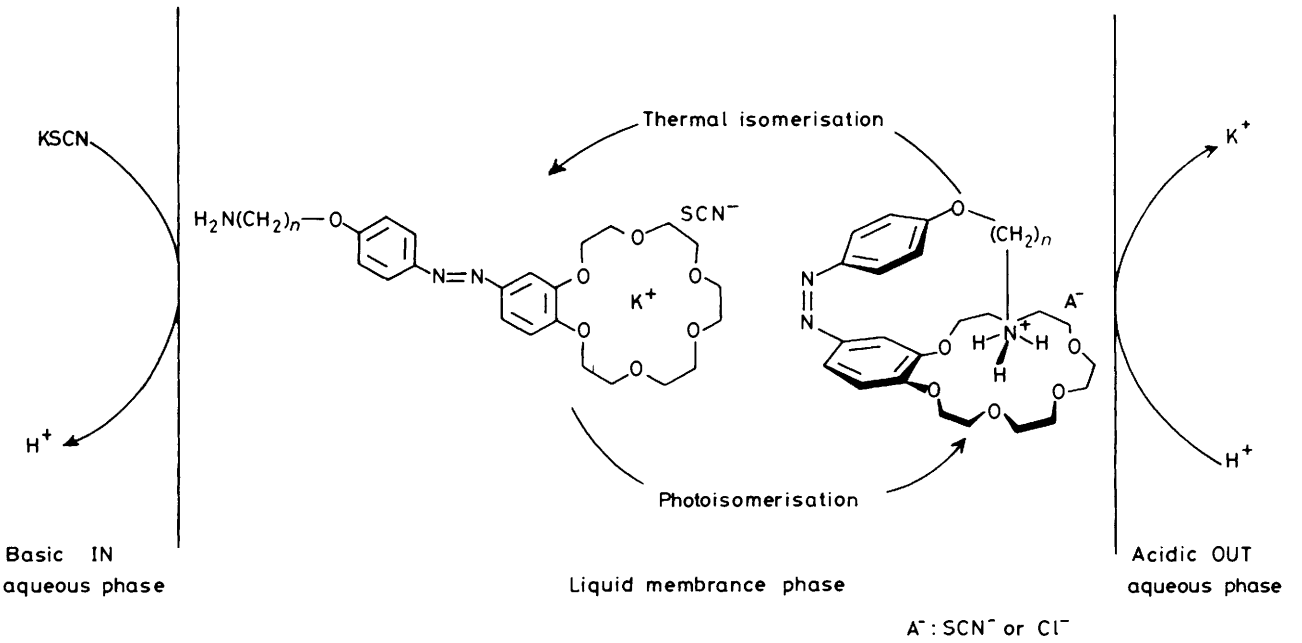


Figure 6. Schematic representation of K^+ transport at the low carrier concentration where the ion-release occurs mainly due to photoinduced intramolecular complexation (*i.e.*, 'tail-biting')

might not be lipophilic enough to recross the membrane phase from the acidic OUT aqueous side, *i.e.*, they might be captured at the interface between the membrane and the OUT aqueous phase. If it occurs, this phenomenon would lead to a rate retardation at the steady state. As an attempt to probe this possibility, we added picrate, a hydrophobic anion to the OUT aqueous phase (entries 4—6 in Table 4). In these runs, we found that K^+ in OUT increases linearly for up to 30 h and that the overall transport rate is significantly enhanced. We suggest that *trans*-(**1**H$^+$)(n = 10) and *cis*-(**1**H$^+$)(n = 10) form ion-pairs with the picrate anion and diffuse back through the membrane to the IN aqueous phase. We confirmed that the concentration of picrate ion in the IN aqueous phase increases with elapsed transport time.

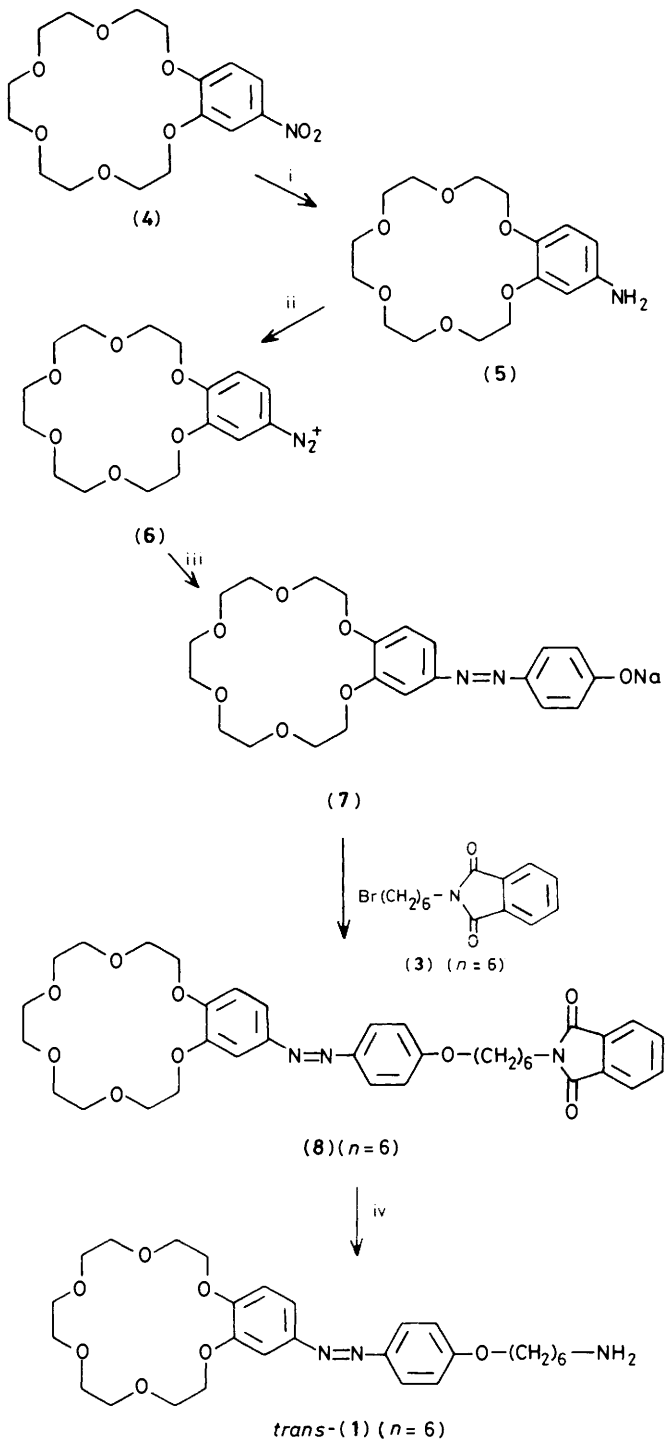
The results of the active ion-transport studies are recorded in entries 7—10. In the experiments, we first used 1.00×10^{-3} M-(**1**)(n = 6) as the carrier. We are surprised to find that active ion-transport took place readily in the dark and was not affected by photoirradiation: that is, active transport can be mediated not only by *cis*-(**1**H$^+$)(n = 6) in which intramolecular complexation is favoured but also by *trans*-(**1**H$^+$)(n = 6) in which intermolecular complexation is occurring. Recently, Nakatsuji *et al.*[13] demonstrated an example of active ion-transport using a crown (**2**) bearing an intramolecularly complexable ammonium group (carrier concentration in the membrane 2.5×10^{-3} M). In their system, however, it is difficult to distinguish the accelerating effect of intramolecular complexation from that of the intermolecular one. For *trans*-(**1**H$^+$), on the other hand, contributions from intramolecular complexation are hardly conceivable, and active transport (if it occurs) is therefore attributed to intermolecular complexation at the acid OUT aqueous phase side (Figure 5). In this connection, it should be pointed out that Tsukube[30] previously reported a proton-driven amino acid transport system in which a lipophilic primary ammonium cation–crown ether complex effectively mediated both active and passive transport. In fact, the transport scheme illustrated in Figure 5 is essentially analogous to that operating in his system.

In order to suppress the contribution from intramolecular complexation, we used a more lipophilic carrier, (**1**)(n = 10), and reduced the concentration to 1.00×10^{-4} M (entries 9 and 10). For *trans*-(**1**)(n = 10) inefficient active transport was observed in the dark (v 6.6×10^{-8} mol h^{-1}). We found, however, that the rate is enhanced up to 1.4×10^{-7} mol h^{-1} by photoirradiation. This significant rate increase can be rationalised in terms of a photoinduced intramolecular 'tail-biting' which facilitates a competitive ion ejection into the OUT aqueous phase (Figure 6). It appears, therefore, that the photoinduced 'tail-biting' mechanism becomes effective when the carrier concentration is lowered enough for the carrier to exist as a discrete monomeric unit.

Conclusions.—This study has demonstrated that photo-regulation of metal-binding to a crown ether ring can be achieved by means of induced structural changes arising from the photoisomerisation of azobenzene. In extensions to membrane transport studies, it was found that these photo-induced changes in affinity could be used to enhance the rate of ion-release from an artificial carrier, thereby increasing the overall rates of either passive or active transport across a membrane. The present study suggests that, although the relative ratio of intra- to inter-molecular complexation is still difficult to control, further elaborations of this concept might lead to the eventual development of a series of photocontrollable membranes.

Experimental

Materials.—The three crown ethers used in this study were synthesized according to Scheme 2. Since the preparation methods are similar to each other, only the synthesis of *trans*-(**1**)(n = 6) is described as an example and the analytical data for the other two crown ethers are merely recorded.



Scheme 2. *Reagent:* i, Pd–C, H_2; ii, $NaNO_2$–HCl; iii, C_6H_5OH; iv, NH_2NH_2

N-(6-*Bromohexyl*)*phthalimide* (**3**)(n = 6).—1,6-Dibromohexane (22.6 g, 0.090 mol) was treated with potassium phthalimide at 170—180 °C for 11 h. The reaction mixture was poured into chloroform, and the precipitate was removed by

filtration. The addition of ligroin to the filtrate afforded crystals (0.56 g), m.p. 135—143 °C, which were identified to be 1,6-bis-(*N*-phthalimido)hexane from elemental analysis. The filtrate was subjected to steam distillation to remove excess of 1,6-dibromohexane. The remaining solution was extracted with chloroform. The chloroform solution was concentrated *in vacuo*, and the solid residue was recrystallised from ligroin, yield 33%, m.p. 46.5—48.0 °C; δ($CDCl_3$) 1.70 [m, $(CH_2)_4$, 8 H], 3.42 (t, NCH_2, 2 H), 3.70 (t, $BrCH_2$, 2 H), and 7.7—7.9 (m, aromatic protons, 4 H) (Found: C, 54.6; H, 5.2; N, 4.65. Calc. for $C_{14}H_{16}BrNO_2$: C, 54.2; H, 5.2; N, 4.5%).

N-(4-*Bromobutyl*)*phthalimide* (**3**)(n = 4). This was formed in 52% yield, m.p. 69.5—71.5 °C (Found: C, 53.0; H, 4.5; N, 5.4%. Calc. for $C_{12}H_{12}BrNO_2$: C, 51.1; H, 4.3; N, 5.0%).

N-(10-*Bromodecyl*)*phthalimide* (**3**)(n = 10). This was formed in 36% yield, m.p. 55.5—56.5 °C (Found: C, 60.2; H, 6.8; N, 3.9. Calc. for $C_{18}H_{24}BrNO_2$: C, 59.0; H, 6.6; N, 3.8%).

Sodium Salt of 4′-(p-*Hydroxyphenylazo*)*benzo*-18-*crown*-6 (**7**).—4′-Aminobenzo-18-crown-6 (**5**) was prepared by catalytic hydrogenation of 4′-nitrobenzo-18-crown-6 (**4**) (5.00 g, 0.014 mol) on Pd–C and used without further purification. Compound (**5**) was diazotised to (**6**) according to the method previously described[31] and treated with phenol (1.58 g, 0.0168 mol) in an aqueous solution (40 ml) containing NaOH (1.00 g, 0.025 mol) and Na_2CO_3 (0.50 g, 0.0047 mol). Compound (**7**) precipitated as orange crystals on the addition of NaCl, yield 85% [from (**4**)], m.p. 114—117 °C, single spot on t.l.c.

Compounds (**8**)(n = 6) *and* trans-(**1**)(n = 6).—Compounds (**3**)(*n* = 6) (0.50 g, 1.61 mmol) and (**7**) (0.30 g, 0.66 mmol) were dissolved in dimethyl sulphoxide (4 ml) and heated at 100 °C for 6 h. The mixture was poured into water, the aqueous solution being extracted with chloroform. The chloroform solution was concentrated *in vacuo* and subjected to t.l.c. separation (silica gel, chloroform–methanol 25:1 v/v), yield 25%, m.p. 32—36 °C; $\nu_{max.}$(KBr) 1 110, 1 250, 1 500, 1 710, and 1 770 cm^{-1}. Compound (**8**)(*n* = 6) (0.11 g, 0.17 mmol) thus obtained was treated with hydrazine hydrate (0.10 ml, 1.95 mmol) in ethanol (20 ml) at reflux. The progress of the reaction was followed by t.l.c. (silica gel, chloroform–methanol 25.1 v/v). After 2 h, the reaction mixture was cooled and the precipitate was removed by filtration. The filtrate was evaporated to dryness, and the residue taken up in chloroform. The insoluble residue was removed by filtration. Compound *trans*-(**1**)(*n* = 6) was obtained as orange crystals on the addition of ligroin to the chloroform filtrate, yield 100%, m.p. 100—102 °C; *m*/*z* 531 (M^+); $\nu_{max.}$(KBr) 1 110, 1 250, and 1 500 cm^{-1}; δ($CDCl_3$) 1.11—2.07 [m, $(CH_2)_4$, 8 H], 2.39 (t, NCH_2, 2 H), 2.73br (NH_2, 2 H), 3.43—4.63 (m, crown protons and OCH_2, 22 H), 6.97(d), 7.27(s), and 7.53(d) (aromatic protons in benzocrown ether), and 6.97(d) and 7.85(d) (aromatic protons in phenoxy). It was very difficult to obtain good elemental analysis data because *trans*-(**1**)(*n* = 6) readily absorbed CO_2 to form the carbamic acid (Found: C, 60.9; H, 7.5; N, 7.4. Calc. for $C_{28}H_{41}N_3O_7 \cdot 0.5\ H_2CO_3$: C, 60.8; H, 7.5; N, 7.5%).

Compound trans-(**1**)(n = 4).—This was formed in 11% yield [from (**7**)], m.p. 114—116 °C (Found: C, 59.6; H 7.3; N, 7.6. Calc. for $C_{26}H_{37}N_3O_7 \cdot 0.5\ H_2CO_3$: C, 59.5; H, 7.2; N, 7.9%).

Compound trans-(**1**)(n = 10).—This was formed in 7.1% yield [from (**7**)], m.p. 107—109 °C (Found: C, 63.3; H, 8.0; N, 6.6. Calc. for $C_{32}H_{49}N_3O_7 \cdot 0.5\ H_2CO_3$: C, 63.1; H, 8.1; N, 6.8%).

Photoisomerisation and Kinetic Measurements of Thermal cis–trans *Isomerisation.—trans–cis* Isomerisation was carried out by using a 500 W high-pressure Hg lamp with a coloured glass filter (Toshiba UV-D35, 330 nm < λ < 380 nm). When the concentration of (**1**) [or ($1H^+$)] was *ca.* 10^{-4}M, the photostationary state was attained in 30 s. The kinetic measurements were carried out spectrophotometrically at 30 °C in *o*-dichlorobenzene : butan-1-ol 80:20 v/v by monitoring the increase in the absorption maxima ($\pi-\pi^*$ bands) of the *trans*-forms. Usually, metal salts were added after photoisomerisation. Further details of the method have been described previously.[7,14,15]

Solvent Extraction.—The method of solvent extraction has been described previously.[7,14] In this study, the organic phase (3 ml) (*o*-dichlorobenzene:butan-1-ol 45:55 v/v) containing 1.18×10^{-4}M-(**1**) or -($1H^+$) was agitated thoroughly with the aqueous phase (3 ml) [pH 4.7 with 10mM-phosphate for ($1H^+$) and 10mM-MOH for (**1**)] containing 0.0102M-alkali toluene-*p*-sulphonates. U.v. light was irradiated (when necessary) before mixing. After agitation, the mixture was equibrated at 30 °C and then separated. The concentrations of alkali toluene-*p*-sulphonates extracted into the organic phase were determined by atomic absorption spectroscopy (Shimadzu AA-640): specifically, the organic phase was evaporated to dryness and the residue was dissolved in water (3 ml). The aqueous solutions thus obtained were subjected to determination of the concentrations.

Ion-transport.—Transport of K^+ across a liquid membrane (*o*-dichlorobenzene:butan-1-ol 45:55 v/v) with the aid of (**1**) or ($1H^+$) was carried out in a U-tube (diameter 1.0 cm). The transport system consisted of the membrane phase (10 ml) and the first (IN) and the second (OUT) aqueous phase (5 ml), and the membrane phase was stirred (400 r.p.m.). The tube was immersed in a thermostatted water-bath (30 °C) and, when required, irradiated by a 500 W high-pressure Hg lamp with a UV-D35 filter. We confirmed spectrophotometrically that when the lamp was switched on for 10 min, 60% of (**1**) or ($1H^+$) in the membrane phase was isomerised to *cis*-(**1**) or *cis*-($1H^+$). The rates of ion transport were determined by monitoring the K^+ concentration in the OUT aqueous phase by atomic absorption spectroscopy. Further details of the transport conditions are recorded in the footnotes to Table 4.

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