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Photoresponsive Crown Ethers. 4. Influence of Alkali Metal Cations on Photoisomerization and Thermal Isomerization of Azobis(benzocrown ether)s

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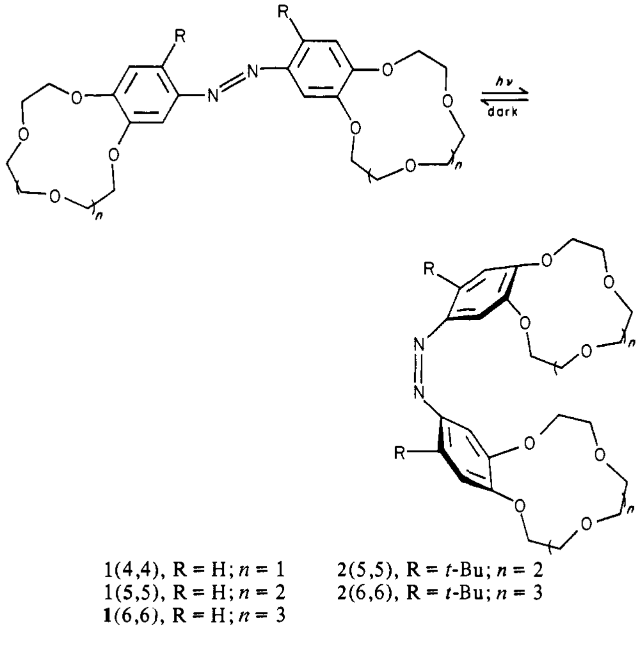
Abstract: Five photoresponsive azobis(benzocrown ether)s, **1**(4,4), **1**(5,5), **1**(6,6), **2**(5,5), and **2**(6,6), were synthesized, where numbers in parentheses denote the number of oxygens in benzocrown ethers, and crown series **2** have two *tert*-butyl groups in the 2 and 2′ position of the azo linkage. We have found that (i) in the presence of alkali metal cations, the concentration of cis isomers (cis %) under the photostationary state is enhanced and the rate of the thermal cis-to-trans isomerization (k) is suppressed, the optima of *cis*-**1**(5,5) and *cis*-**1**(6,6) being observed for Rb$^+$ and Cs$^+$, respectively, (ii) Rb$^+$ and Cs$^+$ are extracted most efficiently from an aqueous solution to an organic phase (*o*-dichlorobenzene) with *cis*-**1**(5,5) and *cis*-**1**(6,6), respectively, (iii) cis % and k of **2**(5,5) and **2**(6,6) are affected by alkali metal cations smaller than those of corresponding **1**(5,5) and **1**(6,6), and (iv) cis % and k of **1**(4,4) are less affected by added alkali metal cations and the extractability is very low. The increase in cis % and the suppression of the thermal isomerization rate are rationalized in terms of the "tying effect" of complexed cations requiring the additional energy to disrupt the crown–cation interaction. The correlation of the extractability with cis % and k implies that alkali metal cations are extracted under photoirradiation as intramolecular 1:2 cation/crown complexes and the ion selectivity is associated with the fitness between the ion size and the size of the spacial cavity provided by two crown ethers of cis forms. The ion selectivity suggests that (i) the cavity size of *cis*-**1**(6,6) is greater than that of *cis*-**1**(5,5) and (ii) the cavity sizes of crown series **2** are smaller than those of crown series **1** probably owing to the steric repulsion of the *tert*-butyl groups. Hence, the ion selectivity in the photocontrolled solvent extraction is effected by the crown ring size and the steric crowding around the azo linkage.

Photoresponsive systems are ubiquitously seen in nature, and light is frequently used as a trigger to cause the subsequent life processes. In these systems, a photoantenna to capture a photon is combined with a functional group to mediate some subsequent event, and the physiological events are frequently linked with photoinduced structural changes of photoantennas. When mimicking the fundamental functions of the photoresponsive systems, chemical substances which exhibit photoinduced structural changes become the candidates for the photoantennas. Azobenzene derivatives which exhibit photoinduced cis–trans isomerism[3,4] are one of the best candidates because of their large geometrical change and good reversibility. With the aid of azobenzene derivatives as photoantenna, several groups have been attempting the photocontrol of the chemical and physical functions of membranes,[5] micelles,[6] microemulsions,[7] polypeptide chains,[8] synthetic polymers,[9] cyclodextrins,[10] and crown ethers.[11-13] We have been aiming at utilizing the phenomenon in controlling the chemical and physical functions of crown ethers.[11,12] We previously synthesized azobis(benzo-15-crown-5) (**1**(5,5)) which has two crown ethers as functional group and an azo linkage as a photoantenna.[12] Photoisomerized *cis*-**1**(5,5) exhibited greater binding abilities for large alkali metal cations than *trans*-**1**(5,5) due to the formation of intramolecular, sandwich-type 1:2 cation/crown complexes. We



1(4,4), R = H; n = 1
1(5,5), R = H; n = 2
1(6,6), R = H; n = 3
2(5,5), R = t-Bu; n = 2
2(6,6), R = t-Bu; n = 3

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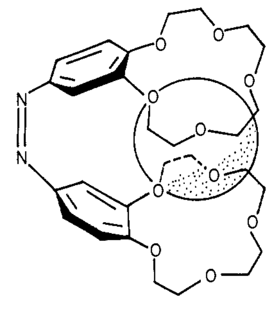
demonstrated that ion extraction and ion transport can be controlled by light by utilizing the difference.[12] In the course of the study, we unexpectedly found that by the addition of large alkali metal cations, the concentration of *cis*-**1**(5,5) under the photostationary state is markedly enhanced and the rate of the thermal cis-to-trans isomerization of the azo linkage is suppressed.[12c] The novel findings were accounted for by the high stability of the intramolecular 1:2 cation/crown complexes (**3**) between *cis*-**1**(5,5) and relatively large alkali metal cations (especially, Rb$^+$ ion).[12c,14]



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As an extention of the study, we here report the influence of alkali metal cations on the photoisomerization and thermal isomerization of several azobis(crown ether)s illustrated above. We found that when the cavity provided by two crown ethers of the cis forms best fits the size of alkali metal cations, the extractability and the concentration of the cis forms at the photostationary state become maximum and the rate of the thermal isomerization becomes minimum.

Results and Discussion

The specific interaction of macrocyclic polyethers with metal ions stems from a host–guest relationship.[15] Alkali metal cations which exactly fit the cavity of crown ethers form 1:1 complexes, whereas those which have larger ionic radii form 1:2 cation/crown complexes. This view was substantiated by the use of bis(crown ether)s,[16] polymeric crown ethers,[17] and the crystal structure of crown ether–alkali metal cation complexes.[18] For example, Mollison and Turter[18] have established that 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$^+$. In a previous stuydy on **1**(5,5),[12c] we reported that (i) the concentration of cis % at the photostationary state is increased by added Rb$^+$ and Cs$^+$, (ii) the rate of the thermal cis-to-trans isomerization is suppressed by K$^+$, Rb$^+$, and Cs$^+$, (iii) *trans*-**1**(5,5) extracts Na$^+$ efficiently from an aqueous phase to an organic phase (*o*-dichlorobenzene), whereas *cis*-**1**(5,5) extracts K$^+$, Rb$^+$, and Cs$^+$ efficiently, and (iv) in all cases, optimum effects are observed for Rb$^+$. These results consistently suggest that *cis*-**1**(5,5) forms stable 1:2 cation/crown complexes (**3**) with large alkali metal cations and in particular the most stable one with Rb$^+$, supporting that the ionic radius of Rb$^+$ best fits the cavity provided by two crown ethers of *cis*-**1**(5,5). We have examined which metal cation fits the cavity of other photoresponsive bis(crown ethers) through the studies on the cis % at the photostationary state, the rate of the thermal cis-to-trans isomerization, and the solvent extraction of alkali metal cations.

Table I. λ_{max} and ϵ_{max} of Trans Isomers, Cis/Trans Ratio at the Photostationary State, and First-Order Rate Constants (k) for Thermal Isomerization[a]

crown ether	λ_{max}, nm	ϵ_{max}, cm^{-1} M^{-1}	cis/trans[b]	$k \times 10^4$, s^{-1}
1(4,4)	370	27100	71/29	2.90
1(5,5)	377	26700	52/48	18.5
1(6,6)	377	22700	65/35	8.52
2(5,5)	394	18900	55/45	5.49
2(6,6)	395	19200	49/51	5.60

[a] 30 °C, *o*-dichlorobenzene:*n*-butyl alcohol = 86.8:13.2 in volume. [b] Room temperature.

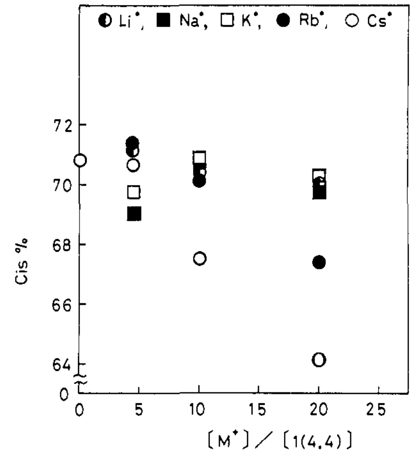

Figure 1. Influence of added metal cations on the cis % of **1**(4,4) (5.00 × 10^{-5} M).

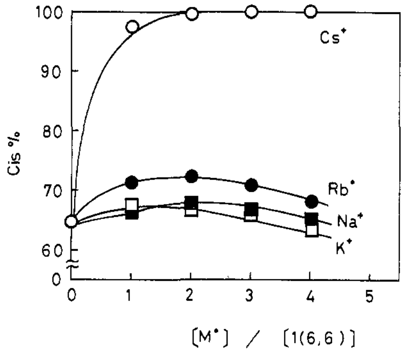

Figure 2. Influence of added metal cations on the cis % of **1**(6,6) (5.00 × 10^{-5} M).

Concentration of Cis % at the Photostationary State and Rate of Thermal Isomerization. When an *o*-dichlorobenzene–*n*-butyl alcohol mixed solution (86.8:13.2 in volume) of bis(crown ethers) was irradiated at room temperature with a 500-W high-pressure Hg lamp, the photostationary state was attained within 5 min. The cis/trans ratio under the photostationary state was calculated from the decrease in the absorption maxima of trans isomers (Table I). The cis/trans ratio in Table I was corrected for the absorbance of each cis isomer at the employed wavelength.[12c] Holding the concentration of bis(crown ether)s constant, we determined the cis % at the photostationary state as a function of the concentration of alkali metal cations (Figures 1–4). For the sake of experimental convenience, dodecanoic acid salts were used for the source of alkali metal cations.[12c] The concentration of cis % at [cation]/[bis(crown ether)] = 4.0 is summarized in Table

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[14] A referee has pointed out that complexed large cations such as Rb$^+$ and Cs$^+$ may increase the decay of the active excited state due to spin–orbit coupling, probably making the cis % higher. E.g.: Larson, J. M.; Sousa, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 1943. The heavy-atom effects may be partly operating, but the increasing order of the cis % for *cis*-**1**(5,5) (i.e., Rb$^+$ > Cs$^+$ > K$^+$ > Na$^+$) indicates that the host–guest relationship is more important than the heavy-atom effects.

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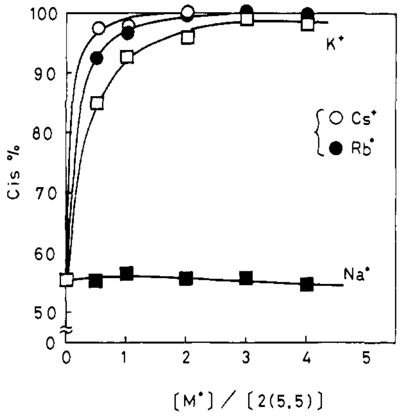

Figure 3. Influence of added metal cations on the cis % of **2**(5,5) (5.00 × 10^{-5} M).

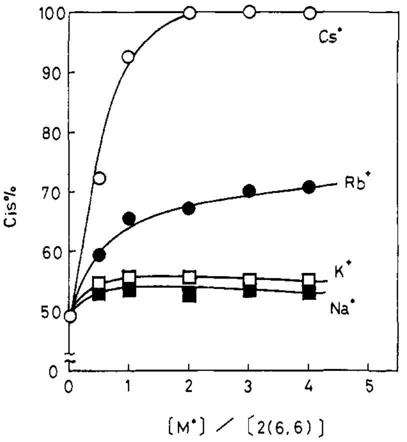

Figure 4. Influence of added metal cations on the cis % of **2**(6,6) (5.00 × 10^{-5} M).

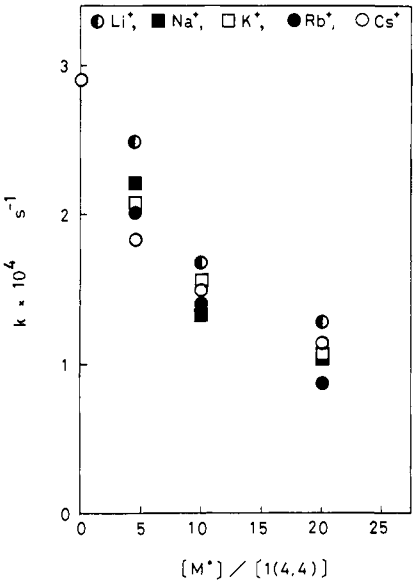

Figure 5. Influence of added metal cations on the rate of thermal isomerization of **1**(4,4).

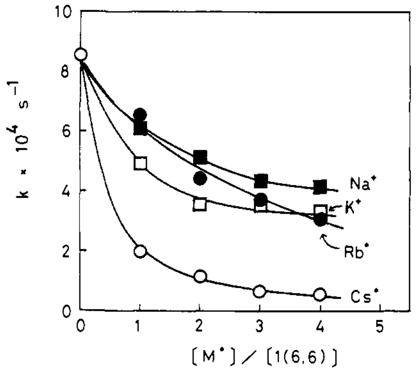

Figure 6. Influence of added metal cations on the rate of thermal isomerization of **1**(6,6).

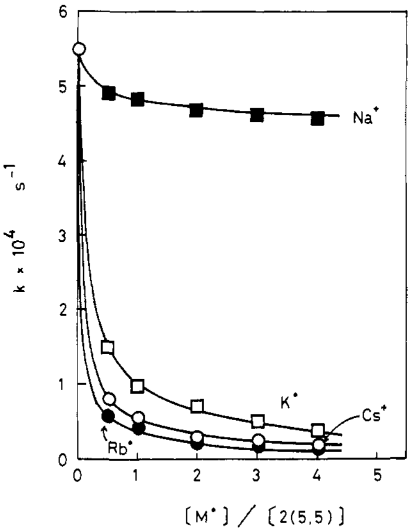

Figure 7. Influence of added metal cations on the rate of thermal isomerization of **2**(5,5).

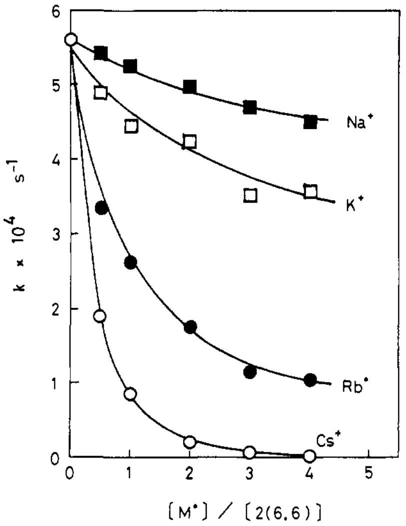

Figure 8. Influence of added metal cations on the rate of thermal isomerization of **2**(6,6).

II. The data on **1**(5,5) have been reported previously,[12c] but some of them were newly determined in this study in order to discuss the results under the identical reaction conditions.

The thermal cis-to-trans isomerization in the absence of metal cations was relatively fast, and the initial spectra were regenerated within a few hours. Hence, the cis–trans isomerism was completely reversible. The first-order rate constants (k) for thermal isomerization were determined spectrophotometrically by following the increase in the absorption band of trans isomers. In Figures 5–8, the rate constants are plotted as a function of the concentration of alkali metal cations, and the k values at [cation]/[bis(crown ether)] = 4.0 are summarized in Table II.

Examination of Table I reveals that (i) the isomerization rates of crown series **1** are in the order **1**(5,5) > **1**(6,6) > **1**(4,4), (ii) the isomerization rates of **2**(5,5) and **2**(6,6) are smaller than those of **1**(5,5) and **1**(6,6), and (iii) in crown series **1**, the bis(crown ether) having the greater rate constant has the smaller cis % at the photostationary state. Factor ii is accounted for by the steric

Table II. Influence of Added Alkali Metal Cations on the Cis/Trans Ratio at the Photostationary State and the Rate of Thermal Isomerization[a]

bis(crown ether)	metal cation[b]	cis %[c]	$k \times 10^4$,[d] s^{-1}	k_{rel}[e]
1(4,4)	Li^+	71	2.48	0.855
	Na^+	69	2.21	0.762
	K^+	70	2.06	0.710
	Rb^+	71	2.02	0.697
	Cs^+	71	1.83	0.631
1(4,4)[f]	Li^+	70	1.28	0.441
	Na^+	70	1.02	0.352
	K^+	70	1.03	0.355
	Rb^+	67	0.87	0.300
	Cs^+	64	1.14	0.393
1(5,5)	Na^+	55	16.5	0.892
	K^+	57	6.66	0.360
	Rb^+	98	2.02	0.109
	Cs^+	92	3.39	0.183
1(6,6)	Na^+	65	4.15	0.487
	K^+	63	3.38	0.397
	Rb^+	68	3.08	0.362
	Cs^+	100	0.53	0.062
2(5,5)	Na^+	53	4.57	0.832
	K^+	98	0.39	0.071
	Rb^+	100	0.11	0.020
	Cs^+	100	0.14	0.026
2(6,6)	Na^+	53	4.49	0.802
	K^+	56	3.55	0.634
	Rb^+	71	1.07	0.191
	Cs^+	100	0.027	0.005

[a] [Cation]/[bis(crown ether)] = 4.0, *o*-dichlorobenzene:*n*-butyl alcohol = 86.8:13.2 in volume. [b] Dodecanoic acid salts were used for alkali metal cations. [c] Room temperature. [d] 30 °C. [e] $k_{rel} = k/k$ at $[M^+] = 0$. [f] [Cation]/[bis(crown ether)] = 10.0.

effect of two *tert*-butyl groups which are introduced into the 2 and 2′ positions of the azo linkage. The steric effect may also be reflected by the red shift of the absorption maxima (17–18 nm) and the smaller molar extinction coefficients. Factor iii implies that the stability of cis isomers in the photoisomerization process is correlative to the magnitude of the free energy of activation in the thermal isomerization process. It is conceivable, therefore, that both the thermal isomerization and photoisomerization processes are governed by a similar mechanistic factor. In the cis %–*k* correlation map (Figure 9), crown series **2** are plotted at a lower area than crown series **1**. The result also suggests the significance of the steric effect in **2**.

It is difficult to rationalize why the rate of **1**(4,4) is smaller by a factor of 6 and why the cis % is greater by 19% than those of **1**(5,5). The result implies that the transition state of **1**(4,4) may be less stabilized than that of **1**(5,5) and **1**(6,6). It is known that the rate of thermal isomerization is facilitated by the resonance stabilization of substituents.[19] It may be said, therefore, that two phenolic ether groups of the crown ether of **1**(4,4) stabilize the transition state to a smaller extent than those of **1**(5,5) and **1**(6,6). At present, we speculate that two phenolic ether oxygens of benzo-12-crown-4, which is classified as a relatively rigid medium ring, may be somewhat distorted from the position suitable to full resonance.

Examination of Figures 1–4, which show the influence of added alkali metal cations on the cis % at the photostationary state, reveals that (i) the cis % of **1**(4,4) is affected to a smaller extent by alkali metal cations and only Cs^+ slightly diminishes the cis %, (ii) as has been reported for **1**(5,5),[12c] the cis % of **1**(6,6), **2**(5,5), and **2**(6,6) is significantly enhanced in the presence of relatively large alkali metal cations and in some cases the cis % reaches 100% (**1**(6,6) and **2**(6,6) in the presence of Cs^+ and **2**(5,5) in the presence of Rb^+ or Cs^+), (iii) in order to induce the distinct increase in the cis %, crown series (6,6) require alkali metal cations larger than crown series (5,5), (iv) when comparing crown series **1** with crown series **2**, the cis % of **2** can be enhanced by alkali metal cations smaller than that of **1** (for example, K^+ is effective to increase the cis % of **2**(5,5) (Figure 3), whereas the cis % of **1**(5,5) is hardly affected by K^+,[12c] and (v) Na^+, K^+, and Rb^+ in **1**(6,6) (Figure 2) and Na^+ and K^+ in **2**(6,6) (Figure 4) apparently provide small maxima at $[M^+]/[\text{bis(crown ether)}] = 1$–2. Similarly, examination of Figures 5–8, which show the influence of added alkali metal cations on the thermal isomerization rate, reveals that (i) the rate of the thermal isomerization of *cis*-**1**(4,4) is retarded to a smaller extent by alkali metal cations, (ii) the rates for **1**(6,6), **2**(5,5), and **2**(6,6) are efficiently suppressed by larger alkali metal cations and, in particular, the isomerization of **2**(6,6) is quenched most efficiently, the rate constant at $[Cs^+]/[\mathbf{2}(6,6)] = 4.0$ being smaller by a factor of 200 than that in the absence of metal cation (Table II), (iii) in order to induce the distinct rate suppression, crown series (6,6) require alkali metal cations larger than crown series (5,5), and (iv) when comparing crown series **1** with crown series **2**, the rate of **2** can be retarded by smaller cations than that of **1** (for example, see Rb^+ in Figures 6 and 8).

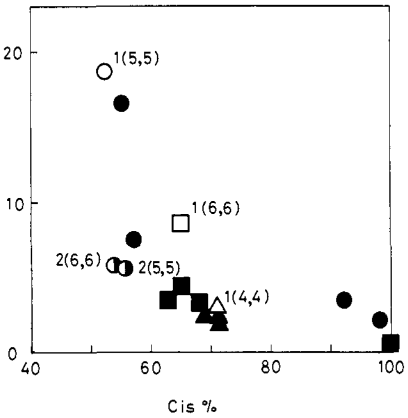

Figure 9. Cis %–*k* correlation map. Filled points are plots in the presence of alkali metal cations for crown series **1**.

The phenomena i–iv are common to both cis % and thermal isomerization rate and are essentially related to the stability of sandwich-type 1:2 complexes between cations and cis isomers. The difference between (5,5)- and (6,6)-bis(crown ether)s (factor iii) could be rationalized such that (6,6)-bis(crown ether)s provide a larger sandwich-type inner cavity than (5,5) analogues due to the larger crown ring size. Thus, only large alkali metal cations such as Cs^+ can interact efficiently with two crown rings of (6,6)-bis(crown ethers).

Comparison of *cis*-**1** with *cis*-**2** suggests that the inner cavity between two crown ethers of *cis*-**2** may be somewhat smaller than that of *cis*-**1** (factor iv). For example, the distinct increase in the cis % for **1**(6,6) occurs only in the presence of Cs^+ (Figure 2), whereas Rb^+ can cause considerable increase in the cis % of **2**(6,6) (Figure 4). Similarly, the cis % of **2**(5,5) becomes almost 100% even in the presence of K^+ (Figure 3), whereas that of **1**(5,5) is hardly affected by K^+ (Figure 2 in ref 12c). A similar trend is seen for the suppression of *k*. We consider that the difference between crown series **1** and **2** is probably ascribed to the buttressing effect of the *tert*-butyl groups.[20] *cis*-Azobenzenes are sterically crowded, and the introduction of *tert*-butyl groups into the ortho positions of the azo linkage would further increase the steric crowding of *cis*-**2**. Probably the distance between two crown rings is enforced to become narrow owing to this steric repulsion. This problem will be discussed again later.

cis-**1**(4,4) was found to be less effective as a sandwich-type ligand (factor i). Based on the complexation of affinity of *cis*-

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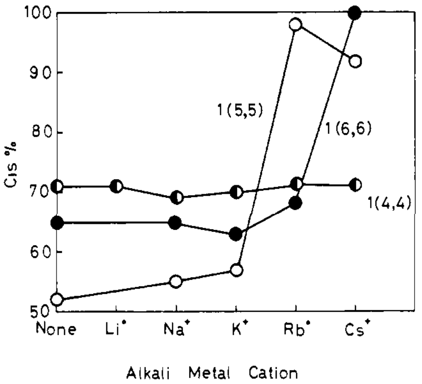

Figure 10. Ion specificity of crown series **1** in the cis % of the photostationary state.

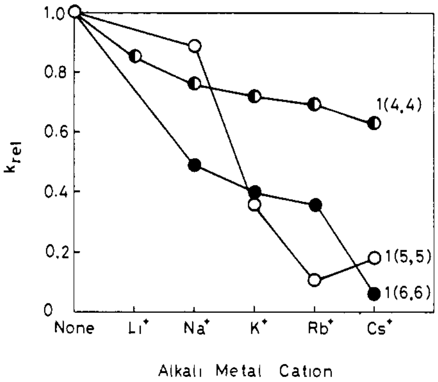

Figure 11. Ion specificity of crown series **1** in the rate constant for the thermal isomerization.

1(5,5) and *cis*-**1**(6,6), one may presume that the inner cavity of *cis*-**1**(4,4) would best fit the size of K^+ or Rb^+. The presence results show, however, that *cis*-**1**(4,4) is not a ligand strong enough to bind these alkali metal cations in a sandwich-type manner. This finding shows that the formation of stable 1:2 cation/crown complexes is dependent not only on the fitness between the inner cavity of cis isomers and the size of alkali metal cations but also on the binding ability of each crown ether. The stability of the complexes of *cis*-**1**(5,5) and *cis*-**1**(6,6) must be aided by the binding ability of benzo-15-crown-5 and benzo-18-crown-6 toward Rb^+ and Cs^+,[15] whereas the binding ability of benzo-12-crown-4 toward K^+ and Rb^+ is so weak that the stability of *cis*-**1**(4,4) also becomes very poor.

It is not clear why **1**(6,6) and **2**(6,6) give rise to the small maxima in the cis %–[cation]/bis(crown ether)] plots (factor v). The phenomenon was not seen for crown series (5,5). Monobenzo-18-crown-6 easily forms 1:1 cation/crown complexes with Na^+ and K^+.[15] Therefore, the most likely explanation is that the formation of 1:2 cation/crown complexes at low cation concentrations leads to the increase in the cis %, and the formation of 2:2 cation/crown (i.e., 2:1 cation/bis(crown ether)) complexes at high cation concentrations causes the decrease in the cis % due to the electrostatic repulsion between two complexed metal cations. If so, Figures 2 and 4 suggest that the concentration of 1:2 cation/crown complexes becomes greatest at [cation]/bis(crown ether)] = 1–2.

The foregoing results are summarized in Figures 10 and 11. The effects of added alkali metal cations on **1**(4,4) are generally small. The maximum effects of **1**(5,5) and **1**(6,6) are observed for Rb^+ and Cs^+, respectively, reflecting the difference in the size of each inner cavity of the sandwich-type complexes. A similar conclusion is valid for **2**(5,5) and **2**(6,6) except that even smaller alkali metal cations induced the changes in the cis % and the thermal isomerization rate.

Solubility of Bis(crown ether)s and Solvent Extraction of Alkali Metal Cations. When an *o*-dichlorobenzene solution of trans isomers was agitated with an aqueous solution of 0.01 M NaOH, only *trans*-**1**(6,6) was transferred to the aqueous phase (2 mol%, Table III). On the other hand, when the photoirradiated *o*-dichlorobenzene solution was agitated with the same aqueous solution, appreciable amounts of cis isomers of crown series **1** were transferred to the aqueous phase. The remarkable difference in solubility is attributed to the difference in the molecular structure:[21] symmetrical trans isomers are classified as a nonpolar molecule, while cis isomers have relatively large dipole moment across the azo linkage due to two dipoles in the same direction. The solubility order of *cis*-**1**(6,6) > *cis*-**1**(5,5), > *cis*-**1**(4,4) simply reflects the number of the oxyethylene group. On the other hand, neither *trans*-**2** nor *cis*-**2** was transferred into the aqueous phase. This is, of course, due to the lipophilic nature strengthened by the *tert*-butyl groups.

Table III. Solubility of Bis(crown ether)s in Water[a]

crown ether	mol % extracted in 0.01 M NaOH	
	trans	cis[b]
1(4,4)	0	3.3
1(5,5)	0	14
1(6,6)	2.0	24
2(5,5)	0	0
2(6,6)	0	0

[a] Equal volumes of an *o*-dichlorobenzene (3.00×10^{-4} M 1 or 2) and an aqueous solution (0.01 M NaOH) were agitated thoroughly for 2 min. [b] Mol % of the cis form extracted in 0.01 M NaOH solution.

Table IV. Extraction of Alkali Metal Salts of Methyl Orange with Photoresponsive Bis(crown ether)s

bis(crown ether)		counterion (methyl orange) extracted, %				
		Li^+	Na^+	K^+	Rb^+	Cs^+
1(4,4)[a]	dark	0	0	1.3	0	1.8
	light	2.2	0	1.0	5.7	3.4
1(5,5)[b]	dark		29.6	1.3	29.3	24.1
	light		17.1	29.0	49.6	29.9
1(6,6)[b]	dark		7.1	14.8	6.0	5.2
	light		8.0	10.3	14.0	22.6
2(5,5)[c]	dark		3.4	32.1	14.9	8.0
	light		0.3	20.4	20.8	14.3
2(6,6)[c]	dark		1.4	58.4	31.6	57.7
	light		3.6	57.4	37.3	76.1

[a] *o*-Dichlorobenzene phase, [1(4,4)] = 3.74×10^{-3} M; aqueous phase, [methyl orange] = 3.74×10^{-5} M, [MOH] = 0.01 M, [MCl] = 0.04 M. [b] *o*-Dichlorobenzene phase, [1(5,5) or 1(6,6)] = 3.00×10^{-4} M; aqueous phase, [methyl orange] = 8.10×10^{-6} M, [MOH] = 0.01 M. [c] *o*-Dichlorobenzene phase, [2(5,5) or 2(6,6)] = 1.70×10^{-3} M; aqueous phase, [methyl orange] = 8.10×10^{-6} M, [MOH] = 0.01 M, [MCl] = 0.04 M.

The binding ability of five photoresponsive bis(crown ethers) was compared by the results of solvent extraction of alkali metal salts. It is seen from Table IV that (i) the extraction ability of **1**(4,4) is generally weak although *cis*-**1**(4,4) appreciably extracts relatively large cations such as Rb^+ and Cs^+ and (ii) *cis*-**1**(5,5) and *cis*-**1**(6,6) exhibit a maximum extractability (Ex %) for Rb^+ and Cs^+, respectively. These results are summarized in Figure 12. Clearly, the ion selectivity of crown series **1** shows the identical trend with that of the inhibitory effect on thermal isomerization rate (k) and cis % at the photostationary state (Figures 10 and 11). It is concluded, therefore, that the extractability under photoirradiation is also associated with the stability of intramolecular 1:2 cation/crown complexes and the Ex % increase of the cis forms is also rationalized by considering the formation of the intramolecular complexes as extraction species.

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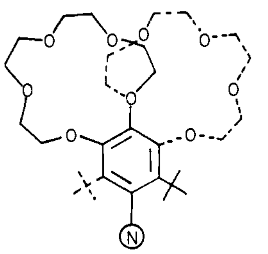
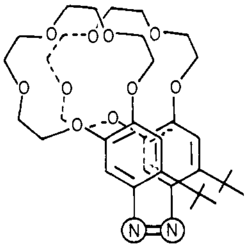
(21) (a) McCellan, A. L. "Tables of Experimental Dipole Moments"; W. H. Freeman: San Francisco, 1963; p 713. (b) Hartley, G. S. *J. Chem. Soc.* **1938**, 633.

The Ex % of crown series **2** was also improved by photoirradiation (in particular, in the extraction of Rb^+ and Cs^+). The examination of Table IV manifests, however, that the Ex % for K^+ is rather decreased by photoirradiation. The Ex % decrease in the **2**(5,5)–K^+ system (32.1% → 20.4%) is clearly incompatible with the trend of the thermal isomerization rate and the cis %. Conceivably, one has to take another extraction mode, in addition to the formation of 1:2 cation/crown complexes, into consideration to rationalize the discrepancy. It is most probable that the discrepancy is associated with the steric effect of the *tert*-butyl groups.

We noticed that an essential difference exists between the experimental methods: to determine *k* and cis %, photoirradiation was performed after the addition of metal cations, while to determine Ex %, photoirradiation was performed before the agitation with the aqueous solution containing metal cations. An inspection of the CPK model suggests that the steric crowding of *cis*-**2** is reduced by placing each *tert*-butyl group on the opposite side of the azo linkage (*cis*-**2**-(*E*)), but two crown rings cannot overlap each other. On the other hand, the *cis*-**2**-(*Z*) conformation in which two *tert*-butyl groups are placed on the same side of the azo linkage bears a serious steric hindrance due to the steric repulsion of two *tert*-butyl groups, but two crown rings overlap each other.

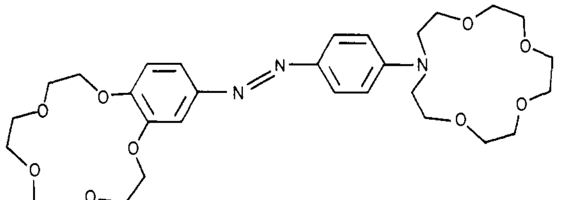


cis-2(5,5)-(*E*)

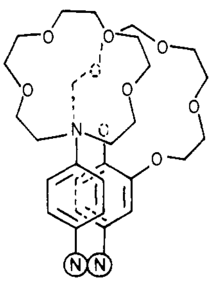


cis-2(5,5)-(*Z*)

In a separate study, we have noticed that symmetrical azobis(crown ether)s, the cis forms of which have the overlapped crown rings, easily form the stable sandwich-type complexes, whereas unsymmetrical ones are unable to form such stable sandwich-type complexes.[22] A typical example for unsymmetrical crown ethers is **4**. Conceivably, the cis form bears an unsymmetrical cavity between disordered crown caps and thus becomes disadvantageous to catch "round" alkali metal cations. Therefore, *cis*-**2**-(*E*) is sterically favorable but would form less stable sandwich-type complexes, whereas *cis*-**2**-(*Z*) is sterically unfavorable but would form very stable sandwich-type complexes.



trans-**4**



cis-**4**

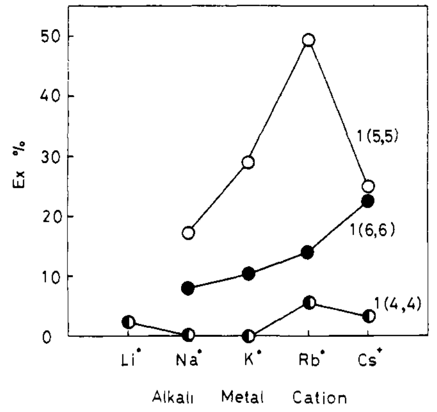


Figure 12. Ion selectivity in the solvent extraction with crown series 1.

Table V. Influence of Treatment Methods on Thermal Isomerization Rates[a]

bis(crown ether)	metal cation	$k \times 10^4$, s^{-1} M^+ method A[b]	 M^+ method B[c]
1(5,5)	K^+	6.66	6.69
	Rb^+	2.02	2.02
	Cs^+	3.39	3.44
1(6,6)	Rb^+	3.08	3.10
	Cs^+	0.53	0.54
2(5,5)	K^+	0.39	1.81
	Rb^+	0.11	0.15
	Cs^+	0.14	0.20
2(6,6)	K^+	3.55	4.96
	Rb^+	1.07	3.12
	Cs^+	0.027	0.061

[a] For the reaction conditions see Table II. [b] M^+ added before photoirradiation. [c] M^+ added after photoirradiation.

Based on the foregoing consideration, the discrepancy observed between Ex % and *k* (or cis %) of crown series **2** may be accommodated as following: photoirradiation in the absence of metal cations predominantly gives sterically favored *cis*-**2**-(*E*), which may poorly tweeze alkali metal cations in the aqueous phase because of the unsymmetrical location of two crown rings, whereas photoirradiation in the presence of metal cations gives *cis*-**2**-(*Z*) owing to the "tying effect" of complexed alkali metal cations. In other words, the steric hindrance in *cis*-**2**-(*Z*) is offset by the stabilization energy of the metal–crown interaction. To confirm the hypothesis, we determined the *k* for crown series **2** by a different treatment: that is, we added metal cations after photoirradiation of the sample solutions and followed the increase in the trans forms spectrophotometrically. If the hypothesis is correct, the rate constants (particularly, that for **2**(5,5) + K^+) should be greater than those determined by photoirradiation after mixing with metal cations.

Reexamination of Thermal Isomerization Rates. The rate constants for thermal isomerization were redetermined by adding metal cations after photoirradiation (method B) and were compared with those determined by adding metal cations before photoirradiation (method A, Table V). The rate constants for crown series **1** were almost unaffected by the difference in the treatment methods. In contrast, the rate constants for crown series **2** treated with method B were appreciably greater than those treated with method A. In particular, the rate constant for the **2**(5,5) + K^+ system was enhanced by a factor of 4.6. The fact that the spectrum of the photochemical products of crown series **2** is affected by the treatment methods strongly supports the above hypothesis. Conceivably, the cavity between two crown rings of *cis*-**2**–(*E*) is not "round" and is somewhat larger than that of *cis*-**2**-(*Z*).

In the foregoing paragraph, we have concluded on the basis of the ion selectivity of *k* and cis % that the cavity size of *cis*-**2**(5,5) is smaller than that of *cis*-**1**(5,5). It is not clear that this *cis*-**2**(5,5) in fact denotes *cis*-**2**(5,5)-(*Z*). On the other hand, the cavity size of *cis*-**2**(5,5)-(*E*) may be comparable with that of *cis*-**1**(5,5), for

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[22] Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manage, O. *J. Chem. Soc., Perkin Trans. 2* **1981**, 3279.

the relative rate constants for *cis*-**2**(5,5)-(*E*) (i.e., K^+ added after photoirradiation) and *cis*-**1**(5,5) at $[K^+]/[\text{bis(crown ether)s}] = 4.0$ are quite comparable (0.33 and 0.36, respectively).

Concluding Remark. The ion selectivity has been one of the most outstanding characteristics of cyclic polyethers. The present study establishes that the photoresponsive bis(crown ether)s with a butterfly-like motion also show the high ion selectivity. The ion selectivity observed for *k*, cis %, and Ex % can be accounted for by the stability of intramolecular 1:2 cation/crown complexes. Thus, the ion selectivity in the present system is associated with the fit between the cavity size provided by two crown rings and the size of alkali metal cations. Since the cavity size can be changed not only by the crown ring size but also by the bulky substituents and the distance between azo linkage and crown rings,[22] further modification of bis(crown ether)s would make it possible to bear the new ion selectivity. Applications to photocontrol of ion transport are currently in progress in these laboratories.

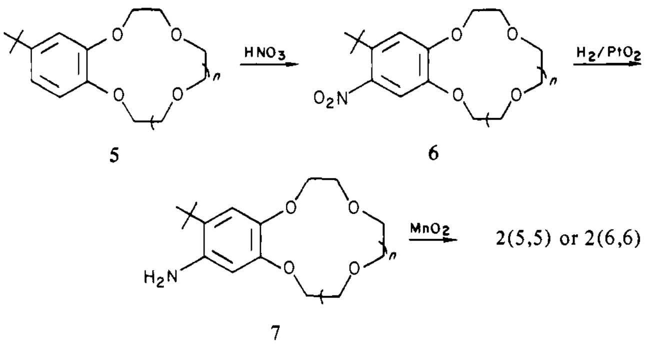
Experimental Section

Materials. The preparation of **1**(5,5) was described previously.[12c] **1**(4,4). Catechol (40 g, 0.36 mol) in 300 mL of *n*-butyl alcohol was mixed with sodium hydroxide (31 g, 0.77 mol) in 40 mL of water and the reaction mixture was gently refluxed with stirring under a nitrogen stream. 1,8-Dichloro-3,6-dioxaoctane (68 g, 0.36 mol) was added dropwise. After 30 h, the solution was cooled and then acidified with concentrated HCl to pH 2–3. Precipitated sodium chloride was filtered off and washed with methanol. The combined solution was concentrated in vacuo and the residue was subjected to continuous liquid–liquid extraction with *n*-heptane. The solid recovered after evaporation of the *n*-heptane solution was found to be a mixture of benzo-12-crown-4 and dibenzo-24-crown-8 by the measurement of mass spectroscopy. The mixture was used without further purification for the following nitration.

The mixture (40 g) was dissolved in a mixed solvent of acetic acid (450 mL) and chloroform (400 mL) and 155 mL of nitric acid (70%) were added dropwise at room temperature. After 24 h, excess acids were neutralized with sodium carbonate and the organic layer was separated. The evaporation of the organic layer in vacuo resulted in 21.7 g of the solid product. The mass spectrum gave two strong peaks at 269 and 538, which are attributable to 4′-nitrobenzo-12-crown-4 and dinitrodibenzo-24-crown-8, respectively. The solid product (17.8 g) was treated with 70 mL of hot chloroform and the insoluble solid was filtered off. The addition of 10 mL of methanol to the filtrate gave a slightly yellow precitate (dinitrodibenzo-24-crown-8). The precipitate was filtered, the filtrate being evaporated in vacuo. The oily residue was solidified by washing with a small amount of methanol. The slightly yellow solid (4′-nitrobenzo-12-crown-4) was recrystallized from benzene: 3.70 g; mp 105–108 °C; M^+ 269; IR (KBr disk) ν_{NO_2} 1580–1600 cm^{-1}. Anal. ($C_{12}H_{15}NO_6$) C, H, N. **1**(4,4) was synthesized from 4′-nitrobenzo-12-crown-4 in a manner analogous to that of **1**(5,5) from 4′-nitrobenzo-15-crown-5:[12c] yield 10.9%; mp 149–150 °C; M^+ 474; IR (KBr disk) $\nu_{N=N}$ 1590 cm^{-1}. Anal. ($C_{24}H_{30}N_2O_8$) C, H, N.

1(6,6) was also synthesized from 4′-nitrobenzo-18-crown-6 according to a similar synthetic manner: yield 1.6%; mp 173–174 °C; IR (KBr disk) $\nu_{N=N}$ 1600 cm^{-1}. Anal. ($C_{32}H_{46}N_2O_{12}$) C, H, N.

2(5,5) and **2**(6,6) were synthesized according to the following reaction scheme.



To 30 mL of a chloroform solution containing 1 g (3.1 mmol) of 4′-*tert*-butylbenzo-15-crown-5 (**5**, *n* = 2) and acetic acid (5 mL) was added dropwise 1 g of nitric acid (*d* = 1.42) in 3 mL of acetic acid over a 10-min period at 35 °C. After the reaction was continued for 6 h at 35 °C, the mixture was diluted with 30 mL of ice water and neutralized to pH 4 by adding sodium carbonate. The chloroform layer was separated, the aqueous layer being extracted with chloroform. The combined chloroform solution was washed with water and then dried over magnesium sulfate. The solution was concentrated in vacuo, the yellow residue (oil: **6**, *n* = 2) being purified by passing through a short alumina column (solvent, chloroform). The solid thus obtained was recrystallized from *n*-hexane: mp 91.1–92.2 °C (pale yellow crystals); yield 61%; IR (KBr disk) ν_{NO_2} 1381 and 1526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (9 H, 1.35 *t*-Bu), 3.75–4.35 (16 H, *O*–CH_2), 6,88 and 6.95 (2 H, aromatic); ^{13}C NMR ($CDCl_3$) 30.65 (CH_3), 35.28 (>C<), 69.10, 69.29, 70.32, and 70.95 (*O*–CH_2), 110.13 and 113.44 (aromatic CH), 135.28, 144.38, 146.78, and 150.43 (aromatic C). Anal. ($C_{18}H_{27}NO_7$) C, H, N.

4′-Nitro-5′-*tert*-butylbenzo-18-crown-6 (**6**, *n* = 3) was prepared in a similar manner: mp 59.2–60.3 °C (pale yellow crystals); yield 67%; IR (KBr disk) ν_{NO_2} 1390 and 1528 cm^{-1}; ^1H NMR ($CDCl_3$) 1.35 (9 H, *t*-Bu), 3.62–4.30 (20 H, *O*–CH_2), 6.86 and 6.93 (2 H, aromatic). Anal. ($C_{20}H_{31}NO_8$) C, H, N.

To a solution of **6** (*n* = 2) (500 mg, 1.4 mmol) in 30 mL of methanol was added PtO_2 (30 mg) with stirring under hydrogen atmosphere. The reaction mixture was stirred at room temperature until the absorption of hydrogen ceased (about 4 h). The catalyst was removed by filtration. The concentration of the filtrate gave white crystals (**7**, *n* = 2): mp 135.9–137.0 °C; yield 98%; IR (KBr disk) ν_{NH_2} 3340 and 3460 cm^{-1}; ^1H NMR ($CDCl_3$) 1.33 (9 H, *t*-Bu), 2.71–4.2 (16 H, *O*–CH_2), 6.12 and 6.78 (2 H, aromatic).

4′-Amino-5′-*tert*-butylbenzo-18-crown-6 (**7**, *n* = 3) was prepared in a similar manner: colorless oil; yield 96%; IR (KBr disk) ν_{NH_2} 3350 and 3470 cm^{-1}; ^1H NMR ($CDCl_3$) 1.37 (9 H, *t*-Bu), 3.64–4.3 (20 H, *O*–CH_2), 6.19 and 6.81 (aromatic).

The oxidative coupling of **7** by MnO_2 was preformed without further purification of **7**. **7** (*n* = 2) obtained by hydrogenation of 300 mg (0.81 mmol) of **6** (*n* = 2) was dissolved in 40 mL of dry benzene. MnO_2 (300 mg, 3.4 mmol), freshly prepared according to the method of Attenburrow et al.,[23] was added and the mixture was stirred at 100 °C for 3 h. About half of the benzene solvent was distilled off during this period. The hot solution was filtered, the filtrate being evaporated to dryness in vacuo. The oily residue thus obtained was subjected to column purification (alumina–chloroform). The chloroform eluent was evaporated to dryness and the crystallization of the residue from diethyl ether gave orange crystals (**2**(5,5)): mp 143.7–145.5 °C; yield 40%; ^1H NMR ($CDCl_3$) 1.35 (9 H, *t*-Bu), 3.71–4.2 (16 H, *O*–CH_2), 6.16 and 6.81 (2 H, aromatic). Anal. ($C_{36}H_{54}N_2O_{10}$) C, H. N. **2**(6,6) was synthesized in a similar manner from **6** (*n* = 3) via **7** (*n* = 3). The analysis data for **2**(6,6) are following: mp 173.1–174.0 °C (orange crystals); yield 33%; ^1H NMR ($CDCl_3$) 1.32 (9 H, *t*-Bu), 3.65–4.3 (20 H, *O*–CH_2), 6.98 and 7.21 (2 H, aromatic). Anal. ($C_{40}H_{62}N_2O_{12}$) C, H, N.

The position of the nitro group in **6** was identified by comparing the de-*tert*-butylated nitro compounds with the authentic nitro samples prepared by nitration of benzo-15-crown-5 and benzo-18-crown-6.[24] The de-*tert*-butylated nitrobenzocrown ethers showed identical IR and NMR spectra whith those of the authentic samples. The result indicates that the nitration occurs on the 4′ position (ortho position of the *tert*-butyl group), although the *tert*-butyl group is an effective positional protecting group.[25] The details of the identification will be described in a separate paper.

Methods of Kinetic Measurements and Solvent Extraction. The rate of the thermal cis-to-trans isomerization was determined at 30 °C in *o*-chlorobenzene–*n*-butyl alcohol (86.8:13.2 in volume) by monitoring spectrophotometrically the appearance of trans isomers. A quartz cuvette containing a trans isomer (5.0×10^{-5} M) was placed in a thermostated cell holder, and after equilibration to 30 °C the solution was irradiated with a 500-W high-pressure Hg lamp. The absorption band of the trans isomer decreased rapidly with photoirradiation and reached a photostationary state within 5 min. The cuvette was quickly transferred to a thermostated cell holder in a spectrophotometer (Hitachi 200), and the increase in the absorption maximum of the trans isomer was monitored as a function of time. No filter was used for the photoisomerization of **1**(4,4), **1**(5,5), and **1**(6,6). Since the spectrum for the thermal isomerization held tight isosbestic points and the initial spectrum was finally regenerated, the photoisomerization and thermal isomerization of crown series **1** are reversible. On the other hand, when the solution of **2**(5,5) and **2**(6,6) is a quartz cuvette was irradiated without a filter, the spectrum had no isosbestic point, suggesting that some side reaction takes place under the photoirradiation. We found that the photoisomerization and thermal isomerization of crown series **2** become completely reversible

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[23] Attenburrow, J.; Cameron, A. F. B.; Chanpman, J. H. *J. Chem. Soc.* **1952**, 1094.

[24] Ungaro, R.; Haj, B. El.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198.

[25] Tashiro, M. *Synthesis* **1979**, 921.

J. Am. Chem. Soc. **1982**, *104*, 1967–1972

when the photoirradiation is performed with a glass filter plus a visible-cut filter (Toshiba UV-D35) which cuts light >400 nm. As an alkali ion source, we used alkali metal salts of dodecanoic acid for the sake of experimental convenience. Further details of the kinetic method were described previously.[12c] The method of solvent extraction was also described previously.[12c]

Acknowledgment. The authors thank Professors T. Kunitake and M. Takagi (Kyushu University) for helpful discussions. Acknowledgment is also made to Professor T. C. Bruice for encouragement and advice. This research was supported in part by a grant from the Ministry of Education of Japan (No. 56850214).

Registry No. *cis*-**1**(4,4), 80764-64-3; *trans*-**1**(4,4), 80764-65-4; *cis*-**1**-(5,5), 73491-38-0; *trans*-**1**(5,5), 73491-37-9; *cis*-**1**(6,6), 80764-66-5; *trans*-**1**(6,6), 80764-67-6; *cis*-**2**(5,5), 80764-68-7; *trans*-**2**(5,5), 80764-69-8; *cis*-**2**(6,6), 80764-70-1; *trans*-**2**(6,6), 80764-71-2; **6** (n = 2), 80764-72-3; **6** (n = 3), 80764-73-4; **7** (n = 2), 80764-74-5; **7** (n = 3), 80764-75-6; Li^+, 17341-24-1; Na^+, 17341-25-2; K^+, 24203-36-9; Kb^+, 22537-38-8; Cs^+, 18459-37-5.

Photoresponsive Crown Ethers. 5. Light-Driven Ion Transport by Crown Ethers with a Photoresponsive Anionic Cap

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Abstract: Three photoresponsive ionophores (Cr-*o*, Cr-*m*, and Cr-*p*) in which benzo-18-crown-6 and a phenol group are linked with a photoisomerizable azo linkage were synthesized. On the irradiation of UV light, the azo linkage isomerized to the cis forms (46–73%) in which the crown ring wears an anionic phenoxide cap. The cis forms isomerized back to the trans forms slowly in the dark and rapidly by the irradiation of visible light. In solvent extraction, the extractability of alkali and alkaline earth metal cations with Cr-*o*, Cr-*m*, and Cr-*p*, which have the cap of 2-hydroxy-5-nitrophenyl, 3-hydroxyphenyl, and 4-hydroxyphenyl, respectively, was in most cases enhanced by UV light irradiation. In particular, cis-formed Cr-*o* exhibited markedly improved extractabilities for Na^+ and Ca^{2+}. The result suggests that the enhanced extractability is due to the formation of an intramolecular sandwich-type complex like $PhO^{-}\cdots M^{+(+)}\cdots$crown. In ion transport across a liquid membrane (90 vol % *o*-dichlorobenzene + 10 vol % *n*-butyl alcohol) in a U-tube, the rates of Na^+ and Ca^{2+} transport were enhanced by 4.0- and 276-fold, respectively, by adding 0.01 N HCl into the second OUT aqueous phase. The rates were further enhanced by irradiating the liquid membrane phase by UV light (1.7- and 2.8-fold, respectively), and the rate of Ca^{2+} transport was greater than that of Na^+ transport in spite of the lower concentration in the first IN aqueous phase ($[Na^+]$ = 0.10 M, $[Ca^{2+}]$ = 0.0225 M). The finding implies that transport of the Ca^{2+} ion is efficiently mediated with an anionic, photoresponsive ionophore Cr-*o* under a countercurrent of proton flux and UV light irradiation. This is the first example of the light-driven Ca^{2+} transport across a liquid membrane.

A substantial part of the ion transport phenomena across cell and organelle membranes is well mimicked by a liquid membrane which is an organic liquid phase separating two other aqueous phases with which it is immiscible. Cations are transported from one water phase (IN aqueous phase) to the other water phase (OUT aqueous phase) through membranes with the aid of synthetic macrocyclic polyethers such as crown ethers as well as with the aid of naturally occurring antibiotic macrocycles.[1-7] In contrast to numerous studies on the transport of alkali metal cations, the study on the transport of alkaline earth metal cations has been very limited[1-3] and the transport rate mediated by simple crown ethers is usually much slower than that of alkali metal cations.[2,3] In a biochemical field, the more often employed ionophores for alkaline earth metal cations are the polyether antibiotics which represent the class of monobasic, carrier-type ionophores.[1,8] Similarly, crown ethers which have within a molecule a carboxylate anionic cap can extract and transport alkaline earth metal cations efficiently.[1,9-11] These results imply that an ionophore which has a crown ring and an anionic cap in a suitable geometrical position would act as an efficient carrier for alkaline earth metal cations.

This work aims at developing a new class of ionophores which have within a molecule both a crown ring and a photoresponsive anionic cap and carry alkaline earth metal cations in response to photoirradiation. We previously designed a photoresponsive crown ether which combines monobenzo-15-crown-5 and a carboxylate function through a photoisomerizable azo linkage, expecting that the photoisomerized cis form would bind alkaline earth metal cations in a cavity between the crown and the carboxylate group.[12] However, the extractability of this ionophore was rather inferior owing to its relatively low lipophilicity. Here, we newly synthesized three ionophores, Cr-*m*, Cr-*p*, and Cr-*o*, with a phenoxide anion cap. To strengthen the lipophilicity, we chose a phenoxide function instead of a carboxylate function and introduced an *n*-butyl group. A 5-nitro group in Cr-*o* was introduced to lower the pK_a of the phenol group so that Cr-*o* may extract the Ca^{2+} ion at almost

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