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Photoresponsive Crown Ethers. 2. Photocontrol of Ion Extraction and Ion Transport by a Bis(crown ether) with a Butterfly-like Motion[1]

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Abstract: A photoresponsive bis(crown ether) with an azo linkage (**1**) was synthesized. *trans*-**1** was isomerized by UV light to *cis*-**1** and *cis*-**1** was isomerized thermally to *trans*-**1**, the interconversion being reversible such as the motion of a butterfly. We found that (i) the concentration of *cis*-**1** under the photostationary state is markedly enhanced by added Rb^+ and Cs^+, (ii) the rate of the thermal isomerization (cis → trans) is suppressed by added alkali metal cations, the order of the inhibitory effect being $Rb^+ > Cs^+ > K^+ > Na^+$, and (iii) Na^+ is extracted efficiently from an aqueous phase to an organic (*o*-dichlorobenzene) phase by *trans*-**1**, whereas K^+, Rb^+, and Cs^+ are extracted efficiently by *cis*-**1**, and the selectivity between Na^+ and K^+ is 238-fold. These results consistently indicate that *cis*-**1** forms a stable sandwich-type 1:1 cation/**1** complex with large alkali metal cations. The K^+ transport across a liquid (*o*-dichlorobenzene) membrane in a U-tube established that the transport rate is suppressed by light when a hydrophobic counteranion is used, whereas it is accelerated by light when a relatively hydrophilic counteranion is used. Most interestingly, even the transport velocity of potassium picrate (most hydrophobic anion used) was accelerated when the liquid membrane in contact with the IN aqueous phase was partially photoirradiated. This implies that ion transport can be facilitated by the interconversion between *cis*-**1** and *trans*-**1** occurring in the membrane phase. We thus consider that **1** acts as a useful "phototweezers" in solvent extraction and ion-transport systems.

Photoresponsive systems are ubiquitously seen in nature: photosynthesis, vision, phototropism, and phototaxis are typical examples. In these systems, light is used as a trigger to cause subsequent events. We have been interested in the application of the phenomena to biomimetic systems. To mimic the fundamental functions of such photoresponsive systems, one has to combine a photoantenna to capture a photon with a functional group to mediate some subsequent event.

Host molecules have drawn considerable attention as simplified enzyme model systems.[2,3] It seems that the photocontrol of host molecules, as well as that of enzymes themselves,[4] provides a somewhat new field of chemistry. We have combined crown ethers with azobenzene as a photoantenna and have attempted the photocontrol of the solvent extraction of alkali metal and ammonium ions.[1,5] Similarly, several groups have been attempting the photocontrol of the chemical and physical functions of membranes,[6] microemulsions,[7] polypeptide chains,[8] synthetic polymers,[9-11] cyclodextrins,[12] and an anthracene-containing crown ether.[13]

In this paper, we report an attempt to control ion extraction and ion transport across a liquid membrane by light. Cations are known to be transported through membranes with the aid of synthetic macrocyclic polyesters as well as with the aid of antibiotics. Kobuke et al.[14] and Kirch and Lehn[15] independently established that the best carrier for the ion transport is a ligand that gives a moderately stable rather than a very stable complex. The finding clearly indicates a dilemma occurring in the transport system: the very stable complex, which may rapidly extract ion into the membrane phase, cannot release the ion efficiently from the complex. As a result, the plots of K (association constant) vs. transport velocity provide a maximum. In other words, the ion transport with simple ion carriers cannot exceed the maximal, ceiling velocity. Some of the natural ionophores skillfully break the dilemma: for example, monensin utilizes a conformational change between the cyclic and the noncyclic form, attaining a marked difference in the binding ability between the ion-complexation site and the ion-release site.[16] It occurred to us that, if the binding ability of the ion carrier can be changed by light, it would lead to photocontrol of the ion-transport system. Bis(crown ethers) (and also polymeric crown ethers) which are able to adopt the face-to-face orientation exhibit greater binding abilities for large alkali metal cations than the corresponding mono(crown ethers).[17,18] We thus synthesized a bis(crown ether)

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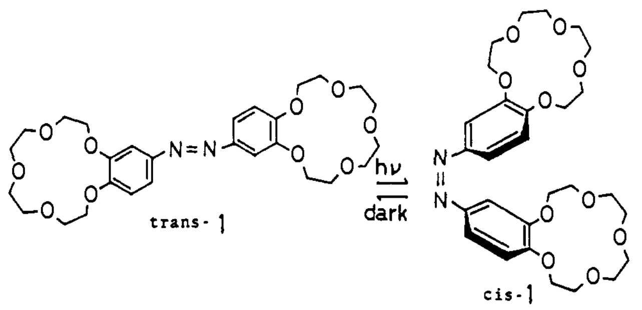
(**1**) which exhibits a butterfly-like motion in response to photoirradiation, expecting that photoisomerized *cis*-**1** would exhibit greater binding abilities for large alkali metal cations than *trans*-**1**.



Experimental Section

Materials. Compound **1** was synthesized from 4′-nitrobenzo-15-crown-5[19] as follows. One gram of NaOH in 1 mL of water and 5.1 g (0.33 mol) of 4′-nitrobenzo-15-crown-5 in 30 mL of benzene were heated at 70–80 °C. The solution was stirred vigorously, and 16 g of KOH and 4 g of zinc powder were added. After 5 h, the hot solution was filtered and the solid was washed with 30 mL of methanol. Air was introduced into the combined solution for 4 h. The solution was then acidified by concentrated HCl, precipitated KCl being filtered off. The resultant filtrate was concentrated in vacuo. Compound **1** was isolated from the residual solid by TLC (silica gel, 3:1 chloroform–acetic acid): mp 187–188 °C (yellow needles); yield 9.1%; IR (KBr disk) $\nu_{N=N}$ 1590, ν_{COC} 1120–1140 cm^{-1}; mass spectrum: *m/z* 563 (M$^+$). Anal. ($C_{28}H_{38}N_2O_{10}$): C, H, N.

2-Nitrodiphenylamine-4-sulfonic acid (NDS) and 4′-butyl-2-nitrodiphenylamine-4-sulfonic acid (BuNDS) were prepared by the reaction of sodium 3-nitro-4-chlorobenzenesulfonate with aniline and 4-butylaniline, respectively, and were isolated as their aniline salts. NDS·$C_6H_5NH_2$: mp 264–269 °C. Anal. ($C_{18}H_{17}N_3O_5S$): C, H, N. BuNDS·$C_6H_5NH_2$: mp 235–240 °C dec. Anal. ($C_{22}H_{25}N_3O_5S$): C, H, N. Picric acid and Methyl Orange were purchased from Woko Pure Chem. Co. and were used without further purification. The absorption maxima (nm) and the extinction coefficients (in parentheses) in 0.01 M NaOH are as follows: NDS, 434 (56 800); BuNDS, 431 (58 700); picrate, 355 (17 300); Methyl Orange, 466 (45 100).

Method of Solvent Extraction. Equal volumes of an *o*-dichlorobenzene containing 3.00 × 10^{-4} M **1** and an aqueous solution containing 0.01 M MOH (M, alkali metal cation) and 8.10 × 10^{-6} M Methyl Orange were agitated thoroughly on a Vortex Junior mixer for 2 min. The solution was equilibrated at 30 °C, the aliquot of the upper aqueous solution was withdrawn, and the spectrum was recorded at 30 °C. A similar extraction was performed with pure *o*-dichlorobenzene. The extractability was determined by reading the difference between two absorbances of Methyl Orange in the aqueous solutions.

The absorption band of *trans*-**1** in *o*-dichlorobenzene (λ_{max} 376 nm, ϵ_{max} 26 700 decreased rapidly with photoirradiation time and reached a constant intensity within 5 min (59% intensity). For the photoisomerization, a 500-W high-pressure Hg lamp was used. The distance from the lamp to the sample tube was 12.5 cm. The thermal recovery of *trans*-**1** in the dark was relatively fast in dry *o*-dichlorobenzene ($t_{1/2}$ = 10.3 min at 30 °C) but became slower in water-saturated *o*-dichlorobenzene ($t_{1/2}$ = 75.5 min at 30 °C). Therefore, we carried out the solvent extraction immediately after the photoirradiation. Since the workup time was shorter than 5 min, the change in the cis/trans composition was neglected.

Kinetic Measurements of the Thermal Isomerization Rates. A cuvette containing a solution of *trans*-**1** (5.0 × 10^{-5} M) was put in a thermostated cell holder, and after equilibration to the desired temperature the solution was irradiated with a 500-W high-pressure Hg lamp for 5 min. The cuvette was quickly transferred to a thermostated cell holder in a spectrophotometer (Hitachi 200), and the increase in the absorption band of *trans*-**1** (376 nm) was monitored as a function of time. Importantly, we noticed that when the absorbance at 376 nm was continuously followed, the rate was significantly suppressed. This is probably due to the occurrence of photoisomerization (trans → cis) by light from the spectrophotometer. We thus measured the absorbance for a few seconds per minute, and except during the measurement time, light from the spectrophotometer was blocked by a black plate. The absorbance plotted against time satisfied a first-order equation for at least 2 half-lives, the correlation coefficient being usually better than 0.99. Finally, it was corroborated that the initial spectrum is regenerated completely.

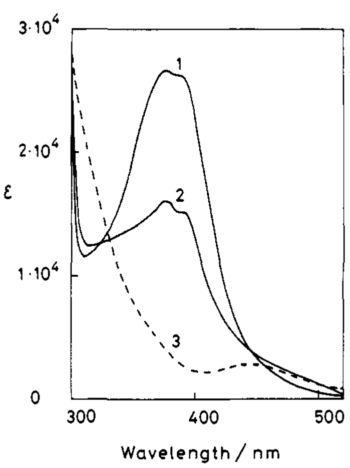


Figure 1. Absorption spectra of **1**: (1) *trans*-**1** in *o*-dichlorobenzene; (2) cis/trans mixture at the photostationary state in *o*-dichlorobenzene; (3) *cis*-**1** in 0.01 M NaOH aqueous solution.

The water content in the reaction media was determined by a coulometric Karl-Fischer apparatus (Kyoto Electric Co., Type MK-AII). The water concentrations recorded in the tables and figures are the average of two to three determinations, the relative error being less than 4%.

Method of Ion Transport across a Liquid Membrane. Transport of K$^+$ across an *o*-dichlorobenzene liquid membrane with the aid of **1** was examined within a U-tube. The tube was immersed in a thermostated water bath and, when required, was irradiated by a 500-W high-pressure Hg lamp which was also immersed in the water bath. The distance from the lamp to the tube was 12.5 cm. The *o*-dichlorobenzene phase (100 mL) contained **1** (2.00 × 10^{-4} M), and the IN aqueous phase (25 mL) contained KOH and a hydrophobic anion as a chromophore. An aliquot (100 μL) was withdrawn from the OUT aqueous phase (25 mL) and dilute to 3 mL, and the spectrum was recorded. The increase in the absorbance began after an induction period (about 2 h). The plots of OD vs. time gave good straight lines. The rates of the K$^+$ transport were determined from the slope. In those cases in which NDS·$C_6H_5NH_2$ was used as the chromophore, the IN aqueous phase containing KOH and the chromophore was extracted twice with 30 mL of *o*-dichlorobenzene to remove aniline. After this treatment, the aqueous solution was used as the IN aqueous phase.

We confirmed in a separate experiment that the photodecomposition of hydrophobic anions does not occur under the present experimental conditions. We also attempted to accelerate the isomerization (cis → trans) by visible light (Xe lamp). However, we could not find any useful wavelength from 400 to 600 nm.

Results and Discussion

Photoisomerization of 1. When an *o*-dichlorobenzene solution of *trans*-**1** was agitated with aqueous solutions (pure water or 0.01 M NaOH solution), *trans*-**1** was not transferred to the aqueous phase at all. On the other hand, appreciable amounts of photoisomerized *cis*-**1** were transferred to the aqueous phase. For example, when a 5-mL sample of *o*-dichlorobenzene solution containing photoirradiated **1** (3.00 × 10^{-4} M) was agitated with 5 mL of 0.01 M NaOH aqueous solution, the aqueous phase contained 2.2 × 10^{-5} M *cis*-**1**. This implies that *cis*-**1** is selectively distributed to the aqueous phase. Figure 1 shows the spectra of *trans*-**1**, the cis/trans mixture under the photstationary state (5-min irradiation, 59% intensity in comparison to that of *trans*-**1**), and the aqueous solution after extraction. The finding leads to two important conclusions: (i) the absorption spectrum of *cis*-azobenzene (λ_{max} 445 nm, ϵ_{max} 2890) can be obtained directly by solvent extraction and (ii) the cis/trans composition under the photostationary state can be determined accurately. The cis percentage has been frequency calculated on the assumption that the absorbance of the cis isomer at the employed wavelength is negligible in comparison to that of the trans isomer. Figure 1 indicates, however, that this assumption is not necessarily valid.

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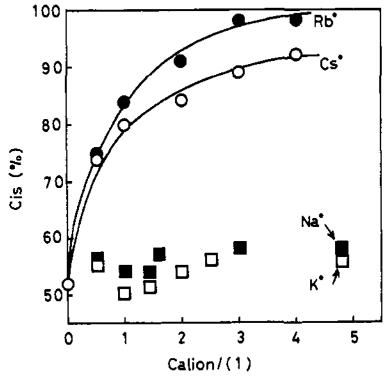


Figure 2. Composition of *cis*-**1** at the photostationary state plotted as a function of added alkali metal cations. [**1**] = 5.0 × 10^{-5} M, *o*-dichlorobenzene:*n*-butyl alcohol = 86.8:13.2 by volume.

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

cation[b]	cis/trans	k_{rel}	$\Delta\Delta G^{\ddagger}$, kcal mol^{-1}
none	52/48	1.00[c]	
Na^+	58/42	0.96	0.02
K^+	64/36	0.41	0.54
Rb^+	98/2	0.13	1.23
Cs^+	89/11	0.18	1.03
$C_6H_5CH_2NH_3^+$	55/45	0.91	0.06
o-$C_6H_4(CH_2NH_3^+)_2$	57/43	0.79	0.41

[a] 30 °C, *o*-dichlorobenzene:*n*-butyl alcohol = 86.8:13.2 by volume, [cation]/[**1**] = 3. [b] Dodecanoic acid salts and chloride salts were used for alkali metal and ammonium cations, respectively. [c] *k* (first-order rate constant) = 1.85 × 10^{-3} s^{-1}.

Assuming that the spectrum of *cis*-**1** in aqueous solution is similar to that in *o*-dichlorobenzene, we estimated the equilibrium composition under the photostationary state to be 51.4/48.6 ([*cis*-**1**]/[*trans*-**1**]). The remarkable difference in solubility is attributed to the difference in the molecular structure:[20] symmetrical *trans*-**1** is a nonpolar molecule, while *cis*-**1** is classified as a relatively polar molecule due to two dipole moments in the same direction.

Influence of Alkali Metal Cations on the Photoisomerizations and Thermal Isomerizations. The specific interaction of macrocyclic polyethers with metal cations stems from a host–guest relationship.[2] 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 ethers),[17] polymeric crown ethers,[18] and the crystal structure of crown ether–alkali metal cation complexes.[21] 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^+.[17,21] We can thus expect that *cis*-**1** forms stable 1:1 cation/**1** complexes with relatively large alkali metal cations.

Figure 2 shows the percentage of *cis*-**1** at the photostationary state plotted as a function of the concentration of added alkali metal cations. For the sake of experimental convenience, we used alkali metal salts of dodecanoic acid and an *o*-dichlorobenzene solvent ([H_2O] = 1.7 mM) containing 13.2 vol % of *n*-butyl alcohol. It is seen from Figure 2 that the relative concentration of *cis*-**1** is scarcely affected by added Na^+ and K^+, whereas it remarkably increases with increasing concentrations of Rb^+ and Cs^+. In particular, the cis isomer was enhanced up to 98% at high Rb^+ concentrations. The compositions at cation/**1** = 3 are listed in Table I. Ammonium ions also increased the cis composition but the effect was rather small. Figure 3 shows the effect of added alkali metal cations on the rate of the thermal (cis → trans) isomerization. Rb^+ and Cs^+ again exhibited a marked inhibitory effect. K^+ also suppressed the rate. The relative rate constants at cation/**1** = 3 are listed in Table I.[22] These results consistently suggest that large alkali metal cations form the stable complexes with *cis*-**1**: the order of the stability of $Rb^+ > Cs^+ > K^+ > Na^+$. In the photoinduced dimerization of anthracene nuclei which incorporate a crown ether, Yamashita et al.[13] found that the rate of thermal reaction (dimer → monomers) is suppressed by alkali metal cations (2–3-fold), whereas the rate of the photoreaction (monomers → dimer) is unaffected by alkali metal cations. In our system, the rate of the thermal reaction (*cis*-**1** → *trans*-**1**) was suppressed efficiently. The rate of the photoreaction (*trans*-**1** → *cis*-**1**) could not be determined quantitatively, but the shift of the *cis*-**1**/*trans*-**1** value at the photostationary state is caused by an increase in the forward reaction rate and/or by a decrease in the reverse reaction rate. Speculating from the data of the thermal isomerization, we consider that the decrease in the reverse reaction rate is responsible for the shift. These results suggest that the sandwich-type complexes of *cis*-**1** with Rb^+ and Cs^+ are farily stable.

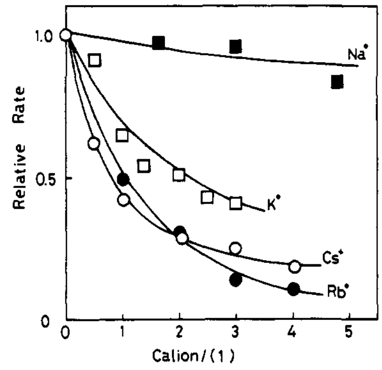
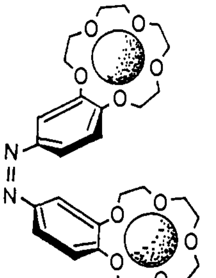


Figure 3. Rate of the thermal isomerization plotted as a function of added alkali metal cations. 30 °C, [**1**] = 5.00 × 10^{-5} M, *o*-dichlorobenzene:*n*-butyl alcohol = 86.8:13.2 by volume.

To account for the effect of added alkali metal cations on the rates of the photoisomerization and thermal isomerizations, one has to take several factors into consideration: (i) the salt effect,[5] (ii) electrostatic repulsion between two metal cations, which is expected for the 2:1 cation/*cis*-**1** complex **2**, (iii) an enhanced electron-withdrawing effect of the crown ether moiety, which is expected for both of the 2:1 and 1:1 cation/*cis*-**1** complexes (**2** and **3**, respectively),[23] and (iv) "tying" of two crown ethers by one alkali metal cation, which is expected only for the sandwich-type 1:1 cation/*cis*-**1** complex **3**. Probably, factors i and



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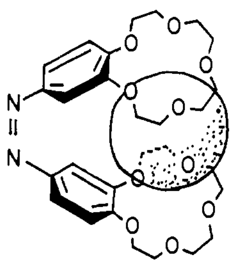

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(22) The association constants with *cis*-**1** may be determined by analyzing the curvature of the plots in Figure 3. However, one has to take many factors into consideration: cis/trans composition, association with both *cis*-**1** and *trans*-**1**, thermal isomerization of both *cis*-**1** and *cis*-**1**-metal complex, etc. We finally abandoned attempts to analyze the results quantitatively. It may be said qualitatively that Cs^+ has a greater association tendency for *cis*-**1** than Rb^+, but as for the thermal isomerization rate, Rb^+-*cis*-**1** complex has a smaller *k* value than Cs^+-*cis*-**1** complex.

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Table II. Extraction of Alkali Metal Salts of Methyl Orange with the Photoresponsive Crown Ether 1

1	alkali metal salt extracted (% Ex)			
	Na^+	K^+	Rb^+	Cs^+
trans-1	29.6	1.3	29.3	24.1
photoirradiated 1	17.1	29.0	49.6	29.9
cis-1[a]	5.3	55.2	68.8	36.2

[a] Calculated by the equation $Ex_{cis\text{-}1} = (Ex_{photoirradiated\ 1} - 0.486Ex_{trans\text{-}1})/0.514$.

ii would accelerate the rate of the thermal isomerization, while factors iii and iv would suppress the rates.[5,24] On the baiss of the host–guest relationship, one can easily presume that Na^+ forms the 2:1 cation/*cis*-**1** complex, while K^+, Rb^+, and Cs^+ form the 1:1 cation/*cis*-**1** complexes. Since the rate suppression was caused only by large alkali metal cations, one can conclude that the most important factor in the present system is iv. This is the first example that the crown–cation interaction is able to suppress the configurational change of crown-containing compounds.

As shown in Table I, $\Delta\Delta G^{\ddagger}$ values (additional free energy of activation required for the thermal isomerization) increase by 1.0–1.2 kcal mol^{-1} in the presence of Rb^+ or Cs^+. The additional energy must be comsumed to disrupt the interaction between these cations and the crown ether in the sandwich-type complexes. Very recently, Sutherland et al.[25] reported that bis(crown ethers) form the intramolecular 1:1 complex with diammonium cations when the geometrical condition is satisfied. On the basis of CPK models, we expected that *cis*-**1** would form the sandwich-type complex with K^+, Rb^+, and Cs^+, but we could not predict which metal cation best fits the cavity constructed by the two crown ether rings of *cis*-**1**. The foregoing results suggest that the complex with Rb^+ most satisfies the geometrical condition. We also found that *o*-xylylenediamine dihydrochloride inhibits the thermal isomerization more efficiently than benzylamine hydrochloride. This may be attributed to the formation of such a 1:1 complex between *cis*-**1** and *o*-phenylenediamine dihydrochloride.

Solvent Extraction of Alkali Metal Cations with 1. The binding ability of *trans*-**1** and *cis*-**1** was estimated by solvent extraction of alkali metal salts of Methyl Orange from water to *o*-dichlorobenzene. The results are summarized in Table II. It is seen from Table II that *trans*-**1** and *cis*-**1** exhibit a contrasting extraction ability: *trans*-**1** extracts Na^+ 5.6 times more efficiently than *cis*-**1**, whereas *cis*-**1** extracts K^+ 42.5 times more effeciently than *trans*-**1**. The selectivity which is expressed by the ratio (trans/cis) of extractability (Ex) for Na^+ against that for K^+ is 238-fold. Rb^+ and Cs^+ are also extracted by *cis*-**1** more efficiently than by *trans*-**1**, although the selectivity is not so striking as for K^+. Conceivable, Na^+ is extracted as a 1:1 cation/benzocrown (i.e., 2:1 cation/**1**) complex, so that the extractability directly reflects the solubilizing power of the bis(crown ether). Since *trans*-**1** is more hydrophobic than *cis*-**1**, $Ex_{trans\text{-}1} > Ex_{cis\text{-}1}$ resulting in the extraction of Na^+. On the other hand, K^+, Rb^+, and Cs^+, the ion radii of which are somewhat greater than the size of benzo-15-crown-5,[2] are extracted as 1:2 cation/benzocrown (i.e., 1:1 cation/**1**) complexes. Hence, *cis*-**1** which is sterically able to form the sandwich-type 1:1 cation/**1** complex, extracts these large alkali metal cations more efficiently. The CPK models suggest that *cis*-**1** has a relatively rigid structure and the conformational fluctuation is very limited. We believe that the high selectivity for Na^+ and K^+ stems from the rigid structure.

Interestingly, the order of the extractability under photoirradiation (% Ex) ($Rb^+ > Cs^+ > K^+ > Na^+$) is identical with that of the inhibitory effect on the thermal isomerization rate (k_{rel}) and the cis percentage at the photostationary state (Figure 4). Presumably, both orders are associated with the stability of the sandwich-type complex with *cis*-**1**. The order of the extractability for *trans*-**1** is Na^+, $Rb^+ > Cs^+ > K^+$. The order is almost equal to that of the complexation constant with benzo-15-crown-5 in 70 wt % methanol.[26] It may be said, therefore, that the two crown ethers of *trans*-**1** behave independently on extraction.

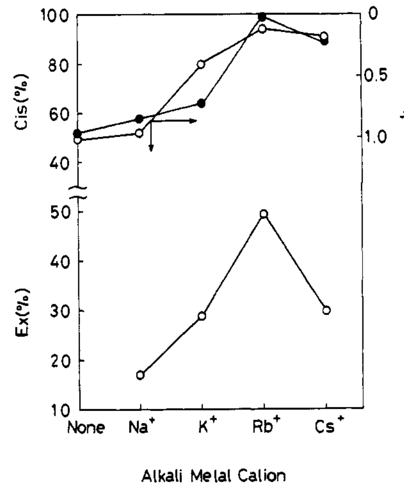

Figure 4. Extractability under photoirradiation (% Ex), the cis percentage at the photostationary state (% cis), and the relative rate constant for the thermal isomerization (k_{rel}).

Table III. Rates of K^+ Transport across an *o*-Dichlorobenzene Liquid Membrane (30 °C)

anion	[anion], mM	$[K^+]$, mM	$10^2 V_{obsd}$, μmol h^{-1}	
			dark	light
picrate	4.00	16	47.6	25.5 (5/30)[a]
			56.3[b]	73.5 (5/30)[c]
BuNDS	2.00	8	6.48	4.15 (5/120)
NDS	4.00	16	0.02[b]	0.34[b] (5/60)

[a] The interval of irradiation, in minutes, is given in parentheses. For example, 5/30 means that the *o*-dichlorobenzene phase was photoirradiated for 5 min at intervals of 30 min. [b] 50 °C. [c] The *o*-dichlorobenzene phase in contact with the IN aqueous phase was photoirradiated. The volume of solution which was photoirradiated was about one-fifth of the total volume of the *o*-dichlorobenzene solution.

The foregoing results demonstrate that the solvent extraction of alkali metal cations is controlled by light. The concept provides basic information for the photocontrol of ion transport across a liquid membrane.

Ion Transport across a Liquid Membrane. Various kinds of chemical phenomena have been utilized to increase the rate of ion transport through membranes: energy of the redox and photoinduced redox systems,[27] countercurrent of different alkali metal cations,[28] pH dependence of lactone cyclization,[29] remote control by heavy metals with crown ethers which incorporate a 2,2′-bipyridyl unit,[30] etc. Some of these systems have been applied to active transport. We considered that light would be one of the most convenient sources to control the rate of ion transport. We thus examined the effect of photoirradiation on K^+ transport across a liquid (*o*-dichlorobenzene) membrane in a U-tube. Three counteranions were employed: picrate, BuNDS, and NDS (in

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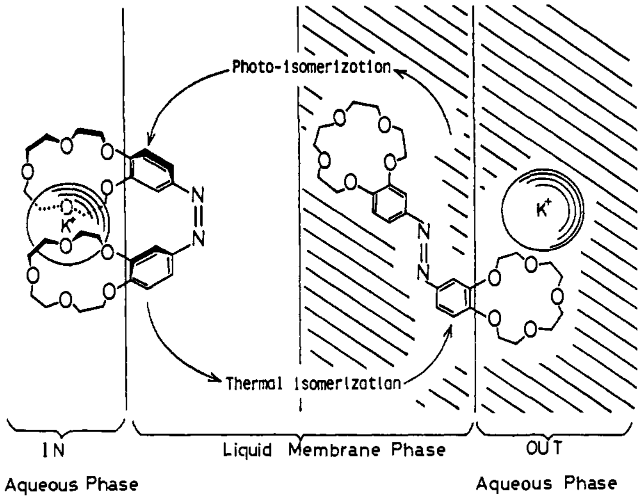
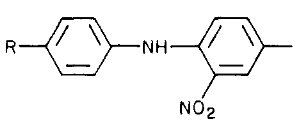


Figure 5. Schematic representation of light-driven ion transport.

the order of their hydrophobicity). The results are summarized in Table III.



NDS, R = H
BuNDS, R = C_4H_9

The rate of ion transport is strongly dependent on the anion present.[31] We also observed that the transport rate is markedly affected by the hydrophobicity of the anion. Under dark conditions, the transport rate of BuNDS·K^+ is greater by a factor of more than 300 than that of NDS·K^+. The transport of picrate·K^+ is 7 times faster than that of BuNDS·K^+. The differences are rationalized in terms of the hydrophobicity of counteranions. Interestingly, the photoirradiation brought about two contrasting influences on the transport rate: the transport of picrate·K^+ and BuNDS·K^+ was decelerated by 1.9-fold and 1.7-fold, respectively, whereas that of NDS·K^+ was markedly accelerated on photoirradiation (17-fold). As described in the introduction, there are two possible rate-limiting steps in an ion-transport system: the rate-limiting step for very stable complexes is at the ion-release site while that for less stable complexes is at the ion-complexation site. The situation is applicable to the effect of counteranions. Probably, the increase in hydrophobicity of counteranions changes the rate-limiting step from the ion-complexation site to the ion-release site. The effect of photoirradiation in Table III is rationalized if one accepts that the rate-limiting step for picrate·K^+ and BuNDS·K^+ is at the ion-release site and that for NDS·K^+ is at the ion-complexation site. In the transport of picrate·K^+ and BuNDS·K^+, photoisomerized *cis*-**1** would further suppress the release of K^+ to the OUT aqueous phase. However, if ion complexation from the IN aqueous phase is rate limiting, it would facilitate the extraction of NDS·K^+, resulting in an enhancement in the overall transport velocity. These results demonstrate that the acceleration of ion transport by light occurs only when the ion transport in the rate-limiting step is modified by light.

Table III shows, however, that there is an exception. We found that when one-fifth of the *o*-dichlorobenzene phase in contact with the IN aqueous phase is partially photoirradiated, the transport of picrate·K^+ is accelerated. As expected, photoisomerized *cis*-**1** rapidly extracts K^+ from the IN aqueous phase, and while moving in the liquid membrane to the ion-relase site, it would isomerize thermally to *trans*-**1**. Hence, the concentratiuon of K^+ in the liquid membrane phase can be enhanced without perturbing the situation in the ion-release site. The enhanced ion concentration would necessarily lead to the acceleration of K^+ transport (Figure 5). This finding implies that the dilemma which may occur in the ion-transport system can be broken by changing the binding ability of ion carrier by light.

Concluding Remarks. The present system demonstrated that, in principle, ion extraction and ion transport through a liquid membrane can be controlled by light. The novel phenomena are attained because **1** combines within a molecule an antenna (azobenzene) which acts as a photoresponsive trigger and a functional group (crown ether) which causes a subsequent event. We expect that this concept might lead to a more efficient control of ion extraction, ion transport, and other effects by switching the light source on and off.

Acknowledgment. We thank Professors T. Kunitake and M. Takagi for helpful discussions. We also thank Professor K. Higashi for bringing some references on the dipole moment of azobenzene to our attention.

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Minor and Trace Sterols in Marine Invertebrates. 19.[1] Isolation, Structure Elucidation, and Partial Synthesis of 24-Methylene-25-ethylcholesterol (Mutasterol): First Example of Sterol Side-Chain Bioalkylation at Position 25

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Abstract: A new C_{30} sterol—mutasterol—has been isolated as a minor component of the sterol fraction from the Caribbean sponge *Xestospongia muta*. Its structure (**5**) (24-methylene-25-ethylcholesterol) has been deduced from spectroscopic data and confirmed by partial synthesis. The side chain contains an acyclic, quaternary carbon—hitherto unknown among sterols—and its biosynthetic origin is discussed. The sterol composition is compared with that of other *Xestospongia* species collected at different locations.

Sterols have been found in all forms of life, from the higher animals and plants down to the protista at the bottom of the evolutionary hierarchy.[3] The only exceptions seem to be found among bacteria.[4] In higher animals and plants only a few major

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