

PHOTOCONTROLLED EXTRACTION ABILITY OF  
AZOBENZENE-BRIDGED AZACROWN ETHER

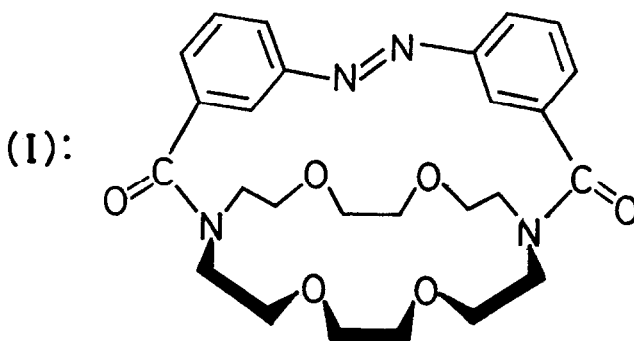
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The extraction equilibrium of alkali metal salts between water and benzene with an azobenzene-bridged azacrown ether (I) is affected by photo(uv)-irradiation. This indicates that the binding ability of (I) can be controlled by photo-induced cis-trans isomerism of the azobenzene moiety.

Considerable interest has recently centered around the function of crown ether family as an ion-transport carrier.<sup>1)</sup> Kobuke et al.<sup>2)</sup> have found that the best carrier for the ion-transport is a ligand that gives the moderately stable rather than the very stable complex. In fact, Kirch and Lehn<sup>3)</sup> reported that an optimum stability of the cryptate complex is  $\log K_s = 5$  (in methanol) for efficient transport. The results clearly offer a dilemma occurring in the transport system: that is, the very stable complex which may enhance the ion concentration in the transport medium cannot release metal cation efficiently from the complex, resulting in the low overall transport efficiency. Some of the natural ionophores skillfully break the dilemma. For example, monensin utilizes a conformation change between the cyclic and the non-cyclic form, attaining a markedly different binding ability between the ion-complexation site and the ion-release site<sup>3)</sup>. This suggests that, if the binding ability of crown ether easily changes in response to reaction conditions, it would function as an efficient ion-transport carrier.

One of the most expeditious sources to control the binding ability would be light. Azobenzene derivatives undergo a photo-induced, reversible cis-trans isomerism. It occurred to us that the binding ability of crown ether which includes the azobenzene unit within the molecule may be controlled by light. We thus synthesized an azacrown ether with an azobenzene bridge (I) and estimated the influence of photo-irradiation on the binding ability.



Compound (I) was prepared from 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 and 3,3'-bis(chlorocarbonyl)azobenzene according to the high-dilution method. The product recrystallized from benzene gave satisfactory elemental analysis and spectral properties consistent with the assigned structure.<sup>5)</sup> Photoisomerization of the trans-azobenzene form (abbreviated by trans-(I)) to the cis-azobenzene form (abbreviated by cis-(I)) was performed by photo-irradiation using a high-pressure Hg-lamp.<sup>6)</sup> The absorption band of trans-(I) ( $\lambda_{\max}$  324 nm in benzene) decreased rapidly with photo-irradiation time and reached an equilibrium intensity within 1 min. From the absorption intensity of 324 nm, the cis-(I)/trans-(I) at the equilibrium was estimated to be 60/40.<sup>7)</sup> The recovery of trans-(I) in the dark was considerably slow, but the spectrum of trans-(I) was regenerated quantitatively. The first-order rate constants ( $\text{hr}^{-1}$ ) estimated by following the increase in the absorption band at 324 nm were: 0.056 at 40°C, 0.150 at 50°C, and 0.347 at 60°C. The activation energy calculated from these rate constants was 19 kcal/mol.

The binding ability of (I) was estimated by preliminary solvent extraction of alkali metal salts of methyl orange from water to benzene.<sup>8)</sup> It took about 10 min to finish the work-up of the solvent extraction.<sup>9)</sup> Since the isomerization of cis-(I) to trans-(I) in the dark is slow enough, the change in the cis-(I)/trans-(I) during the work-up time could be neglected. The result of the solvent extraction at 30°C is summarized in Table 1.

Table 1. Extraction of alkali metal salts of methyl orange with azobenzene-bridge azacrown ether (I)

(I)	Alkali metal salt extracted(%)			
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
trans-(I)	1.1	14.8	15.8	(<0.1)
photo-irradiated (I)	(<0.1)	13.5	27.2	(<0.1)
cis-(I) <sup>a)</sup>	-	12.6	34.8	-

a) Calculated by the equation  $Ex_{cis-(I)} = (Ex_{photo-irradiated (I)} - 0.40 Ex_{trans-(I)}) / 0.60$ , where  $Ex$  denotes the percentage extracted by each azobenzene-bridged azacrown ether (I).

It is seen from Table 1 that (1) the extractability of (I) is in the order,  $K^+ > Na^+ > Li^+ > Cs^+$ , (2) large alkali metal ion such as  $Cs^+$  is hardly extracted, and (3) for small alkali metal ions ( $Li^+$  and  $Na^+$ ) trans-(I) exhibits the greater binding ability than cis-(I), whereas cis-(I) becomes the better ligand for relatively large  $K^+$  ion. The CPK model building suggests that the size of the azacrown ether moiety of cis-(I) is more expanded than trans-(I) due to the steric distortion of the azobenzene bridge. The conjecture well accounts for the fact that trans-(I) favors relatively small alkali metal ions such as  $Li^+$  and  $Na^+$ , whereas relatively large  $K^+$  binds to cis-(I) in preference to trans-(I).

As a summary of the foregoing results, one can conclude that the binding ability of (I) can be controlled by light in principle. To our knowledge, this is the first example that the binding ability of crown ether family is significantly affected by light. Table 1 suggests that, when (I) is employed as an ion-transport carrier, the transport velocity of  $Li^+$  and  $Na^+$  can be accelerated by photo-irradiation of the ion-release site and that of  $K^+$  by photo-irradiation of the ion-complexation site. The application is currently under way in this laboratory.

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## References and Notes

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- 2) Y. Kobuke, K. Hanji, K. Horiguchi, M. Asada, Y. Nakayama, and J. Furudawa, J. Am. Chem. Soc., 98, 7414(1976).
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- 5) Mp 215-216°C. Elemental analysis: Found; H, 6.60; C, 62.76; N, 11.17%. Calcd for  $C_{26}H_{32}N_4O_6$ ; H, 6.50; C, 62.89; N, 11.28%. Mass spectrum:  $M^+$ , 497. IR(KBr disc):  $\nu_{C=O}$ , 1618  $cm^{-1}$ ;  $\nu_{N=N}$ , 1578  $cm^{-1}$ ; ether, 1110  $cm^{-1}$ ;  $\nu_{CH}$ , 2850, 2890, 3040  $cm^{-1}$ . NMR( $CDCl_3$ ): N- $CH_2$ , 3.6-3.9 ppm, 8H; O- $CH_2$ , 4.1-4.8 ppm, 16H; aromatic, 8.1-8.6 ppm, 8H.
- 6) A benzene solution containing (I) was irradiated at room temperature with a high-pressure Hg-lamp(500 W). The distance from the lamp to the sample tube was 12.5 cm.
- 7) The cis percentage was calculated from the absorbance at 324 nm assuming that the absorbance of cis-(I) at this wavelength is negligible in comparison to that of trans-(I).
- 8) The combination of alkali picrates and halogen solvents is frequently employed for the solvent extraction with crown ether family. However, the system was improper under the photo-irradiation, since (1) halogen solvents caused the side reactions and (2) the absorption maximum of picrates(ca. 360 nm) overlapped with that of (I).
- 9) Equal volumes of a benzene solution containing  $1.32 \times 10^{-4}$  M of (I) and an aqueous solution containing  $1.66 \times 10^{-5}$  M of alkali methyl orange were agitated thoroughly on a Vortex Junior mixer for 5 min. All extractions were conducted at  $30 \pm 0.5^\circ C$ . Photo-irradiation of the benzene solution was performed before solvent extraction.

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