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SELECTIVE EXTRACTION OF ALKALI METAL CATIONS BY A PHOTORESPONSIVE BIS(CROWN ETHER)

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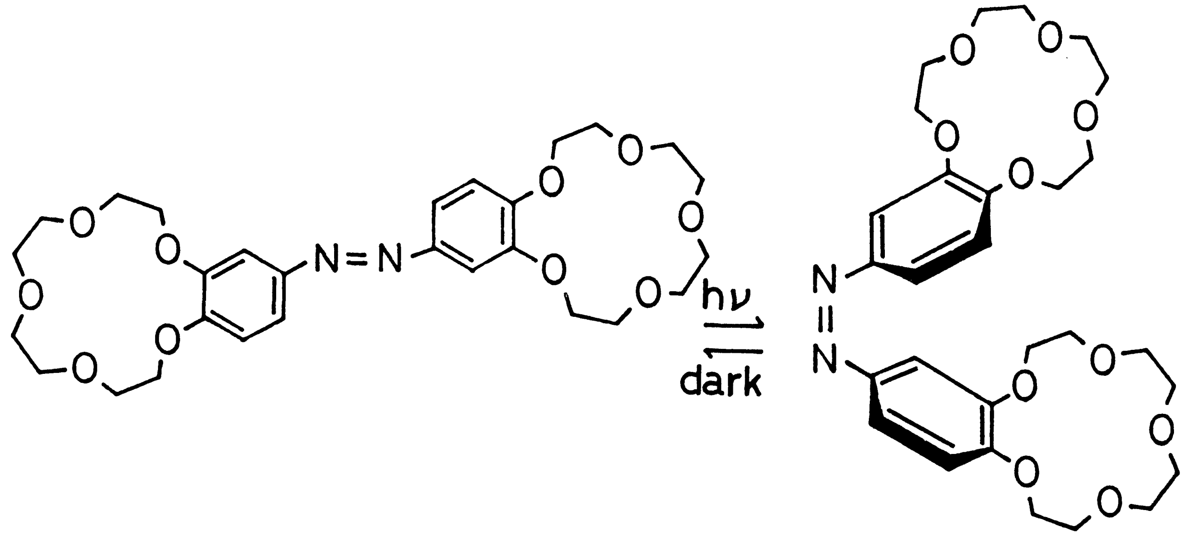
A photo-responsive bis(crown ether) with azo-linkage(I) was synthesized. The solvent extraction study with (I) indicated that K^+ is efficiently extracted by photo-isomerized cis-(I) but not by trans-(I), resulting in a remarkably large selectivity of trans-(I)/cis-(I) for Na^+/K^+ (238 fold). This suggests a possibility of photo-control of selective ion-extraction with (I).

The chemical substance which exhibits photo-induced structural changes is able to become not only chemical condensers for the storage of light energy but also mediators for the conversion of light energy. The derivatives of spirobenzopyran and azobenzene are the candidates. The object of our investigation has been to utilize the photo-induced cis-trans isomerism of azobenzene to control the functions of crown ether family. We have reported that the extraction equilibrium of alkali metal cations between water and benzene with an azobenzene-bridged crown ether is affected by photo-irradiation.1) In this communication, we wish to report a novel bis(crown ether) called "photo-butterfly crown ether" which also changes the extractability in response to photo-irradiation.

The specific interaction of macrocyclic compounds with metal cations and its analogues stems from a host-guest relationship.2,3) It has been established that alkali metal cations which exactly fit the size of crown ether form an 1:1 complex, whereas those which have larger ion radii form an 1:2 complex.2) This view is substantiated clearly by the use of bis(crown ether)s4,5): for example, the maleate derivative (cis form) of benzo-15-crown-5 extracts K^+ ion from aqueous phase 14 times more efficiently than the fumarate derivative (trans form) owing to formation of the intramolecular 1:2 complex.4) The result suggests that the bis(crown ether) in which the C=C double bond is replaced with azo-linkage would exhibit novel extraction behaviors under photo-irradiation. We thus synthesized a new bis(crown ether)(I) and estimated the extraction ability under photo-irradiation and dark conditions.



trans-(I) cis-(I)

Trans-(I) was prepared from 4'-nitrobenzo-15-crown-5 by zinc powder reduction in the presence of KOH, and the structure was confirmed by IR, mass spectrum, and elemental analysis.[6)] Photo-isomerization of trans-(I) was performed in o-dichlorobenzene.[7)] The absorption band of trans-(I)(λ_{max} 376 nm, ε 26700) decreased rapidly with photo-irradiation time and reached a constant intensity within 5 min(59% intensity). The recovery of trans-(I) in the dark was relatively fast($k=1.12\times10^{-3}$ sec^{-1} at 30°C) and the initial spectrum was completely regenerated within 90 min.

Trans-(I) was not extracted from o-dichlorobenzene to aqueous phase by agitation. On the other hand, appreciable amounts of cis-(I) were transfered to aqueous phase. For example, when 5 ml of o-dichlorobenzene solution containing photo-irradiated (I) (3.00×10^{-4} M) were agitated thoroughly with 5 ml of 0.01 M NaOH aqueous solution, the aqueous phase separated contained 2.2×10^{-5} M of cis-(I). The phenomenon leads to two new findings: (i) direct observation of the absorption spectrum of cis-azobenzene(λ_{max} 445 nm, ε 2890) and (ii) accurate estimation of the cis/trans composition under photo-irradiation.[8)] Assuming that the spectrum of cis-(I) in aqueous solution is similar to that in o-dichlorobenzene, we estimated the equilibrium composition to be 51.4/48.6(=cis-(I)/trans-(I)). The remarkable difference in solubility supposedly stems from the difference in the molecular structure: symmetrical trans-(I) is classified as a nonpolar molecule, while cis-(I) belongs to a polar molecule due to two dipole moments in the same direction.

Table 1. Extraction of alkali metal salts of methyl orange with "photo-butterfly" crown ether(I)

(I)	Alkali metal salt extracted(Ex)(%)				
	Li^+	Na^+	K^+	Rb^+	Cs^+
trans-(I)	13.1	29.6	1.3	29.3	24.1
photo-irradiated(I)	23.3	17.1	29.0	49.6	29.9
cis-(I)[a]	32.9	5.3	55.2	68.8	36.2

[a] Calculated by the equation, $Ex_{cis-(I)} = (Ex_{photo-irradiated(I)} - 0.486\ Ex_{trans-(I)})/0.514$

The binding ability of (I) was estimated by solvent extraction of alkali metal salts of methyl orange from water to o-dichlorobenzene.[9] The combination of methyl orange salts and o-dichlorobenzene was chosen because (i) aliphatic halogen solvents such as $CHCl_3$ and CH_2Cl_2 which are frequently used for the solvent extraction with crown ether family caused the side reaction of (I) under photo-irradiation and (ii) the absorption maximum of methyl orange (465 nm) does not overlap with that of (I). The results are summarized in Table 1. The examination of Table 1 reveals that trans-(I) and cis-(I) exhibit a contrasting extraction behavior for Na^+ and K^+: trans-(I) extracts Na^+ 5.6 times more efficiently than cis-(I), whereas cis-(I) extracts K^+ 42.5 times more efficiently than trans-(I). The selectivity of 238 fold, which is expressed by the ratio (trans-(I)/cis-(I)) of extractability for Na^+ against that for K^+, is truly remarkable. Expectedly, trans-(I) would a priori have the greater solubilizing power due to the nonpolar nature than cis-(I)(polar crown ether). The extractability of Na^+ which can be extracted as a simple 1:1 complex[4,5] directly reflects the solubilizing power. On the other hand, K^+, the radius of which is somewhat greater than the size of benzo-15-crown-5,[2] can be solubilized in o-dichlorobenzene as an intramolecular 1:2 complex. Hence, cis-(I) whcih is sterically able to form the intramolecular 1:2 complex transfers K^+ more efficiently than trans-(I).

Methyl orange salts of Rb^+ and Cs^+ were easily transfered to o-dichlorobenzene phase probably owing to their less hydrophilic nature.[2] The order of the extractability for trans-(I), $K^+ < Cs^+ < Na^+$, Rb^+, is almost equal to the order of the complexation constant with benzo-15-crown-5 in 70 wt% methanol.[10] Table 1 shows that cis-(I) again exhibits the greater extraction power for Rb^+ and Cs^+, although the selectivity is not so large as observed for the extraction of K^+.

On the other hand, it is not clear why the Li^+ salt was efficiently extracted by cis-(I). A possible explanation may be that the Li^+ salt forms the aggregate in the o-dichlorobenzene solution, reflecting the additional influence on the extractability.

In conclusion, the present results suggest that, in principle, the photocontrolled, selective ion-extraction can be achieved by the use of photoresponsive bis(crown ether)(I). We believe that the high selectivity is related to the relatively rigid structure of trans-(I) and cis-(I). The application to light-driven ion-transport with (I) is now under way in this laboratory.

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References and Notes

1) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, and O. Manabe, Tetrahedron Lett., 1979, 4569.
2) e. g., J.-M. Lehn, Struct. Bonding, 16, 1(1973); M. Takagi, Kagaku No Ryoiki, 33, 49(1979); Kagaku Zokan, vol. 74, ed. by R. Oda, T. Shono, and I. Tabushi, Kagaku Dojin, Tokyo, 1978; K. Koga, Yuki Gosei Kagaku, 33, 163(1975).
3) B. Dietrich, T. M. Fyles, J.-M. Lehn, L. G. Pease, and D. L. Fyles, J. Chem. Soc., Chem. Commun., 1978, 934; E. Graf and J.-M. Lehn, J. Am. Chem. Soc., 98, 6403(1976); I. Tabushi, Y. Kobuke, and T. Nishiya, Tetrahedron Lett., 1979, 3515.
4) K. Kimura, H. Tamura, T. Tsuchida, and T. Shono, Chem. Lett., 1979, 611.
5) M. Bourgoin, K. H. Wong, J. Y. Hui, and J. Smid J. Am. Chem. Soc., 97, 3462 (1975).
6) Yield 9.1%, mp 187-188°C(yellow needles). Elemental analysis: Found; H, 6.94; C, 59.37; N, 4.82%. Calcd for $C_{28}H_{38}N_2O_{10}$: H, 6.82; C, 59.77; N, 4.98%. Mass spectrum: M^+, 563. Ir(KBr disc): $\nu_{N=N}$, 1590 cm^{-1}; ν_{C-O-C}, 1120-1140 cm^{-1}.
7) An o-dichlorobenzene solution containing (I) was irradiated at room temperature with a high-pressure Hg-lamp.
8) The cis percentage has been frequently calculated on the assumption that the absorbance of cis-isomer at the employed wavelength is negligible in comparison to that of trans-isomer. Fig. 1 shows, however, that the assumption cannot be necessarily admitted.
9) Equal volumes of an o-dichlorobenzene solution(3.00×10^{-4} M (I)) and an aqueous solution(0.01 M MOH and 8.10×10^{-6} M methyl orange) were agitated thoroughly for 2 min. All extractions were conducted at 30±0.5°C.
10) R. M. Izatt, L. D. Hansen, D. J. Eatough, J. S. Bradshaw, and J. J. Christensen, "Metal-Ligand Interactions in Organic Chemistry and Biochemistry", ed. by B. Pullman and N. Goldblum, Reidel Pub. Co., Holland, part 1, p 337, 1977.

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