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A NEW "SWITCHED-ON" CROWN ETHER WHICH EXHIBITS A REVERSIBLE ALL-OR-NONE ION-BINDING ABILITY

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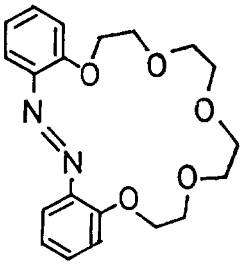
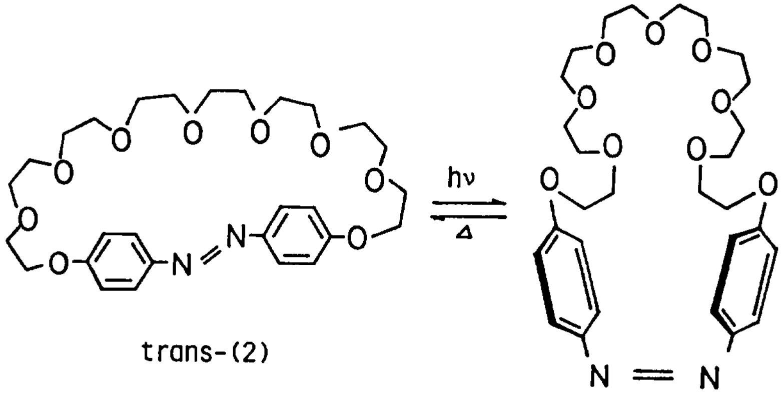
A new photoresponsive crown ether (2) in which the poly(oxyethylene) chain is linked to 4- and 4'-position of azobenzene was synthesized. Trans-(2) completely lacked the affinity to alkali metal cations, while photoisomerized cis-(2) was capable of binding K^+, Rb^+, and Cs^+.

Considerable interest has recently centered around the artificial photoresponsive systems which mimic the photoregulated functions in nature. When photoresponsive chromophores are linked to crown ether compounds, the ion-binding ability of the crown ethers may change in response to photoirradiation and as a result, one may control, for example, solvent extraction and ion-transport across membranes by an on-off light switch. Several photoresponsive crown ethers have been synthesized by our group and others,1-8) but there is no example which exhibits a reversible, all-or-none change in the binding ability in response to photoirradiation. For example, Shiga et al.3) synthesized a photoresponsive crown ether (1) which directly involves a chromophoric azo group in the skeleton. However, the photoisomerization of this compound is extremely slow (probably owing to the steric hindrance at the transition state) and is accompanied by photodecomposition. We thus designed a new photoresponsive crown ether (2) in which the chromophoric azobenzene is linked to the poly(oxyethylene) chain at its 4- and 4'-positions.



(1)

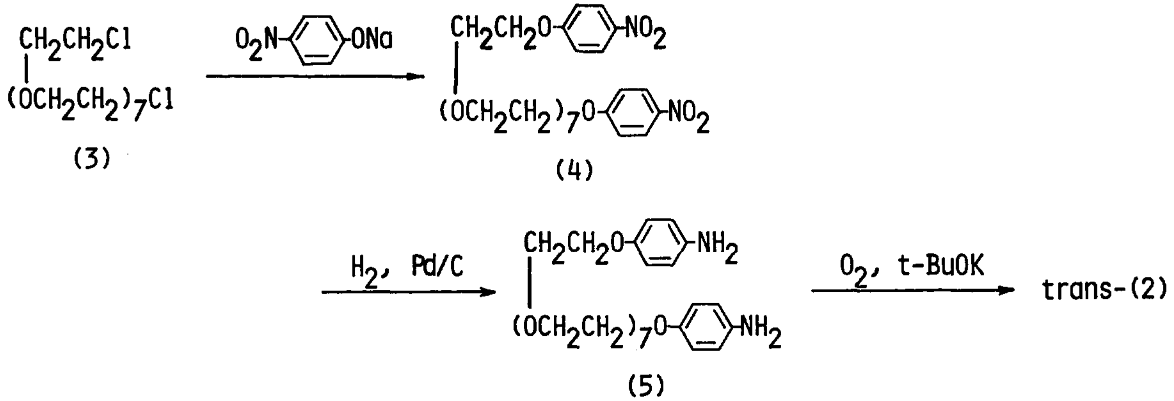


trans-(2)

cis-(2)

The inspection of the CPK models of (2) and its homologues suggests that (i) the smallest ethylene number to form the cyclic structure between 4- and 4'-position of trans-azobenzene is six, (ii) the poly(oxyethylene) chain of the trans-homologues with 6≤ ethylene number ≤ 10 is extended linearly, (iii) there is no significant steric restriction in the course of the cis-trans isomerization, and (iv) the number of oxygen atoms which contribute to the formation of a "crown ring" is n(total oxygen number)-2(phenolic oxygen atoms); that is, cis-(2) would act as an analogue of 21-crown-7.

Trans-(2) (mp 60-63°C) was synthesized according to the following reaction sequence and identified by elemental analysis, IR,[9] NMR,[10] and mass spectrum (M^+, 548). It is worth while mentioning that in NMR ($CDCl_3$), the center four ethylene units of trans-(2) shift to higher magnetic field by 0.2-0.3 ppm.



The absorption band of trans-(2) in o-dichlorobenzene (λ_{max} 361 nm) decreased rapidly by u.v. light irradiation (500 W high-pressure Hg-lamp with a color glass filter, 330 nm < λ < 380 nm) and reached a photostationary state (cis/trans = 68/32) within 30 sec. The observable thermal cis-to-trans isomerization took place in the dark at 30°C (first-order rate constant, $k = 0.114\ h^{-1}$) and the spectrum of trans-(2) was regenerated quantitatively after one day. Thus, trans-cis isomerism of (2) is completely reversible.

The binding ability of (2) was estimated by preliminary solvent extraction of alkali picrates from water to the organic phase (o-dichlorobenzene : n-butyl alcohol = 80 : 20 v/v). The extractability of (2) was determined by the partition of picrate ion between the aqueous and the organic phase. Since the thermal cis-to-trans isomerization was relatively slow, the change in the cis% during the work-up time could be neglected. The result of the solvent extraction at 30°C, together with the extraction conditions as footnotes, is summarized in Table 1.

Table 1. Extraction of alkali metal salts of picrate ion with (2) at 30°C[a)]

Metal	Ex(%)		
	trans-(2)	photoirradiated (2)[b)]	cis-(2)[c)]
Na^+	0	0.9	1.3
K^+	0	12.6	18.5
Rb^+	0	20.4	30.0
Cs^+	0	12.9	19.0

a) Organic phase: o-dichlorobenzene : n-butylalcohol = 80 : 20 v/v, $[(2)] = 3.00 \times 10^{-3}$ M. Aqueous phase: [MOH] = 0.3 M, [picric acid] = 1.00×10^{-4} M. Equal volumes of an organic and an aqueous solution were agitated on a Vortex Junior Mixer for 3 min, and the decrease in the absorption band of picrate ion in the organic phase was measured spectrophotometrically.

b) Concentration of cis-(2), 68%.

c) $Ex_{cis\text{-}(2)} = Ex_{photoirradiated\ (2)}/0.68$.

The examination of Table 1 reveals two noticeable characteristics of (2): that is, (i) trans-(2) completely lacks the affinity with metal ions, whereas photoisomerized cis-(2) is capable of extracting considerable amounts of metal ions and (ii) the maximum extractability is observed for Rb^+. The result (i) indicates that the almost linear poly(oxyethylene) chain of trans-(2) is transformed to the crown-like loop by u.v. light irradiation. The result (ii) means, on the other hand, that as predicted on the basis of the CPK model building, the poly(oxyethylene) loop formed in photoisomerized cis-(2) behaves as an analogue of 21-crown-7. In a separate study, we have found that the cis-to-trans isomerization is efficiently accelerated by visible light irradiation. Thus, an ionophoric loop of cis-(2) appears and disappears reversibly in response to the photoirradiation.

We are now studying the photoirradiation effect on the membrane transport of (2), expecting that the "all-or-none" ion-transport can be effected by an on-off light switch.

REFERENCES

1) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, and O. Manabe, Tetrahedron Lett., 1979, 4569.
2) I. Yamashita, M. Fujii, T. Kaneda, S. Misumi, and T. Otsubo, Tetrahedron Lett., 1980, 541.
3) M. Shiga, M. Takagi, and K. Ueno, Chem. Lett., 1980, 1021.
4) M. Eichner and A. Merz, Tetrahedron Lett., 22, 1315(1981).
5) J.-P. Desvergne and H. Bouas-Lanrent, J. Chem. Soc., Chem. Commun., 1978, 403.
6) S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa, and O. Manabe, J. Am. Chem. Soc., 102, 5860(1980).
7) S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, and O. Manabe, J. Am. Chem. Soc., 103, 111(1981).
8) S. Shinkai, K. Shigematsu, Y. Kusano, and O. Manabe, J. Chem. Soc., Perkin Trans. 1, 1981, 3279.
9) IR(KBr disk): $\nu_{N=N}$ 1600 cm^{-1}, ν_{C-O-C} 1120-1130 cm^{-1}.
10) NMR($CDCl_3$): O-CH_2, 3.38 ppm (16H), 3.60 ppm (8H), 3.88 ppm (4H), 4.35 ppm (4H); aromatic protons, 7.10 ppm (4H), 7.90 ppm (4H).

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