CHEMISTRY LETTERS, pp. 1021-1022, 1980.

AZO-CROWN ETHERS. THE DYES WITH AZO GROUP DIRECTLY INVOLVED IN THE CROWN ETHER SKELETON[1)]

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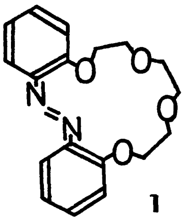
Crown-type polyether azo dyes **1**∿**3** were synthesized, and the ion-pair extraction of sodium and potassium ion was studied. The extraction behavior resembles those of benzo-type crown ethers, but changes on light illumination due to *trans-cis* isomerization of the dyes. The *cis*-form lacks the affinity to metal ions.

The application of crown ethers in analytical chemistry is expanding rapidly.[2)] In order to meet various demands in analytical chemistry, particularly, the demand to use a crown ether structure for the alkali and alkaline earth metal-selective chromogenic reagents,[3)] a new skeletal modification of the crown ether ring is highly desirable. In this communication we would like to report on the synthesis and the metal extraction property of a new family of crown ether dyes **1**∿**3**, in which the chromophoric azo group is directly involved in the crown ether skeleton.



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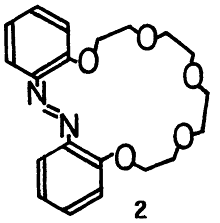

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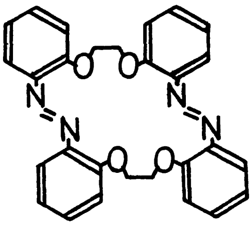

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The dyes **1**∿**3** were synthesized by the reaction of 2,2'-dihydroxyazobenzene with the appropriate oligoethylenglycol dichloride or ditosylate in the presence of a calculated amount of potassium *t*-butoxide in dry THF. In a typical run, the dye **1** was prepared in the following procedure. Triethyleneglycol ditosylate (3.2 g, 1.4 x 10^{-2} mol) in 100 ml THF was added dropwise in 1 h to a solution of potassium *t*-butoxide (3.2 g, 2.8 x 10^{-2} mol) and 2,2'-dihydroxyazobenzene (3.0 g, 1.4 x 10^{-2} mol) in 100 ml dry THF, and the mixture was refluxed for 20 h with vigourous stirring under nitrogen. After filtering the precipitates, the filtrate was concentrated to obtain the residue, which was taken in chloroform, washed with water, and finally recrystallized from heptane. These are reddish orange crystals, soluble in common organic solvents and insoluble in water. The elemental and instrumental analyses fully supported the proposed structure[4)].

Alkali metal ions were extracted from aqueous solution into benzene using the azo-crown ethers and tetrabromophenolphthalein ethyl ester ($TBPE^-$) as a pairing anion at pH 9. The extraction constants ($K_{ex} = [M^+.crown.TBPE^-]_{org}/[M^+][crown]_{org}[TBPE^-]$) for Na^+ and K^+ are summarized in Table 1. Lithium was not extracted by any of these crown ethers. The crown ether **1** extracts Na^+ preferentially over K^+ and thus resembles benzo-15-crown-5 in selectivity. The compound **2** prefers the extraction of K^+, but the selectivity for K^+ is considerably reduced as compared with that of dibenzo-18-crown-6 (DB18C6). The CPK model inspection suggests that the presence of azo group introduces a strain in the crown ether ring, resulting in the effective reduction in the size of the polyether ring to accomodate the alkali metal ion. 2,2,-Dimethoxyazobenzene (**4**), which lacks cylcic polyether linkage, does not extract alkali metals at all. The fact that the azo-crown ethers exhibit the affinity to alkali metals similar to "regular" crown ethers indicates that the azo group is interacting directly with alkali metal ions. The direct interaction between the chromophore and the alkali metal is important because it gives a clue to develop a new type of chromogenic reagent based on crown ethers.

Table 1. Extraction Constants of Crown ethers

M^+	log Kex **1**	**2**	DB18C6
Na^+	4.1_8	4.0_1	3.8_4
K^+	2.7_7	5.0_1	5.6_9

The behavior to light of the dyes **1**,**2** and **4** was studied in benzene under conditions$^{5)}$ similar to those reported.$^{6)}$ The spectral change due to *trans* - *cis* isomerization was similar for the three azo dyes. On exposure to light (λ≥300 nm), 4 showed a general decrease in absorption above 300 nm except for an approximate isosbestic point at 436 nm. **1** and **2**, apart from the decrease in absorption below 400 nm, showed a very slight increase at 410-460 nm region, giving isosbestic points at around 405 (1, **2**), 445 (**2**), and 455 nm (**1**). The rate of reconversion of the *cis*-form to the *trans* in the dark was slow, the half life being several days at room temperature for all of the dyes. The non-cyclic azo deys are characterized by the relative ease of photo-isomerization as compared with the cyclic azo dyes. Thus, while more than 60 % of **4** is readily photo-isomerized to *cis*, only 20 % of 1 or **2** is isomerized under the same conditions, and the attempt to further isomerization resulted in irrevercible spectral change. An extraction study for 20 % photo-isomerized **1** and **2** indicated that while the selectivity among Na^+ and K^+ remained the same, the amount of metal extracted decreased to 80 % of the non-light-irradiated controls. The result suggests that the photo-isomerized form of **1** and **2** lacks the affinity to metal ions. A CPK model inspection of the *cis* structure indicates that the conformation of the crown ether ring is highly strained and unfavorable for the interaction with metals. The present crown ethers can thus serve also as a mediator which responds to light and controls the transport of metal ions between aqueous and organic phases. Quite recently, Shinkai et al.reported a macrocyclic compound with a similar function, in which the diaza-crown ether (Kryptofix 22) was bridged with azobenzene-3,3'-dicarbonyl group through amido linkages leading to a bicyclic structure. The azo group, which is not involved in the coordination, induces a conformational change in the crown ether ring on photo-isomerization.$^{6)}$

REFERENCES AND NOTES

1) Presented at the 41st Annual Meeting of the Chemical Society of Japan, Higashi-osaka, 1980.

2) I. M. Kolthoff, Anal. Chem., **51**, 1R (1979).

3) T. Yamashita, H. Nakamura, M. Takagi, and K. Ueno, Bull. Chem. Soc. Jpn., **53**, 1550 (1980).

4) **1**. Yield 14 %. Mp 67.5-68.0°C. Mass spectrum: M^+, 328. IR(KBr disk); 2900(C-H); 1598(N=N); 1132 cm^{-1}(C-O-C). NMR($CDCl_3$); 3.62-4.00(O-CH_2), 4.12-4.32(Ar-O-CH_2), 6.71-7.75 ppm (aromatic). λ_{max},(ε): 352, (12000); 453 nm, (1200).

2. Yield 23 %. Mp 111.0-113.0°C. Mass spectrum: M^+, 372. IR(KBr disk); 2850(C-H); 1585(N=N); 1120 cm^{-1}(C-O-C). NMR($CDCl_3$); 3.32-3.95(O-CH_2), 4.10-4.42(Ar-O-CH_2), 6.71-7.45 ppm (aromatic). λ_{max}, (ε): 346, (11300); 453 nm, (1700).

3. Yield 2 %. Mp 113.5-114.5°C. Mass spectrum: M^+, 480. IR(KBr disk); 2920(C-H); 1592 cm^{-1}(N=N). NMR($CDCl_3$); 4.08-4.60(O-CH_2), 6.55-7.37 ppm (aromatic). λ_{max}, (ε): 367, (21200); 450 nm, (3500).

5) A benzene solution containing azo-crown ether was irradiated for one minuite at room temperature with a high-pressure Hg-lamp (100 w) at a 20 cm distance.

6) S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, and O. Manabe, Tetrahedron Lett., **1979**, 4569.

(Received May 19, 1980)