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Photoresponsive Crown Ethers. 9. Cylindrical and Phane Crown Ethers with Azobenzene Segments as a Light-switch Functional Group[1]

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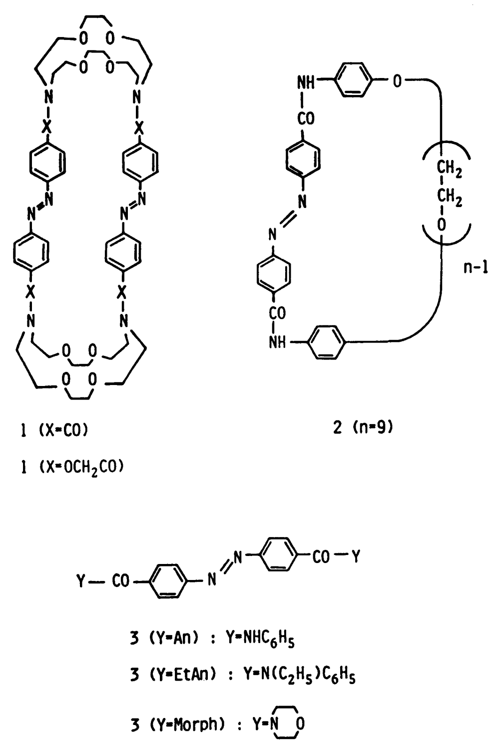
Cylindrical and phane crown ethers with azobenzene segments as a light-switch functional group were synthesized. Cylindrical ionophores in which two diazacrown ethers are linked by two photoresponsive azobenzene pillars change their binding ability for polymethylenediammonium salts in response to photoirradiation. Thus, the distance between the two crown rings can be photocontrolled. A phane-type ionophore in which 1,23-bis(*p*-aminophenoxy)-3,6,9,12,15,18,21-heptaoxatricosane is linked by a *trans*-4,4′-azobenzenedicarbonyl segment exhibits no affinity with all alkali metal cations but significantly binds Rb^+ and Cs^+ under UV-light irradiation. This is the example of the "all-or-nothing" control of the ion-binding ability and implies that a crown-like loop emerges only when the azobenzene segment is photoisomerized to the *cis*-configuration. These ionophores are categorized to novel photoresponsive crown ethers.

The importance of macrocyclic ligands has been recognized not only in organic chemistry but also in relation to biological chemistry. One of the recent exploration is associated with the combination of a photoresponsive function with macrocyclic ligands, which leads to photocontrol of chemical and physical functions of a crown ether family by an on-off light switch.[2–7] For example, we and others have reported that a photoresponsive crown ether that combines within a molecule both a crown ether and a photoresponsible chromophore changes its conformation in response to the photoinduced configurational change in the chromophore,[2–7] resulting in a change in the complexation ability. The finding has been applied to the novel photocontrol of solvent extraction and ion transport across membranes.[8–10]



Scheme 1.

We here wish to address two new classes of photoresponsive crown ethers, cylindrical and phane ionophores. A cylindrical ionophore, in which two macrocyclic ligands are linked by two (or more than two) pillars, is an interesting receptor molecule which is able to bind diammonium ions and plural metal ions.[11–14] Since the metal affinity of cylindrical ionophores is crucially governed by the pillar length, one may expect that the binding ability and the binding selectivity would be readily controlled by changing the length of the two pillars. Thus, cylindrical ionophores with azobenzene pillars would act as "elastic" ionophores in response to photoinduced *trans-cis* isomerization of the azobenzene pillars. Meanwhile, a phane ionophore, in which a poly(oxyethylene) chain is linked by 4,4′-azobenzene, may exhibit the photoresponsive "all-or-noting" change in the ion-binding ability.[15] Since the distance between the 4- and 4′-positions of *trans*-azobenzene is 9.0 Å while that of *cis*-azobenzene is 5.5 Å, one may visualize that an ionophoric polyoxyethylene loop would appear in *cis*-isomers and disappear in *trans*-isomers reversibly in response to photoirradiation. With these objects in view we synthesized cylindrical and phane ionophores (**1** and **2**, respectively) and evaluated their photoresponsive behaviors in comparison with their model compounds **3**.

Experimental

Materials. Compound **1**(X=CO) was synthesized in benzene from equimolar amounts of 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 and 4,4′-bis(chloroformyl)azobenzene[4] according to the high-dilution method. In a 1-l three-necked flask with a reflux condenser were placed 200 ml of benzene and 5 ml of triethylamine, and 2.10 g (8.0 mmol) of 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 in 100 ml of benzene from one dropping funnel and 2.46 g (8.0 mmol) of 4,4′-bis(chloroformyl)azobenzene in 100 ml of benzene from another dropping funnel were added simultaneously. The reaction mixture was stirred vigorously at room temperature. It took about 1 h to complete the addition of two reactants, and the reaction was continued for 1 h. The precipitate was removed by filtration, the filtrate being washed with water. The benzene was evaporated to dryness *in vacuo*. When the residual red solid was redissolved in 50 ml of benzene, insoluble, viscous material(polymer?) was removed. The benzene solution was concentrated again, and the residue was recrystallized three times from xylene; mp 224—226 °C, yield 21%, hygroscopic. IR(KBr): $\nu_{C=O}$ 1635 cm^{-1}. NMR(Me$_2$SO-d_6, 80 °C): crown protons, 3.5—3.8 ppm, 48H; 2′-H of azobenzene, 7.56 ppm, 8H; 3′-H of azobenzene, 7.88 ppm, 8H. Mass spectrum: M$^+$ (*m*/*e*) 992. Found: C, 62.36; H, 6.64: N, 11.01%. Calcd for $C_{52}H_{64}N_8O_{12}$: C, 62.89; H, 6.50; N, 11.28%. Gel permeation chromatography gave a single peak at 1000±40.

Compound **1**(X=OCH_2CO) was similarly synthesized by the high-dilution method from equimolar amounts of 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 and 4,4′-bis(chloroformylmethoxy)azobenzene. 4,4′-Bis(carboxymethoxy)azobenzene was prepared from 4,4′-dihydroxyazobenzene and chloroacetic acid in aqueous solution containing NaOH: mp 250 °C, yield 73%. 4,4′-Bis(chloroformylmethoxy)azobenzene was obtained by treating this compound with thionyl chloride: mp 140—145 °C, yield 69%. The condensation to synthesize **1**(X=OCH_2CO) was carried out in benzene in the presence of triethylamine. The raw product was purified by the TLC method(silica gel, chloroform–methanol (8 : 2 v/v)) and finally recrystallized from chlorobenzene: mp 219—221 °C yield 37%. IR(KBr): $\nu_{C=O}$ 1660 cm^{-1}, ν_{C-O-C} 1060—1160 cm^{-1}. NMR(CDCl$_3$): crown protons, 3.4—3.8 ppm, 48H; OCH$_2$, 4.80 ppm, 8H; 3′-H of azobenzene, 6.92 ppm, 8H; 2′-H of azobenzene, 7.72 ppm, 8H. Found: C, 60.47; H, 6.59; N, 9.73%. Calcd for $C_{56}H_{72}O_{16}N_8$: C, 60.42; H, 6.52; N, 10.07%. Gel permeation chromatography gave a single peak at 1000±50.

Compound **2**(*n*=9) was synthesized according to the high-dilution method from equimolar amounts of 1,23-bis(*p*-aminophenoxy)-3,6,9,12,15,18,21-heptaoxatricosane[16] and 4,4′-bis(chloroformyl)azobenzene[4] in benzene in the presence of triethylamine. The precipitate was a mixture of triethylamine hydrochloride and orange solid. The colored solid(polymer?) was insoluble in usual organic solvents. The filtrate was washed with water and concentrated to dryness *in vacuo*. The residue was recrystallized from benzene: mp 179—183 °C, yield 8.4%. IR(KBr): ν_{NH} 3450 cm^{-1}, $\nu_{C=O}$ 1670 cm^{-1}, ν_{C-O-C} 1120—1126 cm^{-1}. NMR(Me$_2$SO-d_6, 70 °C): central methylene protons at 8, 10, 11, 13, 14, and 16 positions, 3.21 ppm, 12H; 5, 7, 17, and 19 methylene protons, 3.46 ppm, 8H; 4 and 20 methylene protons, 3.57 ppm 4H; 2 and 22 methylene protons, 3.79 ppm, 4H; 1 and 23 methylene protons, 4.22 ppm, 4H; aromatic protons of the aminophenol moiety, 7.02 ppm (4H), 7.40 ppm (4H); aromatic protons of the azobenzene moiety, 7.88 ppm (4H), 8.00 ppm (4H); NH, 10.04 ppm, 2H. Mass spectrum: M$^+$ (*m*/*e*) 786. Found: C, 63.57: H, 6.38; N, 7.11%. Calcd for $C_{42}H_{50}O_{11}N_4$: C, 64.11; H, 6.40; N, 7.12%. Gel permeation chromatography gave a single peak at 770±50.

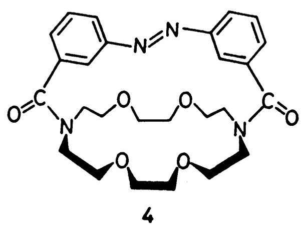
Compound **3**(Y=An) and **3**(Y=EtAn) were prepared by the reaction of 4,4′-bis(chloroformyl)azobenzene[4] with aniline and *N*-ethylaniline, respectively, in benzene in the presence of triethylamine. **3**(Y=An): mp>260 °C. Found: C, 74.37; H, 4.66; N, 13.47%. Calcd for $C_{26}H_{20}N_4O_2$: C, 74.27; H, 4.79; N, 13.32%. **3**(Y=EtAn): mp 135—140 °C. Found: C, 70.23; H, 6.19; N, 10.98%. Calcd for $C_{30}H_{28}N_4O_2 \cdot 2H_2O$: C, 70.29; H, 6.29; N, 10.93%. The preparation of **3**(Y-Morph) was described previously.[4]

Miscellaneous. The method of solvent extraction was described priviously.[4,8] The deteils of the work-up conditions are recorded in footnotes to Table 2. A 500-W high-pressure Hg-lamp with a color glass filter (330 nm$<\lambda<$380 nm) was used for the *trans*-to-*cis* photoisomerization unless otherwise stated. The ionophore concentration for the solvent extraction was usually higher than that for the kinetic measurements. In case the concentration was extremely high, the *trans*-to-*cis* photoisomerization was slow and the *cis*-percentage at the photostationary state was not sufficiently high. We thus prepared a thin solution layer between two glass plates and photoirradiated the solution. This method enabled a satisfactory photoconversion to the *cis*-isomers. The *cis*% at the photostationary state was estimated from the decrease in the absorption maximum of the *trans*-isomers, assuming that the absorbance of the *cis*-isomers at the wavelength is neglible in comparison to that of the *trans*-isomers. In all cases, the *cis*-*trans* isomerism was reversible within the experimental error.

The method of kinetic measurements was also described in the previous papers.[4,8] After a cuvette containing an ionophore solution was photoirradiated, the cuvette was transferred to a thermostated cell-holder (30 °C) in a spectrophotometer. The reaction was monitored by following the appearance of the absorption maximum of the *trans*-isomers.

Results and Discussion

Syntheses, Spectroscopic Properties, and Photoresponsiveness. We previously synthesized an azobenzene-capped azacrown ether **4** (*i.e.*, 1 : 1 adducts) from 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 and 3,3′-bis(chloroformyl)azobenzene in 23% yield.[4] On the other hand, the reaction between the azacrown ether and 4,4′-bis(chloroformyl)azobenzene mainly gave the polymer.[4] The difference was rationalized in terms of the steric factor that the distance between 1-*N* and 10-*N* of the azacrown ether is almost equal to that between two carbonyl groups of the 3,3′-isomer but significantly shorter than that between two carbonyl groups of the 4,4′-isomer. The present result indicates that when the distances between two reaction centers do not fit each other, the 2 : 2-adduct such as **1** (X=CO) and (**1** X=OCH_2CO) results under high-dilution conditions



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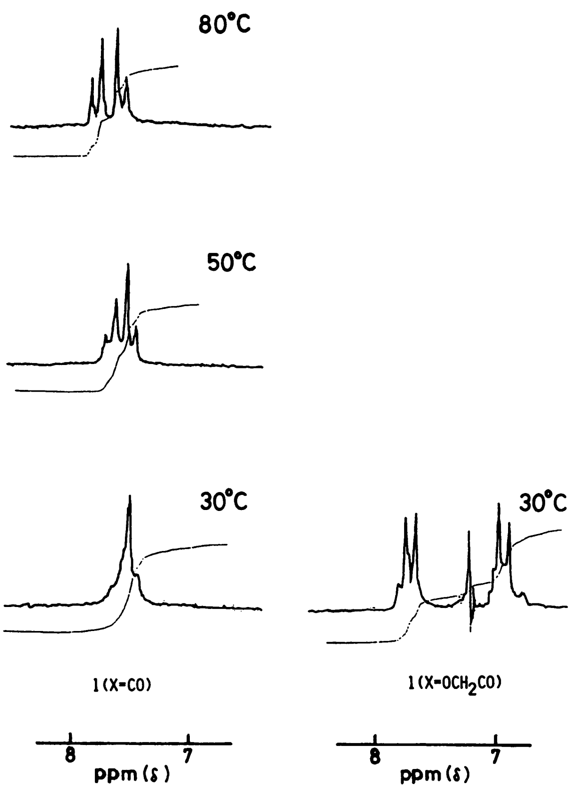
An azobenzenophane **2** (*n*=9) was also synthesized according to the high-dilution method. The CPK model of **2** (*n*=9) suggests that the poly(oxyethylene) clain is almost linearly extended when the azobenzene segment adopts the *trans*-configuration. We attempted the synthesis of the homologues with the smaller ring-size (*e.g.*, **2** (*n*=7 and 8)), but we could not isolate any cyclic compound by the TLC method. The result suggests that eight oxyethylene units are the shortest chain to form the cyclic adduct.

In the NMR measurements, the crown protons of **1** (X=CO) and **1** (X=OCH_2CO) appeared at 3.5—3.8 ppm and 3.4—3.8 ppm, respectively, as a broad single

Table 1. Spectroscopic and kinetic properties of cylindrical and phane azobenzene derivatives in o-dichlorobenzene (30 °C)

Properties	**1** (X=CO)a)	**1** (X=OCH$_2$CO)	**2** (n=9)b)	**3** (Y=An)c)	**3** (Y=EtAn)	**3** (Y=Morph)
λ_{max}/nm	332	356	340	345	343	331
ε_{max}	53200	42900	25240	30200	22300	26200
Time/min to reach photostationary state	60	1.5	30	6	10	10
cis(%) at photostationary state	65	63	10	28	40	26
$k_{cis \to trans}$/s^{-1}	6.33×10^{-6}	1.55×10^{-3}	*ca.*1×10^{-5} d)	1.58×10^{-5}	1.26×10^{-5}	2.22×10^{-5}

a) *o*-Dichlorobenzene: butyl alcohol=86.8 : 13.2 by volume. b) *o*-Dichlorobenzene: butyl alcohol=4 : 1 by volume. c) 9 vol% *N*,*N*-dimethylformamide in *o*-dichlorobenzene. d) The rate constant could not be determined accurately because the spectral change was slight.



1(X-CO) 1(X-OCH$_2$CO)

Fig. 1. Temperature dependence of the NMR spectra of **1** (X=CO) (in Me$_2$SO-d_6) and **1** (X=OCH$_2$CO) (in CDCl$_3$).

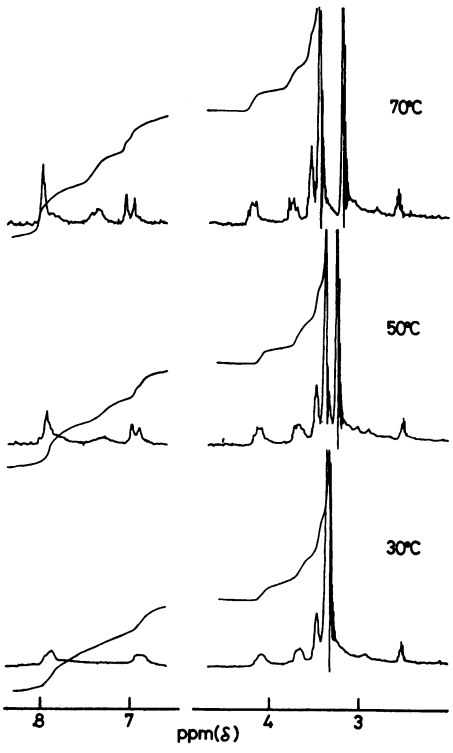


Fig. 2. Temperature dependence of the NMR spectra of **2** (n=9) (in Me$_2$SO-d_6).

peak. On the other hand, the NMR spectrum of **4** gave two resolved peaks at 3.6—3.9 ppm (8H) and 4.1—4.8 ppm (16H), which were attributed to *N*-CH$_2$ and *O*-CH$_2$ of the crown ring, respectively.[4] The comparison of these data suggests that the *O*-methylene protons of **4** are somewhat deshielded by the ring current of the azobenzene moiety. The finding is in line with our previous prediction that the azobenzene moiety of *trans*-**4** stands vertically over the crown ether plane.[4]

Another interesting finding in the NMR measurements is the fact that the NMR peaks of **1** (X=CO) and **2** (n=9) are significantly broad at 30 °C, whereas those of **1** (X=OCH$_2$CO) are not subject to such a broadening effect (Figs. 1 and 2). The peaks are sharpened with increasing temperature. Conceivably, the broadening effect is induced by the steric rigidity of these molecules and in fact, the CPK models of **1** (X=CO) and **2** (n=9) are more rigid than that of **1** (X=OCH$_2$CO). It is interesting to know whether the steric rigidity is reflected by photoresponsive behaviors of these molecules. As shown is Table 1, we have found that it takes a long time for **1** (X=CO) and **2** (n=9) to reach the photostationary states as compared with the time required for **1** (X=OCH$_2$CO) and model compounds such as **3** (Y=An), **3** (Y=EtAn), and **3** (Y=Morph). In contrast, the significant difference was not found for the rate of the thermal *cis*-to-*trans* isomerization: the rate constants ($k_{cis \to trans}$) for **1** (X=CO) and **2** (n=9) are comparable with those for the model compounds. These results may mean that the transition state of **1** (X=CO) and **2** (n=9) in the photoisomerization process is more destabilized than that of **1** (X=OCH$_2$CO) and model compounds. Previously, Shiga *et al.*[3] synthesized phane-type crown ether in which a poly(oxyethylene) chain is linked directly by 2,2′-azobenzene. It was found, however, that the photoisomerization of this compound is extremely slow and sometimes accompanied by photodecomposition. This would be also due to the sterically-destabilized transition state. Fortunately, the *trans*-isomers used in the present study were photochemically converted to the *cis*-isomers and the *cis*-isomers were thermally converted back to the *trans*-isomers: the *cis-trans* isomerism was reversible within the allowable experimental error. Meanwhile, we consider that the enhanced rate constant ($k_{cis\rightarrow trans}$) observed for **1** (X=OCH_2CO) is attributable to the electronic effect but not to the steric effect.

Along the isomerization process of the photoresponsive cylindrical ionophores there exist three different isomers: *trans-trans*, *trans-cis*, and *cis-cis*. The thermal isomerization of these cylindrical ionophores satisfied the first-order rate equation for up to four half-lives and the UV-visible spectra of the thermal isomerization showed sharp isosbestic points. The results support that no intermediate is accumulated along the isomerization pathway. One may suppose, therefore, that 65% *cis*-**1** (X=CO) means, for example, 65% *cis-cis*-**1** (X=CO) and 35% *trans-trans*-**1** (X=CO).

Solvent Extraction of Alkali Metal Cations. Solvent extraction of alkali picrates with cylindrical and phane ionophores is summarized in Table 2. Ex% denotes the partition of picrate to organic phase. At the start of this experiment, we expected that *trans-trans*-**1** (X=CO) would form a 1 : 1 crown/metal (*i.e.*, 1 : 2 **1** (X=CO)/metal) complex, whereas *cis-cis*-**1** (X=CO) would form a 2 : 1 crown/metal (*i.e.*, 1 : 1 **1** (X=CO)/metal) sandwich-type complex with large alkali metal cations. The Ex% of picrate salts in Table 2 reveals, however, that the formation of the sandwich-type complex is rather unlikely: *cis-cis*-**1** (X=CO) generally exhibits a metal affinity greater than *trans-trans*-**1** (X=CO), but the enhancement in the Ex% is not limited to large alkali metal cations. We consider at present that the steric rigidity of the crown rings is somewhat relaxed through the photoisomerization of the azobenzene pillars, resulting in the improved affinity toward all alkali metal cations. Similarly, *cis-cis*-**1** (X=OCH_2CO) has the larger Ex% than *trans-trans*-**1** (X=OCH_2CO) and exhibits the selectivity for small alkali metal cations.

It is speculated on the basis of the CPK model building that the poly(oxyethylene) chain of *trans*-**2** (n=9) is almost linearly extended while that of *cis*-**2** (n=9) may form a crown-like loop. The examination of Table 2 reveals that *trans*-**2** (n=9) completely lacks the affinity with metal ions, whereas photoisomerized *cis*-**2** (n=9) is capable of extracting large alkali metal cations such as Rb^+ and Cs^+ in the significant Ex%. Thus, an ionophoric, crown-like loop appears and disappears in response to photoirradiation and the loop size is roughly comparable with that of 21-crown-7.

Solvent Extraction of Polymethylenediammonium Salts. One of the most interesting characteristics of photoresponsive cylindrical ionophores would be the possibility that the distance between two crown rings changes reversibly by an on-off light-switch. The possibility was tested by the solvent extraction of polymethylenediammonium salts as a molecular measure. The inspection of CPK models suggests that, assuming that the polymethylene chain adopts an extended conformation, the distances between the two crown rings of *trans-trans*-**1** (X=CO) and *cis-cis*-**1** (X=CO) are almost equal to those between the two terminal ammonium groups of decamethylenediamine and hexamethylenediamine, respectively.

TABLE 2. EXTRACTION OF PICRATE SALTS OF ALKALI METAL CATIONS WITH CYLINDRICAL AND PHANE CROWN ETHERS (30 °C)

Crown	Ex(%)			
	Na^+	K^+	Rb^+	Cs^+
1 (X=CO)[a)], dark	4.4	3.9	5.3	4.7
light (*cis* 54%)	6.5	6.3	6.8	8.5
1 (X=OCH_2CO)[b)], dark	4.8	1.7	0	0
light (*cis* 67%)	10.2	2.6	2.6	0
2 (n=9)[c)], dark	0	0	0	0
light (*cis* 10%)	0	0	4	1

a) Aqueous phase: [picric acid]=1.00×10^{-4} M, [MOH] =1.00×10^{-2} M, [MCl]=0.49 M. Organic phase: [**1** (X=CO)]=1.00×10^{-3} M, *o*-dichlorobenzene: butyl alcohol=9 : 1 by volume. b) Aqueous phase: [picric acid] =1.00×10^{-4} M, [MOH]=1.00×10^{-2} M, [MCl]=0.49 M. Organic phase: [**1** (X=OCH_2CO)]=3.00×10^{-3} M, chloroform: butyl alcohol=9: 1 by volume. c) Aqueous phase: [picric acid]=3.90×10^{-3} M, [MOH]=6.00×10^{-3} M, [MCl]=0.59 M. Organic phase: [**2** (n=9)]= 9.91×10^{-3} M, *o*-dichlorobenzene: butyl alcohol=4: 1 by volume.

TABLE 3. EXTRACTION OF POLYMETHYLENEDIAMMONIUM SALTS WITH CYLINDRICAL CROWN ETHERS (30 °C)

Crown	Ex(%) of $H_3N^+(CH_2)_nNH_3^+\cdot(\text{picrate})_2$				
	n=4	6	8	10	12
1 (X=CO)[a)], dark	0.5	3.0		20.0	27.2
light(*cis* 22%)	0.8	8.9		12.3	22.0
light(*cis* 38%)	2.4	12.6		9.3	18.9
light(*cis* 54%)	3.0	19.0		6.7	13.1
1 (X=OCH_2CO)[b)], dark		0	0	3.0	7.6
light(*cis* 67%)		0	0	0.4	4.2

a) Aqueous phase: [picric acid]=4.00×10^{-4} M, [HCl] = 5.96×10^{-2} M, [$H_2N(CH_2)_nNH_2$] = 3.00×10^{-2} M. Organic phase: [**1** (X=CO)]=3.00×10^{-3} M, *o*-dichlorobenzene: butyl alcohol=9 : 1 by volume. b) Aqueous phase:[picric acid]=4.00×10^{-4} M, [HCl]=5.96×10^{-2} M, [$H_2N(CH_2)NH_2$]=2.99×10^{-2} M. Organic phase: [**1** (X=OCH_2CO)]=2.98×10^{-3} M in chloroform.

The Ex% was evaluated on the basis of the partition equilibrium of picrate ion added as counter-anion between an organic phase and an aqueous phase (see footnote b) in Table 3). The results in Table 3 substantiates several important points: (i) *trans-trans*-**1** (X=CO) extracts decamethylane and dodecamethylenediammonium salts efficiently but hardly extracts tetramethylene and hexamethylenediammonium salts, (ii) hexamethylenediammonium salt gives the greatest Ex% value under UV-light irradiation, and (iii) with increase in the concentration of *cis-cis*-**1** (X=CO), Ex% of tetramethylene and hexamethylenediammonium salts increases while Ex% of decamethylene and dodecamethylenediammonium salts decreases. The findings are basically compatible with the prediction from CPK model building. Similarly, *trans-trans*-**1** (X=OCH_2CO)

is capable of extracting diammonium salts with long methylene units but scarcely extracts those with short methylene units. As expected, the Ex% of decamethylene and dodecamethylenediammonium salts is suppressed by UV irradiation.

Conclusion

The present paper represents two novel findings. One is the fact that in the photoresponsive cylindrical ionophores, the distance between two crown rings is readily convertible by photoinduced *cis-trans* isomerism of the azobenzene pillars. The other is the all-or-noting change in the metal affinity observed for the azobenzenophane-type ionophore. These novel photoresponsive behaviors would be applicable to the photocontrol of solvent extraction, membrane transport, spatial distance between two metal ions, *etc.*

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