The approximate equivalence of T_{CH} values for corresponding methylene groups in the DMODCS-reacted and DMOCS-reacted samples leads one to challenge the suitability of spectral density curves B and C of Figure 4 to explain the proton relaxation data of the DMODCS-reacted and DMOCS-reacted samples, respectively. The T_{CH} results, together with "chemical intuition," lead to the conclusion that *on the average* the methylene C–H bond vectors must be *more* mobile for larger attached alkyl chains (a smaller fraction of methylenes near the surface); this is opposite to what is implied in identifying curve B with the DMODCS-reacted case and curve C with the DMOCS-reacted case.

The apparent dilemma can be explained as follows. If proton spin–lattice relaxation, sensitive to motional frequency components at 150 MHz, is due primarily to methyl group rotation, then the CH_3 group serves as a "T_1 sink." In this case, the system with more methylene protons has a larger Zeeman heat capacity and will manifest less efficient overall ^{1}H spin–lattice relaxation (larger T_{1H}). In this case one could identify curve C of Figure 4 with the average chain motion of CH_2 groups in the DMODCS-reacted sample (having greater average methylene mobility) and curve B with methylene motion in the DMOCS-reacted sample (with less average mobility of methylene C–H vectors).

In summary, ^{13}C relaxation measurements have shown that motional behavior is quite heterogeneous for methyl and methylene environments in silica-attached alkylsilane phases. Future studies can be expected to elucidate more fully the nature of the interactions responsible for such behavior in these and other surface-immobilized systems.

Acknowledgment. The authors gratefully acknowledge partial support of this research by the U.S. Department of Energy (Contract No. DE-AT20-81LC0652 from the Laramie Energy Technology Center) and the assistance of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE 78-18581.

Registry No. DMOCS, 18162-84-0; DMODCS, 18643-08-8.

Photoresponsive Crown Ethers. 8. Azobenzenophane-Type "Switched-On" Crown Ethers Which Exhibit an All-or-Nothing Change in Ion-Binding Ability[1]

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Abstract: Three new azobenzenophane-type crown ethers, cr(O_7), cr(O_8), and cr(O_9), in which 4,4′ positions of azobenzene are linked by a polyoxyethylene chain, were synthesized. The trans isomers were isomerized by UV light to the cis isomers, and the cis isomers were isomerized thermally or by visible light to the trans isomers, the interconversion being completely reversible. The solvent extraction showed that the trans isomers totally lack affinity toward metal ions, whereas the cis isomers are able to bind considerable amounts of alkali metal cations. The result is in accord with the prediction by the CPK model building that the polyoxyethylene chains of the trans isomers are linearly extended, whereas those of the cis isomers form the crown-like loops. The cis isomers showed spheric recognition patterns in the binding of alkali metal cations, typical of crown ethers in solution; the metal cations which provided the maximum extractability are Na^+ for *cis*-cr(O_7), K^+ for *cis*-cr(O_8), and Rb^+ for *cis*-cr(O_9). The rate of the thermal cis-to-trans isomerization was significantly suppressed by added alkali metal cations, indicating that the additional energy is required to disrupt the crown–metal interaction. The order of inhibitory effect is well correlated with that of extractability. From plots of the rate constant against metal concentration, we estimated association constants (K) and rate constants for the crown–metal complexes (k_{CM}). Conceivably, the increment in free energy of activation in the presence of metal cations reflects the magnitude of the "template effect" of metal ions. This is the first example for photoresponsive crown ethers which exhibit an "all-or-nothing" change in ion-binding ability.

Photoresponsive systems are ubiquitous in nature, and light is frequently the trigger for subsequent life processes. As a first step to mimic natural photoresponsive systems, one has to design a molecule (or system) which combines a photoantenna to capture a photon with a functional group to mediate some subsequent event. Photoresponsive crown ethers have azobenzene or anthracene as a photoantenna and crown ether as a functional group and change their chemical and physical functions in response to photoirradiation.[2-8] Similarly, azobenzene derivatives have been utilized as a light trigger to control the functions of metal ligands,[9] β-cyclodextrin,[10] membranes,[11] micelles,[12] and microemulsions.[13]

In spite of these efforts, few examples have ever attained an "all-or-nothing" photoregulation. Shiga et al.[8] synthesized azobenzenophane-type crown ethers in which the 2,2′ positions of azobenzene are linked by a polyoxyethylene chain. Although the

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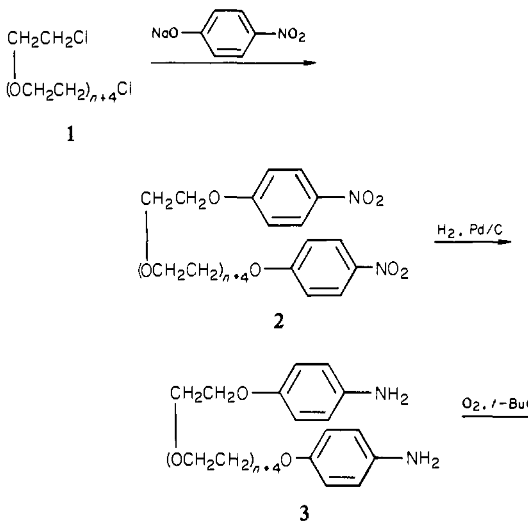
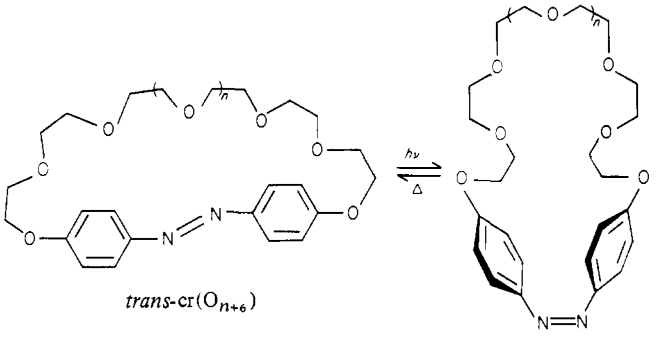
Scheme I



cis forms of these crown ethers lack affinity for metal ions, the photoisomerization is inevitably accompanied by photodecomposition, probably due to steric strain of the cis forms. Therefore, these crown ethers do not reversible photoresponsiveness. To attain the "all-or-nothing" change and the good reversibility at the same time, one has to utilize the large geometrical change without inducing any steric strain. Thus, we newly synthesized azobenzenophane-type crown ethers cr(O_7), cr(O_8), and cr(O_9), in which 4,4′ positions of azobenzene are linked by a polyoxyethylene chain. As expected, these photoresponsive crown ethers exhibited both the "all-or-nothing" change and the excellent reversibility.



trans-cr(O_{n+6})

cis-cr(O_{n+6})

Experimental Section

Materials. 1,4,7,10,13,16,19-Heptaoxa[19](4,4′)azobenzenophane (cr(O_7)), 1,4,7,10,13,16,19,22-octaoxa[22](4,4′)azobenzenophane (cr(O_8)), and 1,4,7,10,13,16,19,22,25-nonaoxa[25](4,4′)azobenzenophane (cr(O_9)) were synthesized according to Scheme I (n = 1, 2, 3). Since the preparation methods for three crown ethers are similar to each other, we shall describe the synthesis of cr(O_7) as an example and simply record the analytical data for the synthesis of the other two crown ethers.

1,17-Bis(*p*-nitrophenoxy)-3,6,9,12,15-pentaoxaheptadecane (**2**, n = 1) was prepared by the reaction of sodium *p*-nitrophenolate and 1,17-dichloro-3,6,9,12,15-pentaoxaheptadecane (**1**, n = 1). To a dehydrated sulfolane solution of sodium *p*-nitrophenolate (40.3 g, 0.25 mol) was added dropwise 31.9 g (0.10 mol) of **1** (n = 1), and the reaction was continued at 150 °C for 30 h. Precipitated sodium chloride was removed by filtration and washed with methanol. The combined solution was evaporated to dryness in vacuo and the residue was dissolved in benzene. The benzene solution was washed with aqueous NaOH solution and then boiled in the presence of 20 g of silica gel. After filtration, benzene was evaporated in vacuo. The residue crystallized on cooling: mp 55–62 °C; yield 74.2%; IR (KBr disk) ν_{NO_2} 1340 and 1510, ν_{Ar-O-C} 1040, ν_{C-O-C} 1110 cm^{-1}; mass spectrum, *m/e* 524 (M^+); NMR ($CDCl_3$) δ 3.68 (16 H, m, OCH_2), 3.88 (4 H, t, Ar–O–C–CH_2–), 4.21 (4 H, t, Ar–O–CH_2), 6.98 (4 H, d, *m*-H to nitro), 8.19 (4 H, d, *o*-H to nitro). Anal. ($C_{24}H_{32}N_2O_{11}$) C, H, N.

2 (n = 2): oil; yield 80.9%; IR(neat) ν_{NO_2} 1340 and 1510, ν_{Ar-O-C} 1050, ν_{C-O-C} 1120 cm^{-1}; NMR ($CDCl_3$) δ 3.68 (20 H, m, OCH_2), 3.88 (4 H, t, Ar–O–C–CH_2), 4.21 (4 H, t, Ar–O–CH_2), 6.95 (4 H, d, *m*-H to nitro), 8.18 (4 H, d, *o*-H to nitro).

2 (n = 3): oil; yield 82.4%; IR (neat) ν_{NO_2} 1350 and 1510, ν_{Ar-O-C} 1060, ν_{C-O-C} 1120 cm^{-1}; mass spectrum, *m/e* 612 (M^+); NMR ($CDCl_3$) δ 3.68 (24 H, m, OCH_2), 3.90 (4 H, t, Ar–O–C–CH_2), 4.28 (4 H, t, Ar–O–CH_2), 7.00 (4 H, d, *m*-H to nitro), 8.21 (4 H, d, *o*-H to nitro). Anal. ($C_{28}H_{40}N_2O_{13}$) C, H, N.

1,17-Bis(*p*-aminophenoxy)-3,6,9,12,15-pentaoxaheptadecane (**3**; n = 1) was prepared by catalytic hydrogenation of **2** (n = 1). **2**: (n = 1) (10.0 g, 0.019 mol) was dissolved in 500 mL of methanol and reduced by hydrogen in the presence of 2 g of Pd on carbon. The reaction mixture was filtered in a nitrogen stream, the fitrate being evaporated to dryness. The residue which crystallized on cooling was recrystallized from benzene: mp 55–60 °C; yield 84.7%; IR (KBr disk) ν_{NH_2} 3360 and 3440, ν_{Ar-O-C} 1060, ν_{C-O-C} 1110 cm^{-1}; mass spectrum, *m/e* 464 (M^+); NMR ($CDCl_3$) δ 3.40 (4 H, broad, NH_2), 3.65 (16 H, m, OCH_2), 3.79 (4 H, t, Ar–O–C–CH_2), 4.02 (4 H, t,Ar–O–CH_2), 6.67 (8 H, q, aromatic). Anal. ($C_{24}H_{36}N_2O_7$) C, H, N.

3 (n = 2): oil; yield 85.0%. The oil was used for the following reaction without identification.

3 (n = 3): mp 70–72 °C; yield 95.8%; IR (KBr disk) ν_{NH_2} 3380 and 3440, ν_{Ar-O-C} 1050, ν_{C-O-C} 1120 cm^{-1}; mass spectrum, *m/e* 552 (M^+); NMR ($CDCl_3$) δ 3.42 (4 H, broad, NH_2), 3.68 (24 H, m, OCH_2), 3.82 (4 H, t, Ar–O–C–CH_2), 4.08 (4 H, t, Ar–O–CH_2), 6.69 (8 H, q, aromatic). Anal. ($C_{28}H_{44}N_2O_9$) C, H, N.

cr(O_7) was prepared by oxygen oxidation of **3** (n = 1) in the presence of base. **3** (n = 1) (5.0 g, 0.01 mol) and potassium *tert*-butoxide (4.83 g, 0.043 mol) are dissolved in 300 mL of a mixed solvent of dimethyl sulfoxide and *tert*-butyl alcohol (80:20 in volume). A dry air stream was introduced into the reaction mixture and the reaction was continued for 4 h at room temperature. The precipitate (unknown: polymer?) was removed by filtration, the filtrate being concentrated in vacuo. The residue was diluted with water and then extracted by chloroform. The chloroform layer was washed with water and evaporated in vacuo; the residue was subjected to isolation by TLC (silica gel and ethanol–chloroform (1:10 v/v)): mp 87–91 °C; yield 10.5%; IR (KBr disk) $\nu_{N=N}$ 1590, ν_{Ar-O-C} 1050, ν_{C-O-C} 1120–1160 cm^{-1}; mass spectrum, *m/e* 460 (M^+); NMR($CDCl_3$) δ 3.02, 3.37, 3.75, 4.40 (8 H, 8 H, 4 H, 4 H, respectively, all m, OCH_2), 7.10 (4 H, d, 3,3′-H of azobenzene), 7.82 (4 H, d, 2,2′-H of azobenzene). Anal. ($C_{24}H_{32}N_2O_7$) C, H, N.

cr(O_8): mp 77–80 °C; yield 6.3%; IR (KBr disk) $\nu_{N=N}$ 1580, ν_{Ar-O-C} 1050, ν_{C-O-C} 1120–1160 cm^{-1}; mass spectrum *m/e* 504 (M^+); NMR($CDCl_3$) δ 3.28, 3.55, 3.81, 4.40 (12 H, 8 H, 4 H, 4 H, respectively, all m, OCH_2), 7.13 (4 H, d, 3,3′-H of azobenzene), 7.89 (4 H, d, 2,2′-H of azobenzene). Anal. ($C_{26}H_{36}N_2O_8$) C,H,N.

cr(O_9): mp 60–63 °C; yield 5.0%; IR (KBr disk) $\nu_{N=N}$ 1600, ν_{Ar-O-C} 1050, ν_{C-O-C} 1120–1130 cm^{-1}; mass spectrum, *m/e* 548 (M^+); NMR($CDCl_3$) δ 3.38, 3.60, 3.88, 4.35 (16 H, 8 H, 4 H, 4 H, respectively, all m, OCH_2), 7.10 (4 H, d, 3,3′-H of azobenzene), 7.90 (4 H, d, 2,2′-H of azobenzene). Anal. ($C_{28}H_{40}N_2O_9$) C, H, N.

Method of Solvent Extraction. The method of solvent extraction was described previously.[2,3] The details of the workup conditions are recorded in footnotes to Table II. A 500-W high-pressure Hg lamp with a color glass filter (330 nm < λ < 380 nm) was used for the trans-to-cis photoisomerization. As described in the Results and Discussion section, the thermal recovery of the trans forms in the dark was slow, so that the change in the cis/trans ratio during the workup time was neglected.

Kinetic Measurements. The method for the measurement of the thermal cis-to-trans isomerization rates was also described previously.[2,3] The reaction was monitored at 30 °C by following the appearance of the absorption maximum of the trans isomers. To enhance the accuracy and the reproducibility, we measured the absorbance for a few seconds per minute in order to obviate the trans-to-cis isomerization by light from the spectrophotometer. Further details are recorded in the captions to Figures 3–5.

Results and Discussion

Comments on The Synthesis Methods and Spectral Properties. The synthesis of azobenzoenophane-type crown ethers was one of the most difficult experiments we have ever experienced. Before we reached the synthesis route described in the Experimental Section, we had tried several synthetic methods: (i) the reaction of 4,4′-dihydroxyazobenzene and $Cl(CH_2CH_2O)_7CH_2CH_2Cl$ in the preaence of base, (ii) the reaction of 4-hydroxy-4′-(9-hydroxy-1,4,7-trioxanonyl)azobenzene and $Cl(CH_2CH_2O)_3CH_2CH_2Cl$ in the presence of base, (iii) cyclization of 4-(9-hydroxy-1,4,7-trioxanonyl)-4′-(12-chloro-1,4,7,10-tetraoxadodecyl)azobenzene in the presence of base, (iv) the reductive coupling of **2** in the presence of zinc powder and potassium hy-

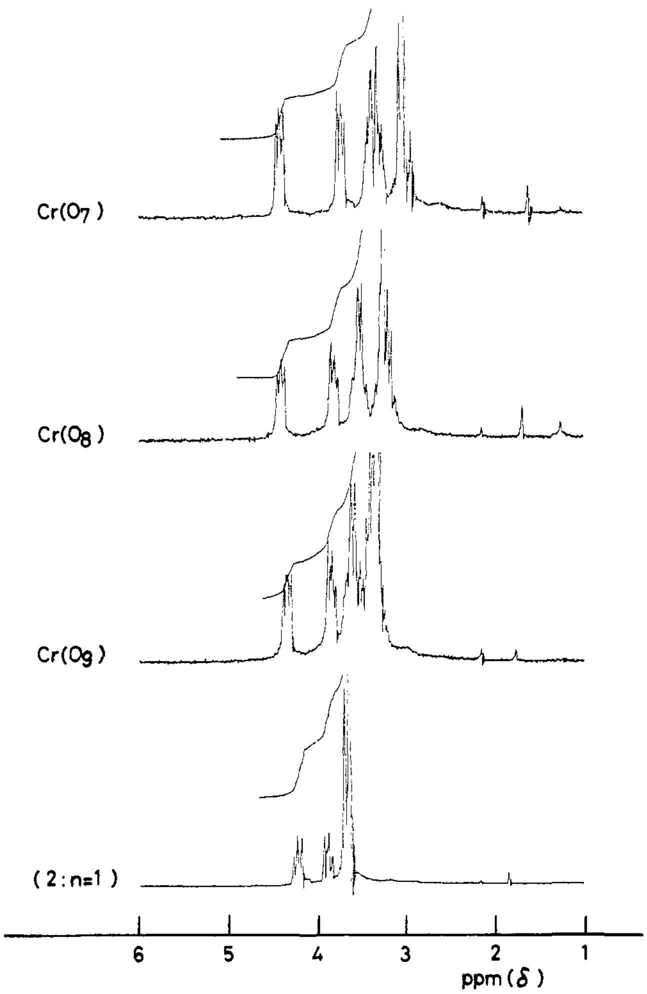


Figure 1. ^{1}H NMR spectra of the polyoxyethylene chains (solvent, $CDCl_3$).

droxide,[3] and (v) the oxidative coupling of **3** in pyridine in the presence of Cu(I) under an oxygen stream.[14] These methods were all unsuccessful, resulting in viscous polymers. On the other hand, the cyclization of **3** in the presence of potassium *tert*-butoxide under an oxygen stream (method vi) gave the target molecules in 5–10% yields. The difference can be explained as follows. In methods i–iii, the reactions involve the cyclization between 4,4′ positions of trans azobenzenes. In method iv, the primary cyclization product of the reductive coupling is presumed to be *trans*-azoxybenzene, which is subsequently reduced to azo- and hydrazobenzene. Therefore, one cannot expect the template effect of metal ions on the cyclization step since the polyoxyethylene chain is almost linearly extended. In contrast, the reaction of method vi proceeds via a hydrazobenzene intermediate which is able to adopt, like *cis*-cr(O_{n+6}), a cyclic structure involving the polyoxyethylene loop. Thus, the success by method vi is probably due to the template effect of K^+. In method v, copper cannot be a good template metal for the polyoxyethylene loop.

In the NMR measurements, we found that the chemical shift of center ethylene protons moves to higher magnetic field (Figure 1). For example, acyclic precursors such as **2** (n = 1) and **3** (n = 1) have three different types of protons at about 3.7, 3.8, and 4.1 ppm in the ratio of 16 H:4 H:4 H. These are assigned respectively to protons of the center four ethylenes, methylene protons of terminal ethylenes far from the benzene ring (Ar–O–C–CH_2), and methylene protons of terminal ethylenes near the benzene ring (Ar–O–CH_2). In cr(O_7), a new peak appears at higher magnetic field (3.02 ppm), and the ratio of the peak intensity of four different protons is 8 H:8 H:4 H:4 H (from high to low magnetic field). The result indicates that the protons of center two ethylenes are affected by magnetic anisotropy of the azobenzene. Similarly, cr(O_8) and cr(O_9) have new peaks at higher magnetic field, the ratio of the peak intensity in their spectra being 12 H and 16 H, respectively. Therefore, the protons of the center three (in cr(O_8)) and four (in cr(O_9)) ethylenes are subjected to the ring current of the azobenzene. Also significant is the fact that the smaller the azobenzenophane ring, the greater the shift to higher magnetic field. These NMR spectral results provide important information for the structure and the conformation of the azobenzenophane-type crown ethers.

Table I. Properties of Azobenzenophane-Type Switched-On Crown Ethers[a]

crown	λ_{max} (ϵ_{max}), nm in *o*-dichlorobenzene	cis %[b]	$k \times 10^5$,[c] s^{-1}
cr(O_7)	363 (25 200)	71.5	2.65
cr(O_8)	363 (24 200)	72.2	3.08
cr(O_9)	361 (27 600)	73.6	3.16

[a] At 30 °C, *o*-dichlorobenzene. [b] Cis % of the azobenzene moiety at the photostationary state. [c] First-order rate constant for the thermal cis-to-trans isomerization in *o*-dichlorobenzene/*n*-butyl alcohol = 86.8:13.2 v/v.

The absorption bands of the trans isomers in *o*-dichlorobenzene decreaed rapidly by UV light irradiation and reached photostationary states within 30 s. The observable thermal cis-to-trans isomerization took place in the dark at 30 °C and the spectra of the trans isomers were regenerated quantitatively after 1 day. The cis-to-trans isomerization was further accelerated by irradiation with a 200-W tungsten lamp through a color glass filter ($\lambda > 460$ nm); for example, 100% *trans*-cr(O_9) was regenerated by the 2-min irradiation. Hence, one may consider that trans–cis isomerism of the azobenzophanes is completely reversible. The cis at the photostationary state and the first-order rate constants (k) for the thermal cis-to-trans isomerization are recorded in Table I. Inspection of the CPK model suggests that the isomerization of cr(O_7) may be a little more restricted than that of cr(O_8) and cr(O_9). Examination of Table I reveals, however, that cis % and k are scarcely different among three azobenzenophanes.

Solvent Extraction of Alkali Metal Cations. Inspection of the CPK models of cr(O_{n+6}) suggests that (i) the smallest ethylene number to form a phane structure between 4,4′ positions of *trans*-azobenzene is six (i.e., cr(O_7)), (ii) the polyoxyethylene chain of the trans homologues with 6 ≤ ethylene number ≤ 10 is extended linearly on the azobenzene ring, (iii) there is no (or little) significant ant steric restriction in the course of the cis–trans isomerization, and (iv), most importantly, the number of oxygen atoms which can contribute to the formation of a crown-like ring in the cis homologues is "total oxygen number" −2 (i.e., two phenolic oxygen atoms); for example, *cis*-cr(O_7) forms a polyoxyethylene loop analogous to 15-crown-5.

The results of solvent extraction of alkali metal cations with cr(O_7)–cr(O_9) (Table II) indicate that the predictions based on the CPK model building are almost reasonable. As expected, the trans isomers totally lack the affinity for metal ions, whereas the cis isomers extracted considerable amounts of metal ions to the organic phase (*o*-dichlorobenzene :*n*-butyl alcohol = 80:20 in volume). The maximum extractability (Ex %) was observed for Na^+ in *cis*-cr(O_7), K^+ in *cis*-cr(O_8), and Rb^+ in *cis*-cr(O_9) (Figure 2). The result implies that the spheric recognition patterns, typical of crown ethers in solution, are well reproducible in the azobenzenophanes with the polyoxyethylene chain. The ion selectivity supports the previous conjecture that the ring sizes of *cis*-cr(O_7), *cis*-cr(O_8), and *cis*-cr(O_9) would correspond to those of 15-crown-5, 18-crown-6, and 21-crown-7, respectively. cis-cr(O_7) cannot bind large alkali metal cations, whereas *cis*-cr(O_9) can bind, although not strongly, both small and large alkali metal cations. Probably, *cis*-cr(O_9) has a characteristic of so-called "induced fit" to small alkali metal cations.

The foregoing results establish that in azobenzenophanes with a polyoxyethylene chain the crown-like loop appears and disappears in response to the photoirradiation, and the "all-or-nothing" change

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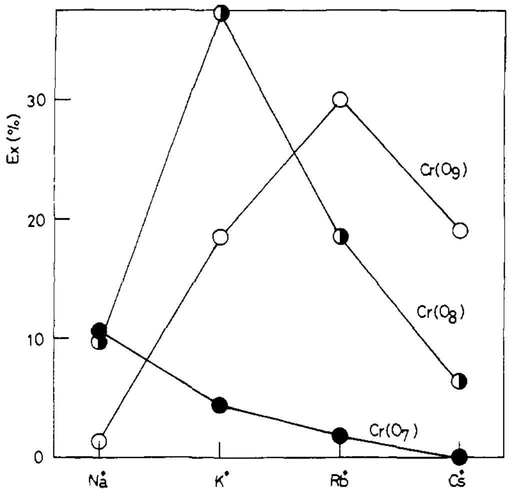


Figure 2. Extractability (Ex %) of the cis isomers calculated by $Ex_{cis} = 100Ex_{light}/cis$ %.

Table II. Extraction of Alkali Metal Picrates with Azobenzenophane-Type Crown Ethers[a]

crown		cis %[b]	picrate ion extracted (Ex %)			
			Na^+	K^+	Rb^+	Cs^+
$cr(O_7)$	trans (dark)		0	0	0	0
	light	83	8.8	3.7	1.5	~0
	cis[c]		10.6	4.4	1.8	~0
$cr(O_8)$	trans (dark)		0	0	0	0
	light	80	7.7	29.8	14.8	5.0
	cis[c]		9.6	37.3	18.5	6.3
$cr(O_9)$	trans (dark)		0	0	0	0
	light	68	0.9	12.6	20.4	12.9
	cis[c]		1.3	18.5	30.0	19.0

[a] Organic phase: *o*-dichlorobenzene/*n*-butyl alcohol = 80:20 v/v, [crown] = 3.00×10^{-3} M. Aqueous phase: [MOH] = 0.30 M; [picrate] = 1.00×10^{-4} M. [b] Cis % of the extractants used under the "light" conditions. [c] $Ex_{cis} = 100Ex_{light}/cis$ %.

in the ion-binding ability is effected.

Influence of Complexed Metal Ions on Photoisomerization and Thermal Isomerization. In previous papers of this series,[3,5] we have reported that the photostationary state and the rate of the thermal cis-to-trans isomerization of azobis(benzocrown ether)s are affected by complexed metal ions. The novel phenomena are rationalized in terms of the "tying" of two crown ethers by a sandwiched metal cation. A similar effect is expected for the present azobenzenophane-type crown ethers: if *cis*-$cr(O_{n+6})$ forms a stable complex with a metal cation, the rate of the thermal isomerization would be suppressed and the concentration of cis % at the photostationary state would be enhanced. As illustrated in Figures 3–5, alkali metal cations exhibit a considerable inhibitory effect on the thermal isomerization. On the other hand, the cis % at the photostationary state scarcely change in the presence of alkali metal cations. Probably, the present metal–crown complexes are not so stable as to affect the photoisomerization process. Yamashite et al.[7] also observed an inhibitory effect on the thermal isomerization and no effect on the photoisomerization for the anthracene-containing phane-type crown ethers. These samples imply that the sandwich-type 1:2 metal/crown complexes of *cis*-azobis(benzocrown ether)s[3,5] are very stable, for the significant effect on the photoisomerization process has been observed only for this class of photoresponsive crown ethers.

Examination of Figures 3–5 reveals that (i) Rb^+ and Cs^+ exhibit no inhibitory effect on the thermal isomerization of *cis*-$cr(O_7)$; (ii) similarly, Cs^+ exhibits no inhibitory effect on that of *cis*-$cr(O_8)$; (iii) although the thermal isomerization of *cis*-$cr(O_9)$ is inhibited by all alkali metal cations, the magnitude of the inhibitory effect is relatively small; (iv) the metal cations which provide the maximum inhibitory effect are Na^+ for *cis*-$cr(O_7)$, K^+ for *cis*-$cr(O_8)$, and Rb^+ for *cis*-$cr(O_9)$. The results again demonstrate that the polyoxyethylene loops of the cis isomers have spheric recognition patterns. The ion selectivity of the cis isomers is well correlated with that in solvent extraction (vide supra); that is,

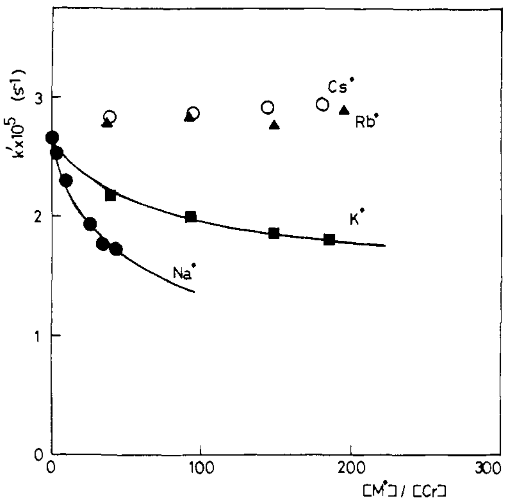


Figure 3. First-order rate constant for the thermal cis-to-trans isomerization of *cis*-$Cr(O_7)$: 30 °C, *o*-dichlorobenzene/*n*-butyl alcohol = 86.8:13.2 v/v, [$cr(O_7)$] = 2.40×10^{-5}M. Dodecanoic acid salts were used for alkali metal cations.

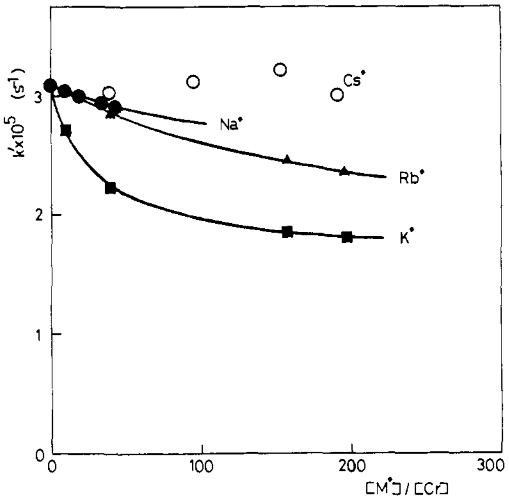


Figure 4. First-order rate constant for the thermal cis-to-trans isomerization of *cis*-$cr(O_8)$. [$cr(O_8)$] = 2.40×10^{-5} M. The reaction conditions are recorded in Figure 3.

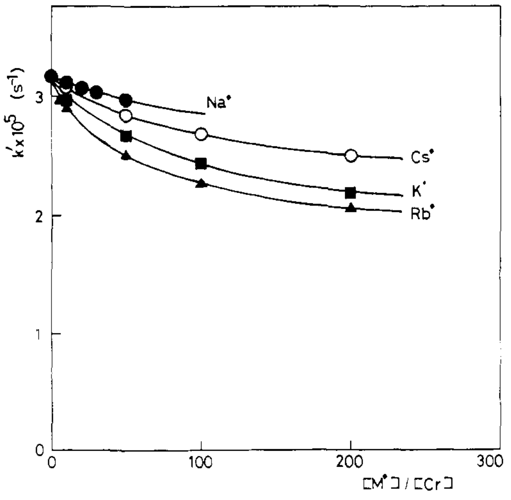


Figure 5. First-order rate constant for the thermal cis-to-trans isomerization of *cis*-$cr(O_9)$. [$cr(O_9)$] = 2.57×10^{-5} M. The reaction conditions are recorded in Figure 3.

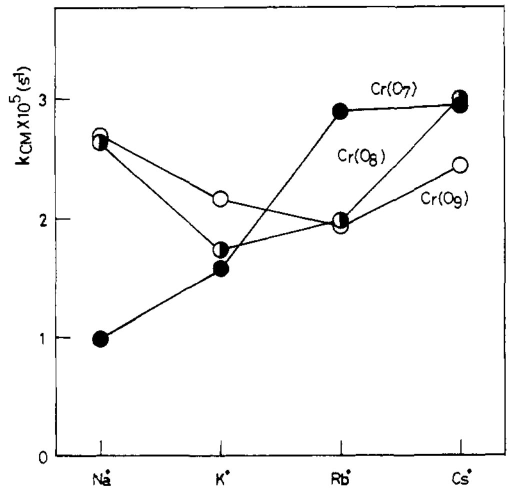
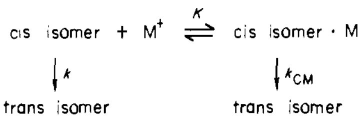


Figure 6. First-order rate constant for the thermal cis-to-trans isomerization of the cis isomer-metal complexes.

Scheme II



cis-cr(O_{n+6}) behaves like a crown ether with $n + 4$ oxygen atoms.

From the curvatures of the k vs. [M$^+$] plots one can estimate the association constants (K) with the cis isomers and the first-order rate constants (k_{CM}) for the thermal isomerization of the cis isomer-metal complexes. In Scheme II, k and k_{CM} are the first-order rate constants in the absence of and in the complex with metal cation, respectively.

In the presence of excess M$^+$ over cis isomer, the relation in Scheme II is expressed by a kinetic equation which has a linear correlation between $k/(k - k')$ and $[M^+]^{-1}$:

$$\frac{k}{k - k'} = \frac{1}{qK[M^+]} + \frac{1}{q} \tag{1}$$

where k' is the observed first-order rate constant in the presence of metal cations and $q = 1 - (k_{CM}/k)$.[15] Plots of the rate data according to eq 1 gave good straight lines with correlative coefficient better than 0.99. We estimated the slope ($= 1/qK$) and the intercept ($= 1/q$) from least-squares computation and determined K and k_{CM}. The results are summarized in Table III.

Table III shows that the ion selectivity observed for K and k_{CM} is well correlated with that expected from Ex %. For example, the metal cations which provide the maxium association constants (and also the maximum inhibitory effects) are Na$^+$ for *cis*-cr(O$_7$), K$^+$ for *cis*-cr(O$_8$), and Rb$^+$ for *cis*-cr(O$_9$). Thus, plots of k_{CM} vs. alkali metal cations (Figure 6) are approximately in reverse to the plots of Ex % vs. alkali metal cations (Figure 2). The result suggests that three parameters (Ex %, K, and k_{CM}) are governed by a single factor, that is, the affinity of the polyoxyethylene loops with metal ions.

The magnitude of the metal affinity may be expressed more quantitatively by a difference of free energy of activation between k and k_{CM} ($\Delta\Delta G^\ddagger$). The largest $\Delta\Delta G^\ddagger$ value is observed for the Na$^+$-*cis*-cr(O$_7$) complex, and the $\Delta\Delta G^\ddagger$ value for the K$^+$-*cis*-cr(O$_8$) complex is second largest (Table III). On the other hand, $\Delta\Delta G^\ddagger$ values for *cis*-cr(O$_9$) are relatively small and less ion selective. The result suggests again that the ion-binding of *cis*-cr(O$_9$) has the characteristic of "induced-fit".

Table III. Association Constants (K), Rate Constants (k_{CM}) for the Thermal Cis-to-Trans Isomerization of cis-Form Metal Complexes, and Template Energy ($\Delta\Delta G^\ddagger$)

crown	metal	K, M^{-1}	$10^5 k$, s^{-1}	$10^5 k_{CM}$, s^{-1}	$\Delta G^\ddagger$, kcal/mol	$\Delta\Delta G^\ddagger$,[a] kcal/mol
cr(O$_7$)	none		2.65		24.1	
	Na$^+$	1370		0.99	24.7	−0.6
	K$^+$	787		1.58	24.4	−0.3
	Rb$^+$	*b*		*b*	*b*	0
	Cs$^+$	*b*		*b*	*b*	0
cr(O$_8$)	none		3.08		24.0	
	Na$^+$	576		2.64	24.1	−0.1
	K$^+$	1590		1.74	24.4	−0.4
	Rb$^+$	348		1.98	24.3	−0.3
	Cs$^+$	*b*		*b*	*b*	0
cr(O$_9$)	none		3.16		24.0	
	Na$^+$	562		2.69	24.1	−0.1
	K$^+$	948		2.17	24.2	−0.2
	Rb$^+$	1140		1.94	24.3	−0.3
	Cs$^+$	710		2.44	24.2	−0.2

[a] $\Delta\Delta G^\ddagger = \Delta G^\ddagger$ (from k) $- \Delta G^\ddagger$ (from k_{CM}). [b] The association is too small to analyze with eq 1.

The thermal cis-to-trans isomerization of azobenzenes has been a controversial problem since two opposing mechanisms have been proposed: the reaction may proceed either via a rotational mechanism involving rotation about the N=N bond or an inversion mechanism involving flip-flop of one of the nitrogen atoms.[16-19] Recent studies support the mechanism where the thermal isomerization proceeds via an inversion intermediate unless the azobenzene has push-pull substituents (e.g., couple of amino and nitro groups).[20-23] Since the present azobenzenophanes have no such push-pull substituents, the isomerization most probably proceeds via an inversion intermediate in which one of the nitrogen atoms must employ an sp hybrid orbital. The CPK model predicts that the polyoxyethylene chain is almost linearly extended at the inversion transition state, and one can hardly expect interaction with alkali metal cations. If so, the transition states are all similar apart from the kind of metal ions. Hence, $\Delta\Delta G^\ddagger$ is the additional energy required to disrupt the metal-loop interaction when the loop disappears. In other words, $\Delta\Delta G^\ddagger$ would correspond to the stabilization energy due to the "template effect" of metal ions.

Concluding Remarks.

To design the photoresponsive system with the "all-or-nothing" change, one must select large geometrical change without steric hindrance. In fact, however, these are quite opposing factors. The distance between the 4,4′ positions of azobenzene changes largely in response to photoirradiation, and the "all-or-nothing" change would be effected if one can link these two positions without accompanying steric hindrance. The present paper demonstrates that the azobenzenophane-type crown ethers completely satisfy these prerequisites and act as "switched-on" crown ethers which exhibit both the "all-or-nothing" change in the ion-binding ability and the reversible photoresponsiveness. We are now attempting the application of the novel crown functions to the membrane systems.

Acknowledgment. We thank Professors T. Kunitake and M. Takagi for helpful discussions and Miss K. Ueda for technical assistance. This research was supported by a grant from the Ministry of Education of Japan (No. 57470068).

Registry No. **1** (n = 1), 52559-90-7; **2** (n = 1), 84649-38-7; **2** (n = 2), 84649-39-8; **2** (n = 3), 82959-74-8; **3** (n = 1), 84649-40-1; **3** (n = 2), 84649-41-2; **3** (n = 3), 82959-75-9; *cis*-cr(O$_7$), 84649-42-3; *cis*-cr(O$_8$),

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84649-43-4; *cis*-cr(O_9), 82959-76-0; *cis*-cr(O_7)Na complex, 84649-46-7; *cis*-cr(O_7)K complex, 84649-47-8; *cis*-cr(O_7)Rb complex, 84680-87-5; *cis*-cr(O_7)Cs complex, 84649-48-9; *cis*-cr(O_8)Na complex, 84649-49-0; *cis*-cr(O_8)K complex, 84649-50-3; *cis*-cr(O_8)Rb complex, 84649-51-4; *cis*-cr(O_8)Cs complex, 84649-52-5; *cis*-cr(O_9)Na complex, 84680-88-6; *cis*-cr(O_9)K complex, 84680-89-7; *cis*-cr(O_9)Rb complex, 84680-90-0; *cis*-cr(O_9)Cs complex, 84680-91-1; *trans*-cr(O_7), 84649-44-5; *trans*-cr(O_8), 84649-45-6; *trans*-cr(O_9), 82959-73-7.

Temperature Dependence of the Photochemistry of Aryl Alkyl Ketones[1]

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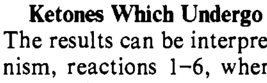
Received May 7, 1982

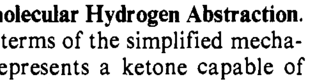
Abstract: The photochemistry of several phenyl alkyl and *p*-anisyl alkyl ketones has been examined using laser flash photolysis and conventional quantum yield techniques. The methoxy-substituted ketones show higher activation energies ($\Delta E_a \sim 3$ kcal mol^{-1}) for the Norrish type I and type II processes. It is concluded that both reactions are adiabatic processes occurring from the triplet $n\pi^*$ surface. In the case of *p*-methoxy-substituted ketones the upper $n\pi^*$ surface is reached from the low-lying $\pi\pi^*$ triplet, with the energy gap between both states reflected as an increase in the activation energy.

The photochemistry of alkyl and phenyl alkyl ketones has been extensively studied, and the main factors which determine the rate constants for the type I cleavage and type II intramolecular hydrogen abstraction are now well characterized.[5-18] In the case of phenyl alkyl ketones, their photobehavior for a given alkyl group is determined by the relative positions of the $n\pi^*$ and $\pi\pi^*$ excited states.[8,10,19-26] In particular, Wagner et al.[20,21] have carried out extensive studies of the effect of ring substituents on the type II photoreaction of aryl alkyl ketones in order to understand how interactions between nearby excited triplets affect chemical reactivity; they concluded that *p*-methoxy ketones react primarily from equilibrium concentrations of the higher $n\pi^*$ triplet state. Data on the type I cleavage of ketones with lower $\pi\pi^*$ excited triplets have been obtained only employing *p*-methoxyphenyl *tert*-butyl ketone at a single temperature.[9] The results obtained also suggest that the reaction takes place from the $n\pi^*$ triplet surface. In order to have a more complete understanding of the reactivity of $\pi\pi^*$ excited triplets, we have carried out a detailed study of the temperature dependence of the photochemistry of phenyl alkyl and *p*-anisyl alkyl ketones which react via both type I and type II photoprocesses. The measurements were carried out employing conventional steady-state and laser flash photolysis techniques.

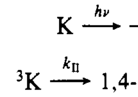
The ketones studied have the structures I–IV.



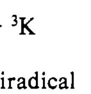
I



II



III



IV

a, X = H, b, X = CH_3O

Results

Ketones Which Undergo Intramolecular Hydrogen Abstraction. The results can be interpreted in terms of the simplified mechanism, reactions 1–6, where K represents a ketone capable of undergoing the Norrish type II reaction.

$$K \xrightarrow{h\nu} \rightarrow {}^3K \tag{1}$$

$$^3K \xrightarrow{k_{II}} \text{1,4-biradical} \tag{2}$$

$$^3K \xrightarrow{k_d} K \text{ (or products)} \tag{3}$$

$$\text{1,4-biradical} \rightarrow \text{fragmentation} \tag{4}$$

$$\text{1,4-biradical} \rightarrow \text{cyclization} \tag{5}$$

$$\text{1,4-biradical} \rightarrow K \tag{6}$$

k_d includes the interaction with the solvent and/or solvent impurities. Both the steady-state photolysis method and the direct detection of the triplet state have shortcomings when applied to these ketones. The kinetics of triplet decay are controlled by (k_{II} + k_d); thus an estimation of k_d is required to obtain the value of k_{II}. Further, the presence of the relatively long-lived 1,4-biradical can interfere with the direct determination of the triplet lifetime. In those cases where the corresponding activation energies (E_{II} and E_d) are substantially different, the first difficulty can be solved by working over an extended temperature range.

The second difficulty (biradical interference or too short a lifetime)[27] can be overcomed by using an indirect approach in the

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