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Changes of Cation Binding Ability of Cyclic Alkene Enhanced by Photosensitized Isomerization from *cis* to *trans* Form

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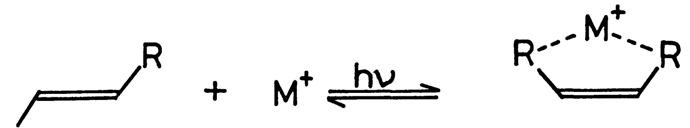
A cyclic polyether (**1**) showed enhanced cation binding ability by *trans* to *cis* photoisomerization in the presence of benzophenone. The results were explained in terms of the profitable structural arrangement of oxygen atoms of the polyether linkage in *cis*-**1**.

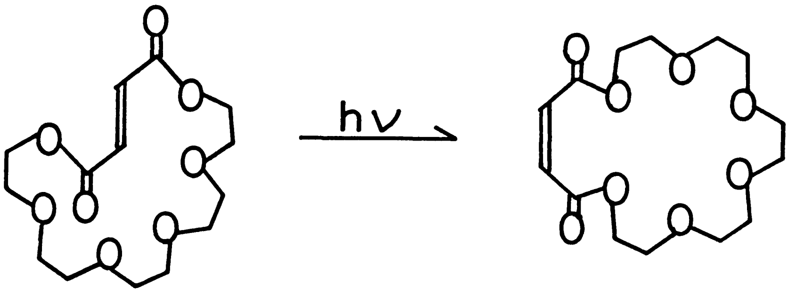
Switching of various molecular functions is a current topic.1,2) In connection with photocontrol of metal ion binding, many photoresponsive crown ethers have been prepared.3-5) The basic idea for the switching is mostly photo-assisted binding of a metal ion by two ligands as shown in scheme 1.



Scheme 1.

R: Polyether unit

We report here a new photosensitive system **1**, in which oxygen atoms change their positions by photosensitized fumarate to maleate isomerization in its cyclic linkage.6)



trans-**1**

cis-**1**

trans-**1** was synthesized by esterification reaction of fumaryl chloride (1.6 g, 10.5 mmol) with pentaethylene glycol (2.5 g, 10.5 mmol) in dichloromethane (100 ml) containing triethylamine (2.3 g, 22.7 mmol) at room temperature for 24 h. Treatment of the crude product with active charcoal followed by column chlomatography on silica-gel with dichlomethane:ethanol (15:1) gave trans-**1** (0.40 g, 12 %) as a colorless oil. Found : C, 52.54 ; H, 7.21%. Calcd for $C_{14}H_{22}O_8$: C, 52.83 ;H, 6.97%. ^{1}H-NMR ($CDCl_3$) δ 3.5-3.9 (16H, m), 4.2-4.5 (4H, m), 6.9 (2H, s). IR $\nu_{C=O}$ 1720 cm^{-1} (ester).

In dichloromethane, trans-**1** (1×10^{-2} $mol\cdot dm^{-3}$) was isomerized by photoirradiation in the presence of benzophenone. Photoirradiation was performed with 500 W xenon lamp using Pyrex glass filter (270 nm $< \lambda$). The maleate (cis-**1**) formation was followed by ^{1}H-NMR spectroscopy, the peak positions of fumarate and maleate being 6.9 ppm and 6.3 ppm, respectively. A photostationary state was achieved by photoisomerization within 150 min, the cis content being 90%. This value is in agreement with that reported for benzophenone-sensitized photoisomerization of diethyl fumarate and diethyl maleate.[7)]

Table 1 shows the results of liquid-liquid extraction of alkali metal ions. According to the extraction data, the photoirradiated sample of **1** exhibits larger cation binding ability than trans-**1**, the extents of photoinduced enhancement ranging from 2.9-fold for Cs^+ to 4.0-fold for Na^+.

Table 1. Liquid-liquid extraction by **1**[a)]

	Alkali metal picrate extracted (%)			
	Na^+	K^+	Rb^+	Cs^+
trans-**1**	6	7	9	8
photoirradiated-**1**[b)]	24	27	30	23

a) Organic phase (2 ml of dichloromethane) : [**1**]=1×10^{-3} $mol\cdot dm^{-3}$; [Benzophenone]=1×10^{-3} $mol\cdot dm^{-3}$. Aqueous phase (2 ml of water) : [Alkali metal picrate]=1×10^{-5} $mol\cdot dm^{-3}$; [Alkali metal chloride] =1 $mol\cdot dm^{-3}$.

b) cis-**1** content: 90% .

Table 2 shows the results of liquid-membrane transport. The experiments were performed using a U-tube shown in Fig. 1. The velocities of the picrate transport from source phase (a) to receiving phase (b) were obtained by measuring the absorbance changes of the receiving phase. The data reveal that the velocity was remarkably accelerated by photoirradiation, ranging from 2.7-fold for Cs^+ to 6.6-fold for Na^+. The above results may be explained in terms of the photoinduced structural change from less suitable form (trans-1) to more suitable one (cis-1) for cation binding. The examination of molecular models indicates that cis-1 can take a structure similar to usual crown ethers, while trans-1 is incapable of forming an appropriate cavity for metal-ion accommodation.

Table 2. Alkali metal cation transport by 1

	Alkali metal cation transported (10^{-7} mol·dm^{-3}·h^{-1})			
	Na^+	K^+	Rb^+	Cs^+
trans-1	7	11	10	22
photoirradiated-1[a)]	46	72	53	59

a) cis-1 content: 90% .

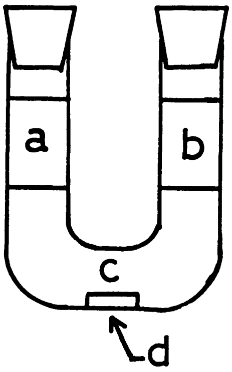


Fig. 1. Schematic representation of the U-tube for transport experiments.

a(source phase): 1×10^{-3} mol·dm^{-3} of alkali metal picrate solution (5ml), diameter; 17 mm.
b(receiving phase): water (5ml), diameter, 17 mm.
c(membrane phase): 7.5×10^{-4} mol·dm^{-3} of 1 and 7.5×10^{-4} mol·dm^{-3} of benzophenone solution (20ml of dichloromethane), diameter, 17 mm.
d: Stirring bar

Unlike the azobenzene-containing photoresponsive crown ethers, the present system is stable in both trans and cis forms, so it may be used for construction of unique memory materials, in which metal species are preferentially deposited into the photoirradiated parts.

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In contrast to the present system, their system is virtually the same as the two-ligand systems.

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