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Synthesis and Properties of a New Photoresponsive Crown Ether with a Fluorescent Stilbene-cap[1]

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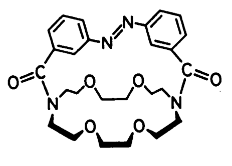
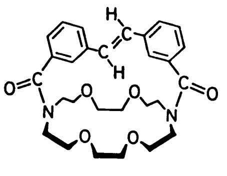
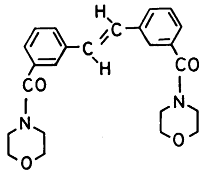
Synopsis. A new photoresponsive crown ether **2** with a stilbene-cap was synthesized. The crown *trans*-**2** could extract Li^+ and Na^+ into the organic phase, and UV light irradiation which produces photoisomerized *cis*-**2** enhanced the extractability. Thus, the stilbene-cap induces the conformational change in the crown ether moiety by photoirradiation.

Macrocyclic polyethers contain intramolecular cavities delineated with molecular segments capable of binding cations. Previously, we synthesized an azobenzene-capped crown ether *trans*-**1**[2,3] which was one of the early examples of photoresponsive crown ethers.[4—6] In **1**, the azobenzene-cap undergoes photoinduced reversible interconversion between the trans- and cis-configuration, and thus the three-dimensional cavity structure changes in response to photoirradiation. Here, we wish to address a new photoresponsive crown ether, **2** which has a photoresponsive stilbene-cap on the N_2O_4 crown ether. We used **3** as a reference compound.


trans-1


trans-2


trans-3

Experimental

Materials. Stilbene-3,3′-dicarboxylic acid was prepared according to the method of Toland *et al.*[7] This was treated with thionyl chloride to yield 3,3′-bis(chloroformyl)stilbene: mp 179—181 °C, yield 73%. Found: C, 62.64; H, 3.30%. Calcd for $C_{16}H_{10}O_2Cl_2$: C, 62.98; H, 3.30%.

The crown *trans*-**2** was prepared in chlorobenzene from equimolar amounts of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane(N_2O_4 crown) and 3,3′-bis(chloroformyl)stilbene according to the high-dilution method. The basic operation is similar to that described for the preparation of *trans*-**1**.[3] The raw product was subjected to the TLC separation (silica gel, chloroform–ethyl acetate (1:1 v/v) and finally recrytallized from benzene: mp 193.5—195 °C, yield 8.8%. IR (KBr) $\nu_{C=O}$ 1625 cm^{-1} and $\nu_{C=C}$ 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.08—3.35 (8H, m), 3.65—4.32 (16H, m), 7.07 (2H, s), and 7.41—7.58 (8H, m); M^+ (*m/z*) 494. Found: C, 68.02; H, 7.02; N, 5.63%. Calcd for $C_{28}H_{34}N_2O_6$: C, 68.00; H, 6.93; N, 5.66%.

The compound *trans*-**3** was prepared by treatment of 3,3′-bis(chloroformyl)stilbene with excess morpholine in chlorobenzene. Recrystallization from benzene gave white crystals: mp 198—200 °C, yield 93%. IR (KBr) $\nu_{C=O}$ 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.68 (16H, s), 7.07 (2H, s), and 7.20—7.51 (8H, m). Found: C, 70.28; H, 6.47; N, 6.83%. Calcd for $C_{24}H_{26}N_2O_4$: C, 70.92; H, 6.45; N, 6.89%.

Results

Absorption Spectra, Fluorescence Spectra, and Photoisomerization. Absorption maxima of *trans*-**2** and *trans*-**3** were 290 nm (ε_{max} 21900) and 297 nm (ε_{max} 26800) in acetonitrile at 30 °C, respectively. The light-mediated trans-to-cis isomerization was carried out by using a 100 W high-pressure Hg-lamp through a color glass filter (330 nm$<\lambda<$380 nm). The lamp and a N_2-substituted Thunberg cuvette containing 1-butanol solution of *trans*-**2**(or *trans*-**3**)(1.12×10^{-5} M (1 M=1 mol dm^{-3})) were immersed in a thermostated (30 °C) water bath. The absorption maxima decreased with photoirradiation time and finally reached equilibrium values: *cis*%'s at the photostationary state were 52% for **2** and 48% for **3**. The time-dependence could be approximated by a first-order rate equation with $r>0.99$: k_1 (first-order rate constant)= 3.25×10^{-3} s^{-1} for **2** and 1.15×10^{-3} s^{-1} for **3**. In the trans-to-cis photoisomerization of **1** and its reference compound, 3,3′-bis-(morpholinocarbonyl)azobenzene, we could not find a significant rate difference between these two compounds.[3] The larger rate constant for **2** relative to **3** suggests, therefore, that *trans*-**2** in the initial state should be somewhat destabilized.

Fluorescence maxima of *trans*-**2** and *trans*-**3** appeared at 373 nm and 365 nm in acetonitrile at 30 °C, respectively (excitation 320 nm). The absolute fluorescence intensity of *trans*-**3** was greater by about 4-fold than that of *trans*-**2**.[8] We found, interestingly, that fluorescence emission of *trans*-**2** is quenched by LiI and NaI more efficiently than that of *trans*-**3** (Fig. 1). Such a large difference was not observed for KI, RbI, and CsI. As described below, Li^+ and Na^+ are bound to the crown ether moiety of *trans*-**2**, while other alkali metal ions are not. The finding suggests, therefore, that the metal-crown interaction is responsible for the efficient fluorescence quenching observed for *trans*-**2**. The efficiency of fluorescence quenching was similar between Li^+ and Na^+ in spite of the efficient binding of Li^+ relative to Na^+ (*vide post*). This reason is not clear yet. Conceivably, the quenching can occur through the weak metal-crown interaction in dehydrated acetonitrile.

Two-Phase Solvent Extraction of Alkali Metal Ions. The ionophoric functions of *trans*-**2** and *cis*-**2** were evaluated through solvent extraction. We used the mixture containing 44% *cis*-**2** for solvent extraction. First, we employed extraction conditions used for **1**[3]

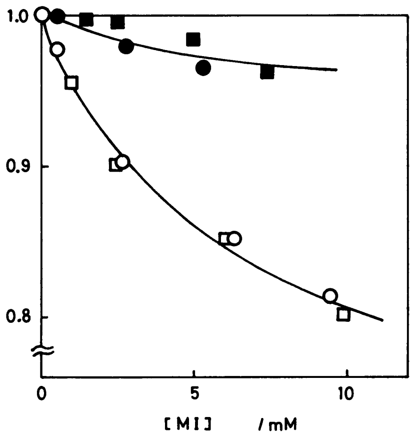


Fig. 1. Relative fluorescence intensity of *trans*-**2** and *trans*-**3** (3.20×10^{-5} M) plotted against the concentration of alkali iodides. ○: *trans*-**2**+LiI, □: *trans*-**2** +NaI, ●: *trans*-**3**+LiI, ■: *trans*-**3**+NaI.

Table 1. Solvent extraction of alkali picrates from water to the organic phase (*o*-dichlorobenzene: 1-butanol = 50 : 50 v/v) at 30 °C$^{a)}$

Metal	Ex(%)	
	trans-**2**	Photoirradiated-**2**$^{b)}$
Li^+	11	13
Na^+	4	11
K^+	1	6
Rb^+	(<1)	(<1)
Cs^+	(<1)	(<1)

a) Organic phase: [**2**] = 2.70×10^{-3} M. Aqueous phase: [MCl] = 0.50 M, [MOH] = 7.00×10^{-3} M, [picric acid] = 5.00×10^{-3} M. b) *Cis*-form 44%.

but none of alkali metal salts was extracted into the benzene phase. This indicates that the stilbene-cap has some negative effect on the metal-binding ability of the N_2O_4 crown moiety. We thus changed the extraction conditions as recorded in a footnote to Table 1.

Examination of Table 1 reveals that in contrast to the ion selectivity of *trans*-**1** for Na^+ and K^+,[3] *trans*-**2** shows the highest selectivity for Li^+ having the smallest ion radius. It extracts K^+ only by 1%. Interestingly, the extractabilities for Na^+ and K^+ are efficiently improved by photoirradiation. The finding suggests that apparently, the size of the crown ether ring is enlarged upon photoinduced *trans*-to-*cis* isomerization of the stilbene-cap.

Discussion

The crown *trans*-**2**, in comparison with *trans*-**1** or *trans*-**3**, can be characterized by (i) low yield in the high-dilution synthesis, (ii) low fluorescence intensity, (iii) fast light-mediated trans-to-cis isomerization, and (iv) specific ion-selectivity for Li^+. These results consistently suggest that *trans*-**2** should be destabilized by some steric strain. Two possible explanations emerge. According to X-ray crystallographic studies and theoretical calculations,[9,10] the C=C bond of *trans*-stilbene (1.453 Å) is longer than the N=N bond of *trans*-azobenzene (1.23 Å) by 0.22 Å. One possible explanation is, therefore, that the distance between two carbonyl groups of 3,3′-bis(chloroformyl)stilbene is a little too longer to intramolecularly react with 7-*N* and 16-*N* of N_2O_4 crown. If so, this explanation can readily accommodate the low yield and the inferior ion-binding ability of *trans*-**2**. N_2O_4 crown ether itself shows the K^+-selectivity.[11] The previous X-ray studies on an analogue of *trans*-**1** showed that the crown ether ring is oval-shaped,[12] and the N_2O_4 crown ether moiety in *trans*-**1** showed the Na^+-selectivity.[3] The result implies that when the crown ether is stretched and enforced to adopt the oval-shaped conformation, the crown ether ring would favorably bind smaller alkali metal ions. The Li^+-selectivity observed for *trans*-**2** suggests that the N_2O_4 crown of *trans*-**2** is more stretched than that of *trans*-**1**.

Examination of Corey-Pauling-Koltun (CPK) molecular models of *trans*-**2** offers another possible explanation: one of the olefin protons in the CH=CH bond, which are absent in the azo linkage, deeply penetrates into the crown cavity and seems to interfere metal-binding. The low metal-affinity of *trans*-**2** relative to *trans*-**1** may be related to this steric disadvantage. On the other hand, CPK models of *cis*-**2** show that the olefinic protons in the *cis*-stilbene-cap exist apart from the crown ether plane. This favorable configuration would largely improve the metal-binding ability (especially, for large metal ions).

In conclusion, the present study indicates that the N_2O_4 crown with a fluorescent stilbene-cap acts as a new photoresponsive crown ether. Furthermore, the stilbene unit which apparently seems to be sterically equivalent to the azobenzene unit brought forth several marked differences in ion-binding ability, isomerization process, *etc.* The efforts to modify *trans*-**2** as a metal-selective fluorescence probe are now continued in this laboratory.

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