

On-Off-switched Crown Ether-Metal Ion Complexation by Photoinduced Intramolecular Ammonium Group 'Tail-biting'

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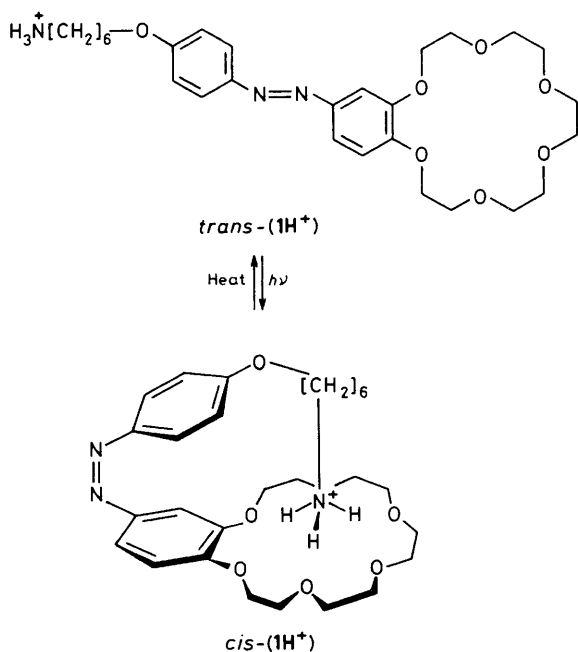
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A new photoresponsive crown ether with an ammonium-group tail was synthesised in which the ion-binding ability changes in response to photoirradiation because of competitive intramolecular 'tail-biting' in the *cis*-form produced by photoisomerisation.

Cations are known to be transported through membranes by synthetic macrocyclic polyethers as well as by antibiotics.¹⁻³ In particular, polyether antibiotics such as nigericin and monensin interconvert between the cyclic and acyclic forms in the membrane phase, a property which is believed to be responsible for rapid ion-transport through the membranes. This phenomenon suggests that reversible interconversion between two states can be responsible for the high efficiency of carrier molecules. Azobenzene exhibits photoinduced reversible *cis-trans* isomerism. The geometrical change involved is so large that it has frequently been employed as a

photoantenna for photocontrol of functional molecules such as crown ethers,⁴⁻⁸ cyclodextrins,⁹ and polymers.^{10,11}

Recently, Nakatsuji *et al.*¹² reported a new synthetic ionophore having a crown ether ring and an attached ammonium ion capable of intramolecular complexation. Herein we report on a new photoresponsive crown ether (**1H**⁺) with an ammonium-group tail. This 'tail-biting' crown ether is designed so that the crown ether ring can bind intramolecularly to the ammonium group only when it is photoisomerised to the *cis*-form. The Corey-Pauling-Koltun (CPK) model of (**1H**⁺) shows that the hexamethylene spacer



group is of sufficient length for the ammonium group to reach the crown ether ring plane in *cis*-(**1H**⁺). We have found that (i) the ion affinity of (**1H**⁺) is markedly reduced by u.v. irradiation, (ii) the rate of the thermal isomerisation of *cis*-(**1H**⁺) to *trans*-(**1H**⁺) is slower than that of the free amino analogue [*cis*-(**1**) → *trans*-(**1**)], and (iii) the rate is accelerated by addition of K⁺ ions.

trans-(**1**) was prepared by condensation of 4'-(4''-hydroxyphenylazo)benzo-18-crown-6 and *N*-(6-bromohexyl)phthalimide followed by treatment with hydrazine [*trans*-(**1H**⁺)Cl⁻ m.p. 180–181.5 °C]. The product gave satisfactory elemental analyses and mass (*M*⁺ 531), n.m.r., and i.r. spectra.

The photoisomerisation was carried out using a 500 W high-pressure Hg lamp with a colour glass filter (330 < λ < 380 nm). In *o*-dichlorobenzene (containing 20 vol% *n*-butyl alcohol), the isomerisation reached a photostationary state after 30 s [*cis*-(**1**) 72.5%, (**1H**⁺) 79.6%]. The initial spectra of the *trans*-forms [λ_{max}, (**1**) 370 nm, (**1H**⁺) 368 nm] were quantitatively regenerated thermally or by irradiation with a 200 W tungsten lamp.

The first-order rate constants (*k*₁) for the thermal *cis*-*trans* isomerisation were determined in *o*-dichlorobenzene (containing 20 vol% *n*-butyl alcohol) at 30 °C by following the increase in the absorption bands of the *trans*-forms. We found that *k*₁ for *cis*-(**1H**⁺) (1.59 × 10⁻⁵ s⁻¹) is significantly smaller than that for *cis*-(**1**) (2.77 × 10⁻⁵ s⁻¹). Figure 1 shows the influence of added K⁺ ion (as potassium dodecanoate) on the isomerisation rates. It can be seen that *k*₁ for *cis*-(**1H**⁺) increases with increasing K⁺ concentration and reaches a maximum value (3.1 × 10⁻⁵ s⁻¹) at [K⁺] ca. 10⁻⁴ M. The thermal isomerisation can be suppressed when interaction between azo-substituents exists.⁶ The K⁺-dependent rate acceleration is due to competitive complexation of K⁺ to the crown ether ring. Therefore, our results can be rationalised in terms of intramolecular complexation of the terminal ammonium group with the crown ether ring in *cis*-(**1H**⁺). Interestingly, *k*₁ for *cis*-(**1**) also increased, although to a smaller extent, with increasing K⁺ concentration. The rate constants of simple *cis*-azobenzenes were unaffected by the addition of

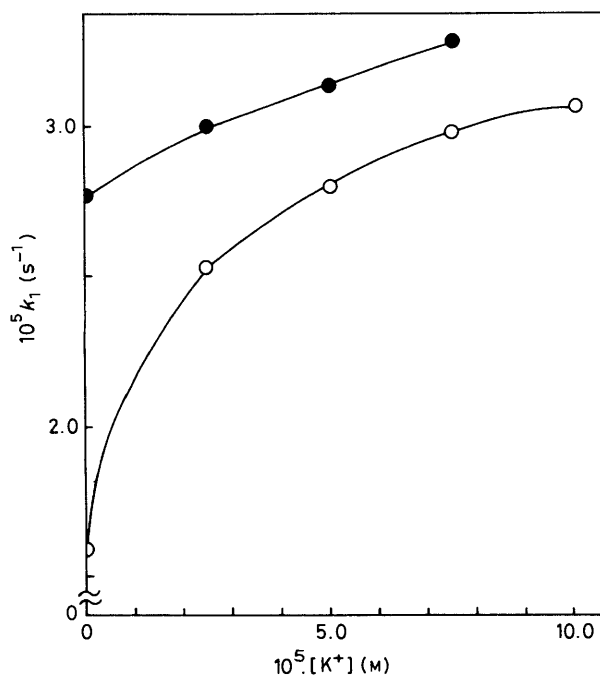


Figure 1. First-order rate constants (*k*₁) for the thermal *cis*-*trans* isomerisation plotted against the K⁺ concentration; 30 °C, *o*-dichlorobenzene : *n*-butyl alcohol 8:2 v/v, [(**1H**⁺)] or [(**1**)] 1.14 × 10⁻⁵ M. ● = *cis*-(**1**); ○ = *cis*-(**1H**⁺).

Table 1. Extraction of alkali toluene-*p*-sulphonates (M⁺Ts⁻) with (**1H**⁺) and (**1**) at 30 °C.^a

Metal ion	10 ⁴ ·[M ⁺] in the organic phase			
	<i>trans</i> -(1H ⁺)	<i>cis</i> -(1H ⁺) ^b	<i>trans</i> -(1) ^c	<i>cis</i> -(1) ^{b,c}
Li ⁺	0.09	0.01	0.12	0.03
K ⁺	0.22	0.04	1.16	0.39
Rb ⁺	0.30	0.17	0.66	0.43
Cs ⁺	0.38	0.24	0.60	0.63

^a Aqueous phase (3 ml): [M⁺Ts⁻] 0.0102 M, pH 4.7 with 10 mM phosphate. Organic phase (*o*-dichlorobenzene : *n*-butyl alcohol 45 : 55 v/v, 3 ml): [(**1**) or [(**1H**⁺)] 1.88 × 10⁻⁴ M. ^b 82.9% *cis*-Form by irradiation with a 500 W high-pressure Hg lamp (330 < λ < 380 nm) for 10 min. ^c Aqueous phase: [M⁺Ts⁻] 0.0102 M, [MOH] 10 mM.

such low concentrations of K⁺ ion. The result suggests that the amino group in *cis*-(**1**) also interacts with the crown ether ring. In fact, there are many precedents that amino groups form stable complexes with 18-crown-6 and its analogues.¹³

The photoresponsive ionophoric properties of (**1**) were evaluated through solvent extraction of alkali toluene-*p*-sulphonates. Usually, the extractions can be conveniently determined by spectroscopic measurement of the counter-anion (A⁻) extracted into the organic phase. However, this method was unsuitable in the present system because A⁻ could be extracted not only as M⁺A⁻ but also as (**1H**⁺)A⁻. We thus measured the concentration of M⁺ in the organic phase by atomic absorption spectroscopy. While this method has merit in that the metal concentrations are obtained directly, practically it is somewhat inconvenient and the concentration of Na⁺ could not be determined because of subtle changes in the Na⁺ background owing to the glassware

used.† The results are summarised in Table 1. Under the extraction conditions, leaks of (1) or (1H⁺) into the aqueous phase could be neglected.

Examination of Table 1 reveals that (i) *trans*-(1) exhibits the highest affinity for K⁺, as expected for an 18-crown-6 analogue, (ii) the extracted ion concentrations decrease in the order *trans*-(1) > *trans*-(1H⁺) > *cis*-(1H⁺), and (iii) the most conspicuous change is seen for K⁺ ion where *cis*-(1H⁺) shows very small ion affinity. The lower extraction ability of *trans*-(1H⁺) relative to *trans*-(1) can be attributed to intermolecular complexation of the ammonium group in *trans*-(1H⁺), but the further decrease observed in *cis*-(1H⁺) relative to *trans*-(1H⁺) could be rationalised in terms of intramolecular complexation of the ammonium tail by the crown ether ring. In other words, the intramolecular-complexed ammonium-group tail in the *cis*-configuration is capable of ejecting K⁺ ion from the crown ether ring.

The less prominent changes with Rb⁺ and Cs⁺ relative to K⁺ may be explained as follows: K⁺ (best-fit metal ion) nests in the benzo-18-crown-6 ring while the larger Rb⁺ and Cs⁺ perch on its edge, so that the interaction with Rb⁺ and Cs⁺ would be less affected by the ammonium group bound (probably) to the opposite side of the crown ether ring.

† We attempted solvent extraction into quartz vessels but could not stabilise the background to a satisfactory level.

S. S. thanks the Ministry of Education of Japan for a Grant-in-aid for Scientific Research.

Received, 6th February 1984; Com. 154

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