

## Photoresponsive Crown Ethers. Part 6.† Ion Transport Mediated by Photoinduced *cis*—*trans* Interconversion of Azobis(benzocrown ethers)

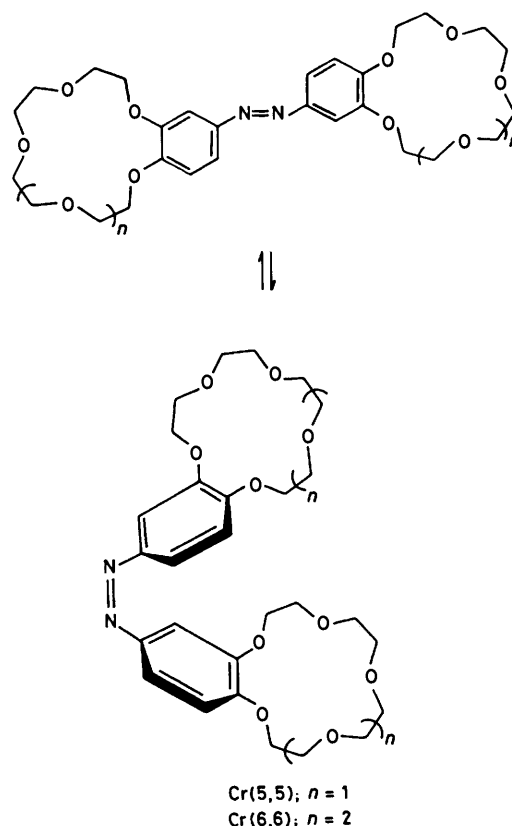
Seiji Shinkai,\* Kazuyoshi Shigematsu, Michiko Sato, and Osamu Manabe\*

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

In the light-driven membrane (*o*-dichlorobenzene) transport with azobis(benzo-15-crown-5) (Cr(5,5)), we have found that by alternate irradiation with u.v. light and visible light the rate of K<sup>+</sup> is considerably accelerated while the rates of Na<sup>+</sup> and Rb<sup>+</sup> transport are accelerated only a little. This result indicates that efficient light-driven ion-transport is achieved with moderately stable complexes (e.g. K[*cis*-Cr(5,5)]) rather than with unstable (Na[*cis*-Cr(5,5)]) or very stable (Rb[*cis*-Cr(5,5)]) complexes. The rate ratio of K<sup>+</sup> versus Na<sup>+</sup> independent transport in the dark ([M<sup>+</sup>] in the aqueous phase/[Cr(5,5)] in the membrane phase = 80) was only 2.7-fold, whereas that in competitive ion transport ([M<sup>+</sup>] in the aqueous phase/[Cr(5,5)] in the membrane phase = 1 000) was enhanced up to 27-fold. In competitive ion transport, the rates of Na<sup>+</sup> and K<sup>+</sup> transport were both suppressed by u.v. light irradiation and significantly enhanced under alternate irradiation with u.v. and visible light. Since the photoirradiation effect is similar to that of K<sup>+</sup> transport, it is proposed that the rate of competitive ion transport is primarily governed by the affinity of K<sup>+</sup> for the carrier molecule.

Cations are known to be transported through membranes by synthetic macrocyclic polyethers as well as by antibiotics.<sup>1-6</sup> In particular, some polyether antibiotics such as nigericin and monensin feature the interconversion between the cyclic and the acyclic form in the membrane phase, a feature which is believed to lead to the high functionality of these antibiotics as ion carriers.<sup>1-7</sup> For example, the interconversion to the acyclic form is responsible for the rapid release of ions from the ion-carrier complex in the membrane phase to the second (OUT) aqueous phase. The object of our investigation has been to mimic such an enforced ion release by using members of the crown ether family.<sup>8-11</sup> Recently we and others have reported that the complexation abilities of photoresponsive crown ethers and ligands which combine within a molecule both a crown ether (or a ligand) and a photosensitive chromophore change in response to photoirradiation.<sup>8-10,12,13</sup> These results suggest that light energy is a promising candidate to control the change in the binding ability of crown ethers and that light-driven ion transport across membranes may be effected with the aid of photoresponsive crown ethers.

In previous publications of this series,<sup>10,14</sup> we have reported that azobis(benzo-15-crown-5) [Cr(5,5)] and azobis(benzo-18-crown-6) [Cr(6,6)] isomerise photo(u.v.)-chemically from *trans* to *cis* and thermally from *cis* to *trans* and that the *cis*-forms extract relatively large alkali-metal cations more favourably than the corresponding *trans*-forms. This is due to the formation of intramolecular 1 : 2 cation/crown complexes as (1). In the liquid (*o*-dichlorobenzene) membrane transport of alkali picrates, however, we found that u.v. light irradiation rather retards the rate of K<sup>+</sup> transport.<sup>10</sup> The result indicates that the ion-release to the OUT aqueous phase from (1) in the membrane phase is involved in the rate-limiting step and that the rate of thermal *cis*-to-*trans* isomerisation occurring in the membrane phase is too slow to enforce the ion release to the OUT aqueous phase. There is therefore the new possibility that the rate of K<sup>+</sup> transport would be further speeded up if the *cis*-to-*trans* isomerisation is accelerated by visible light. This we have found to be so, the *cis*-to-*trans* isomerisation being facilitated by visible light ( $\lambda > 460$  nm) irradiation and the rate of K<sup>+</sup> transport being accelerated by alternate ir-

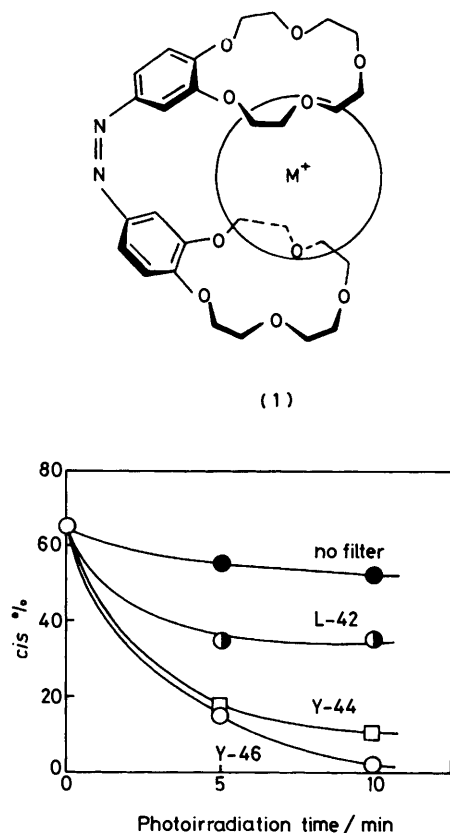


radiation with u.v. and visible light. This phenomenon constitutes a new system for light-driven ion-transport through a liquid membrane.

### Results and Discussion

*Acceleration of the cis-to-trans Isomerisation Rate by Visible Light.*—It is well-known that *trans*-azobenzene derivatives are readily isomerised to *cis*-forms by u.v. light irradiation and *cis*-azobenzene derivatives to *trans*-forms by visible

† Part 5, S. Shinkai, T. Minami, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, 1982, **104**, 1967.

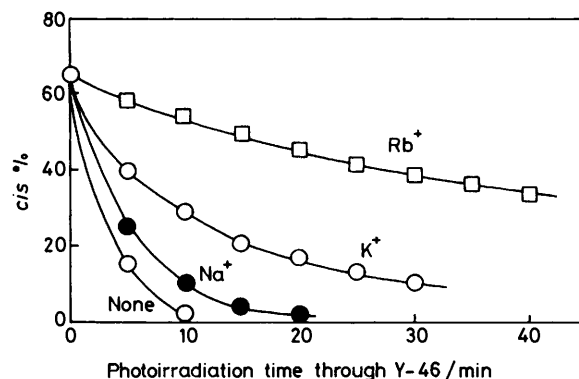


**Figure 1.** Rate of photoinduced *cis*-to-*trans* isomerisation at 30 °C.  $[\text{Cr}(5,5)] = 4.00 \times 10^{-5} \text{M}$  in *o*-dichlorobenzene : *n*-butyl alcohol = 86.8 : 13.2 by volume. Filters: L-42 ( $\lambda > 420 \text{ nm}$ ), Y-44 ( $\lambda > 440 \text{ nm}$ ), Y-46 ( $\lambda > 460 \text{ nm}$ ).

light irradiation.<sup>15-18</sup> This phenomenon is associated with the fact that *trans*-forms have  $\pi-\pi^*$  bands in the u.v. region (ca. 330 nm) and *cis*-forms have  $n-\pi^*$  bands in the visible region (ca. 430 nm). On the other hand, the  $\pi-\pi^*$  bands of *trans*-Cr(5,5) and *trans*-Cr(6,6) shift to longer wavelength (377 nm) and overlap partially with the  $n-\pi^*$  bands of the *cis*-forms. As a result the photostationary states attained by u.v. and visible light irradiation are both 'intermediary'.

We sought the optimum wavelength to induce the efficient photoisomerisation using a number of coloured glass filters.\* The best for *trans*-to-*cis* isomerisation in *o*-dichlorobenzene-*n*-butyl alcohol (86.8 : 13.2, v/v) was found to be a UV-36 filter ( $\lambda > 360 \text{ nm}$ ), which affords 65% *cis*-Cr(5,5) at the photostationary state. The *cis* percentage further increased in the presence of metal ions (72% for  $[\text{C}_{11}\text{H}_{23}\text{CO}_2\text{K}]/[\text{Cr}(5,5)] = 4.0$  and 100% for  $[\text{C}_{11}\text{H}_{23}\text{CO}_2\text{Rb}]/[\text{Cr}(5,5)] = 4.0$ , where  $[\text{Cr}(5,5)] = 4.00 \times 10^{-5} \text{M}$ ). The visible-light-mediated *cis*-to-*trans* isomerisation in the absence of metal ion is illustrated in Figure 1. When a 500-W high-pressure Hg-lamp was used without a filter, a new photostationary state with 52% *cis*-Cr(5,5) was attained. When the solution was irradiated through shorter wavelength cut-off filters, the rate of the *cis*-to-*trans* isomerisation was further accelerated; specifically, the light through a Y-46 filter ( $\lambda > 460 \text{ nm}$ ) is capable of completing the *cis*-to-*trans* isomerisation within 10 min.

\* In a previous paper,<sup>10</sup> we examined the influence of visible light irradiation on the *cis*-to-*trans* isomerisation by using monochromatic light from a Xe lamp of a fluorescence spectrophotometer but failed to find a wavelength which gave useful results.



**Figure 2.** Rate of photoinduced *cis*-to-*trans* isomerisation at 30 °C in the presence of alkali-metal cations.  $[\text{Cr}(5,5)] = 4.00 \times 10^{-5} \text{M}$  in *o*-dichlorobenzene : *n*-butyl alcohol = 86.8 : 13.2 by volume,  $[\text{M}^+ \text{ (as dodecanoic acid salt)}] = 2.00 \times 10^{-4} \text{M}$ . Filter: Y-46 ( $\lambda > 460 \text{ nm}$ ) was used.

**Table 1.** Rates of thermal isomerisation and visible-light-mediated isomerisation of Cr(5,5)<sup>a</sup>

| Additive<br>(conc. mM) <sup>b</sup> | $10^4 k/\text{s}^{-1}$ |                            | $\frac{k_{\text{visible}}}{k_{\text{dark}}}$ |
|-------------------------------------|------------------------|----------------------------|--|
|                                     | Dark                   | Visible light <sup>c</sup> |  |
| None                                | 18.5                   | 57.8                       | 3.1  |
| Na <sup>+</sup> (0.20)              | 16.0                   | 31.5                       | 2.0  |
| K <sup>+</sup> (0.20)               | 7.30                   | 14.2                       | 1.9  |
| Rb <sup>+</sup> (0.20)              | 2.02                   | 2.72                       | 1.3  |

<sup>a</sup> 30 °C, *o*-dichlorobenzene : *n*-butyl alcohol = 86.8 : 13.2 by volume,  $[\text{Cr}(5,5)] = 4.00 \times 10^{-5} \text{M}$ . <sup>b</sup> Dodecanoic acid salts were used for alkali-metal cations. <sup>c</sup> Y-46 Filter ( $\lambda > 460 \text{ nm}$ ).

We next examined the influence of added alkali-metal cations on the rate of the visible-light-mediated *cis*-to-*trans* isomerisation. We have previously reported that the rate of the thermal *cis*-to-*trans* isomerisation is efficiently suppressed by alkali-metal cations owing to the formation of sandwich-type 1 : 2 cation/crown complexes (1), the inhibitory effect on *cis*-Cr(5,5) being the order of  $\text{Rb}^+ > \text{Cs}^+ > \text{K}^+ > \text{Na}^+$ .<sup>10,14</sup> As shown in Figure 2 and Table 1, the rate of the isomerisation was retarded in the order of 'no additive' < Na<sup>+</sup> < K<sup>+</sup> < Rb<sup>+</sup>. When comparing the rate of the visible-light-mediated isomerisation with that of the thermal one (Table 1), the visible light ( $\lambda > 460 \text{ nm}$ ) accelerates the rate by 3.1-fold in the absence of metal ion, whereas acceleration of only 1.3-fold is effected in the presence of Rb<sup>+</sup>. The finding implies that the formation of stable sandwich-type complexes, which is an important driving-force to extract cations from the initial (IN) aqueous phase to the membrane phase, is not favourable to the visible-light-mediated *cis*-to-*trans* isomerisation.

**Light-driven Ion-transport across an *o*-Dichlorobenzene Membrane.**—Light-driven ion-transport was carried out by using a U-tube immersed in a thermostatted (30 °C) water-bath. In the transport experiments with Cr(5,5), we found that the irradiation of the membrane phase by light from a Hg-lamp (no filter) retards the rate of K<sup>+</sup> transport (Table 2).<sup>10</sup> The phenomenon is explicable in that ion-release from the membrane phase to the second (OUT) aqueous phase becomes rate-limiting owing to the formation of the stable 1 : 2 K<sup>+</sup>/crown complex with *cis*-Cr(5,5). In other words, the thermal *cis*-to-*trans* isomerisation is not fast enough to eliminate ion-release from the rate-limiting step. As shown in

Table 2. Rates of ion transport across an *o*-dichlorobenzene liquid membrane (30 °C) <sup>a</sup>

| Crown    | Metal ion       | Rate of ion transport ( $\mu\text{mol h}^{-1}$ ) |                          |                    |  |       |       |
|----------|-----------------|--|--------------------------|--------------------|--|-------|-------|
|          |                 | Dark   | Hg-lamp irradiation with |                    |  |       |       |
|          |                 |  | No filter <sup>b</sup>   | UV-36 <sup>b</sup> | UV-36 $\rightleftharpoons$ Y-46 <sup>c</sup> |       |       |
| Method A | Method B        | Method C   |                          |                    |  |       |       |
| Cr(5,5)  | Na <sup>+</sup> | 0.176  |                          | 0.301              | 0.170  |       |       |
| Cr(5,5)  | K <sup>+</sup>  | 0.476 <sup>d</sup>                               | 0.255 <sup>d</sup>       | 0.431              | 0.861  |       | 1.22  |
| Cr(5,5)  | Rb <sup>+</sup> | 0.244  |                          | 0.401              | 0.459  | 0.302 | 0.558 |
| Cr(6,6)  | Cs <sup>+</sup> | 0.680  |                          | 0.987              | 1.06   |       |       |

<sup>a</sup> *o*-Dichlorobenzene phase: [Cr] =  $2.00 \times 10^{-4}$  M. IN aqueous phase: [MOH] =  $1.60 \times 10^{-2}$  M, [picrate] =  $4.00 \times 10^{-3}$  M. OUT aqueous phase: water. <sup>b</sup> The *o*-dichlorobenzene phase was photoirradiated for 5 min at intervals of 30 min. <sup>c</sup> UV-36 and Y-46 were used alternatively. Method A: UV-36 (5 min)  $\rightarrow$  dark (10 min)  $\rightarrow$  Y-46 (5 min)  $\rightarrow$  dark (10 min)  $\rightarrow$  repeated. Method B: UV-36 (5 min)  $\rightarrow$  Y-46 (25 min)  $\rightarrow$  repeated. Method C: the half volume in contact with the IN aqueous phase and that in contact with the OUT aqueous phase were photoirradiated alternatively through UV-36 and Y-46, respectively, for 5 min at intervals of 30 min. <sup>d</sup> Cited from ref. 10.

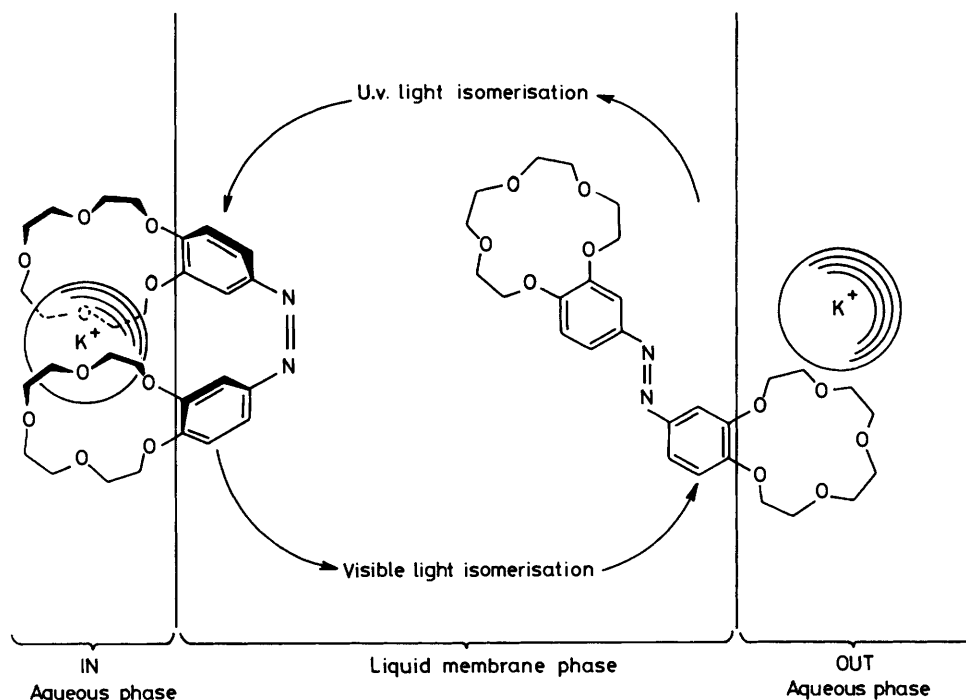


Figure 3. Schematic representation of ion-transport mediated by alternative irradiation of u.v. and visible light.

Table 2, alternate irradiation of the membrane by u.v. light (UV-36 filter,  $\lambda > 360$  nm) and visible light (Y-46 filter,  $\lambda > 460$  nm) significantly accelerated the rate of K<sup>+</sup> transport (method A). This result implies that the visible-light-mediated *cis*-to-*trans* interconversion of the carrier facilitates ion-release to the OUT aqueous phase. The rate was further enhanced when the half-volume of the membrane in contact with the IN aqueous phase was irradiated by u.v. light and that in contact with the OUT aqueous phase was irradiated by visible light (method C). Hence, the transport phenomenon may be illustrated schematically as Figure 3.

Interestingly, the result of Na<sup>+</sup> transport provided a contrasting photoirradiation effect, the rate being enhanced by u.v. light irradiation and retarded by alternate irradiation with u.v. and visible light (Table 2). This result shows that whilst the rate-limiting step for u.v. light irradiation is ion-extraction from the IN aqueous phase to the membrane phase, visible light irradiation decreases the concentration of *cis*-Cr(5,5) in the membrane phase and leads to rate retardation. In other

words, the rate of Na<sup>+</sup> transport is simply related to the concentration of *cis*-Cr(5,5). A similar rate enhancement by u.v. light irradiation has been observed for azobis(crown ethers) which form less stable 1 : 2 cation/crown sandwich-type complexes.<sup>19</sup> We consider that in less-stable complexes the release of cations can occur from the *cis*-formed complexes, whereas in stable complexes such as K[*cis*-Cr(5,5)] the release of cations occurs favourably from the *trans*-formed complexes. Thus, the *cis*-to-*trans* interconversion is a prerequisite to ion-release in the latter case.

It has been established that bis(crown ethers) and polymeric crown ethers are capable of binding relatively large alkali-metal cations owing to the formation of 1 : 2 cation/crown sandwich-type complexes.<sup>20-22</sup> Our previous investigation on the rate of the thermal *cis*-to-*trans* isomerisation and solvent extraction suggests that *cis*-Cr(5,5) and *cis*-Cr(6,6) form their most stable complexes with Rb<sup>+</sup> and Cs<sup>+</sup>, respectively.<sup>10,14</sup> The stability is also ascribed to the formation of 1 : 2 cation/crown complexes. Probably, ion-extraction from the IN

Table 3. Rates of competitive ion transport of Na<sup>+</sup> and K<sup>+</sup> with Cr(5,5) and ratios of K<sup>+</sup> versus Na<sup>+</sup> transport (30 °C)<sup>a</sup>

| Treatment of membrane phase                                | Rate of competitive ion transport<br>( $\mu\text{mol h}^{-1}$ ) |                | $v_{\text{K}^+}/v_{\text{Na}^+}$ |             |
|--|---|----------------|----------------------------------|-------------|
|  | Na <sup>+</sup>   | K <sup>+</sup> | Independent <sup>d</sup>         | Competitive |
| Dark   | 0.012   | 0.325          | 2.70                             | 27.1        |
| Light through UV-36 <sup>b</sup>                           | 0.007   | 0.163          | 1.43                             | 23.3        |
| Light through UV-36 $\rightleftharpoons$ Y-46 <sup>c</sup> | 0.049   | 0.740          | 5.06                             | 15.1        |

<sup>a</sup> *o*-Dichlorobenzene phase: [Cr(5,5)] =  $5.00 \times 10^{-5}\text{M}$ . IN aqueous phase: [Na<sup>+</sup>] = [K<sup>+</sup>] =  $5.00 \times 10^{-2}\text{M}$  (as M<sub>2</sub>CO<sub>3</sub>), [picrate] =  $4.00 \times 10^{-3}\text{M}$ . OUT aqueous phase: water. <sup>b</sup> 5 min at intervals of 30 min. <sup>c</sup> UV-36 (5 min)  $\rightarrow$  dark (10 min)  $\rightarrow$  Y-46 (5 min)  $\rightarrow$  dark (10 min)  $\rightarrow$  repeated. <sup>d</sup> Cited from Table 2: note the difference in the transport conditions that [M<sup>+</sup>]/Cr(5,5) is 80 in the independent transport and 1 000 in the competitive transport.

aqueous phase to the membrane phase is rate-limiting in the transport of Rb<sup>+</sup> and Cs<sup>+</sup>. The rate acceleration observed for Rb[Cr(5,5)] and Cs[Cr(6,6)] under u.v. light irradiation could be rationalised in terms of the improved extraction ability of the *cis*-forms. As shown in Figure 2, the visible-light-mediated *cis*-to-*trans* isomerisation of the Rb[*cis*-Cr(5,5)] complex is considerably slower owing to the stability of the complex. Therefore, the irradiation of the membrane phase by visible light scarcely accelerates the rate of Rb<sup>+</sup> (or Cs<sup>+</sup>) transport, unlike that of K<sup>+</sup> transport.

In early studies on the mediation of ion-transport by crown ethers and cryptands, Kobuke *et al.*<sup>23</sup> and Kirch and Lehn<sup>24</sup> independently established that the best carrier for ion transport is a ligand that gives a moderately stable rather than a very stable complex; the generality of this rule has recently been confirmed by Lamb *et al.*<sup>25</sup> It is of interest that the light-driven ion-transport system provides a similar conclusion. Thus, for less-stable complexes such as Na[Cr(5,5)], the rate is proportional to the concentration of the *cis*-formed carrier, irradiation by visible light which efficiently mediates *cis*-to-*trans* isomerisation retarding the transport rate. In contrast, for very stable complexes such as Rb[Cr(5,5)], the extraction is facilitated by u.v. light, which mediates *trans*-to-*cis* isomerisation, but the stable metal-*cis*-form complexes cannot be isomerised rapidly by visible light. Hence, the most efficient light-driven ion-transport is realised in moderately stable complexes such as K[Cr(5,5)].

**Competitive Ion Transport.**—Considerable interest has centred around the competitive ion transport of Na<sup>+</sup> and K<sup>+</sup> because of its practical importance.<sup>1,2,23,26,27</sup> In the present study ([M<sup>+</sup>] in the IN aqueous phase/[Cr(5,5)] in the membrane phase = 80), we observed a 2.7-fold rate difference between K<sup>+</sup> and Na<sup>+</sup> independent transport in the dark (Table 3). The difference was enhanced up to 27-fold in the competitive ion transport where the concentration of Cr(5,5) in the membrane phase was lowered ([M<sup>+</sup>] in the IN aqueous phase/[Cr(5,5)] in the membrane phase = 1 000). The result implies that in the competitive transport K<sup>+</sup> is predominantly bound to, and carried by, *trans*-Cr(5,5) in contrast to the small difference in the independent transport.

Under u.v. light irradiation, K<sup>+</sup> forms a moderately stable complex with *cis*-Cr(5,5), and ion-release from the membrane phase to the OUT aqueous phase is involved in the rate-limiting step. It is expected, therefore, that K<sup>+</sup> ions are accumulated in the membrane phase and a significant fraction of the carriers is occupied by K<sup>+</sup>. Na<sup>+</sup> Transport scarcely occurs with u.v. light irradiation (0.007  $\mu\text{mol h}^{-1}$ ).

When the system is irradiated with u.v. light and visible light alternately, the K[*cis*-Cr(5,5)] complex releases K<sup>+</sup> to the OUT aqueous phase as a result of interconversion to *trans*-Cr(5,5). Hence, the concentration of the free carriers

increases in the membrane phase with the Na<sup>+</sup> ions having a higher probability of being extracted by the carriers. Table 3 shows that both rates are at a maximum with alternate irradiation conditions, whilst ion selectivity ( $v_{\text{K}^+}/v_{\text{Na}^+}$ ) is at a minimum. Examination of Table 3 also reveals that the photoirradiation effect on competitive transport (*i.e.* decrease by u.v. light irradiation and increase by alternate irradiation) is similar to that found for K<sup>+</sup> independent transport but not to that for Na<sup>+</sup> independent transport. This result suggests that selectivity in the competitive ion-transport is primarily governed by the affinity of K<sup>+</sup> ion with the carrier molecule.

**Conclusion.**—The present study demonstrates that the *trans*-*cis* interconversion of azobis(benzocrown ethers) by alternate irradiation of u.v. and visible light leads to a new class of light-driven ion-transport system. Efficient rate-acceleration can be achieved, however, only when ions form moderately stable complexes with the *cis*-formed carriers. This feature would be crucial in designing new light-driven ion-transport systems.

## Experimental

**Materials.**—The preparation of Cr(6,6) has been described previously<sup>14</sup> as has that of Cr(5,5) by the same procedure (reductive coupling).<sup>10</sup> In this work, we synthesised Cr(5,5) by an oxidative coupling method, which provided a much better yield of product than the previous method. 4'-Aminobenzo-15-crown-5 was prepared by catalytic hydrogenation of 4'-nitrobenzo-15-crown-5 (5.0 g, 16 mmol) in ethanol (150 ml) and used without further purification. CuCl (0.35 g) in pyridine (50 ml) was treated with molecular oxygen and then mixed with the ethanolic solution containing 4'-aminobenzo-15-crown-5. The amount of absorbed oxygen was monitored and when it reached 200 ml, the reaction was stopped. The solution was cooled in an ice-water bath and the crystalline precipitate was collected by suction and washed with pyridine. The solid was dissolved in chloroform and washed with 5% ammonia water. The chloroform layer was separated and evaporated to dryness *in vacuo*. The residue was recrystallised from benzene in the presence of activated charcoal; the product (yield 53%) had m.p. 190–191 °C (lit.,<sup>10</sup> 187–188 °C) (Found: C, 59.9; H, 6.9; N, 4.9%. Calc. for C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>O<sub>10</sub>: C, 59.77; H, 6.82; N, 4.98%).

**Miscellaneous.**—The methods of photoirradiation and ion transport have been described in previous publications of this series.<sup>10,14,19</sup> The transport system consists of 100 ml of a liquid membrane phase and 25 ml of two aqueous phases in a U-tube (2.5 cm diam.). The membrane phase was stirred slowly at a constant speed (180 rev min<sup>-1</sup>). The rates of the independent ion transport were determined by monitoring the increase in the absorbance of picrate ( $\lambda_{\text{max}}$ , 355 nm,  $\epsilon_{\text{max}}$ , 17 280)

in the OUT aqueous phase. In the competitive ion transport, a quartz U-tube was used to obviate the dissolution of Na<sup>+</sup> from a glass U-tube, and the rates were determined by estimating the concentration of each ion by an atomic absorption spectrophotometer (Shimadzu AA-640). The linear increase was observed after an induction period (*ca.* 1 h). The sampling was continued for 12 h. In a separate study, we have corroborated that the picrate method and the atomic absorption method give the same transport rate within the experimental error (4% relative error).

#### Acknowledgement

This research was supported by a grant from the Ministry of Education of Japan (No. 56850214).

#### References

- 1 E. M. Choy, D. F. Evans, and E. L. Cussler, *J. Am. Chem. Soc.*, 1974, **96**, 7085.
- 2 J. D. Lamb, J. J. Christensen, S. R. Izatt, K. Bedke, M. S. Astin, and R. M. Izatt, *J. Am. Chem. Soc.*, 1980, **102**, 3399.
- 3 M. Sugiura and T. Shinbo, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 684.
- 4 K. Hiratani, *Chem. Lett.*, 1981, 21.
- 5 N. Yamasaki, S. Nakahama, A. Hirao, and S. Negi, *Tetrahedron Lett.*, 1978, 2429.
- 6 J. M. Timko, R. C. Helgeson, M. Newcomb, G. W. Gokel, and D. J. Cram, *J. Am. Chem. Soc.*, 1974, **96**, 7097.
- 7 Yu. A. Ovchinnikov, V. T. Ivanov, and A. M. Shrob, 'Membrane Active Complexones,' Elsevier, Amsterdam, 1974.
- 8 S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano, and O. Manabe, *Tetrahedron Lett.*, 1979, 4569.
- 9 S. Shinkai, T. Ogawa, T. Nakaji, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1980, 375.
- 10 S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, and O. Manabe, *J. Am. Chem. Soc.*, 1981, **103**, 111.
- 11 S. Shinkai, H. Kinda, T. Sone, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1982, 125.
- 12 I. Yamashita, M. Fujii, T. Kaneda, S. Misumi, and T. Otsubo, *Tetrahedron Lett.*, 1980, 541.
- 13 M. Shiga, M. Takagi, and K. Ueno, *Chem. Lett.*, 1980, 1021; M. Blank, L. M. Soo, N. H. Wassermann, and B. F. Erlanger, *Science*, 1981, **214**, 70.
- 14 S. Shinkai, T. Ogawa, Y. Kusano, O. Manabe, K. Kikukawa, T. Goto, and T. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 1960.
- 15 L. P. Zalukaev, M. G. Voronkov, L. V. Moiseeva, and S. V. Afanasev, *Dokl. Akad. Nauk. SSSR*, 1976, **230**, 136.
- 16 J. Ronayette, R. Arnand, P. Lebourgeois, and J. Lemaire, *Can. J. Chem.*, 1974, **52**, 1848.
- 17 M. Irie and K. Hayashi, *J. Macromol. Sci., Chem.*, 1979, **A13**, 511.
- 18 D. T. Chen and H. Morawetz, *Macromolecules*, 1976, **9**, 463; C. D. Eisenbach, *Makromol. Chem.*, 1979, **180**, 565.
- 19 S. Shinkai, K. Shigematsu, Y. Kusano, and O. Manabe, *J. Chem. Soc., Perkin Trans. I*, 1981, 3279.
- 20 K. Kimura, H. Tamura, T. Tsuchida, and T. Shono, *Chem. Lett.*, 1979, 611.
- 21 T. Maeda, M. Ouchi, K. Kimura, and T. Shono, *Chem. Lett.*, 1981, 1573.
- 22 M. Bourgoin, K. H. Wong, J. Y. Hui, and J. Smid, *J. Am. Chem. Soc.*, 1975, **97**, 3462.
- 23 Y. Kobuke, K. Hanji, K. Horiguchi, M. Asada, Y. Nakayama, and J. Furukawa, *J. Am. Chem. Soc.*, 1976, **98**, 7414.
- 24 M. Kirch and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 555.
- 25 J. D. Lamb, J. J. Christensen, J. L. Oscarson, B. L. Nielsen, B. W. Asay, and R. M. Izatt, *J. Am. Chem. Soc.*, 1980, **102**, 6820.
- 26 C. F. Reusch and E. L. Cussler, *AIChE J.*, 1973, **19**, 736.
- 27 I. Tajima, M. Okada, and H. Sumitomo, *J. Am. Chem. Soc.*, 1981, **103**, 4096.

Received 25th January 1982; Paper 2/132