

# Synthesis of photoresponsive crown ethers having a phosphoric acid functional group as anionic cap and their selective complexing abilities toward alkali metal cations

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New photoresponsive crown ethers (**3a**, **3b** and **3c**) connected to ionizable phosphoric acid moieties by an azobenzene skeleton have been synthesized. The *trans* isomers are isomerized to the *cis* isomers by UV irradiation and the *cis* isomers are reversibly thermally isomerized to the *trans* isomers. The complexing abilities of these compounds have been estimated by measuring the *cis* to *trans* thermal isomerization rate in the presence of various alkali metals and tetramethylammonium ions and by the competitive extraction of alkali metal cations. The first-order rate constant for the thermal isomerization of *cis*-**3a** to *trans*-**3a** is remarkably suppressed in the presence of Na<sup>+</sup> and the extraction ability of *cis*-**3a** for Na<sup>+</sup> was greatly enhanced. In contrast, the recovery of *trans*-**3c** from *cis*-**3c** was significantly suppressed by Li<sup>+</sup> and the extraction of Li<sup>+</sup> by *cis*-**3c** was greatly and selectively enhanced.

Since 1973, many crown ethers have been synthesized that exhibit selective complexing abilities toward alkali, alkaline-earth, heavy and other metals and/or ammonium ions.<sup>1</sup> Recently, several kinds of photoresponsive crown ethers have been reported by several research groups.<sup>2-4</sup> For example, Shinkai and co-workers have reported the synthesis of benzocrown ethers with a photoisomerizable azo linkage and shown that their complexing abilities depended on structural changes that were induced by light and/or heat.<sup>5,6</sup> In previous papers,<sup>7,8</sup> we reported the synthesis of photoresponsive cyclobutane-1,2-dicarbonyl-capped 2*n* diazacrown ethers by intramolecular [2 + 2]photocycloaddition and their selective complexation of alkali and other metal ions. Furthermore, we have recently reported that benzocrown, dibenzocrown and crown ethers having alkylphosphoric acid functional groups as side arms are useful as selective and efficient Li<sup>+</sup> carriers for liquid-liquid extraction and liquid membrane transport.<sup>9-11</sup> In these compounds, both the phosphoric acid group and crown ether moiety cooperatively play important roles in the selective complexation of the Li<sup>+</sup> ion. In connection with the above findings, we have synthesized photoresponsive benzocrown ethers in which the crown ether moiety and a phosphoric acid functional group are joined by an azobenzene linkage and studied their complexing abilities with alkali metal ions.

## Results and discussion

Photoresponsive crown ethers, **3a** and **3b**, were prepared by the treatment of crown ethers **2a** and **2b** with octyl dichlorophosphate followed by hydrolysis, in 7.8 and 7.3% yields, respectively. Compound **3c** was also prepared using the above method from **2b** and hexadecyl dichlorophosphate, which was obtained by the reaction of phosphorus oxychloride with hexadecanol, in 1.2% yield. The structures of **3a**–**3c** were established using elemental analyses and mass, IR and <sup>1</sup>H NMR spectroscopy. The <sup>1</sup>H NMR spectrum of **3a** showed the signals of the aromatic protons at δ 6.55–7.96 (7 H, m), the methylene protons at 3.12–4.99 (18 H, m) and the methylene and methyl protons at 0.50–1.95 (17 H, m).

As shown in Table 1, the *trans* isomers of **3** showed strong absorption maxima at 362 nm (**3a**) and 365 nm (**3b** and **3c**) from

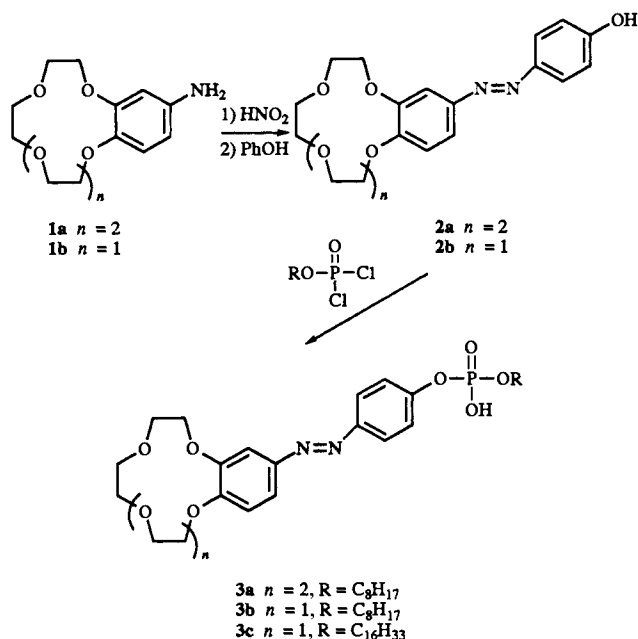


Table 1 Properties of photoresponsive crown ethers

Crown ether	$\lambda_{\text{max}}/\text{nm}^a$	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}^a$	<i>cis</i> : <i>trans</i> ratio at the photostationary state <sup>a</sup>
<b>3a</b>	362	30 500	6:4 <sup>b</sup>
<b>3b</b>	365	22 000	7:3 <sup>c</sup>
<b>3c</b>	365	22 800	7:3 <sup>c</sup>

<sup>a</sup> MeOH–H<sub>2</sub>O (11:1) at room temperature. <sup>b</sup> Irradiated with 362 nm light using Xe lamp monochromator. <sup>c</sup> Irradiated with 365 nm light using a Xe lamp monochromator.

$\pi$ – $\pi^*$  transitions, respectively. An aqueous methanol solution of the *trans*-**3a** was irradiated at 362 nm using a grating monochromator with a 500 W xenon lamp. As shown in Fig. 1,

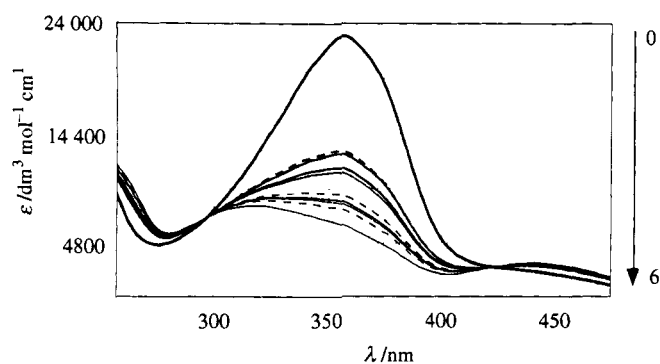
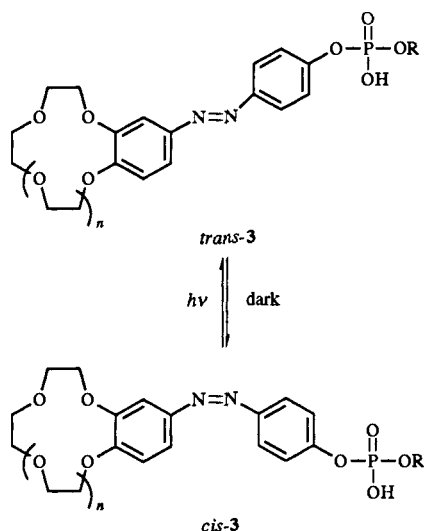


Fig. 1 Spectral changes of *trans*-**3a** to *cis*-**3a** in methanol-water (11:1). The numbers beside the arrow are the elapsed irradiation times (min).



the absorption band at 362 nm decreased and a steady state was attained after 6 min. Similar results were also obtained for *trans*-**3b** and *trans*-**3c**. The *cis*:*trans* ratios of the irradiated mixtures of **3a**, **3b** and **3c** at the photostationary states were estimated to be 6:4, 7:3 and 7:3, respectively, compared with the initial absorbances of the *trans* isomers of unirradiated **3a**, **3b** and **3c**. Furthermore, the *cis*:*trans* ratios are not affected by added cations during the *trans* to *cis* isomerization. The influence of alkali metals and tetramethylammonium cations on the first-order rate constants ( $k_1$ ) for the *cis* to *trans* thermal isomerization of **3** are summarized in Table 2. The first-order rates for the thermal isomerization varied depending on the cation. The added alkali metals and tetramethylammonium ions influenced the rates for **3a** in the following order:  $\text{Na}^+ \gg \text{K}^+ > \text{Rb}^+ = \text{Me}_4\text{N}^+ > \text{Li}^+$ . It is noteworthy that the rate for the *cis* to *trans* isomerization of **3a** was suppressed by  $\text{Na}^+$  ( $k_{\text{rel}}$  0.54). However,  $\text{Li}^+$  and  $\text{Rb}^+$  as well as  $\text{Me}_4\text{N}^+$  had only a slight influence on the rate constant. In contrast, the influence of the added cations on the rates for **3b** and **3c** were in the following order:  $\text{Li}^+ > \text{Na}^+ = \text{K}^+ = \text{Rb}^+ = \text{Me}_4\text{N}^+$  for **3b** and  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ = \text{Rb}^+ > \text{Me}_4\text{N}^+$  for **3c**. In the case of **3c**, the rate for *cis* to *trans* isomerization was suppressed ( $k_{\text{rel}}$  0.72) by  $\text{Li}^+$ . These results suggest that the cooperative interactions of the  $\text{P}-\text{O}^- \cdots \text{Na}^+ \cdots$  crown ring in the *cis* isomer of **3a** and the  $\text{P}-\text{O}^- \cdots \text{Li}^+ \cdots$  crown in the *cis* isomer of **3c** play important roles in the complexation and thermal *cis* to *trans* isomerization.

Using the photoirradiated mixture of *cis* and *trans* isomers at the photostationary state as well as the *trans* isomer as a carrier,

Table 2 Influence of alkali metal cations on the first-order rate constants ( $k_1$ ) for the *cis* to *trans* isomerization of **3a**–**3c**<sup>a</sup>

Metal cation	$k/10^{-3} \text{ min}^{-1}$			$k_{\text{rel}} = k_{\text{M}^+}/k_{\text{non}}$		
	<b>3a</b> <sup>d</sup>	<b>3b</b> <sup>e</sup>	<b>3c</b> <sup>e</sup>	<b>3a</b> <sup>d</sup>	<b>3b</b> <sup>e</sup>	<b>3c</b> <sup>e</sup>
None <sup>b</sup>	3.85	1.47	0.550			
$\text{Li}^+$ <sup>c</sup>	3.57	1.37	0.398	0.93	0.91	0.72
$\text{Na}^+$ <sup>c</sup>	2.07	1.44	0.497	0.54	0.98	0.90
$\text{K}^+$ <sup>c</sup>	3.33	1.44	0.511	0.86	0.98	0.93
$\text{Rb}^+$ <sup>c</sup>	3.46	1.44	0.519	0.90	0.98	0.94
$\text{Me}_4\text{N}^+$ <sup>c</sup>	3.47	1.44	0.509	0.90	0.98	0.98

<sup>a</sup> At room temperature. <sup>b</sup> Crown ether (0.5 mmol dm<sup>-3</sup> in MeOH; 0.5 cm<sup>3</sup>) + MeOH (5.0 cm<sup>3</sup>) + H<sub>2</sub>O (0.5 cm<sup>3</sup>) (MeOH–H<sub>2</sub>O, 11:1). <sup>c</sup> Crown ether (0.5 mmol dm<sup>-3</sup> in MeOH; 0.5 cm<sup>3</sup>) + MeOH (5.0 cm<sup>3</sup>) + aqueous MOH (2.5 mmol dm<sup>-3</sup>; 0.5 cm<sup>3</sup>) (MeOH–H<sub>2</sub>O, 11:1). <sup>d</sup> Irradiated with 362 nm light using Xe lamp monochromator. <sup>e</sup> Irradiated with 365 nm light using Xe lamp monochromator.

Table 3 Competitive extraction of alkali metal ions from the aqueous phase into the organic phase (*o*-dichlorobenzene) with **3a**, **3b** and **3c**

Compd.	Cation	Extractability ( $Ex$ ) (%) <sup>a</sup>		$Ex_{\text{mix}}/Ex_{\text{trans}}$
		<i>trans</i> Isomer	Photoirradiated mixture	
<b>3a</b> <sup>b,c</sup>	$\text{Li}^+$	0.5	0.9	1.8
	$\text{Na}^+$	10.8	25.7	2.4
	$\text{K}^+$	17.7	22.3	1.3
<b>3b</b> <sup>b,d</sup>	$\text{Li}^+$	0	0	
	$\text{Na}^+$	14	16	1.1
	$\text{K}^+$	0	1.4	
<b>3c</b> <sup>b,d</sup>	$\text{Li}^+$	0.44	2.75	6.25
	$\text{Na}^+$	8.27	7.30	0.88
	$\text{K}^+$	7.30	5.30	0.73

<sup>a</sup> Determined by atomic absorption. <sup>b</sup> *cis*:*trans* ratio 5:5 at photostationary state in *o*-dichlorobenzene. Aqueous solution (2.0 cm<sup>3</sup>) of LiOH, NaOH and KOH (each 1.0 mmol dm<sup>-3</sup>) + *o*-dichlorobenzene (2.0 cm<sup>3</sup>) of crown ether (3.0 mmol dm<sup>-3</sup>). <sup>c</sup> Irradiated with 362 nm light using Xe lamp monochromator. <sup>d</sup> Irradiated with 365 nm light using Xe lamp monochromator.

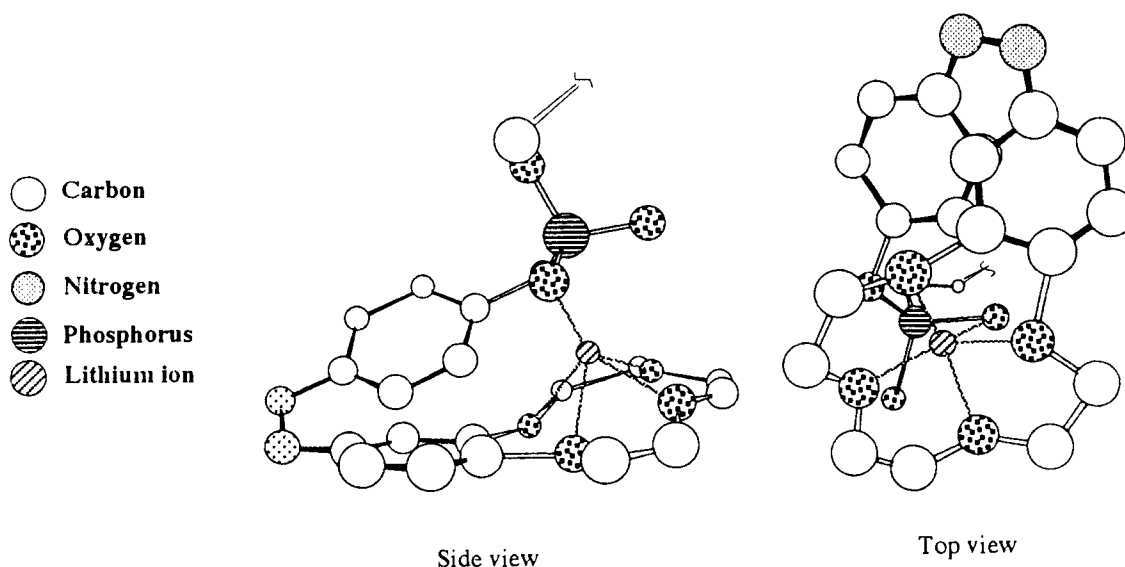
we examined solvent extraction of alkali metal ions under competitive conditions. The results of the extraction studies are summarized in Table 3. In the case of **3a**, the extraction ability for each of the alkali metal cations was enhanced by irradiation with UV light. In particular,  $\text{Na}^+$  was the most selectively extracted cation by the *cis* isomer of **3a** generated by UV light irradiation, and the ratio ( $Ex_{\text{mix}}/Ex_{\text{trans}}$  2.4) of the extracted  $\text{Na}^+$  was especially high. In contrast, the extraction ability of *trans*-**3c** for the alkali metal cations is in order:  $\text{Na}^+ > \text{K}^+ \gg \text{Li}^+$ . However, the ratio ( $Ex_{\text{mix}}/Ex_{\text{trans}}$  6.25) of the extraction ability of a photoirradiated mixture of **3c** and *trans* isomer of **3c** for  $\text{Li}^+$  was greatly enhanced compared with those for  $\text{Na}^+$  and  $\text{K}^+$  of 0.88 and 0.73, respectively. Therefore, these results confirm the effect of alkali metal ions on the thermal *cis* to *trans* isomerization rate. As a result of the introduction of an ionizable phosphoric acid group, the crown ether ring would be effectively bound to  $\text{M}^+$  in combination with the phosphoric anion group as an anionic cap.<sup>9–11</sup> In the case of **3b**, the obvious effect of added alkali metal cations could not be observed owing to its high solubility in the water phase as shown in Table 4.

After the extraction experiments, the ratio of **3** that was transferred from the organic phase into the aqueous phase was determined using a photospectrometer. These results are

**Table 4** Influence of the conditions in the aqueous phase on the ratio of **3** transferred from the organic phase to the aqueous phase at 25 °C

Compd.	Conditions in the aqueous phase	Amount of <b>3</b> transferred from the organic phase to the aqueous phase (%)	
		<i>trans</i> - <b>3</b> <sup>a</sup>	<i>cis</i> and <i>trans</i> mixture of <b>3</b> <sup>b</sup>
<b>3a</b>	H <sub>2</sub> O	20.6	25.8
	3.0 mmol dm <sup>-3</sup> Me <sub>6</sub> NOH 1.0 mmol dm <sup>-3</sup> (LiOH, NaOH, KOH) <sup>c</sup>	55.9	69.8
<b>3b</b>	3.0 mmol dm <sup>-3</sup> Me <sub>6</sub> NOH	92.0	97.4
	1.0 mmol dm <sup>-3</sup> (K <sub>2</sub> OH, NaOH, KOH) <sup>c</sup>	92.2	96.5
<b>3c</b>	H <sub>2</sub> O	47.9	49.0
	3.0 mmol dm <sup>-3</sup> Me <sub>6</sub> NOH 1.0 mmol dm <sup>-3</sup> (LiOH, NaOH, KOH) <sup>c</sup>	57.8	59.0
		60.0	55.9

<sup>a</sup> Aqueous phase (2.0 cm<sup>3</sup>) + 3.0 mmol dm<sup>-3</sup> crown ether in *o*-dichlorobenzene (2.0 cm<sup>3</sup>). <sup>b</sup> *cis:trans*, 5:5 at photostationary state in *o*-dichlorobenzene. <sup>c</sup> After the competitive extraction of alkali metal ions.

**Fig. 2** Postulated conformation of a partial structure of **3c**-Li<sup>+</sup>

summarized in Table 4, together with those of the control experiments under the same conditions. It is known that *cis*-azobenzene is more hydrophilic than the *trans* isomer. Therefore, the finding that less of the *trans* isomer than the *cis-trans* mixture of **3** is transferred to the aqueous phase is quite reasonable.<sup>12-14</sup> On the other hand, the reverse relationship, *trans* isomer > *cis-trans* mixture, only occurred in the presence of alkali metal cations due to the combined action of the phosphoric acid group and the crown ether moiety. Shinkai and co-workers previously reported that a 15-crown-5 moiety that was capped with a carboxylate group, under UV light irradiation can selectively bind K<sup>+</sup>, whose radius is greater than the size of the crown ring.<sup>12-14</sup> However, we showed that compound **3a** and **3c** selectively complexed with Na<sup>+</sup> and Li<sup>+</sup>, respectively, by converting the carboxylate group into a phosphoric acid group. Therefore, these results lead to the conclusion that the phosphoric acid groups of **3a** and **3c** can efficiently bind Na<sup>+</sup> and Li<sup>+</sup>, respectively.

Concerning the differences between the *cis* and *trans* isomers of **3**, computer modelling was investigated using Chem 3D Plus together with the CPK molecular model as shown in Figs. 2 and 3. Minimization of the complexes of *cis*-**3a** and *cis*-**3c** with Na<sup>+</sup> and Li<sup>+</sup>, respectively, were carried out using the Chem 3D Parameter. The distance between the oxygen anion of the phosphoric acid group and the incorporated Li<sup>+</sup> in the Li<sup>+</sup>-(*cis*-**3c**) complex is about 2.0 Å and that between the Li<sup>+</sup> on the oxygen atoms of the crown ether moiety is about 2.0 Å. The lengths of all of the Li<sup>+</sup>-O bonds are closely similar to the

sum (2.0 Å) of the ionic radius of Li<sup>+</sup> (0.6 Å)<sup>15</sup> and the atomic radius (1.4 Å)<sup>15</sup> of the oxygen atom. The values indicate that the Li<sup>+</sup> is bonded with approximately the same strength to the four oxygen atoms of the crown ether moiety and to the one oxygen anion of the phosphoric acid group. In contrast, Li<sup>+</sup> complexed with *trans*-**3c** mainly bonds to the phosphoric site under basic conditions, because of the long distance between the crown ether ring and the phosphoric acid moiety. Similar results were also obtained in the Na complex of **3a**. The distance between the oxygen anion of the phosphoric acid moiety and the incorporated Na<sup>+</sup> in *cis*-**3a** is about 2.4 Å, and the distance between the Na<sup>+</sup> and the oxygen atoms of the crown ether moiety is about 2.4 Å. The distances between the Na<sup>+</sup> and all of the oxygen atoms of the crown ether ring are extremely close to the sum (2.35 Å)<sup>15</sup> of the ionic radius of the Na<sup>+</sup> ion (0.95 Å) and the atomic radius of the oxygen. These findings show that *cis*-**3a** and *cis*-**3c** formed well fitted three-dimensional cavities using the crown ring segment and the oxygen anion of the phosphoric acid moiety as a cap for complexation with Na<sup>+</sup> and Li<sup>+</sup>, respectively.

### Experimental

Melting points were recorded with a Yazawa micro melting point apparatus and are uncorrected. <sup>1</sup>H NMR spectra were recorded with a Bruker AC250 spectrometer (250 MHz) using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Hitachi M-80 spectrometer. Elemental

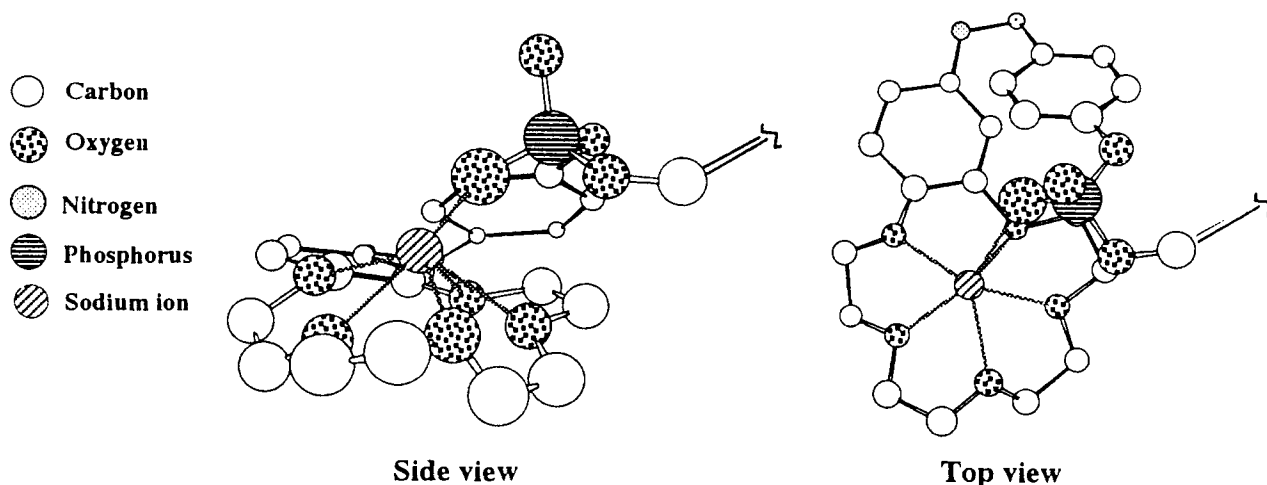


Fig. 3 Postulated conformation of a partial structure of **3a**-Na<sup>+</sup>

analyses were carried out using a Perkin-Elmer 2400 instrument. The concentrations of the alkali metal cations were determined with a Perkin-Elmer 5100 atomic spectrometer. The UV-VIS spectra were measured using a Hitachi 330 spectrometer. The photoisomerization of *trans*-**3** to *cis*-**3** was carried out at UV wavelengths of 362 nm (**3a**) and/or 365 nm (**3b** and **3c**) using a grating monochromator (Model JASCO CT-10) with a 500 W xenon lamp (JASCO PS-X500) and a band width of 0.5 nm.

#### Materials

1<sup>4</sup>-Amino-2,5,8,11,14-pentaoxa-1(1,2)-benzenacyclotetradecaphane (4-aminobenzo-15-crown-5) **1a**,<sup>16</sup> 1<sup>4</sup>-amino-2,5,8,11-tetraoxa-1(1,2)-benzenacycloundecaphane (4-aminobenzo-12-crown-4) **1b**,<sup>17</sup> octyl dichlorophosphinate (dichlorooctylphosphate)<sup>18</sup> and hexadecyl dichlorophosphinate (dichlorohexadecylphosphate)<sup>18</sup> were prepared according to the methods described in the literature. All solvents were purified by distillation in the usual manner.

#### Preparation of 1<sup>4</sup>-(4-hydroxyphenyldiazenyl)-2,5,8,11,14-pentaoxa-1(1,2)-benzenacyclotetradecaphane **2a**

To a solution of crown ether **1a** (6.82 g, 24.1 mmol) and sodium nitrate (1.72 g, 24.9 mmol) in hydrochloric acid (7.5 mol dm<sup>-3</sup>; 12.0 cm<sup>3</sup>), was added a solution of sodium hydroxide (1.72 g, 43.0 mmol), sodium carbonate (0.910 g, 8.58 mmol) and phenol (2.72 g, 28.9 mmol) in water (30 cm<sup>3</sup>) in one portion at 0–5 °C. The mixture was stirred for 3 h, and was then acidified with acetic acid. The reaction mixture was extracted with chloroform and the extract was washed with water and dried (MgSO<sub>4</sub>). Concentration of the solution gave a dark reddish oil, which was crystallized from methanol to give the title compound **2a** as reddish purple crystals, mp 119.0–121.5 °C (lit.,<sup>19</sup> 72–74 °C);  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 3.65–4.36 (16 H, m, CH<sub>2</sub>) and 6.80–7.82 (7 H, m, Ar-H),  $\nu(\text{KBr})/\text{cm}^{-1}$  3300, 1595, 1261 and 1130;  $m/z$  (20 eV) 388 (M<sup>+</sup>, 100%).

#### Preparation of the sodium salt of crown ether **2a**

An aqueous solution containing sodium hydroxide (0.701 g, 1.75 mmol), sodium carbonate (0.349 g, 3.29 mmol) and **2a** (1.54 g, 3.97 mmol) was irradiated with an ultrasonic wave, and the resulting solid was collected by filtration. The crude material was recrystallized from ethanol to give the sodium salt of crown ether **2a** (84.8%), mp 260.0–260.7 °C;  $\delta_{\text{H}}$ (250 MHz;

CD<sub>3</sub>OD) 3.70–4.60 (16 H, m, CH<sub>2</sub>) and 6.51–7.90 (7 H, m, Ar-H);  $\nu(\text{KBr})/\text{cm}^{-1}$  1590, 1500, 1261 and 1130.

#### Preparation of 1<sup>4</sup>-(4-[hydroxy(octyloxy)phosphoryloxy]-phenyldiazenyl)-2,5,8,11,14-pentaoxa-1(1,2)-benzenacyclotetradecaphane **3a**

To a benzene solution (10 cm<sup>3</sup>) of octyl dichlorophosphinate (2.16 g, 8.74 mmol) at reflux was added dropwise the sodium salt of 15-crown-5, **2a** (1.09 g, 2.77 mmol) in pyridine (25 cm<sup>3</sup>). The reaction mixture was stirred for a further 31 h and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and then water (25 cm<sup>3</sup>) was added. The aqueous solution was stirred for 35 h at 90 °C. The reaction mixture was concentrated under reduced pressure and the residue was extracted with chloroform. The extract was washed with water and dilute aqueous sodium sulfate, dried (Na<sub>2</sub>SO<sub>4</sub>) and then concentrated. The residue was separated by chromatography on silica gel (chloroform–methanol, 2:1 as eluent) followed by gel-permeation chromatography (Sephadex LH-20, EtOH as eluent) to give the title compound **3a** as a reddish oil (7.8%), mp 179–180 °C;  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.55–7.96 (7 H, m), 3.12–4.99 (18 H, m) and 0.50–1.95 (15 H, m);  $\nu(\text{KBr})/\text{cm}^{-1}$  2250 and 1605;  $m/z$  (20 eV) 580 (M<sup>+</sup>, 5%) (Found: C, 56.4; H, 7.3; N, 4.5%. Calc. for C<sub>28</sub>H<sub>43</sub>N<sub>2</sub>O<sub>10</sub>P: C, 56.18; H, 7.24; N, 4.68%).

#### Preparation of 1<sup>4</sup>-(4-hydroxyphenyldiazenyl)-2,5,8,11-tetraoxa-1(1,2)-benzenacycloundecaphane **2b**

To a solution of crown ether **1b** (1.0 g, 4.2 mmol) and sodium nitrate (0.3 g, 3.5 mmol) in hydrochloric acid (7.5 mol dm<sup>-3</sup>; 2.1 cm<sup>3</sup>), was added dropwise an aqueous solution (12 cm<sup>3</sup>) of sodium hydroxide (0.31 g, 7.8 mmol), sodium sulfate (0.15 g, 1.4 mmol) and phenol (0.48 g, 5.1 mmol) at 0–5 °C. The reaction mixture was stirred for 24 h and was then concentrated. To the residue was added in one portion sodium hydroxide (0.31 g, 7.8 mmol) and sodium carbonate (0.15 g, 1.4 mmol) in water (12 cm<sup>3</sup>). The orange coloured precipitate was filtered off. The solid was crystallized from ethanol–water to give the crude product, which was purified using silica gel chromatography (eluent, ethyl acetate–methanol) followed by gel-permeation chromatography (Sephadex LH-20, ethanol as an eluent) to give the title compound **2b** as pale yellow crystals (29.8%), mp 150–152 °C;  $\delta_{\text{H}}$ (250 MHz; CDCl<sub>3</sub>) 6.85–8.00 (7 H,

m, Ar-H) and 3.78–4.45 (12 H, m, CH<sub>2</sub>); *m/z* 345 (M<sup>+</sup> + 1, 100%) (Found: C, 62.7; H, 5.7; N, 7.9%. Calc. for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>: C, 62.78; H, 5.85; N, 8.13%).

**Preparation of 1<sup>4</sup>-{4-[hydroxy(octyloxy)phosphoryloxy]-phenyldiazenyl}-2,5,8,11-tetraoxa-1(1,2)-benzenacyclo-undecaphane 3b**

To a solution of crown ether **2b** (0.55 g, 1.5 mmol) in toluene (50 cm<sup>3</sup>), dichlorooctylphosphate (2.23 g, 9.0 mmol) was added dropwise under a nitrogen atmosphere at 80 °C. The reaction mixture was stirred for 24 h and was then cooled to room temperature after which water (5 cm<sup>3</sup>) was added to it and the aqueous solution was stirred for 3 h at 0–5 °C. The organic layer was separated and the aqueous phase was extracted with chloroform (20 cm<sup>3</sup> × 3). The extracts were combined with the organic layer and then concentrated under reduced pressure. The residue was purified by gel-permeation chromatography (Sephadex LH-20, ethanol–chloroform, 1:2 as eluent) followed by preparative TLC (silica gel, methanol–chloroform 1:2 as eluent) to give the crude material as a yellowish powder. Rechromatography of the crude material using Sephadex LH-20 (ethanol as an eluent) gave the title compound **3b** as a pale yellowish powder (7.3%), mp 170–173 °C; *m/z* (20 eV) 536 (M<sup>+</sup>, 5%); δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 6.70–7.80 (7 H, m, Ar-H), 3.32–4.41 (14 H, m, CH<sub>2</sub>O) and 0.54–1.62 (15 H, m, OCH<sub>2</sub>C<sub>7</sub>H<sub>15</sub>); ν(KBr)/cm<sup>-1</sup> 2910, 2250, 1240 and 1040 (Found: C, 58.4; H, 7.2; N, 5.3. Calc. for C<sub>26</sub>H<sub>37</sub>N<sub>2</sub>O<sub>8</sub>P: C, 58.20; H, 6.95; N, 5.22%).

**Preparation of 1<sup>4</sup>-{4-[hexadecyloxy(hydroxy)phosphoryloxy]-phenyldiazenyl}-2,5,8,11-tetraoxa-1(1,2)-benzenacyclo-undecaphane 3c**

To a benzene solution (20 cm<sup>3</sup>) of crown ether **2b** (1.06 g, 3.07 mmol), hexadecyl dichlorophosphinate (3.10 g, 9.45 mmol) was added dropwise at reflux. The reaction mixture was stirred for 60 h at reflux and then cooled to room temperature. Water (10 cm<sup>3</sup>) was added to the reaction mixture in one portion and the mixture was stirred for 48 h. The organic layer was separated and concentrated under reduced pressure. The residue was separated by silica gel chromatography [ethyl acetate–acetone (3:1) to methanol–chloroform (1:5)] followed by thin layer chromatography [Wakogel B-5F, methanol–chloroform (1:10)] to give crude **3c**. Rechromatography of the crude **3c** by gel-permeation chromatography (Sephadex LH-20, methanol) gave the title compound **3c** as a yellowish oil in 1.2% yield, δ<sub>H</sub>(250 MHz; CDCl<sub>3</sub>) 6.18–7.86 (7 H, m, Ar-H), 3.67–4.30 (14 H, m, OCH<sub>2</sub>) and 0.28–1.62 (31 H, m, OCH<sub>2</sub>C<sub>15</sub>H<sub>31</sub>); ν(KBr)/cm<sup>-1</sup> 2920, 2230, 1595, 1499, 1262, 1110 and 1050; *m/z* (20 eV) 648 (M<sup>+</sup>, 5.4%) (Found: C, 62.7; H, 8.5; N, 4.6. Calc. for C<sub>34</sub>H<sub>53</sub>N<sub>2</sub>O<sub>8</sub>P: C, 62.94; H, 8.23; N, 4.32%).

**Photoisomerization of trans-3 to cis-3**

An aqueous methanol solution (MeOH–H<sub>2</sub>O, 11:1) of *trans*-**3** (0.045 mmol dm<sup>-3</sup>) was placed in a quartz cell (1 × 1 × 4 cm) and irradiated at 25 ± 2 °C with 362 and/or 365 nm UV light using a grating monochromator with a xenon lamp (500 W). The steady states were attained within 6 min and the percentages of *cis*-**3** were calculated from the intensity of the absorption band at 362 and/or 365 nm. The ratios of *cis*:*trans* isomers were 6:4 (in **3a**) and 7:3 (in **3b** and **3c**).

**Kinetic measurement of the thermal isomerization of cis-3 to trans-3**

An aqueous methanol solution (3.0 cm<sup>3</sup>; MeOH–H<sub>2</sub>O, 11:1) that contained **3** (0.045 mmol dm<sup>-3</sup>) with or without an alkali metal cation was placed in a quartz cell (1 × 1 × 4 cm) and

irradiated for 10 min at 25 ± 2 °C with a 362 and/or 365 nm UV light using a grating monochromator with a xenon lamp (500 W) and the irradiation was then stopped. The photo-stationary state solution was observed spectrophotometrically at 25 ± 2 °C by monitoring the appearance of the absorption maxima of *trans*-**3** at 5 min intervals.

**Extraction experiments**

(a) **By trans-3.** A mixture of equal volumes (5.0 cm<sup>3</sup>) of dichlorobenzene containing **3** (3.0 mmol dm<sup>-3</sup>) and an aqueous solution containing LiOH, NaOH and KOH (each 1.0 mmol dm<sup>-3</sup>) was thoroughly agitated at 25 ± 2 °C, and then an aliquot of the lower organic solution was withdrawn. The organic solution was extracted with hydrochloric acid (1 mol dm<sup>-3</sup>; 5.0 cm<sup>3</sup>) and the amounts of metal cations were then determined using atomic absorption spectrometry.

(b) **By photoirradiated 3.** A solution of *trans*-**3** (3.0 mmol) in *o*-dichlorobenzene (2.0 cm<sup>3</sup>) was irradiated at 25 ± 2 °C with 362 and/or 365 nm UV light using a grating monochromator with a xenon lamp (500 W). The steady states were attained within 6 min. The percentages of *cis*-**3** were calculated from the intensities of the absorption band at 362 and/or 365 nm in the steady state. The ratios of *cis* and *trans* isomers were 1:1 (in **3a**, **3b** and **3c**). To the solution, an aqueous solution (2.0 cm<sup>3</sup>) containing LiOH, NaOH and KOH (each 1.0 mmol dm<sup>-3</sup>) was added and was then thoroughly agitated. The solution was then equilibrated at 25 ± 2 °C, and an aliquot of the lower organic solution was withdrawn. The organic solution was extracted with hydrochloric acid (1 mol dm<sup>-3</sup>; 5.0 cm<sup>3</sup>) and the amounts of metal ions were determined using atomic absorption spectrometry.

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