

Photoresponsive Crown Ethers. Part 20.† Reversible Photocontrol of Association–Dissociation Equilibria between Azobis(benzo-18-crown-6) and Diammonium Cations

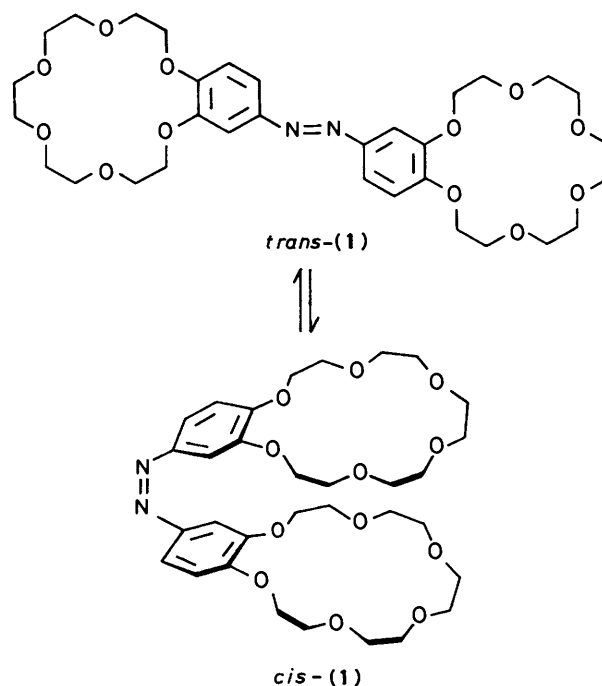
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The solution properties of complexes formed from azo(benzo-18-crown-6) (**1**) and polymethylene- α,ω -diammonio cations [$\text{H}_3\text{N}^+(\text{CH}_2)_n\text{NH}_3^+$ (**2**)] have been evaluated through measurements of average molecular weights, viscosity, n.m.r. spectra, and electrical conductance. The *trans* compound (**1**) and (**2**; $n = 6$) forms a polymeric complex with N_{av} (average aggregation number) = 20 while *trans*-(**1**) and (**2**; $n = 12$) form a 1:1 pseudocyclic complex. The difference is related to the geometrical fitness of the two terminal ammonium cations to the two crown rings in *trans*-(**1**), i.e. when the distance between the two ammonium cations in (**2**) is shorter than that between the two crown rings in (**1**), they form a polymeric complex. When the two distances are comparable, they form the 1:1 pseudocyclic complex. The n.m.r. chemical shift of the methylene protons in the 1:1 *trans*-(**1**)–(**2**; $n = 12$) complex move to higher magnetic field by 0.10–0.58 p.p.m., findings which support the view that in the complex these methylene protons lie exactly on the azobenzene moiety of *trans*-(**1**). Photoisomerised *cis*-(**1**) shows different aggregation modes because of the change in the distance between the two crown rings: a 1:1 complex for *cis*-(**1**) + (**2**; $n = 6$) and a 2:2 complex for *cis*-(**1**) + (**2**; $n = 12$). The photoinduced depolymerisation from the polymeric complex to the low molecular weight 1:1 complex for (**1**) + (**2**; $n = 6$) has been detected by viscosity measurements: $\eta_{\text{sp}}/C = 0.440$ for *trans*-(**1**) + (**2**; $n = 6$) and 0.354 for *cis*-(**1**) (*cis*% 70–78%) + (**2**; $n = 6$). The photoresponsive change in the aggregation mode is accurately reflected by the change in the electrical conductance. The conductance for (**1**) + (**2**; $n = 6$) increases on u.v. irradiation and decreases on visible light irradiation. This photoresponsive wave can be reproduced many times by alternate irradiation with u.v. and visible light. The reverse photoresponsive wave is observed for (**1**) + (**2**; $n = 12$). The conductance changes were well correlated with the changes in the aggregate size of these complexes. This is a novel example of reversible interconversion of polymers and low molecular weight pseudomacrocycles and of the transmission of light energy to electrical conductance.

The development of photofunctional systems which change their chemical and physical properties in response to photoirradiation is currently a focus of interest in the field of bio-organic chemistry.¹ Thus, the photofunctional systems reported so far are related to the photocontrol of ion transport,^{2–6} solution pH,^{7,8} membrane potentials,^{9–12} polymer conformations,^{13–16} host–guest complexation,^{17–20} etc. The purpose of our investigation in this field was to control the functions of a crown ether family by an on–off light switch, which can be extended eventually to photoregulation of ion-extraction and carrier-mediated membrane transport.¹ In 1980, we reported a new photoresponsive crown ether, azo(benzo-crown ether)s which exhibited a butterfly-like motion in response to photoirradiation.^{21,22} These crown ethers have been designed so that the distance between two crown ethers can change upon photoisomerisation of the azobenzene segment. Thus, *trans*-azo(benzo-18-crown-6) [*trans*-(**1**)] forms a 1:1 metal–crown complex with Na^+ and K^+ while *cis*-(**1**) forms an intramolecular 1:2 metal–crown sandwich complex with Cs^+ .²³

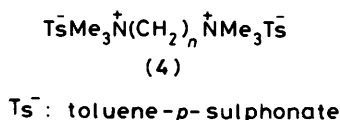
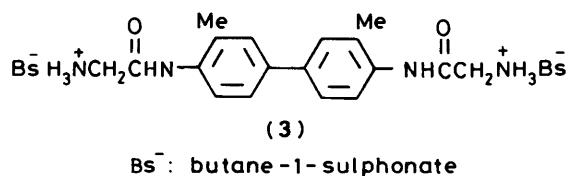
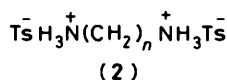
It is well established that 18-crown-6 and its analogues can form stable complexes with ammonium cations, the stability constants being comparable with those of K^+ complexes.^{24–27} Thus, they are frequently employed as receptors to fix the ammonium moiety in guest molecules. For example, bis(crown ether)s and polymethylene- α,ω -diammonio cations can form



1:1 pseudocyclic complexes when the distance between the two crown systems is close to the distance between the two ammonium cations.^{28–31} On the other hand, intermolecular,

† Part 19: S. Shinkai, T. Yoshida, K. Miyazaki, and O. Manabe, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1819.

polymeric complexes result when the two crown systems are not suitably located to form pseudocyclic 1:1 complexes.²⁸⁻³¹ In compound (1) the distance between the two crown systems changes reversibly through photoinduced *trans-cis* interconversion. One may thus expect that *trans*-(1) and the polymethylene- α,ω -diammonio cation $[\text{H}_3\text{N}^+(\text{CH}_2)_n\text{NH}_3^+]$; (2) form either a polymeric complex or a pseudocyclic complex and the complexation mode changes in response to photoirradiation. Examination of Corey-Pauling-Koltun models suggests that (2; $n < 9$) possibly forms a polymeric complex while in (2; $n > 9$) it is sterically possible to form a pseudocyclic complex. To obtain an insight into the photoresponsive properties of (1), we assessed the effect of photoirradiation on electrical conductance, average molecular weights, viscosity, and n.m.r. spectra of (1)-(2) complexes.



Experimental

Materials.—Preparation of azo(benzo-18-crown-6) (1) has been described previously.²³ The diammonium salts (2) were prepared by the treatment of polymethylenediamines with toluene-*p*-sulphonic acid. The products were identified by elemental analysis.

4,4'-Bis(ammonioacetamido)-3,3'-dimethylbiphenyl (3).—3,3'-Dimethylbiphenyl-4,4'-diamine (5.0 g, 23 mmol), *N*-benzyloxycarbonylglycine (9.7 g, 46 mmol), and dicyclohexylcarbodiimide (10.5 g, 51 mmol) were refluxed in tetrahydrofuran (150 ml) for 60 h. The precipitate obtained from the cooled reaction was collected by filtration and washed well with hot methanol to remove dicyclohexylurea. 4,4'-Bis(benzyloxycarbonylaminoacetamido)-3,3'-dimethylbiphenyl was thus obtained (45%), m.p. 209–211 °C; $\delta[(\text{CD}_3)_2\text{SO}]$ 2.26 (6 H, Me), 3.88 (4 H, NCH_2), 5.07 (4 H, OCH_2), 7.37 (5 H, Ph), 7.45, 7.52, and 7.53 (2 H each, biphenyl protons), and 7.60 and 9.31 (2 H, each, NH) (Found: C, 68.9; H, 5.8; N, 9.5. Calc. for $\text{C}_{34}\text{H}_{34}\text{N}_4\text{O}_6$: C, 68.7; H, 5.8; N, 9.4%).

4,4'-Bis(benzyloxycarbonylaminoacetamido)-3,3'-dimethylbiphenyl (1.0 g, 1.7 mmol) was dissolved in methanol-acetic acid-water (50 ml; 8:2:1 v/v/v) and reduced at room temperature with hydrogen in the presence of Pd-C (0.3 g). After 40 h, the reaction mixture was filtered in a nitrogen stream and the filtrate was evaporated to dryness. The residue was dissolved in water (10 ml) and treated with activated charcoal. Addition of a solution of the toluene-*p*-sulphonate (10%) precipitated the bis(toluene-*p*-sulphonate) salt of (3). The

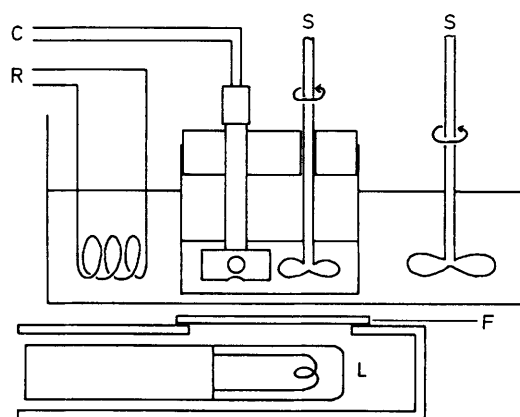


Figure 1. Apparatus for measurements of the photoinduced changes in conductance: L, high-pressure Hg lamp; F, coloured glass filter; S, stirrer; C, conductance electrode; R, thermoregulator

Table 1. Average aggregation numbers (N_{av}) of (1)-(2) complexes^a

(2)	Crown ether	<i>cis</i> % ^b	N_{av}
(2; $n = 6$)	<i>trans</i> -(1)		20.0 ± 5.0
(2; $n = 6$)	<i>cis</i> -(1)	72 → 66	3.0 ± 0.2
(2; $n = 12$)	<i>trans</i> -(1)		2.4 ± 0.4
(2; $n = 12$)	<i>cis</i> -(1)	58 → 45	4.0 ± 0.2

^a 50 °C, butan-1-ol; [(1)] = [(2)], [(1)] + [(2)] = 0.600 g l⁻¹. ^b The values indicate the *cis*% before and after the vapour pressure measurement.

precipitate was recrystallised from water (63%), m.p. 245 °C (decomp.); $\delta(\text{CD}_3\text{OD})$ 2.33 and 2.35 (6 H each, Me), 3.96 (4 H, CH_2), 7.21 and 7.70 (2 H each, aromatic protons in toluene-*p*-sulphonate), and 7.44, 7.50, and 7.54 (2 H each, ArH in biphenyl) (Found: C, 56.5; H, 5.7; N, 8.1; S, 9.5. Calc. for $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}_8\text{S}_2 \cdot 0.5\text{H}_2\text{O}$: C, 56.5; H, 5.8; N, 8.2; S, 9.4%). The salt was not very soluble in butan-1-ol so the counteranion was changed to butane-1-sulphonate by treatment with the ion-exchange resin. The bis(butane-1-sulphonate) salt of (3) showed satisfactory solubility in butan-1-ol.

Measurements of Electrical Conductance.—Conductance measurements were carried out at 30 °C using the apparatus illustrated in Figure 1. Photoisomerisation was conducted using a 100-W high-pressure Hg lamp with a coloured glass filter: Toshiba UV-D35 ($330 < \lambda < 380$ nm) for u.v. and Toshiba Y-46 ($\lambda > 460$ nm) for visible light. The containers for a thermostatted water-bath and a sample solution were made of transparent Pyrex glass. In order to avoid heat effects caused by the Hg lamp on the electrical conductance, both the water-bath and the sample solution were stirred efficiently.

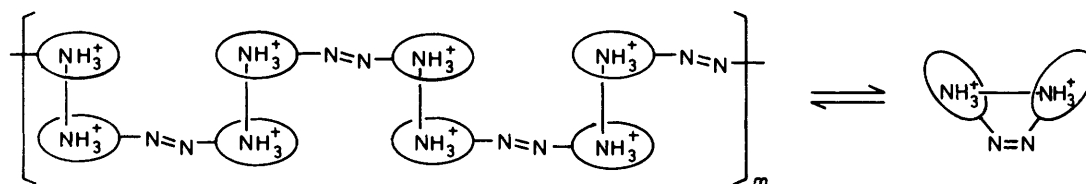
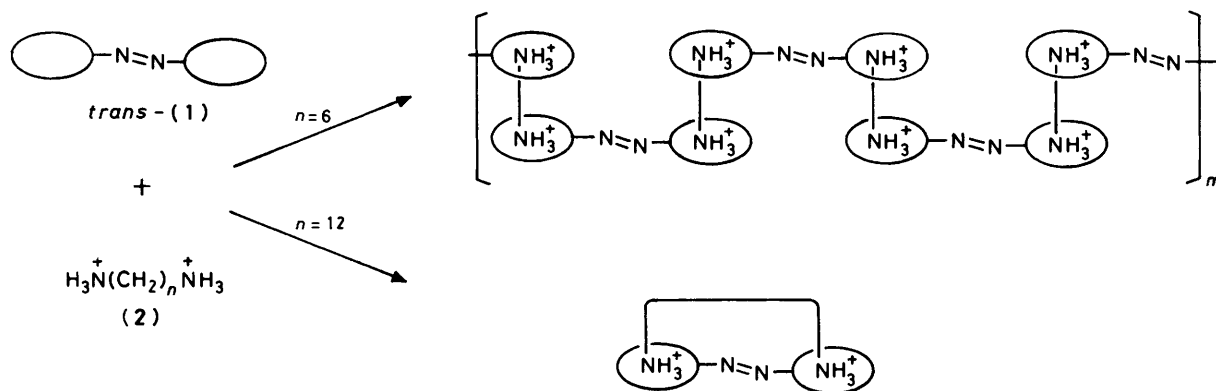
Measurements of Average Molecular Weights.—The average molecular weights (MW_{av}) of the complexes formed between (1) and (2) were determined by vapour pressure osmometry³²⁻³⁴ (50 °C; butan-1-ol). The apparatus (Corona, Type 117) was first calibrated in the presence of equimolar amounts of (1) and *N,N,N',N',N'*-hexamethylpolymethylene- α,ω -diammonio cation $[\text{Me}_3\text{N}^+(\text{CH}_2)_n\text{NMe}_3^+]$ (4) and then used for the measurement of the *trans*-(1)-(2) complexes. The measurement for the *cis*-(1)-(2) complexes is somewhat complicated: the butan-1-ol solution of *trans*-(1) and (2) was irradiated with u.v. light and the percentage *cis* isomer at the photostationary state was determined spectrophotometrically. This solution

was immediately transferred to the apparatus. After the measurement of MW_{av} (ca. 15 min), the percentage *cis* was redetermined spectrophotometrically. The results are summarised in Table 1.

Miscellaneous.—N.m.r. spectra were measured with JEOL JX-400. Viscosities of the (1)—(2) complexes were measured at 34 °C in *o*-dichlorobenzene–butan-1-ol (1:1 v/v) using a modified Ubbelohde viscometer. The % *cis* for (1) was determined before and after the measurement.

Results and Discussion

Osmometric Determination of Average Molecular Weights (MW_{av}). The MW_{av} values for the equimolar mixture of (1) and (2) were determined in butan-1-ol. The aggregation numbers (N_{av}) were computed on the basis of the definition $MW_{monomer} = [MW_{(1)} + MW_{(2)}]/2$ and are recorded in Table 2. As described earlier, examination of Corey–Pauling–Koltun models suggests that the distance between the two ammonium cations in (2; $n = 6$) is shorter than that between the two crown systems in *trans*-(1). In other words, (2; $n = 6$) is too short to form a 1:1 pseudocyclic complex with *trans*-(1). As expected, the equimolar mixture of *trans*-(1) and (2; $n = 6$) forms a polymeric complex with $N_{av} = 20$. However, the distance between the two ammonium cations in (2; $n = 12$) is close to that between the two crown systems in *trans*-(1). Thus, the equimolar mixture of *trans*-(1) and (2; $n = 12$) forms a 1:1 complex with $N_{av} = 2.4$. Most probably, this is a pseudocyclic complex as illustrated in Scheme 1.



Interestingly, we found that the N_{av} changes in response to photoirradiation. The N_{av} for (1) + (2; $n = 6$) decreased from 20 to 3 upon u.v. irradiation. This implies that the polymeric complex is depolymerised by the photoinduced *trans*-to-*cis* configurational change in (1). Since $N_{av} = 3$ was obtained for the mixture of *trans*-(1) (28–34%) and *cis*-(1) (66–72%), the N_{av} for 'pure' *cis*-(1) should be close to 2 indicating the formation of a 1:1 pseudocyclic complex (Scheme 2). As the distance between the two crown rings in *cis*-(1) is much shorter than that in *trans*-(1),^{20,23} the short (2; $n = 6$) chain can now

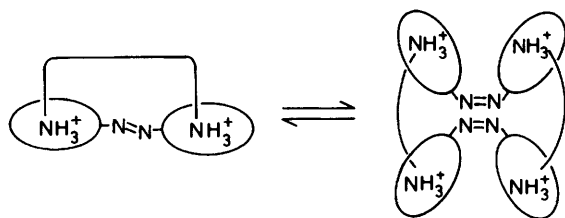
bridge the two crown rings in *trans*-(1). This is a novel example of the reversible interconversion between polymer and low molecular weight pseudomacrocycle.

The N_{av} for (1) + (2; $n = 12$) increased from 2.4 to 4 upon u.v. irradiation. This suggests that *cis*-(1) and (2; $n = 12$) may form a 2:2 complex. We previously synthesized cyclic compounds from 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6 and *trans*-3,3'-(or 4,4')-bis(chlorocarbonyl)azobenzene according to the high dilution method.^{19,35,36} The distance between the two carbonyl groups in *trans*-3,3'-bis(chlorocarbonyl)azobenzene is close to that between the two nitrogens in 1,10-diaza-4,7,13,16-tetraoxa-18-crown-6.^{19,37} As a result, the reaction afforded a 1:1 macrocycle. On the other hand, the distance between the two carbonyl groups in *trans*-4,4'-bis(chlorocarbonyl)azobenzene is too long for the two carbonyl groups to interact with the two nitrogens. In fact, we isolated a 2:2 macrocycle as a major product.^{35,36} The result suggests that when two bifunctional reactants cannot form a 1:1 macrocycle because of steric incompatibility, they tend to form a 2:2 macrocycle which is free from steric constraints.* This is probably the case for *cis*-(1) + (2; $n = 12$); i.e. the $(CH_2)_{12}$ chain is too long for the two terminal ammonium cations to interact with the two crown rings in *cis*-(1). Thus, they form a 2:2 pseudocyclic complex (Scheme 3).

Viscosity Measurements and N.M.R. Studies.—When the reversible interconversion between polymer and pseudomacrocycle takes place in solution, it is reflected by the change in viscosity. Viscosity measurements for (1) + (2; $n = 6$) ($7.68 \times 10^{-3}M$ each) were carried out at 34 °C in *o*-dichloro-

benzene–butan-1-ol (1:1 v/v). We found that η_{sp}/C , where C is the sum of the concentrations of (1) and (2; $n = 6$) = 0.427 g dl⁻¹, decreases from 0.440 to 0.354 upon u.v. light irradiation. The *cis*% of (1) in the solution was 78% before and 70% after the measurement. This indicates that the solution containing *trans*-(1) + (2; $n = 6$) is more viscous than that containing *cis*-

* A similar association mode has been found for the complexation between cationic bis(paracyclophane)s and dianionic guest molecules: C.-F. Lai, K. Odashima, and K. Koga, *Tetrahedron Lett.*, 1985, 26, 5179.



Scheme 3.

(1) + (2; $n = 6$). The viscosity increased again to $\eta_{sp}/C = 0.440$ upon visible light irradiation and the photoresponsive process could be repeated reversibly. Thus, the 'viscous' polymer solution can be converted into the 'fluid' pseudomacrocyclic solution by photoirradiation.

When *trans*-(1) forms a 1:1 pseudomacrocyclic complex with (2; $n = 12$), the polymethylene chain of (2; $n = 12$) should lie on the benzene rings of *trans*-(1). One may thus expect that the n.m.r. chemical shift for these polymethylene protons is strongly affected by the ring current. A similar upfield shift of diammonium guests has been found for the bis(crown ether) systems.^{28,31} As shown in Figure 2, the chemical shift of the methylene protons moved markedly to higher magnetic field in the presence of equimolar *trans*-(1). The largest upfield shift (0.58 p.p.m.) was observed for the central 5- and 6-H₂. On the other hand, the chemical shift of the methylene protons of (4; $n = 12$) which does not interact with *trans*-(1) scarcely moved (less than 0.03 p.p.m.; Table 2). These n.m.r. data support the view that (2; $n = 12$) forms a bridge on the azobenzene plane of *trans*-(1). Interestingly, the specific upfield shift of (2; $n = 12$) disappeared on the addition of an excess of 18-crown-6 (Figure 2, Table 2). This means that added 18-crown-6 binds the ammonium groups competitively, resulting in the dissociation of the *trans*-(1)-(2; $n = 12$) complex.

An n.m.r. spectral change was also observed for *trans*-(1) + (2; $n = 6$) which formed a polymeric complex although the magnitude of the upfield shift was much smaller than that for *trans*-(1) + (2; $n = 12$) (Table 3). Probably, the hexamethylene protons in the polymeric *trans*-(1)-(2; $n = 6$) complex are affected by the ring current of the azobenzene moiety during the molecular motions of the polymer chain.

Photoresponsive Conductance Changes.—Electrical conductance is a function of mobility of charged particles in solution. Therefore, it should be a sensitive monitor of the photoinduced changes in the molecular size. First, we examined the photoirradiation effect on (1), (1) + (4; $n = 6$), and (1) + (4; $n = 12$) ([1] = [4] = $5.41 \times 10^{-4}M$) in butan-1-ol and in *o*-dichlorobenzene–butan-1-ol (4:1 v/v) at 30 °C. We found that none of these systems exhibit a perceptible change in conductance. By contrast, the conductance for *trans*-(1) + (2; $n = 6$) ($\Lambda = 4.09 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; [1] = [(2; $n = 6$)] = $5.41 \times 10^{-4}M$) in *o*-dichlorobenzene–butan-1-ol (4:1 v/v) increased on u.v. irradiation and finally reached the saturation point at $\Lambda = 6.51 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (Figure 3). Visible light irradiation caused it to decrease gradually and finally reach the initial Λ value. This process could be repeated several times by alternate irradiation of u.v. and visible light. The photoirradiation effect on the *cis*% of (1) is shown in Figure 3. The two curves were obtained using the same apparatus (Figure 1) and the same conditions and show excellent agreement supporting the idea that the change in conductance is related to the *trans*–*cis* photoisomerism of (1). Similar agreement between the *cis*% and the conductance was observed for other systems described below.

Very interestingly, the conductance for (1) + (2; $n = 12$) decreased on u.v. irradiation and increased on visible light

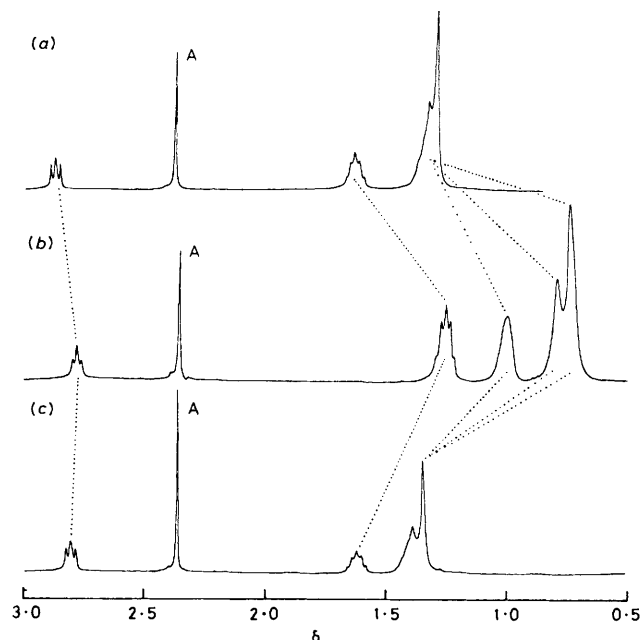


Figure 2. ¹H N.m.r. spectra of (2; $n = 12$) (0.0261M) in CDCl₃-CD₃OD (3:4 v/v) at 20 °C: (a) no additive; (b) (1) (0.0261M); (c) (1) (0.0261M) + 18-crown-6 (0.303M). Peak A is the methyl group of toluene-*p*-sulphonate

Table 2. Chemical shift of the methylene protons in R₃N⁺(CH₂)₁₂N-R₃⁺^a

Methylene protons	δ (p.p.m.)			
	None	<i>trans</i> -(1)	<i>trans</i> -(1) + 18-Crown-6 ^b	δ _{None} - δ ₍₁₎
R = H				
1-H ₂	2.87	2.77	2.80	0.10
2-H ₂	1.63	1.25	1.62	0.38
3-H ₂	1.31	1.00	1.36	0.31
4-H ₂	1.31	0.79	1.36	0.52
5-, 6-H ₂	1.31	0.73	1.36	0.58
R = Me				
1-H ₂	3.30	3.27		0.03
2-H ₂	1.73	1.71		0.02
3-, 4-, 5-, 6-H ₂	1.35	1.33		0.02

^a (R₃N⁺¹CH₂²CH₂³CH₂⁴CH₂⁵CH₂⁶CH₂⁷CH₂⁸CH₂⁹CH₂¹⁰CH₂¹¹CH₂¹²N-R₃⁺); [ammonium salt] = [(1)] = 0.0261M in CDCl₃-CD₃OD (3:4 v/v); 20 °C. ^b [18-Crown-6] = 0.303M.

Table 3. Chemical shift of the methylene protons in R₃N⁺(CH₂)₆NR₃⁺^a

Methylene protons	δ (p.p.m.)			δ _{None} - δ ₍₁₎
	None	<i>trans</i> -(1)		
R = H				
1-H ₂	2.90	2.78		0.12
2-H ₂	1.67	1.46		0.21
3-H ₂	1.38	1.17		0.21
R = Me				
1-H ₂	3.41	3.39		0.02
2-H ₂	1.84	1.82		0.02
3-H ₂	1.51	1.49		0.02

^a (R₃N⁺¹CH₂²CH₂³CH₂⁴CH₂⁵CH₂⁶NR₃⁺); [ammonium salt] = [(1)] = 0.0261M in CDCl₃-CD₃OD (6:1 v/v); 20 °C.

irradiation (Figure 4). This photoresponsive wave shows a large contrast to that for (1) + (2; $n = 6$). A similar trend was observed for the change in conductance in butan-1-ol where the average aggregation numbers were determined (Figure 5). Compound (3) has a rigid segment between the two ammonium

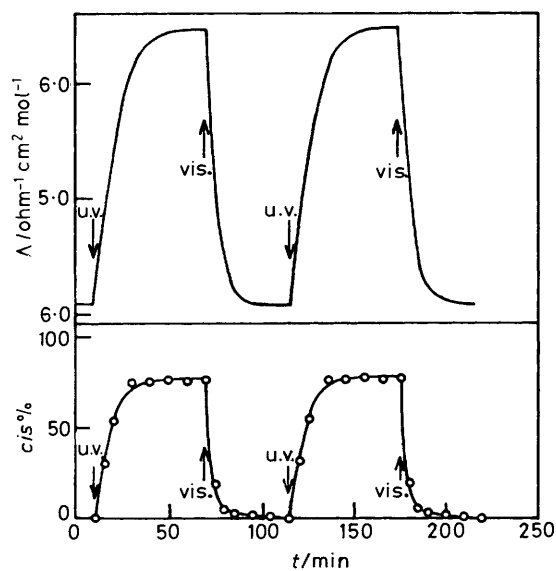


Figure 3. Changes in photoresponsive conductance and *cis*% for (1) ($5.41 \times 10^{-4}M$) + (2; $n = 6$) ($5.41 \times 10^{-4}M$) in *o*-dichlorobenzene-butan-1-ol (4:1 v/v)

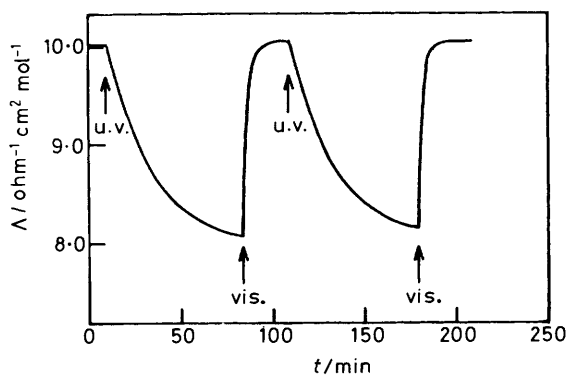


Figure 4. Changes in photoresponsive conductance for (1) ($5.41 \times 10^{-4}M$) + (2; $n = 12$) ($5.41 \times 10^{-4}M$) in *o*-dichlorobenzene-butan-1-ol (4:1 v/v)

cations and the distance is comparable with the extended $(CH_2)_{12}$ chain. The photoresponsive wave for (1) + (3) is similar to that for (1) + (2; $n = 12$) (Figure 5). These findings suggest that the photoresponsive wave becomes inverted with increasing chain length. We thus examined the conductance change in more detail as a function of the chain length (Figure 6 and Table 4). It is seen from Figure 6 that when u.v. light is used, the conductance for (2; $n \leq 8$) increases but the conductance for (2; $n \geq 10$) decreases. Thus, the critical chain length should be ca. $n = 9$.

From the foregoing results, origin of the photoresponsive conductance changes may be envisaged. When *trans*-(1) is mixed with (2; $n < 9$) a polymeric complex is preferentially formed. When subjected to u.v. irradiation it depolymerises to a low molecular weight, pseudocyclic complex. The decrease in the molecular size is reflected by the increase in the conductance. In contrast, when *trans*-(1) is mixed with (2; $n > 9$), a 1:1 pseudocyclic complex is formed preferentially. U.v. irradiation of this converts it into a 2:2 pseudocyclic complex. The increase in the molecular size is reflected by the decrease in the conductance. The largest conductance increase was observed for (2;

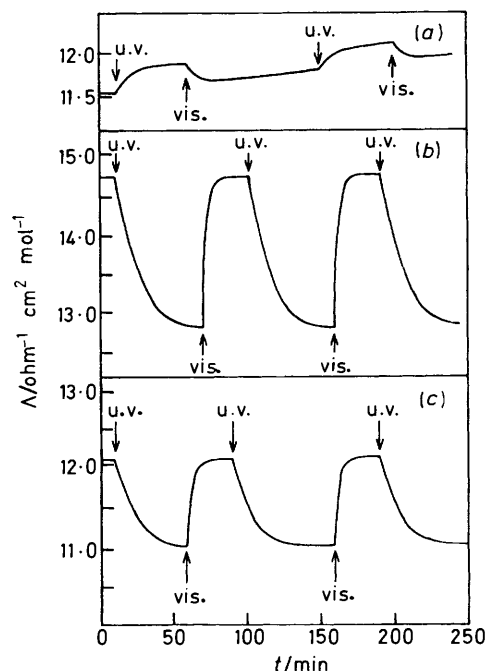


Figure 5. Change in photoresponsive conductance in butan-1-ol: (a) (1) + (2; $n = 6$); (b) (1) + (2; $n = 12$); (c) (1) + (3). Concentrations = $5.40 \times 10^{-4}M$ for all species

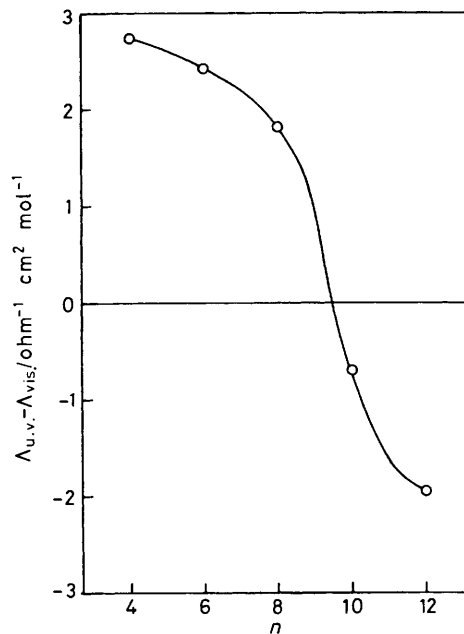


Figure 6. Plot of $\Delta\Lambda_{u.v.} - \Delta\Lambda_{vis.}$ vs. n

$n = 4$) and the largest conductance decrease for (2; $n = 12$). It would be of further interest to use (2; $n = 2$) or (2; $n = 14$); however, (2; $n = 2$) was only sparingly soluble in the solvents used here and (2; $n = 14$) was not available.

As demonstrated by n.m.r. spectroscopy, the upfield shift of the *trans*-(1)-(2; $n = 12$) complex disappeared completely on addition of an excess of 18-crown-6. This is due to the competitive binding of 18-crown-6 to the terminal ammonium groups. Is this phenomenon also reflected by the conductance change? As shown in Figure 7, the photoresponsive conduct-

Table 4. Influence of photoirradiation on electrical conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)^a

Ammonium salt	Solvent	<i>cis</i> % ^d	$\Lambda_{\text{u.v.}}$ ^e	$\Lambda_{\text{vis.}}$ ^e	$\Lambda_{\text{u.v.}} - \Lambda_{\text{vis.}}$
(2; <i>n</i> = 4)	<i>b</i>	72	6.31	3.57	2.74
(2; <i>n</i> = 6)	<i>b</i>	69	6.51	4.09	2.42
(2; <i>n</i> = 8)	<i>b</i>	55	6.86	5.04	1.82
(2; <i>n</i> = 10)	<i>b</i>	61	6.90	7.60	-0.70
(2; <i>n</i> = 12)	<i>b</i>	49	8.09	10.04	-1.95
(2; <i>n</i> = 6)	<i>c</i>	67	12.06	11.82	0.24
(2; <i>n</i> = 12)	<i>c</i>	48	12.84	14.74	-1.90
(3)	<i>c</i>	57	11.05	12.13	-1.08
(4; <i>n</i> = 6)	<i>b</i>	58	3.93	3.91	0.02
(4; <i>n</i> = 12)	<i>b</i>	56	3.68	3.66	0.02

^a [(1)] = [ammonium salt] = $5.41 \times 10^{-4} \text{M}$, 30 °C. ^b *o*-Dichlorobenzene–butan-1-ol (4:1 v/v). ^c Butan-1-ol. ^d The *cis*% at the photo-stationary state under u.v. irradiation. ^e The quantity Λ is defined on the basis of the concentration of ionic species [*i.e.*, (2), (3), or (4)].

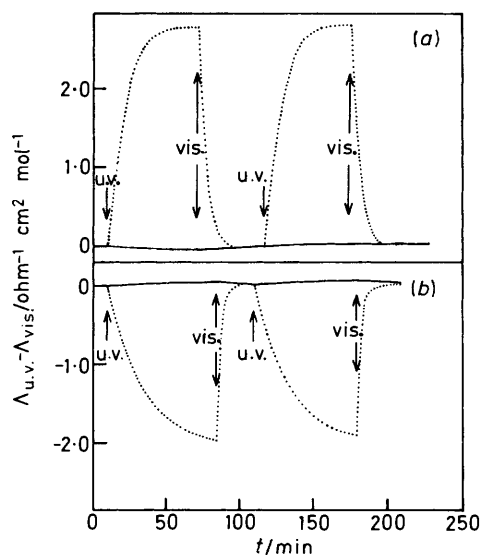


Figure 7. Influence of added 18-crown-6 on the change in photoresponsive conductance in *o*-dichlorobenzene–butan-1-ol (4:1 v/v): (a) (1) ($5.40 \times 10^{-4} \text{M}$) + (2; *n* = 6) ($5.40 \times 10^{-4} \text{M}$) + 18-crown-6 ($1.07 \times 10^{-2} \text{M}$); (b) (1) ($5.40 \times 10^{-4} \text{M}$) + (2; *n* = 12) ($5.40 \times 10^{-4} \text{M}$) + 18-crown-6 ($6.23 \times 10^{-3} \text{M}$). The dotted lines indicate the photoresponsive waves in the absence of 18-crown-6

ance change almost disappears on the addition of an excess of 18-crown-6 {[18-crown-6]/[(2)] = 11–20}. The result is quite complementary to the n.m.r. data and therefore supports the view that 18-crown-6 is capable of dissociating the polymeric complex and the pseudocyclic complex into discrete species. In other words, these complexes are stabilised solely by the hydrogen-bonding interaction between the ammonium groups and the benzocrown ethers in (1).

Conclusions

The present study demonstrates that the reversible interconversion of polymer and low molecular weight pseudomacrocycles is effected by photoirradiation. The novel phenomenon is

ascribed, on the basis of several lines of evidence, to photoinduced association–dissociation between diammonium cations and a photoresponsive crown ether. The concept may therefore be a useful way of controlling various solution properties by an on–off light switch. Also important is the fact that the phenomenon can be sensitively monitored by electrical conductance. This implies that the change occurring in solution is transformed to electrical energy. Thus, the system may be applicable more generally to interdisciplinary fields between photochemistry and electrochemistry including sensors, membrane transport, *etc.*

References

- For comprehensive reviews see S. Shinkai and O. Manabe, *Top. Curr. Chem.*, 1984, **121**, 67; A. Ueno and T. Osa, *Yuki Gosei Kagaku*, 1980, **38**, 207.
- M. Montal, *Biochim. Biophys. Acta*, 1979, **559**, 231.
- D. F. O'Brien, *Photochem. Photobiol.*, 1979, **29**, 679.
- A. Kumano, O. Niwa, T. Kajiyama, M. Takayanagi, K. Kano, and S. Shinkai, *Chem. Lett.*, 1983, 1327.
- T. Shimidzu and M. Yoshikawa, *Polym. J.*, 1983, **15**, 631.
- T. Kinoshita, M. Sato, A. Takizawa, and Y. Tsujita, *J. Chem. Soc., Chem. Commun.*, 1984, 929.
- M. Irie, *J. Am. Chem. Soc.*, 1983, **105**, 2078.
- N. Negishi, K. Tsunemitsu, K. Ishihara, I. Shinohara, T. Okano, K. Katooka, T. Akaike, and Y. Sakurai, *Kobunshi Ronbunshu*, 1980, **37**, 287.
- S. Kato, M. Aizawa, and S. Suzuki, *J. Membr. Sci.*, 1977, **2**, 39.
- J. R. Duchek and J. S. Huebner, *Biophys. J.*, 1979, **27**, 317.
- J. Anzai, H. Sasaki, A. Ueno, and T. Osa, *J. Chem. Soc., Perkin Trans. 2*, 1985, 903; *Chem. Lett.*, 1985, 1443.
- K. Honda, H. Komizu, and M. Kawasaki, *J. Chem. Soc., Chem. Commun.*, 1982, 253.
- A. Ueno, K. Takahashi, J. Anzai, and T. Osa, *J. Am. Chem. Soc.*, 1981, **103**, 6410.
- O. Pieroni, J. L. Houben, A. Fissi, P. Costantino, and F. Ciardelli, *J. Am. Chem. Soc.*, 1980, **102**, 5913.
- M. Irie, 'Molecular Models of Photoresponsiveness,' ed. G. Montanagnoli and B. F. Erlanger, Plenum, New York, 1983, p. 291.
- For a comprehensive review see G. Smets, *Adv. Polym. Sci.*, 1983, **50**, 17.
- H. Bouas-Laurent, A. Castellan, and J.-P. Desvergne, *Pure Appl. Chem.*, 1980, **52**, 2633.
- A. Ueno, H. Yoshimura, R. Saka, and T. Osa, *J. Am. Chem. Soc.*, 1979, **101**, 2779.
- S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa, and O. Manabe, *J. Am. Chem. Soc.*, 1980, **102**, 5860.
- S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu, and O. Manabe, *J. Am. Chem. Soc.*, 1981, **103**, 111.
- S. Shinkai, T. Ogawa, Y. Kusano, and O. Manabe, *Chem. Lett.*, 1980, 283.
- S. Shinkai, T. Ogawa, T. Nakaji, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1980, 375.
- S. Shinkai, T. Ogawa, Y. Kusano, O. Manabe, K. Kikukawa, T. Goto, and T. Matsuda, *J. Am. Chem. Soc.*, 1982, **104**, 1960.
- D. J. Cram, *Acc. Chem. Res.*, 1978, **11**, 8.
- J.-M. Lehn, *Acc. Chem. Res.*, 1978, **11**, 49.
- E. Weber and V. Vögtle, *Top. Curr. Chem.*, 1981, **98**, 1.
- G. W. Gokel and S. H. Korzeniowski, 'Macrocyclic Polyether Syntheses,' Springer-Verlag, Berlin, 1982.
- M. R. Johnson, I. O. Sutherland, and R. F. Newton, *J. Chem. Soc., Chem. Commun.*, 1979, 306; *J. Chem. Soc., Perkin Trans. 1*, 1980, 586.
- J.-P. Kintzinger, F. Kotzyba-Hibert, J.-M. Lehn, A. Pagelot, and K. Saigo, *J. Chem. Soc., Chem. Commun.*, 1981, 833.
- A. H. Alberts, R. Annunziata, and J.-M. Lehn, *J. Am. Chem. Soc.*, 1977, **99**, 8502.
- R. Mageswaran, S. Mageswaran, and I. O. Sutherland, *J. Chem. Soc., Chem. Commun.*, 1979, 722.

- 32 F. Y. Lo, B. M. Escott, E. J. Fendler, E. T. Adams, Jr., R. D. Larsen, and P. W. Smith, *J. Phys. Chem.*, 1975, **79**, 2609.
- 33 U. Herrmann and Z. A. Schelly, *J. Am. Chem. Soc.*, 1979, **101**, 2665.
- 34 K. Tamura and Z. A. Schelly, *J. Am. Chem. Soc.*, 1981, **103**, 1013.
- 35 S. Shinkai, Y. Honda, Y. Kusano, and O. Manabe, *J. Chem. Soc., Chem. Commun.*, 1982, 848.
- 36 S. Shinkai, Y. Honda, T. Minami, K. Ueda, O. Manabe, and M. Tashiro, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1700.
- 37 H. L. Ammon, S. K. Bhattacharjee, S. Shinkai, and Y. Honda, *J. Am. Chem. Soc.*, 1984, **106**, 262.

Received 28th May 1987; Paper 7/938