Stilbene Bis-Crown Ethers: Synthesis, Complexation and Photoisomerization

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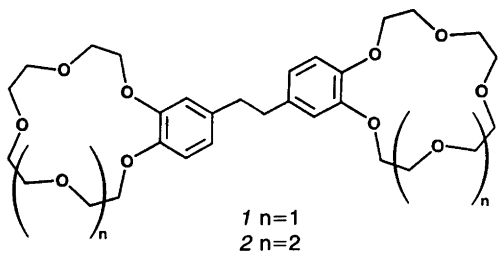
Bis-(benzo crown ethers) with ethylene (-CH_2-CH_2-) and vinylene (-CH=CH-) links have been prepared and their complexing properties towards alkali metal and ammonium ions studied. The *E* and *Z* isomers of the bis crown ethers with vinylene bridges interconvert on irradiation, the two isomers having different complexing properties. A bis sandwich structure is proposed for the *E* isomer complex with potassium ions.

Pedersen and Frensdorff[1] have suggested that the stability of a cation crown ether complex depends on the cation diameter and the ligand hole size. This has been largely accepted, even if it is not undisputed.[2] According to this hole size/cation diameter relationship, 18-crown-6 binds potassium ion more effectively than sodium ion, because the potassium ion fits better into the ligand. When the cation is too large to fit well into the ligand, it has been observed that two ligands coordinate to each cation.[1] Several ligands with two macrocyclic ether rings have been synthesized in order to enhance this sandwich complex formation. Smit *et al.*[3–5] examined the influence of the length of the connecting bridge between the two crown ether groups on the cation binding ability.



1 n=1
2 n=2

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In 1:1 crown ether to metal ion complexes, the cation and the anion form a tight ion pair in apolar organic solvents. In the 2:1 crown to ion complex of a bis-crown ether, however, the ion pair is separated even in apolar solvents, i.e. the anions are more "naked" in the 2:1 complex. Since many applications of crown ethers rely on the "naked anion" principle,[6–9] it seemed worthwhile to attempt to design a bis-crown ether that had parallel macrocyclic ether rings. In a bis-crown ether based on the bibenzyl moiety as in *1* and *2*, the crown ether rings can be close but not completely parallel.

Izatt and coworkers[10] have investigated the relationship between the stability constant of a crown ether-metal ion complex and the rate of the crown ether-facilitated transport of the metal ion through a liquid membrane (cf. Fig. 1). They found that maximum cation transport for a certain complex stability varies with the metal ion. Thus, there was a low transport rate if the complex was either too weak or too strong. The same effect had also been noted previously by Kirch and Lehn.[11]

It would be of interest to be able to regulate by some mechanism the relative positions of the crown ether moieties in a bis-crown ether, thus making it possible to influence the distance between the crown ether rings. Such a process could form the basis for a system that, "on re-

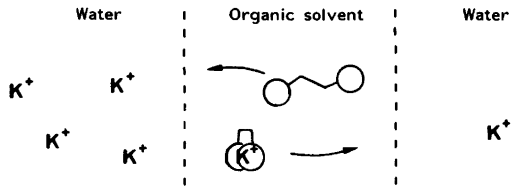
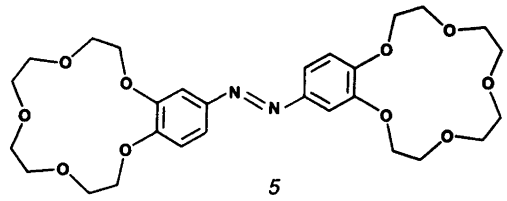


Fig. 1. Cation transport through a liquid membrane.



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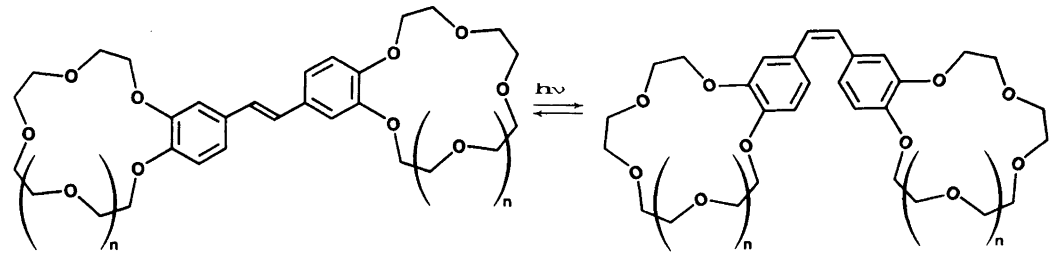
quest", would start to extract or transport a specific ion from one hydrophilic phase to another (Fig. 1).

By introducing a double bond in the bridge connecting the two crown ether rings of a bis-crown ether, as in *3* and *4*, the two complexing sites can no longer move freely relative to each other. In the *trans* configuration (*E-3* and *E-4*), the ether rings are relatively remote, but in the *cis* configuration (*Z-3* and *Z-4*), the rings are close. This interconversion is hindered by a large energy barrier (Scheme 1). However, by excitation of the stilbeno-crown ethers with UV light, the isomerization should become facile. Other similar bis-crown ethers have been reported, the best example being the azobis-crown ether *5*.[12,13] This *trans* azobis-crown ether was found to isomerize to the *cis* isomer when irradiated by UV light, the new species showing different complex formation constants for alkali metal ions as compared to the *trans* isomer.[14] Dix and Vögtle[15] synthesized some related bis-crown ethers in the course of preparing crown ether dyes. Maleic and fumaric acid esters with hydroxymethyl-benzo-crown ethers have also been used to obtain configurationally well defined bis-crown ethers.[16]

Synthesis

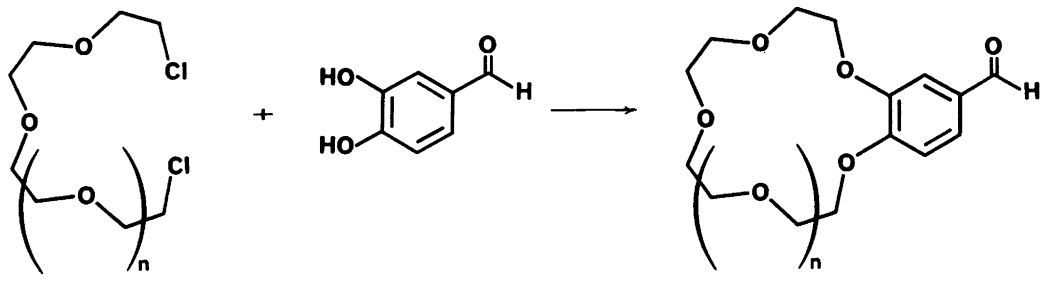
Methods for the synthesis of stilbenes have recently been reviewed by Becker.[17] It is, of course, very attractive to prepare symmetrical stilbenes like *3* and *4* via some kind of coupling of two identical units, a recent method being the reductive coupling of a benzaldehyde by a low valent titanium species.[18] More general methods for the preparation of substituted ethenes, for instance the Wittig reaction, are also of interest. The titanium-mediated reductive coupling requires the crown ether benzaldehydes *9* and *10* as starting materials for the synthesis of *3* and *4* respectively, and the preparation of these aldehydes is straightforward from 3,4-dihydroxybenzaldehyde *8*. The preparation of 4'-formylbenzo-15-crown-5 (*9* Scheme 2) was performed under the same conditions which Pedersen[19] used for preparing benzo-15-crown-5, i.e. with 1-butanol as solvent and aqueous sodium hydroxide in five percent excess as base. The yield of the isolated aldehyde *9* was 56 %. The yield was strongly influenced by the water content of the reaction mixture, the yield of the desired product being decreased when the sodium hydroxide was dissolved in



E-3 n=1
E-4 n=2

Z-3 n=1
Z-4 n=2

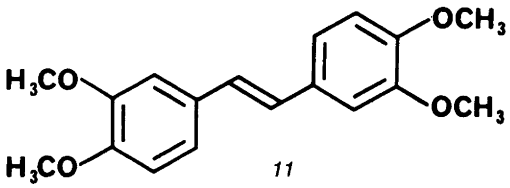
Scheme 1. Photoisomerization of the stilbeno-crown ethers *3* and *4*.



Scheme 2. Synthesis of the crown ether aldehydes *9* and *10*.

more than about 1 ml water per gram. Alternative preparations by formylation of the benzocrown ether have been reported by Hyde *et al.*[20] (9) and Wada and coworkers[21] (10). Smid *et al.*[3] used the Williamson ether synthesis in which 3,4-dihydroxybenzaldehyde is alkylated in alkaline solution by an α,ω-dichloropolyethylene glycol. (Scheme 2)

In order to try out experimental conditions for the titanium-mediated coupling of the aldehydes, 3,3′,4,4′-tetramethoxystilbene[22] (*11*) was chosen as a model compound. Thus, a simple procedure[23,24] using titanium tetrachloride, zinc, and pyridine in THF gave the stilbene *11* in 67 % yield. The Wittig route to *11* was also evaluated via reduction of 3,4-dimethoxybenzaldehyde, bromination of the resultant 3,4-dimethoxybenzyl alcohol, and preparation of the corresponding phosphonium salt. The final Wittig reaction yielded the desired tetramethoxystilbene but the overall yield for the sequence was inferior to that described above. An alternative method for the preparation of *3* and *4* is to alkylate 3,3′,4,4′-tetrahydroxystilbene with the appropriate polyethylene glycol dichloride. An attempt to completely demethylate 3,3′,4,4′-tetrahydroxystilbene, *11*, with boron tribromide in dichloromethane was made, but the product turned out to be a mixture of partly methylated compounds. This route was not pursued further.



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The crown ether aldehyde *9* was reductively coupled to the stilbeno-bis-crown ether *3* via low valent titanium using the same conditions as mentioned above but the yield was very low. A better yield, 26 %, was achieved by adding one equivalent of *N,N,N′,N′*-tetramethyl-1,8-diaminonaphthalene "proton sponge" together with the aldehyde.[25] The bis-crown ether *4* was prepared in a similar yield, 31 %, by the same procedure. The ^{1}H NMR spectra of the products showed that, in both cases, only one isomer was formed, and comparison of the UV spectra with those of other stilbenes showed that the products obtained had, as expected, the *E* configuration. The stilbene derivatives *E-3* and *E-4* were then catalytically hydrogenated (Pd on charcoal) in glacial acetic acid to yield the desired bibenzyl-bis-crown ethers *1* and *2*, both of which were colourless crystalline compounds. *E-4* was then irradiated on an analytical scale in acetonitrile at 350 nm in a photoreactor. This process was followed by UV spectroscopy. A photostationary state was reached quickly but after prolonged irradiation, absorptions typical for phenanthrenes were also observed. This photoisomerization was then carried out on a preparative scale. The ^{1}H NMR spectrum of the mixture at the photostationary state showed a composition of 80 % *Z* and 20 % *E*. The two isomers were separated by crystallization, the *E* isomer (13 %) being the less soluble of the two. The UV spectrum of the pure *Z* isomer was recorded and a sample of the *Z* isomer was then irradiated to give the same photostationary state as judged from the UV spectrum. The isomer composition at the photostationary state was also determined from the UV spectra and found to be about 15 % of the *E* isomer. The

stilbeno-bis-crown ether *E-3* was photoisomerized in a similar manner and the *E* and *Z* isomers were separated by crystallization. At the photostationary state, the isomer distribution was similar to that of the bis-crown ether *4*. In an attempt to establish the structure of the phenanthrene[26] formed after prolonged UV irradiation, a solution of the bis-crown ether *4* in dichloromethane was irradiated. A photostationary state was reached; then a small amount of iodine was added and the irradiation was continued in the presence of air. The mixture was separated by flash chromatography and a major component was identified as the crown ether aldehyde *10* by NMR spectroscopy. No phenanthrene derivative was detected.

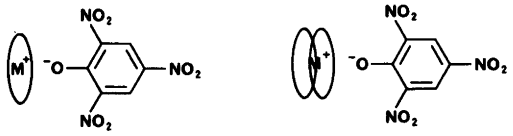
Complexation

Crown ethers can extract metal salts from their aqueous phase into an organic phase, and this property has been used to measure the stability of the complex formed. Frensdorff[27] extracted aqueous solutions of alkali metal (M^+) picrates (A^-) with crown ethers (L) into organic solvents and characterised this heterogeneous reaction by an extraction equilibrium constant, K_e.

$$M^+_{aq} + A^-_{aq} + L_{org} \overset{K_e}{\rightleftharpoons} MLA_{org} \quad (1)$$

$$K_e = \frac{[MLA]_{org}}{[M^+_{aq}\,[A^-]_{aq}\,[L]_{org}} \quad (2)$$

Complex (MLA_{org}) is considered to be the ion pair (ML^+, A^-). The stoichiometry of the complexes can be determined spectroscopically. Smid and coworkers[3] found a shift of the main UV band of the picrate when the metal ion was complexed by a crown ether in tetrahydrofuran. They concluded that when a 1:1 crown ether to metal ion complex was formed, the picrate salt existed



Contact ion pair Crown-separated ion pair

Fig. 2. Illustration of the ion pairing in crown ether complexes.

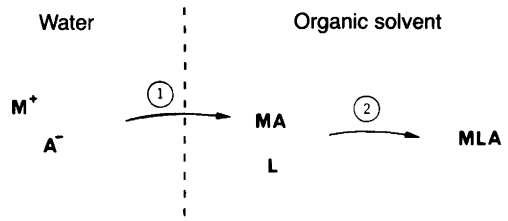


Fig. 3. The complexation taking place in the organic phase. M^+ = metal cation, A^- = picrate anion, L = crown ether.

as a contact ion pair and showed absorption maxima below 370 nm. When a 2:1 crown to metal complex formed, the ion pair was separated by the crown ether and the resulting absorption maximum was close to 380 nm (Fig. 2). Cram and coworkers[28] found similar effects in chloroform saturated with water. The actual complexation can be considered to take place in the organic layer. In this case, some metal picrate has to be extracted into the organic phase as the first step (Fig. 3). This process can be described by equations 3 to 7.

$$M^+_{aq} + A^-_{aq} \overset{K_d}{\rightleftharpoons} MA_{org} \quad (3)$$

$$K_d = \frac{[MA]_{org}}{[M^+]_{aq}\,[A^-]_{aq}} \quad (4)$$

$$MA_{org} + L_{org} \overset{K}{\rightleftharpoons} MLA_{org} \quad (5)$$

$$K = \frac{[MLA]_{org}}{[MA]_{org}\,[L]_{org}} \quad (6)$$

$$K_e = K_d K \quad (7)$$

The distribution coefficient K_d for the chloroform system has been reported[29] to depend on the concentration of alkali picrate. It is therefore essential that K_d be determined at the same concentration as used in the actual crown ether extraction experiment. Extraction of alkali metal picrates from water into chloroform and subsequent spectrophotometric determination of extracted picrate is a rapid and convenient method to screen the complexation ability of a crown ether. However, it should be noted that the chloroform is saturated with water and the pi-

crate salt, the crown ether, and the complex are hydrated to various extents,[30] Helgeson and coworkers[31] state that this method is of low precision. The error in the logarithmic complex constant values can vary from ±1.4 % to ±2.6 %. This is consistent with the results in this work.

When complexes of the sandwich type do not form, the second complexing site of a bis-crown ether can bind a second metal ion (eqn. 8). The

$$2\,MA_{org} + L_{org} \overset{K_1}{\rightleftharpoons} MLA_{org} + MA_{org} \overset{K_2}{\rightleftharpoons} (M_2LA_2)_{org} \quad (8)$$

two complex constants K_1 and K_2 are in principle independent of each other. However, if the affinities of the crown ether units for metal ions are the same and do not change when a complex is formed in another part of the molecule, i.e. when there is no allosteric effect, then $K_1 = 4\,K_2$. Using

$$K_1 = \frac{[MLA]_{org}}{[MA]_{org}[L]_{org}} \quad (9)$$

$$K_2 = \frac{[M_2LA_2]_{org}}{[MA]_{org}\,[MLA]_{org}} \quad (10)$$

equations 9 to 10 and mass balance relationships for the picrate salt and the crown ether, K_1 and K_2 can be calculated. It should be noted that the affinity, K, of the crown ether units for an ion is

$$K = \tfrac{1}{2}\,K_1 = K_2 \quad (11)$$

given by eqn. 11. The affinity, K, can be used in comparisons between different types of crown ethers. Values of ε and K_d determined by Moore and coworkers[22] were used in these measurements since they used approximately the same initial picrate concentrations.

The complexes of bibenzyl-bis-15-crown-5 (*1*) with potassium, rubidium, and cesium showed λ_{max} typical for crown-separated ion pairs, i.e. these complexes were of the sandwich type (Fig. 4). The *trans*-stilbeno-15-crown-5 (*E-3*) had a strong band with λ_{max} at 333 nm. This band interfered in the determination of the λ_{max} of the picrate. It was, however, clear that the complexes with potassium and rubidium were of the sandwich type. This was unexpected since the two

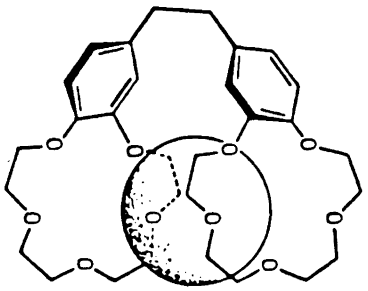


Fig. 4. The sandwich structure of the *1*-potassium complex.

Table 1. Log *K* of picrates for water/chloroform at 23 °C as defined by eqn. 6. For simplicity $k = 2\,K_2 = \tfrac{1}{2}\,K_1$ is used when complexation is a two-step process (see eqn. 8). The numbers in italics were calculated for sandwich complexes because the absorption spectra of the picrates showed maxima at 370–380 nm. The numbers in parenthesis are log K_e, extraction constants, as defined by eqn. 2. These give a direct measure of the extractability of the picrate salt into chloroform.

Crown ether		Conc. /mM	Picrate salts				
			Na^+ 15 mM	K^+ 15 mM	NH_4^+ 15 mM	Rb^+ 15 mM	Cs^+ 15 mM
Bibenzyl-bis-crown-5	(*1*)	1.50	6.0 (3.2)	*6.5 (3.9)*	5.6 (3.2)	*6.0 (3.7)*	*5.5 (3.2)*
E-stilbeno-bis-15-crown-5	(*E-3*)	37.5	5.9 (3.1)	*5.5*[a] *(2.9)*[a]	5.9 (3.5)	*7.0 (4.6)*	4.8 (2.5)
E-stilbeno-bis-15-crown	(*E-3*)	1.87	5.9 (3.1)	*7.2 (4.6)*	5.5 (3.1)	*6.6 (4.2)*	5.0 (2.7)
Z-stilbeno-bis-15-crown-5	(*Z-3*)	1.33	5.9 (3.2)	*6.1 (3.5)*	5.4 (3.0)	*5.6 (3.2)*	5.2 (2.4)
Bibenzyl-bis-18-crown-6	(*2*)	1.98	5.9 (3.2)	7.6 (5.0)	7.3 (4.9)	7.1 (4.8)	*8.1 (5.8)*
E-stilbeno-bis-18-crown-6	(*E-4*)	1.50	5.9 (3.1)	7.1 (4.5)	8.0 (5.6)	7.1 (4.8)	*7.2 (4.9)*
Z-stilbeno-bis-18-crown-6	(*Z-4*)	2.15	5.9 (3.1)	6.9 (4.3)	6.7 (4.3)	6.9 (4.5)	6.2 (4.0)

[a] A precipitate formed before the sample was withdrawn.

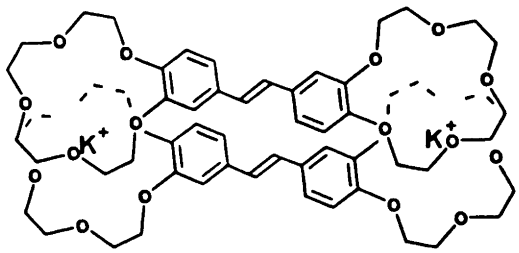


Fig. 5. Proposed structure of the *E-3*-potassium complex.

crown ether rings in the *trans*-stilbene crown ether cannot cooperate in the binding of the same metal ion. Instead, a bis-sandwich structure is proposed for these complexes, Fig. 5.

When a chloroform solution of *E-3* (37.5 mM) was added to a potassium picrate solution, an orange precipitate (m.p. 295–300 °C dec.) formed within a few minutes. A similar precipitate was also formed when a more dilute (1.87 mM) solution of *E-3* was used, but in this case, only after several hours. The *cis*-stilbeno-15-crown-5 had λ_{max} of 301 nm and did not interfere with the picrate absorption to the same extent as the *trans*-stilbene. The potassium complex of *Z-3* is of the sandwich type and this might also be the case for the rubidium complex. The structure of *Z-3* as calculated by a molecular mechanics program[26] is shown in Fig. 6. The two crown ether rings of *Z-3* obviously do not have the correct alignment, whereas the rings of *E-3* in the proposed structure (Fig. 5) can adjust to the requirement of the cation.

Cesium picrate formed contact ion pairs both in the complex with *trans*-stilbeno-bis-15-crown-5 and *cis*-stilbene-bis-15-crown-5. Ammonium picrate formed contact ion pairs in the complexes with all crown ethers investigated here. The radius of the ammonium ion is comparable to that of potassium but ammonium has tetrahedral symmetry whereas potassium is spherical. Of the 18-crown-6 crown ethers, it was only bibenzyl-bis-18-crown-6 and *trans*-stilbeno-bis-18-crown-6 which formed sandwich type complexes and this only with cesium. The *cis*-stilbeno-bis-18-crown-6 formed a contact ion pair with cesium picrate.

Both *trans*-stilbeno-bis-15-crown-5 (*E-3*) and *trans*-stilbeno-bis-18-crown-6 (*E-4*) showed very interesting complex properties. Although the crown ether units are locked in positions remote from each other they formed sandwich type complexes as indicated by the existence of crown-separated ion pairs. The bis-crown ether with the smaller 15-crown-5 ring formed sandwich complexes with potassium and rubidium while the crown ether with the larger 18-crown-6 ring did this only with cesium. Furthermore, these complexes were also very stable; in the case of cesium, its complex stability with *trans*-stilbeno-bis-18-crown-6 (*E-4*) was matched only by its complex with bibenzyl-bis-18-crown-6 (*2*).

The complex of *trans*-stilbeno-bis-15-crown-5 (*E-3*) with rubidium was the most stable of the rubidium complexes in the 15-crown-5 series except for the complex with bibenzyl-bis-15-crown-5 (*1*), which was of equal stability. In the 15-crown-5 series, potassium formed the most

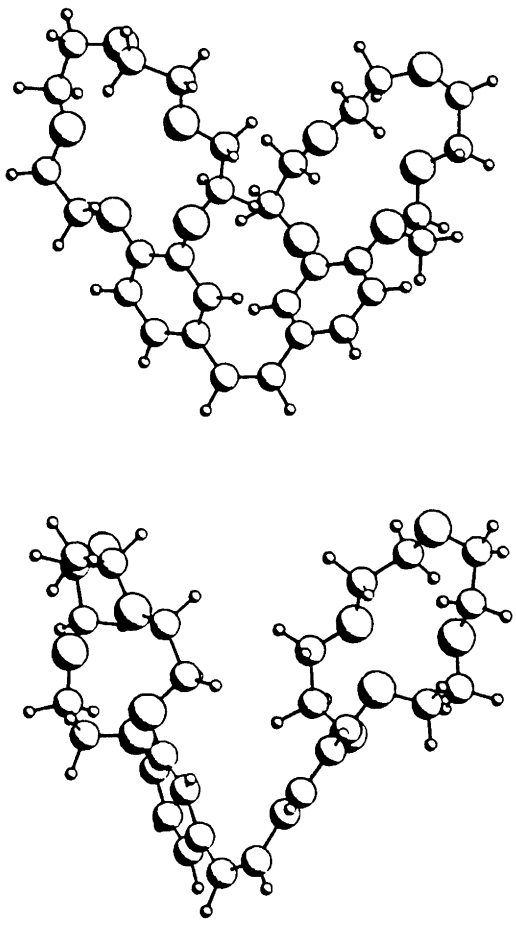


Fig. 6. The calculated structure of *Z-3*.

stable complex with the *trans*-stilbeno-bis-15-crown-5 (*E-3*). These properties of the *trans*-stilbene crown ethers are unexpected.

The differences in complex stability between *trans*- and *cis*-stilbeno-bis-5-crown-5 can be used in an extraction system in which light-induced *cis-trans* isomerization is used to regulate the efficiency and selectivity. In the *trans* configuration, this bis-crown ether will extract potassium and rubidium more than ten times better than sodium, ammonium, or cesium. In the *cis* configuration, this selectivity is reduced and potassium and rubidium will be extracted only slightly better than the others. In the same way, *trans*-stilbeno-bis-18-crown-6 selectively extracts ammonium picrate and, to some extent, cesium picrate; in the *cis* configuration, this bis-crown ether does not show the same selectivity.

Concluding remarks

A series of bis-crown ethers has been prepared and their complex properties have been studied. The original idea, to enhance the stability of complexes with metal ions too large to fit well into the cavity of a crown ether ring, was realized with bibenzyl-bis-15-crown-5 and bibenzyl-bis-18-crown-6. (These compounds were prepared independently by another group[33,34] during the course of this work.) The more rigid *cis*-stilbeno-bis-15-crown-5 and *cis*-stilbeno-bis-18-crown-6 did not show this enhancement of complex stability. The *trans*-stilbeno-bis-15-crown-5 and *trans*-stilbeno-bis-18-crown-6 formed surprisingly stable complexes with large cations. A bis-sandwich structure is proposed for the *trans*-stilbeno-bis-15-crown-5 – potassium complex.

Experimental

General Diethyl ether, tetrahydrofuran, and 1,4-dioxan were distilled from sodium benzophenone ketyl and dry dichloromethane from calcium hydride immediately before use. Dichloromethane, hexane, methanol, and ethyl acetate were distilled through an efficient column. All other solvents were used as purchased. Titanium tetrachloride and tin tetrachloride were freshly distilled through a 20 cm Vigreux column.

The NMR spectra were recorded on a Bruker WH 270 and mass spectra on an AEI MS 902 instrument. Absorbances for complex constant measurements and UV spectra were recorded on a Varian Cary 210 spectrophotometer. The IR spectra were obtained on a Perkin-Elmer 197 spectrophotometer. The melting points were obtained on a Mettler FP 5 apparatus.

17-Formyl-2,5,8,11,14-pentaoxabicyclo[13.4.0] nonadeca-1(15),16,18-triene, 4'-formylbenzo-15-crown-5 (9). 3,4-Dihydroxybenzaldehyde (*8*) (4.1 g, 30 mmol, Fluka) was dissolved in 1-butanol (45 ml). The solution was purged with argon, charged with aqueous sodium hydroxide (2.5 g, 63 mmol in 2.5 ml water) and refluxed for 10 min. To the resulting grey suspension, tetraethylene glycol dichloride (*6*) (6.9 g, 30 mmol) was added. The mixture was refluxed for 48 h, cooled, and filtered through Celite. The filtrate was evaporated and the resulting dark brown oil (6.3 g) was mixed with Celite to give a powder which was extracted continuously in a solid-liquid extractor for 10 h with distilled hexane. The hexane was evaporated to yield a grey crystalline material (5.1 g) which was recrystallized from di-isopropyl ether/hexane 1:1, to give 5.0 g (56 %), m.p. 78–80 °C, lit.[35] 78–79 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.76 (8 H, m), 3.93 (4 H, m), 4.19 (4 H, m), 6.94 (1 H, d, *J* 8.2 Hz), 7.39 (1 H, d, *J* 1.8 Hz), 7.43 (1 H, dd, *J* 8.2 Hz, 1.8 Hz), 9.84 (1 H, s).

20-Formyl-2,5,8,11,14,17-hexaoxabicyclo[16.4.0] docosa-1(18),19,21-triene, 4'-formylbenzo-18-crown-6 (10). This compound was prepared from 3,4-dihydroxybenzaldehyde (*8*) (4.1 g, 30 mmol) and pentaethylene glycol dichloride (*7*) (8.2 g, 30 mmol) with potassium hydroxide (3.5 g, 63 mmol) as base by the same procedure as described for *9*. The yield of recrystallized *10* was 7.0 g (69 %), m.p. 61–63 °C, lit.[30] 60–62 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.69 (4 H, m), 3.73 (4 H, m), 3.78 (4 H, m), 3.95 (4 H, m), 4.22 (4 H, m), 6.96 (1 H, d, *J* 8.1 Hz), 7.39 (1 H, d, *J* 1.9 Hz), 7.44 (1 H,dd, *J* 8.1 Hz, 1.9 Hz), 9.83 (1 H, s).

E-1',2'-Bis(2,5,8,11,14-pentaoxabicyclo[13.4.0] nonadeca-1(15),16,18-trien-17-yl)ethene, E-*1,2-bis(4'benzo-15-crown-5)ethene,* E-*stilbeno-bis-15-crown-5* (E-3). Tetrahydrofuran (40 ml) was placed in a flask purged with argon and cooled to −78 °C. Titanium tetrachloride (2.2 ml, 20 mmol) was added slowly, followed by zinc dust (1,3 g, 20

mmol) and dry pyridine (1 ml). The mixture was refluxed for 30 min, and the resulting black mixture cooled in an ice/water bath. A solution of 4'-formylbenzo-15-crown-5 (*9*) (0.6 g, 2 mmol) and *N,N,N,N*-tetramethyl-1,8-diaminoaphthalene (0.42 g, 2 mmol) in THF (5 ml) were added via a syringe. The mixture was slowly warmed to reflux and the reaction followed by TLC (10% methanol in dichloromethane). The mixture was refluxed for 5 h, cooled, and 20% aqueous sodium carbonate (50 ml) added followed by dichloromethane (50 ml). This mixture was filtered through silica gel (1 cm thick, 63–200 μm) and the filter cake washed with dichloromethane. The two phases of the filtrate were separated and the aqueous phase extracted with dichloromethane (2 × 50 ml). The combined organic phases were washed with saturated sodium bicarbonate until neutral, and then with water (2 × 50 ml). The organic phase was dried ($MgSO_4$), filtered, and the solvent evaporated to give a white, crystalline product. The product was recrystallized in dichloromethane/methanol (148 mg, 26%, m.p. 190–192 °C). Found (%): C, 63.8; H, 7.8; $C_{30}H_{40}O_{10}$; required C, 64.3; H, 7.2; O, 28.5. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.77 (16 H, s), 3.92 (8 H, m), 4.15 (4 H, m), 4.19 (4 H, m), 6.84 (2 H, d, *J* 8.1 Hz), 6.87 (2 H, s), 7.02 (4 H, m). MS (50 eV): *m/z* 561 (33%), 560 (M^+, 100), 296 (6), 149 (7). Mol. wt., obs. 560.262, calc. for $C_{30}H_{40}O_{10}$ 560.262. UV[acetronitrile (log ε)]: 333 (4.55).

E-*1',2'-Bis(2,5,8,11,14,17-hexaoxabicyclo-[16.4.0]docosa-1(18),19,21-trien-20-yl)ethene,* E-*1,2-bis(4'-benzo-18-crown-6)ethene,* E-*stilbeno-bis-18-crown-6* (E-4). This compound was prepared by the same procedure as described for the 15-crown-5 analogue *E-3*. Thus, reductive coupling of 4'-formylbenzo-18-crown-6(*10*) (3.0 g, 10 mmol) with titanium tetrachloride/Zn in THF gave the crystalline *E-4* (1.0 g, 31%, m.p. 154–156 °C). Found (%): C, 62.5; H, 7.8; $C_{34}H_{48}O_{12}$; required C, 62.9; H, 7.5; O, 29.6. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.69 (8 H, s), 3.75 (8 H, m), 3.78 (8 H, m), 3.95 (8, m), 4.18 (4 H, m), 4.23 (4 H, m), 6.85 (2 H, d, *J* 8.5 Hz), 6.86 (2 H, s), 7.01 (2 H, dd, *J* 8.5 Hz, 1.9 Hz), 7.05 (2 H, d, *J* 1.9 Hz). MS (50 eV): *m/z* 649 (37%), 648 (M^+, 100), 604 (6), 296 (41), 240 (11), 197 (12), 149 (23), 115 (16). Mol. wt., obs. 648.310, calc. for $C_{34}H_{48}O_{12}$ 648.315. UV[acetonitrile (log ε)]: 335 (4.56).

3,3',4,4'-Tetramethoxystilbene (11). 3,3',4,4'-Tetramethoxystilbene (*11*) was prepared by the same procedure as used for the preparation of stilbeno-bis-15-crown-5 (*E-3*) with the exception that *N,N,N,N*-tetramethyl-1,8-diaminonaphthalene was not added. Recrystallization from dichloromethane/methanol gave colourless crystals (0.2 g, 67%, m.p. 149–152 °C, lit.[22] 155 °C). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.90 (6 H, s), 3.94 (6 H, s), 6.86 (2 H, d, *J* 8.0 Hz), 6.92 (2 H, s), 7.03 (4 H, m).

Z-1',2'-Bis(2,5,8,11,14-pentaoxabicyclo-[13.4.0]nonadeca-1(15),16,18-trien-17-yl)ethene, Z-1,2-bis(4'-benzo-15-crown-5)ethene, Z-stilbeno-bis-15-crown-5 (Z-3). *E*-Stilbeno-bis-15-crown-5 (*E-3*) (50 mg, 0.89 mmol) was dissolved in acetonitrile (10 ml) and ethanol (50 ml) added. The solution was purged with nitrogen and irradiated by UV light (300 nm, Rayonet reactor). The reaction was followed by UV spectroscopy on samples which were taken out evey 5 min. After irradiation for 35 minutes, a photostationary state was reached and the solvent of the reaction mixture was evaporated. The residue was dissolved in boiling ethanol (5 ml) and allowed to cool (5 °C). The resulting crystals (*E-3*, 7 mg) were collected. The solvent of the filtrate was evaporated to give a colourless oil (*Z-3*, 43 mg, 86%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.78 (16 H, s), 3.81 (4 H, m), 3.89 (4 H, m), 3.95 (% H, m), 4.10 (4 H, m), 6.42 (2 H, s), 6.72 (6 H, m). UV[acetonitrile (log ε)]: 298 (4.10).

Z-1',2'-Bis(2,5,8,11,14,17-hexaoxabicyclo-[16.4.0]docosa-1(18),19,21-trien-20-yl)ethene, Z-1,2-bis(4'-benzo-18-crown-6)ethene, Z-stilbeno-bis-18-crown-6 (Z-4). *E*-Stilbeno-bis-18-crown-6 (*E-4*) (50 mg, 0.77 mmol) was dissolved in acetonitrile (10 ml) and ethanol (50 ml). This solution was irradiated by UV light as described for *Z-3*. After irradiation for 35 min, the *E*.stilbeno-bis-18-crown-6 was crystallized (ethanol, 5 ml) and the crystals collected (6.5 mg). The solvent of the filtrate was evaporated to give a colourless oil (*Z-4*, 43.5 mg, 87%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.68 (8 H, s), 3.73 (16 H, m), 3.84 (4 H, m), 3.91 (4 H, m), 3.97 (4 H, m), 4.13 (4 H, m), 6.41 (2 H, s), 6.75 (6 H, m). UV[acetonitrile (log ε)]: 301 (4.11).

1',2'-Bis(2,5,8,11,14-pentaoxabicyclo[13.4.0]nonadeca-1(15),16,18-trien-17-yl)ethane, 1,2-bis(4'benzo-15-crown-5)ethane, bibenzyl-bis-15-crown-5 (1). *E*-Stilbeno-bis-15-crown-5 (*E-3*) (72 mg, 0.13 mmol) was dissolved in glacial acetic acid (10 ml) and palladium on charcoal (4 mg, 10 % Pd/C) added. The suspension was hydrogenated in a Parr apparatus at 3 bar, 90 °C with efficient agitation for 16 h. The reaction mixture was cooled, filtered, and evaporated to give a colourless crystalline material which was recrystallized from ethanol (50 mg, 69 %, m.p. 114–115 °C, lit. [34] 106.5–108.7 °C). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.79 (4 H, s), 3.76 (16 H, s), 3.90 (8 H, m), 4.10 (8 H, m), 6.72 (6 H, m). MS (50 eV): *m/z* 562 (M^+, 69 %), 281 (70), 149 (100). Mol.wt., obs. 562.280, calc. for $C_{30}H_{42}O_{10}$ 562.278.

1',2'-Bis(2,5,8,11,14,17-hexaoxabicyclo[16.4.0]docosa-1(18),19,21-trien-20-yl)ethane, 1,2-bis(4'-benzo-18-crown-6)ethane, bibenzyl-bis-18-crown-6 (2). *E*-Stilbeno-bis-18-crown-6 (*E-4*) (0.10 g, 0.15 mmol) was hydrogenated in a Parr apparatus (3 bar, 90 °C) with glacial acetic acid (20 ml) as solvent and palladium on charcoal (5 mg, 10 % Pd/C) as catalyst. After 16 h, the reaction mixture was cooled, filtered, and evaporated to give colourless crystals which were recrystallized from ethanol (74 mg, 74 %, m.p. 81–82.5 °C, lit.[34] 87.6–89.4 °C). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.79 (4 H, s), 3.68 (8 H, s), 3.75 (16 H, M), 3.91 (8 H, m), 4.13 (8 H, m), 6.72 (6 H, m). MS (50 eV): *m/z* 650 (M^+, 41 %), 325 (18), 237 (15), 149 (100). Mol.wt., obs. 650.327, calc. for $C_{34}H_{50}O_{12}$ 650.330.

Complex constant measurements

Picric acid, recrystallized from ethanol, was dissolved in distilled water. This solution (10.00 ml) was titrated with 0.0100 M sodium hydroxide (34.3 ml; methyl red). Picrate solutions (0.0150 M) were obtained by dissolving 1.50 mmol of the metal hydroxide or the free amine (corrected for stoichiometry where appropriate) in 43.7 ml (1.50 mmol) of the picric acid solution and adding distilled water to make 100.0 ml. The total concentration of the picrate in the organic phase, $[MA]_{org}$, was determined as follows: A solution of the crown ether (see Table 1) in chloroform was prepared and 0.20 ml of this solution was shaken with 0.50 ml of the aqueous picrate solution for 3 min. The phases were allowed to separate and 0.080 ml of the organic layer was taken out and diluted with acetonitrile to 10.00 ml. The absorbance of this solution was then measured at 380 nm and calculated. When the stoichiometry of the complex was determined, a sample (0.080 ml) was withdrawn from the organic layer as above, diluted to 0.20 ml with chloroform and the UV spectrum recorded. The chloroform sample was subsequently diluted with acetonitrile to 5.00 ml and another UV spectrum recorded.

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