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BIS(BENZOCROWN ETHER)S WITH POLYMETHYLENE BRIDGES AND THEIR APPLICATION IN ION-SELECTIVE ELECTRODES

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Abstract

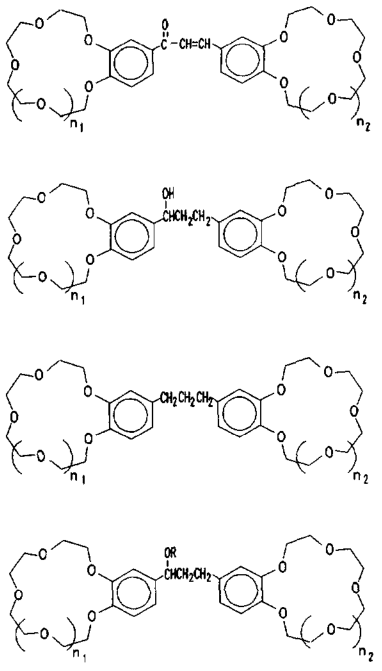
Synthetic procedures based on the condensation of benzocrown ether derivatives leading to bis(benzocrown ether)s with nonhydrolyzable polymethylene bridges have been elaborated. The obtained compounds may have identical or different macrocyclic units. Methods for introducing lipophilic substituents into these compounds also have been described. The synthesized compounds have been applied in ion-selective electrodes and exhibit high selectivities for potassium, rubidium and cesium ions.

INTRODUCTION

Many applications of crown ethers are based on the selectivity of formation of their complexes with different cations.[1] An important application of crown ethers is their use as ion carriers in ion-selective membrane electrodes. The selectivity of monocrowns is usually not sufficient for this purpose although the selectivity of the respective ion-selective membrane electrodes may be increased in some specific cases (due to different stoichiometries of the formed complexes with various cations).[2-4]

Nevertheless bis(crown ether)s forming sandwich-like structures[5] have been found to be very promising electroactive substances in ion-selective electrodes.[6] Bis(crown ether)s exhibit the expected high selectivity in membrane electrodes in recognition of, amongst others, sodium and potassium cations.[6] A variety of bis(benzocrown ether)s have been synthesized in recent years.[7-13]

Most bis(crown ether)s, used as ionophores for ion-selective membrane electrodes, are based on modified crown ethers joined by a bridge with ester or amide bonds susceptible to cleavage caused, for example, by hydrolysis.


1 $n_1=n_2=1$
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7 $n_1=n_2=1$
8 $n_1=2$ $n_2=1$
9 $n_1=n_2=2$
10 $n_1=n_2=1$ $R=n\text{-}C_8H_{17}$
11 $n_1=n_2=1$ $R=n\text{-}C_{12}H_{25}$
12 $n_1=n_2=1$ $R=n\text{-}C_{16}H_{33}$
13 $n_1=2$ $n_2=1$ $R=n\text{-}C_8H_{17}$

Fig. 1. Synthesized compounds 1-13

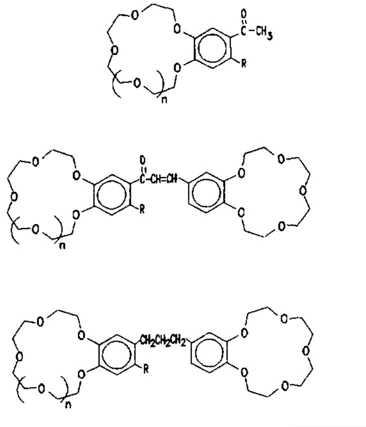

14 n=1 $R=C_2H_5$
15 n=2 $R=C_2H_5$
16 n=1 $R=C_8H_{17}$
17 n=1 $R=C_2H_5$
18 n=2 $R=C_2H_5$
19 n=1 $R=C_8H_{17}$
20 n=1 $R=C_2H_5$
21 n=2 $R=C_2H_5$
22 n=1 $R=C_8H_{17}$

Fig. 2. Synthesized compounds 14-22

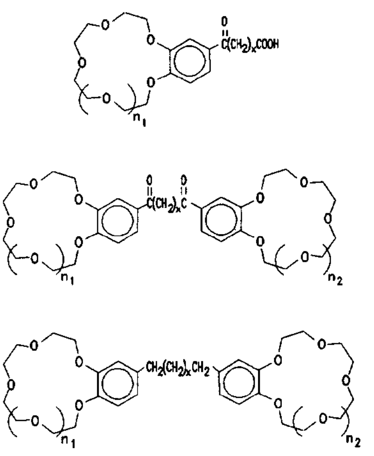
The aim of this paper is to present our findings on replacing the biscrown ester or amide group containing bridges by nonhydrolyzable, stable polymethylene chains or substituted polymethylene chains. In this work we have investigated reactions leading to bis(crown ether)s, derivatives of benzo-15-crown-5 and benzo-18-crown-6, with different lengths of bridging chains. The above compounds have been synthesized as part of our work leading to new, improved ionophores for ion-selective electrodes. The synthesized compounds have been applied in ion-selective electrodes in order to investigate the structure - ion-selectivity relationship. They have very promising electroactive properties. Biscrowns containing two benzo-15-crown-5 units are selective towards potassium while the compounds containing benzo-18-crown-6 units are selective towards rubidium and/or cesium ions.

RESULTS AND DISCUSSION

Synthesis

We have elaborated two methods for the synthesis of bis(benzocrown ether)s. The first route was based on the Claisen-Schmidt reaction of

4-formylbenzocrown with 4-acetylbenzocrown ether[7d] yielding chalcone-type compounds **1-3**. Condensation of 4-formylbenzocrown with 4-acetyl-5-alkylbenzocrown ether (**14-16**) leads to biscrowns substituted in the benzene ring (**17-19**). The 4-alkyl-5-acetyl derivatives (**14-16**) are easily obtained by acylation of *n*-alkyl substituted benzocrowns. All the compounds obtained by this method have a three-carbon bridge. The chalcone-type compounds (**1-3**, **17-19**) were hydrogenated to alcohols using palladium black or palladium on activated alumina as catalysts; unsatisfactory results had been obtained when using palladium on charcoal as catalyst. Some of these alcohols were isolated and characterized (**4-6**). Further hydrogenation of the alcohols using Raney nickel yielded the trimethylene bis(crown ether) derivatives (**7-9**, **20-22**).



23 $n_1=1$ $x=3$
24 $n_1=2$ $x=3$

25 $n_1=n_2=1$ $x=3$
26 $n_1=n_2=1$ $x=11$
27 $n_1=1$ $n_2=2$ $x=3$
28 $n_1=n_2=2$ $x=3$
29 $n_1=n_2=2$ $x=11$

30 $n_1=n_2=1$ $x=3$
31 $n_1=n_2=1$ $x=11$
32 $n_1=1$ $n_2=2$ $x=3$
33 $n_1=n_2=2$ $x=3$
34 $n_1=n_2=2$ $x=11$

Fig. 3. Synthesized compounds **23-34**

A higher lipophilicity of the ionophore increases the life-time of the ion-selective electrode membrane. The lipophilicity of a bis(benzocrown ether), which is a potential ionophore, can be increased, for example, by incorporating alkyl substituents. We have added alkyl substituents to the benzene residue of the substrate (compounds **14-16**) before the Claisen-Schmidt condensation step. Biscrowns **20-22** were obtained by this method. Other lipophilic derivatives, in which the alcoxy substituents are located in the bis(crown ether) bridge (**10-13**), have been obtained starting from the hydroxy derivatives **4-5** and alkyl bromides in the presence of a strong base.

Unsymmetric bis(crown ether)s e.g. compounds **8** and **21** may be obtained by the above method when the condensation is started from two crown derivatives of different sizes of the macrocyclic unit.

The second route leading to bis(crown ether)s with nonhydrolyzable bridging chains was based on the reaction of benzocrown ethers with dicarboxylic acids and subsequent reduction of the diketo derivatives to biscrowns with polymethylene bridges. The reaction of benzocrown ethers with dicarboxylic acids was performed in polyphosphoric acid as a one pot process or in two steps. The one pot process was used to obtain symmetric derivatives e.g. compounds **25**, **26** and **29**. In the two-step procedure the benzocrown ether keto acid derivative (**23**, **24**) was isolated as the first intermediate

Table 1. Properties of synthesized compounds.

No. of compound	Synthetic procedure	m.p. [°C]	Yield [%]	M^+ [m/e]	IR^* (C=O) [cm^{-1}]	^1H NMR δ [ppm] ($CDCl_3$)
1	2a	111-114	58	588	1650	3.60-3.40 (m,32H); 6.53-7.17 (m,4H); 7.30-7.80 (m,4H)
2	2b	77-82	40	632	1655	3.57-4.37 (m,36H); 6.67-7.20 (m,4H); 7.35-7.83 (m,4H)
3	2b	99-101	15	676	1660	3.47-4.40 (m,40H); 6.63-7.70 (m,8H)
4	3	106-109	90	592	-	1.80-2.26 (m,2H); 2.40-2.77 (m,2H); 3.05 (s,1H); 3.60-4.20 (m,32H); 4.35-4.70 (m,1H); 6.57-6.87 (m,2H)
5	3	71-75	70	636	-	1.70-2.20 (m,2H); 2.20-2.73 (m,4H); 3.17 (s,1H); 3.57-4.31 (m,36H); 4.53 (t,1H); 6.57-6.97 (m,6H)
6	3	oil	82	680	-	1.73-2.73 (m,5H); 3.50-4.23 (m,40H); 4.37-4.80 (m,1H); 6.60-6.90 (m,6H)
7	5	83-84	43	576	-	1.50-2.77 (m,6H); 3.50-4.23 (m,32H); 6.50-6.77 (m,6H)
8	5	56-57	23	620	-	1.50-2.20 (m,2H); 2.50 (t,4H); 3.53-4.30 (m,36H); 6.50-6.87 (m,6H)
9	5	83-85	76	664	-	1.67-2.20 (m,2H); 2.20-2.78 (m,4H); 3.57-4.30 (m,40H); 6.55-6.87 (m,6H)
10	4a	57-58	20	704	-	0.63-2.36 (m,17H); 2.36-2.87 (m,2H); 2.93-3.37 (m,2H);3.67-4.30 (m,33H); 6.60-6.90 (m,6H)
11	4a	45-46	27	760	-	0.70-2.30 (m,25H); 2.37-2.80 (t,2H); 2.97-3.40 (m,2H); 3.70-4.37 (m,33H); 6.60-6.87 (m,6H)
12	4a 4b	43-44	21 41	816	-	0.77-2.17 (m,33H); 2.30-2.83 (m,2H); 2.97-3.37 (m,2H); 3.63-4.33 (m,33H); 6.60-6.87 (m,6H)
13	4a	46-48	28	748	-	0.63-3.37 (m,21H); 3.50-4.27 (m,37H); 6.50-6.80 (m,6H)
14	1	108-110	50	-	1680	1.1 (t,3H); 2.48 (s,3H); 2.82 (q,2H); 3.63-4.33 (m,16H); 6.65 (s,1H); 7.23 (s,1H)
15	1	58-62	74	-	1676	1.13 (t,3H); 2.50 (s,3H); 2.85 (q,2H); 3.57-4.40 (m,20H); 6.73 (s,1H); 7.30 (s,1H)
16	1	41-43	36	-	1684	0.80-1.93 (m,15H); 2.47-3.20 (m,2H); 2.67 (s,3H); 3.67-4.47 (m,16H); 6.80 (s,1H), 7.37 (s,1H)
17	2a	81-85	50	616	1660	1.10 (t,3H); 2.40-2.87 (m,2H); 3.60-4.27 (m,32H); 6.60-7.43 (m,7H)

18	2b	90-96	41	660	1650	0.93-1.33 (t,3H); 2.23-2.86 (m,2H); 3.50-4.27 (m,36H); 6.60-7.50 (m,7H)
19	2b	oil	48	700	1658	0.83-1.70 (m,15H); 2.47-3.00 (m,2H); 3.63-4.40 (m,32H); 6.37-7.40 (m,7H)
20	3; 5	54-58	40	604	-	1.10 (t,3H); 1.55-2.15 (m,2H); 2.20-2.80 (m,3H); 3.52-4.35 (m,32H); 6.57-6.90 (m,5H)
21	3; 5	42-46	14	648	-	0.70-2.10 (m,5H); 2.20-2.80 (m,3H); 3.50-4.33 (m,36H); 6.57-6.96 (m,5H)
22	3; 5	49-50	35	688	-	0.70-2.10 (m,17H); 2.10-2.80 (m,6H); 3.60-4.20 (m,32H); 6.50-6.77 (m,5H)
23	6a	115-116	46	382	1732, 1680	1.85-2.70 (m,4H);2.80-3.20 (t,2H); 3.67-4.30 (m,16H); 6.67-6.93 (d,1H); 7.37-7.62 (s+d,2H)
24	6b	62-63	32	426	1728, 1664	1.82-2.65 (q+t,4H); 2.72-3.17 (t,2H); 3.55-4.38 (m,20H); 6.65-6.95 (d,1H); 7.40-7.63 (s+d,2H)
25	7a $7b_1$	124-126	63 25	632	1668	1.93-2.47 (m,2H);2.87-3.23 (t,4H); 3.67-4.40 (m,32H); 6.67-7.00 (m,2H); 7.40-7.73 (m,4H)
26	$7b_2$	93-95	31	744	1672	1.10-1.93 (m,18H); 2.85 (t,4H); 3.67-4.47 (m,32H); 6.67-6.93 (m,2H); 7.43-7.67 (m,4H)
27	7a	121-122	18	676	1670	1.90-2.40 (m,2H); 3.00 (t,4H); 3.63-4.40 (m,36H); 6.87 (d,2H); 7.57 (s,2H); 7.63 (d,2H)
28	7a	75-80	7	720	1680	2.00-2.40 (m,2H); 2.87-3.23 (t,4H); 3.67-4.43 (m,40H); 6.70-7.00 (d,2H); 7.47-7.70 (s+d,4H)
29	$7b_2$	78-80	22	832	1672	1.10-1.92 (m,18H); 2.92 (t,4H); 3.52-4.42 (m,40H); 6.92 (d,2H); 7.56 (s,2H); 7.60 (d,2H)
30	8	68-72	18	604	-	1.20-1.80 (m,6H); 2.23-2.80 (m,4H); 3.53-4.40 (m,32H); 6.50-7.00 (m,6H)
31	8	93-96	42	716	-	1.00-1.90 (m,22H); 2.35-2.68 (m,4H); 3.48-4.25 (m,32H); 6.48-6.75 (m,6H)
32	8	62-66	20	648	-	1.31-1.86 (m,6H); 2.36-2.71 (m,4H); 3.60-4.37 (m,36H); 6.60-6.86 (m,6H)
33	8	56-58	25	692	-	1.10-1.80 (m,6H); 2.20-2.80 (m,4H); 3.48-4.18 (m,40H); 6.52-6.83 (m,6H)
34	8	71-74	22	804	-	1.15-2.00 (m,22H); 2.35-2.70 (m,4H); 3.50-4.30 (m,40H); 6.65-6.90 (m,6H)

* IR spectra in nujol mulls

product. Further reaction of these intermediates with various crown ethers was carried out. Symmetric bis(benzocrown ether)s (**25**, **28**) or the unsymmetric derivative (**27**) were obtained. The reduction of the compounds **25-29**, according to the method described previously gave biscrowns **30-34** with polymethylene bridges.

The preliminary results of the syntheses were presented.[14] In the meantime the method based on the condensation of benzo-15-crown-5 with dicarboxylic acids was published by other authors[15] who reported the synthesis of one of the compounds described here (**30**).

The structural formulae of the synthesized compounds have been presented in Figures 1-3. The properties of the obtained compounds are shown in Table 1.

From the reported yields and reaction conditions a conclusion may be drawn that benzo-15-crown-5 and its acyl derivatives are more reactive than benzo-18-crown-6 and its analogous derivatives in the acylation reaction with dicarboxylic acids as well as in the Claisen-Schmidt condensation.

A different method for the synthesis of the type of compounds described above has been proposed by Kikukawa et al.[7a] who obtained biscrowns with dimethylene and octamethylene bridges.

Ion-Selective Electrode Investigations

Most of the synthesized compounds have been tested in ion-selective electrodes.

The bis(crown ether) derivatives with two benzo-15-crown-5 units act as ionophores for potassium ions. On the basis of CPK models Inoue et al.[15] have stated that biscrowns, benzo-15-crown-5 derivatives, form two types of sandwich complexes with potassium ions. The same authors show that the "open-clam" complex (Figure 4) is typical for biscrowns with bridges shorter than pentamethylene. The "closed clam" complex (Figure 5) is formed for biscrowns with pentamethylene and longer bridges. The stabilities of biscrown complexes with potassium ions increase with the length of the bridge reaching a maximum for 5 carbon atoms, decrease up to an octamethylene bridge and do not change thereafter. The complex formation involves restriction of the freedom of the ligand and cation and is disadvantageous in terms of entropy of the process. The desolvation of the cation as well as the ligand compensates the entropy decrease. In the case of short bridges full desolvation of the cation does not take place and therefore the entropy change of formation of this type of complex is not beneficial.

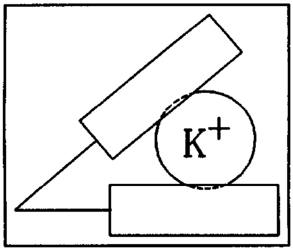


Fig. 4. An "open-clam" type of complex.

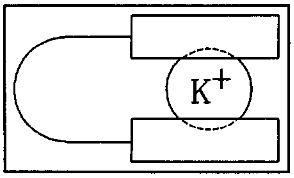


Fig. 5. A "closed-clam" type of complex.

The results of ion-selective electrode investigations concerning the benzo-15-crown-5 biscrown derivatives have been gathered in Figure 6.

A comparison of the K,Na selectivity coefficients of crowns **7**, **25** and **26** shows that the biscrown with the trimethylene bridge exhibits the best selectivity. Without doubt it forms the open-clam type of complex with potassium ions in contrast to the other two compounds with longer bridges. This shows that this type of complex is advantageous from the kinetics point of view of the reaction proceeding at the membrane-water interface. The open-clam conformation of the complex allows a fast exchange of potassium cations increasing the electrode exchange current connected with potassium ions and thus the selectivity of the electrode. The closed-clam type complexes will not induce a fast exchange current at the interface and therefore will not improve K,Na selectivity.

Polar groups as in keto compounds **25** and **26** cause a deterioration of the electrode properties. This may be caused by the negative effect of carbonyl groups on the complexation of potassium ions[15] or the greater rigidity of the bridge, causing the biscrown to be less flexible.

We have modified the lipophilicity of bis(crown ether)s by incorporating alkyl groups into the aromatic rings or to the linking bridge. The electrodes based on compounds **10-12** and **20** show very good properties. The electrodes based on compounds **10-12** have a K,Na selectivity coefficient equal to approx. -3.6 and the compounds a lipophilicity between 8 and 12. They therefore fulfill conditions for application in clinical analysis.

The results of ion-selective electrode investigations concerning the benzo-18-crown-6 biscrown derivatives have been gathered in Figure 7.

Asymmetric aromatic biscrowns, containing benzo-18-crown-6 and benzo-15-crown-5 generally exhibited selectivity towards rubidium ions (compounds **5**, **13**, **27**, **32**) and cesium ions (compounds **8**, **21**) in relation to the other alkali cations. The best selectivity towards rubidium in relation to potassium ions ($\log K_{Rb,K} = -1.3$) was found for compounds **8** and **13** with a three-carbon chain connecting the aromatic rings. Lipophilic substituents did not significantly change the selectivities of the previously mentioned compounds.

Some of the symmetric aromatic biscrowns, containing only benzo-18-crown-6 residues, exhibit selectivity towards cesium ions (compounds **9**, **29**, **33**, **34**). The best result has been obtained for compound **9** ($\log K_{Cs,K} = -2.3$). This compound also has a three-carbon bridge connecting the aromatic rings.

Our ion-selective electrodes compare well with other electrodes based on various bis(crown ether)s reported in the literature. Their selectivity coefficents for potassium over sodium[6] are very similar to values previously reported while the rubidium[7b] and cesium[6,7b] electrodes exhibit selectivities over potassium of an order higher.

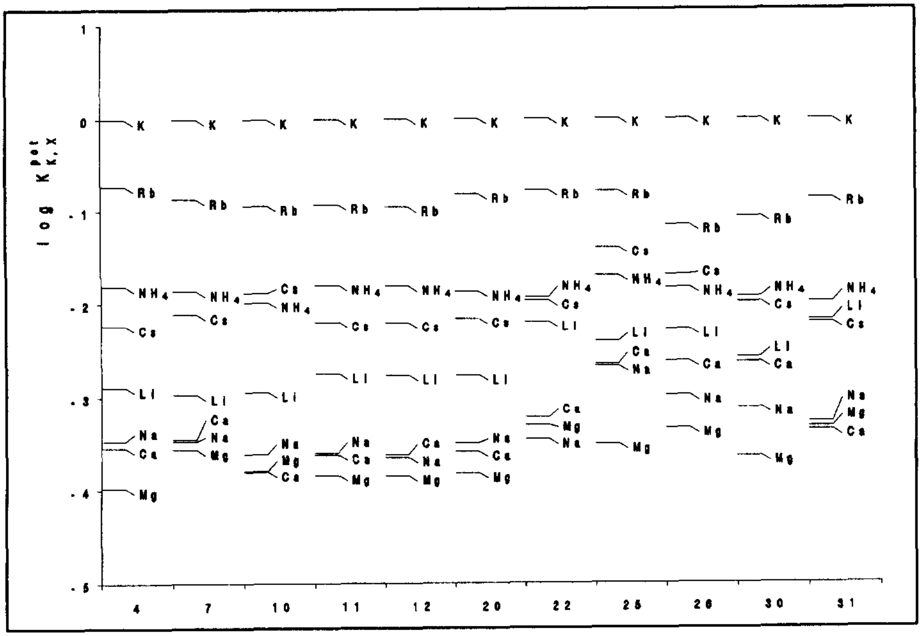


Figure 6. Selectivity coefficients of benzo-15-crown-5 derivatives

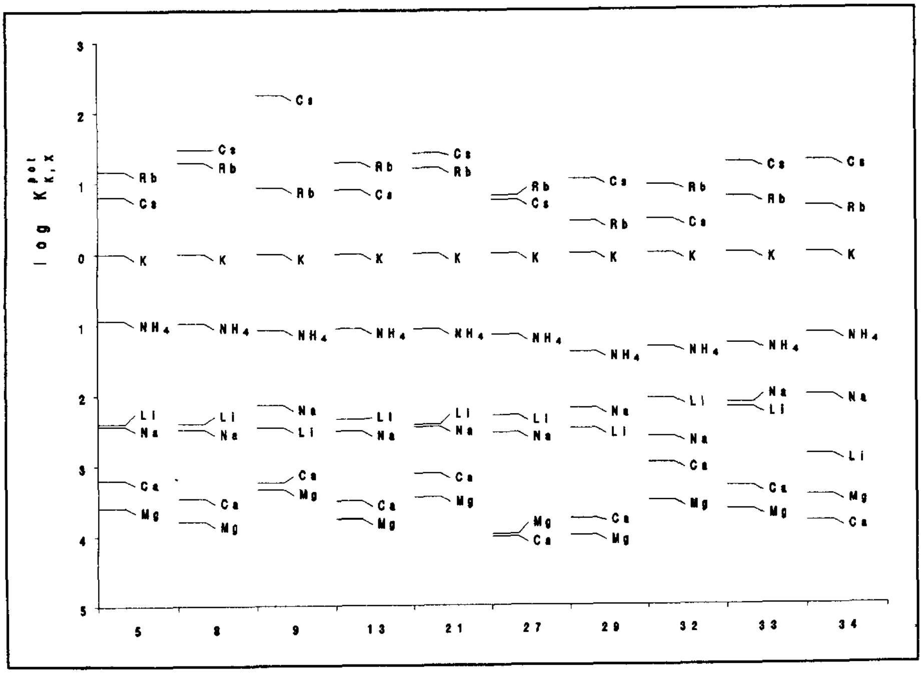


Figure 7. Selectivity coefficients of benzo-18-crown-6 derivatives.

EXPERIMENTAL

Synthesis

Benzo-15-crown-5 and benzo-18-crown-6 were synthesized acc. to Pedersen.[16] The known acyl and alkyl derivatives of benzo-15-crown-5 and benzo-18-crown-6 were synthesized acc. to Bradshaw[17] and Tashmukhamedova.[18] The formyl derivatives were synthesized according to Hyde et al.[19] Polyphosphoric acid (PPA) was obtained by a typical procedure.[20] All solutions were dried using anhydrous magnesium sulphate. Column chromatography was performed using silica gel (MN, 50-100 mesh).

NMR spectra were taken on a Varian 60 MHz spectrometer. IR spectra were taken on a Specord M80 spectrophotometer. The mass spectra were recorded on a Varian MAT 711 spectrometer using the FD technique.

1. 4-Acetyl-5-alkylbenzocrowns - compounds **14-16**.

A mixture of 10 mmoles of 4-alkylbenzocrown, 10 mL of acetic anhydride and 15 mL of PPA was heated for 3 h. at 70°C. After cooling the reaction mixture was diluted with water and the product extracted with chloroform. After evaporation of the solvent the product was extracted with warm *n*-heptane and recrystallized from the same solvent.

2. Condensation of the acetyl- and formyl- derivatives of benzocrowns to chalcone-type compounds **1-3**; **17-19**.

3 mmoles of 4-acetylbenzo-15-crown-5, 4-acetylbenzo-18-crown-6 or the respective alkyl derivatives **14-16** and 3 mmoles of the 4-formylbenzo-15-crown-5 or 4-formylbenzo-18-crown-6 were stirred in 20 mL of methanol in the presence of potassium hydroxide (which was added dropwise as a concentrated solution in methanol to reach pH ≈ 8-9). The reaction was carried out at 50-60°C for 1-10 days under argon. The course of the reaction was controlled by TLC.

The approximate reaction time is (days): compound **1** - (3), **2** - (6), **3** - (10), **17** - (1), **18** -(2), **19** - (4).

The mixture was neutralized with acetic acid and the solvents removed. The product was then extracted with chloroform. After evaporation of the solvent the product was crystallized from izopropyl alcohol (procedure 2a) or purified on a silica gel column (the product was eluted with ethyl acetate and methanol) (procedure 2b) and then crystallized from izopropyl alcohol to give a pale yellow product.

3. Reduction of chalcone-type compounds to alcohols.

Hydrogen was continuously passed through a solution of 2 mmoles of the condensation product (**1-3**, **17-19**) in 40 mL of methanol in the presence of palladium black. The reduction was carried out for approx. 4-5 days at room temperature. After filtration and evaporation of the solution the product was crystallized from *n*-heptane and next recrystallized from izopropyl alcohol (compounds **4**, **5**).

The other alcohols, without initial purification, were further reduced in the presence of Raney nickel as in point 5.

4. O-Alkyl derivatives of the above alcohols - compounds 10-13.

0.25 g of sodium hydride (60% suspension in mineral oil) was washed with dry *n*-hexane, 20 mL of tetrahydrofuran were added and the mixture stirred for 5 minutes. 1.2 mmole of alcohol **4** or **5** were added and the mixture stirred for a further 20 minutes. A solution of 2 mmoles of bromoalkane in 10 mL of tetrahydrofuran was added dropwise. The resulting mixture was stirred for 1 week at room temperature (procedure 4a) or for 3 days at 60°C (procedure 4b). The excesss of sodium hydride was destroyed by adding ice. The solvent was then evaporated. The product was extracted from the neutralized residue with methylene chloride and next extracted with hot *n*-heptane and crystallized from the same solvent (4a) or purified on a silica gel column using ethyl acetate as eluent (4b).

5. Reduction of alcohols to bis(benzocrown ether)s with trimethylene bridges - compounds 7-9, 20-22.

Approximately 1.5 g of Raney nickel (W2) were added to 5 mmoles of alcohol obtained by method 3 in 40 mL of ethanol. The mixture was refluxed for 24 hours. After filtering and evaporation of the solvent the product was extracted with hot *n*-heptane and recrystallized from the same solvent.

6. Acylation of benzocrowns with dicarboxylic acids - the synthesis of keto acid derivatives of benzocrowns - compounds 23-24.

A mixture of 15 mmoles of benzocrown and 30 mmoles of dicarboxylic acid in 12 mL of PPA was heated for 3 h at 85°C. The cooled mixture was diluted with water, the product extracted with chloroform and next crystallized from ethyl acetate (procedure 6a) or purified on silica gel column (procedure 6b), the product was eluted with ethyl acetate and crystallized from ethyl acetate or ethyl acetate - *n*-heptane.

7. Synthesis of compounds 25-29.

7a) A mixture of 6 mmoles of the benzocrown keto acid derivative **23-24**, 12 mmoles of benzocrown and 50 mL of PPA was heated for 24 hours at 80°C. After diluting with water the product was extracted with chloroform and next purified on a silica gel column. The product was eluted with ethyl acetate and crystallized from the same solvent.

7b) A mixture of 2 mmoles of benzocrown, 1 mmole of dicarboxylic acid and 4 mL of PPA was heated for 3 days at 70°C (procedure $7b_1$) or 7 hours at 85-90°C (procedure $7b_2$). Isolation was carried out as in method 7a). Compounds **26**, **29** were crystallized from ethanol.

8. Bis(benzocrown ether)s with polymethylene bridges - compounds **30-34**.

Diketobisbenzocrowns **25** - **29** were hydrogenated to the respective bis(benzocrown ether)s and isolated according to method 3 and 5.

EMF measurements

Electrodes were prepared and tested by procedures described previously.[2] For example: 50 mg of PVC, 11 mg of biscrown **7** and 100 μl of o-nitrophenyloctyl ether were dissolved in 1 mL of THF. The solution was poured into a glass ring and left to evaporate for 24 hours. The discs were incorporated into Ag/AgCl electrode bodies, with 10^{-2}M KCl as the internal electrolyte. Other crowns were used in such amounts so that their molar concentration in the membrane was the same as in the case of compound **7**. In the case of benzo-18-crown-6 derivatives RbCl or CsCl (10^{-2}M) were used as internal electrolytes. Lithium acetate was used as external electrolyte in the double-junction reference electrode (RADELKIS OP-0802OP Ag/AgCl electrode). All measurements were carried out on a N517 (MERA ELWRO) pH-meter with a V-541 digital voltmeter, allowing readings with an accuracy of 0.1 mV. The selectivity coefficients were determined using the mixed solution method.

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