Substituent Effects on Cation-extraction and Transport Properties of a Series of 4′-Substituted Benzo-15-Crown-5 Derivatives

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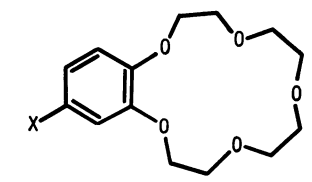
Synopsis. The substituent effects on chemical functions of benzo-15-crown-5 derivatives were found to be considerably large and often comparable to the ring-size effects. For example, 4′-aminobenzo-15-crown-5 transported K^+ ion 14-times faster than 4′-nitrobenzo-15-crown-5, while 4′-nitrobenzo-18-crown-6 showed 12-times higher transport rate than 4′-nitrobenzo-15-crown-5.

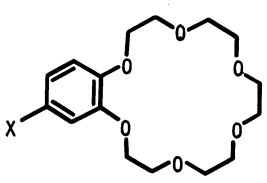
Macrocyclic crown ethers form stable and selective complexes with alkali and alkaline earth cations, and show characteristic cation-transport and related functions.[1] Since their cation-binding properties are largely changed by chemical modifications of crown ether structures,[2] a variety of functional substituents have been introduced into crown ether skeletons. Here we examined the cation-extraction and transport properties of a series of 4′-substituted benzo-15-crown-5 derivatives, and found that the substituent effects on chemical functions of crown ethers were considerably large and often comparable to the crown ring-size effects. Although several types of benzo-crown ether derivatives have been prepared as cation-binders, carriers, and catalysts,[3] this is the first report concerning substituent effects on the cation-transport phenomena.[4] Therefore, the present study may offer the further possibilities in the designing new functional benzo-crown ethers and related polymers.

Results and Discussion

1. Substituent Effects on Cation-extraction Properties of Benzo-15-Crown-5 Derivatives. The cation-extraction properties of a series of benzo-15-crown-5 derivatives **1**, **3**, **4**, and **5** were examined by equilibrating a CH_2Cl_2 solution of a crown ether with an aqueous solution of metal perchlorate.



1: X=NH_2
2: X=t-C_4H_9
3: X=H
4: X=Br
5: X=NO_2



6: X=NO_2

Fig. 1. Examined benzo-crown ethers.

The examined benzo-15-crown-5 derivatives extracted Na^+ and K^+ ions much more effectively than Li^+ and Cs^+ ions under the employed conditions (Table 1). Their extraction properties were generally controlled by guest cation-crown ring size fitness, and also largely influenced by the natures of 4′-substituents attached to benzene ring. For example, crown **1** bearing electron-donating -NH_2 group showed higher extraction abilities for Na^+ and K^+ ions than crowns **4** and **5** bearing electron-withdrawing -Br and -NO_2 substituents. Smid *et al.* have measured the stability constants for some Na^+·benzo-15-crown-5 complexes in acetone and observed somewhat similar substituent effects: $K\times10^{-3}$ (M^{-1})=8.21 for **1**; 2.05 for **4**; 0.165 for **5**.[4a] As shown before,[4] substituent groups attached to benzene rings may change basicities of two aromatic ether oxygen atoms. (1 M=1 mol dm^{-3}).

4′-Nitrobenzo-18-crown-6 (**6**) extracted K^+ ion more effectively than 4′-nitrobenzo-15-crown-5 (**5**). Since K^+ ion fits ring size of 18-membered crown ether more tightly than that of 15-membered one, crown ring size effects seemed to be a dominant factor as reported frequently.[1] However, its extraction efficiency and selectivity for K^+ ion were lower than those of benzo-15-crown-5 derivatives **1** and **3**. These observations strongly suggest that the nature of substituent is a more important factor in determining extraction ability than ring size of parent crown ether.

2. Substituent Effects on Cation-transport Properties of Benzo-15-Crown-5 Derivatives. The transport experiments were performed in the CH_2Cl_2 liquid membrane,[5] in which crown ether solubilizes guest cation salt into the membrane and facilitates transport from source aqueous phase through CH_2Cl_2 membrane to receiving aqueous phase. The measured values of initial cation-transport rates are summarized in Table 2.

The transport rates of Na^+ and K^+ ions with benzo-

Table 1. Extraction properties of benzo-crown ethers

Crown	Extraction Percentage/%[a]			
	Li^+	Na^+	K^+	Cs^+
1	0	3.6	13.6	0.4
3	0.4	3.8	10.4	0
4	0	0.8	2.8	0
5	0.2	1.8	3.6	0
6	0	3.4	4.6	2.1

Conditions: Aqueous phase; Metal perchlorate, 0.02 mmol/H_2O, 2 ml. Organic phase; Crown, 0.15 mmol/CH_2Cl_2, 3 ml. a) [Metal salt extracted in CH_2Cl_2]/[Metal salt added initially]×100 was shown, which was calculated from the difference in the extraction percentages of crown-containing and blank (no crown) systems.

Table 2. Transport properties of benzo-crown ethers

Crown	Transport Rate ($\times 10^6$ mol/h)[a]			
	Li^+	Na^+	K^+	Cs^+
1	0.1	0.7	9.9	1.1
2	<0.1	0.6	9.1	1.2
3	<0.1	0.6	8.9	0.7
4	<0.1	0.2	2.3	0.3
5	<0.1	0.1	0.7	<0.1
6	<0.1	0.4	8.7	3.0

Conditions; Source aqueous phase; Metal perchlorate, 0.5 mmol/H_2O, 5 ml. Membrane phase; Crown, 0.05 mmol/CH_2Cl_2, 12 ml. Receiving aqueous phase; H_2O, 5 ml. a) The values indicated were calculated from the difference in the transport rates of carrier-containing and blank (no carrier) systems. Reproducibility was confirmed as ±15% or better.

15-crown-5 derivatives also showed a pronounced dependence on the natures of 4′-substituents attached to benzo-crown ring. The electron-withdrawing substituents such as -Br and -NO_2 groups largely decreased transport rates of Na^+ and K^+ ions, though electron-donating -NH_2 and -t-C_4H_9 groups offered fast transport rates. As a result, a 14-fold difference in the transport rates of K^+ ion was observed between benzo-15-crown-5 derivatives **1** and **5**. When 4′-nitrobenzo-18-crown-6 (**6**) was employed as a carrier, its transport rate of K^+ ion was 12-times higher than that of 4′-nitrobenzo-15-crown-5 (**5**), but lower than those of 4′-amino- and 4′-t-butylbenzo-15-crown-5 derivatives **1** and **2**. Since we confirmed that the leakages of the examined benzo-crown ethers **1**—**6** were almost negligible,[6] the present results demonstrate that transport profiles are easily modified by simple substitution of benzo-crown ether. In other words, the nature of substituent introduced into crown ether skeleton should be seriously considered in the modification and functionalization of benzo-crown ether type ligand system.

Experimental

1. Materials. 4′-Substituted benzo-crown ethers **1**, **4**, **5**, and **6** were prepared as decribed before,[4a] and showed satisfactory Mass, ^{1}H-NMR, and ir spectral data. Crowns **2** and **3** were purchased from Merck Japan and Parish Chemical, respectively. Other employed reagents were commercially available and used without further purifications.

2. Extraction Procedures. The extraction abilities of crown ethers were estimated on the basis of the partition of metal perchlorate between CH_2Cl_2 (3 ml) and aqueous solution (2 ml). After extraction experiments (3 h), the aqueous phase was separated and the concentrations of K^+, Na^+, and ClO_4^- ions were determined by means of ion-selective electrodes (Orion Model 931901, 971100, and 938100). The crown **2** was not examined here, because of its low solubility into the CH_2Cl_2.

3. Transport Procedures. The transport experiments were carried out at room temperatue in a U-tube glass cell (2.0 cm, i. d.) as reported before.[5] The crown in CH_2Cl_2 (12 ml) was placed in the base of the U-tube, and two aqueous phases (5 ml, each) were placed in the arms of the U-tube, floating on the CH_2Cl_2 membrane. The membrane phase was constantly stirred with a magnetic stirrer. The transported amounts of K^+, Na^+, and ClO_4^- ions were also determined by ion-selective electrode techniques.

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6) After transport experiments, the employed benzo-crown ethers remained in the membrane phase quantitatively, excepting for crown **1** (≈91%).