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EFFECT OF SIDEARM OF 15-CROWN-5 ON Na^+/K^+ SELECTIVITY

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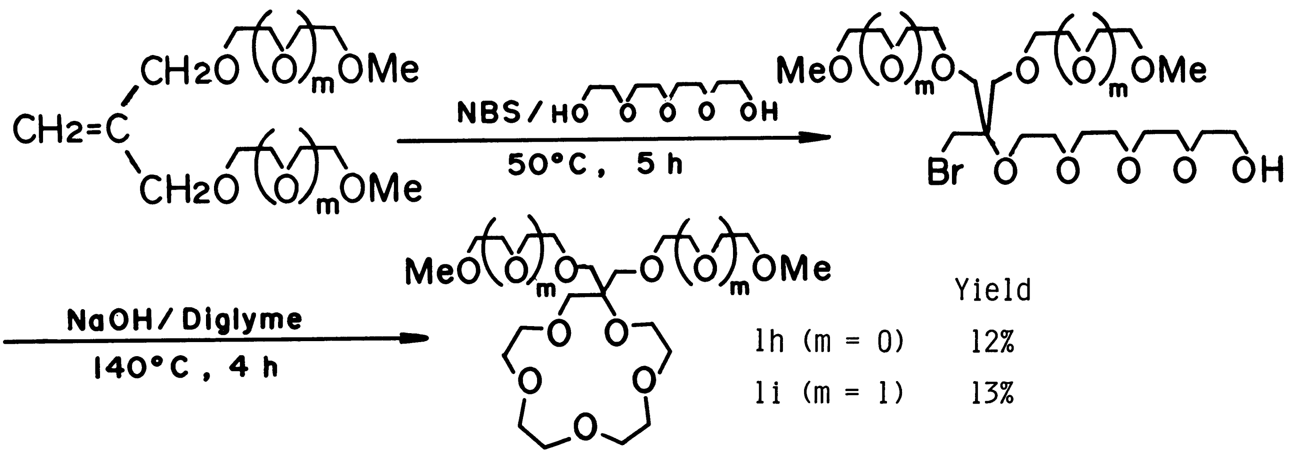
Certain host molecules having electrondonating sidearm derived from 15-crown-5 were found to display excellent Na^+/K^+ selectivity.

Although a lot of factors are known to influence the complexation of macrocyclic multidentate ligands with cations, the relative size of the cation and the hole in the macrocyclic compound is considered to be one of the most important factors dominating the complexing ability and the selectivity.[1,2] As for crown compounds, the ligand suitable for a specified cation is not necessarily obtained because the hole size is determined by its own ring structure. For example, even 15-crown-5, which seems to have most suitable ring structure for Na^+, does not display the sufficient complexing ability toward Na^+ and the Na^+/K^+ selectivity, as shown by the binding data(Table). Some cryptands having three-dimensional structure are known to display much higher complexing ability and the good selectivity.[2] However, the modification of the ring structure has its own limits and too strong complexation is not always desirable in compliance with purpose, as indicated in membrane transport velocity of cations by some groups.[3,4]

Functionalized crown ethers such as bis-crown ethers[5-7] and lariat ethers[8,9] had been extensively studied[10] because the suitability of the structure for a variety of cations can be delicately modified. Recently, lariat ethers[8] having a secondary electrondonating part were found to increase the complexing ability toward cations such as Na^+, K^+, and NH_4^+, but the contribution of the sidearm to the selectivity was not fully clarified in the preceding studies. However, the binding data obtained in 2-methyl-15-crown-5 derivatives having an oligo-oxyethylene sidearm at the pivot position showed that one oxyethylene unit increased the complexing ability toward Na^+ without the increase of that toward K^+.[9] This finding suggests the possibility that the modification of sidearms can improve not only the complexing ability but also the selectivity. We now report the synthesis of novel 15-crown-5 derivatives and the function of the secondary electrondonating sidearm on the Na^+/K^+ selectivity by considering following aspects: 1) fixation of the conformation of the electrondonating sidearm on the crown ring; 2) bulkiness of the terminal branch of the electrondonating sidearm; 3) rigidity of the electrondonating sidearm near the pivot position; 4) interference from the access of cations from backside.

Methyl lariat ethers(1a-1e) were easily obtained from the nucleophilic substitution reaction of 2-bromomethyl-2-methyl-15-crown-5[11] by using the corresponding alkoxides or phenoxides(120-130°C, 24-48 h). Hexyl lariat ethers (1f and 1g) were also obtained from 2-bromomethyl-2-hexyl-15-crown-5, which was prepared in 25% yield according to the intramolecular bromoalkoxylation of tetraethylene glycol mono 2-hexylallyl ether,[12] by the similar procedure.

The two-armed crown ethers having geminal electrondonating sidearms (1h and 1i) were prepared according to the method shown below.

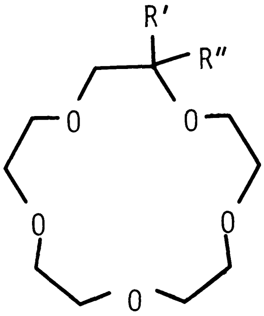


	Yield
1h (m = 0)	12%
1i (m = 1)	13%

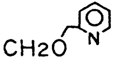
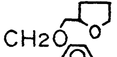
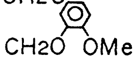
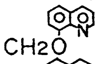
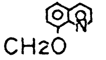
The stability constants at 25°C in methanol determined according to the potentiometric method[14] are shown in the Table.

As the fact that methyl group geminal to oxyethylene group increased the stability constant was considered to display the importance of the fixation of conformation of the electrondonatng sidearm,[9] we introduced more rigid electrondonating sidearm into 15-crown-5 ring in order to enhance the fixation effect. The higher binding data obtained for 1c having tetrahydrofuran-type sidearm in comparison with those for 1a having methoxy-type sidearm show the importance of restricting the interference by the terminal branch movement. The effectiveness of the rigidity of the electrondonating sidearm near the pivot position was disclosed in the binding data of 1e having quinoline-type sidearm, compared with those of 1b having pyridine-type sidearm. The stability constant(4.87) toward Na^+ of 1e was found as to be about 40 times that of unsubstituted 15-crown-5(1j) and, as far as we know, the highest among the values for crown ether derivatives. The fact that the complexing ability toward K^+ of 1e was not so increased turned out to give 1e good Na^+/K^+ selectivity. In addition, introduction of long alkyl chain on the pivot position was found to further contribute to the increase of the selectivity by suppressing the complexation of ligand for K^+.

Table Influence of Electrondonating Sidearm on Complexing Ability



(1)

Compound[a]	R'	R''	log K' Na^+	log K' K^+	K'(Na)/K'(K)
1a	CH_3	CH_2O⌒OMe	$(3.87)^b$	$(3.42)^b$	2.8
1b	CH_3		3.58	3.08	3.2
1c	CH_3		4.02	3.49	3.4
1d	CH_3		3.79	3.35	2.8
1e	CH_3		4.87	3.56	20.4
1f	C_6H_{13}		4.85	3.41	27.5
1g	C_6H_{13}	CH_2O⌒OMe	3.90	3.29	4.1
1h	CH_2O⌒OMe	CH_2O⌒OMe	3.84	3.44	2.5
1i	CH_2O⌒O⌒OMe	CH_2O⌒O⌒OMe	3.86	3.98	0.8
1j	H	H	$(3.27)^b$	$(3.3\text{-}3.6)^c$	< 1

a) All new compounds had IR, NMR, and combustion analyses in accordance with the assigned structures. b) ref. 9 c) The value depends on the concentrations of crown ether and potassium ion because of the formation of 2:1 complex.

The complexing ability of two-armed crown ether having two electrondonating groups on the same carbon(**1h** and **1i**) is very similar to that of the corresponding methyl lariat ether. This finding is reasonable because two oxyethylene chains of **1h** and **1i** can not coordinate the cation at the same time as suggested by the examination of Corey-Pauling-Koltun molecular models.

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