The Synthesis of Li^+-selective Polyether Carriers and Thier Behavior in Cation Transport through Liquid Membranes[1)]

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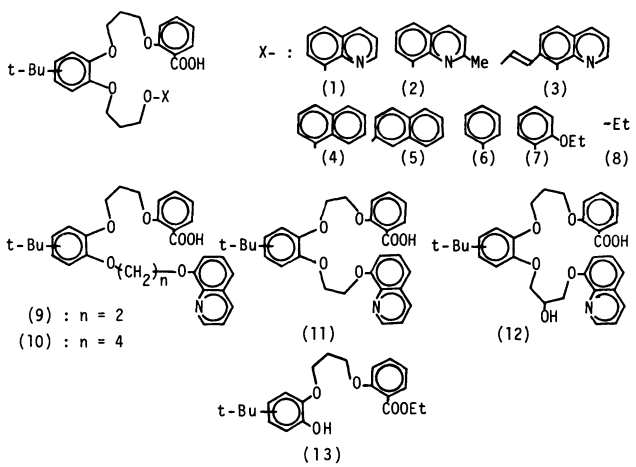
(Received November 18, 1983)

Noncyclic polyethers exhibiting lithium ion selectivity have been synthesized. Their competitive alkali-metal-ion transport through liquid membranes has been investigated, and the influence of their structures on the rates and selectivities of cation transport has been demonstrated. It has been found that the introduction of the oxytrimethylene chain on the polyethers is significant for the appearance of a high selectivity for the lithium ion, and also that the kind of terminal group might play an important role either in determining the rates of cation transport or the selectivity for the lithium ion. The introduction of a methyl group at the 2-position on the quinolyl terminal group of the polyether increased largely the selectivity for the lithium ion compared with that of the polyether having an unsubstituted quinolyl group. The cause of this was discussed on the basis of the NMR spectroscopic method and the CPK-model building.

The lithium ion has the smallest naked ionic radius (0.66 Å) among the alkali metal ions, whereas it has the largest hydrated one (3.40 Å) and also the strongest hydrated energy (ΔH=124 kcal/ mol) among them.[2)] Therefore, it is not easy to design a compound with lithium ion-selectivity, and there have been few reports about available compounds which exhibit lithium ion-selective transport through liquid membranes or which extract the lithium ion into organic solvents, compared with the cases of other alkali metal ions.[3)] In addition, the lithium is an important cation practically, and its selective separation and concentration from a diluted aqueous solution will become of significance in the future. For example, there is a possibility that large amounts of lithium are required for the production of tritium, which is used as a reactant in the nuclear-fusion reaction. Thus, the synthesis of lithium ion-selective compounds is a very interesting target.

In a previous paper, one of the present authors has reported that 1-[3-(*o*-carboxyphenoxy)propoxy]-2-[3-(8-quinolyloxy)propoxy]-4(or 5)-*t*-butylbenzene (**1**) can transport the lithium ion selectively through liquid membranes and against its concentration gradient.[4)] So far, there has been no report of a noncyclic polyether carrier exhibiting uphill transport for the lithium ion selectively.[5)] Though some cyclic polyethers, *e.g.*, 12-crown-4 and its derivatives, and cryptand[211], can take up the lithium ion selectively, they do not always transport it selectively and efficiently.[6)]



In this paper, we wish to report that analogues of **1**, **2**—**12**, were newly synthesized in order to investigate the effects of their structural modification on the transport rates and selectivities. In the cation-transport experiments, the competitive cation transport of alkali metal ions from an alkaline aqueous solution (source phase) through a chloroform phase to an acidic aqueous solution (receiving phase) by these noncyclic polyethers was examined.

Results and Discussion

Dependence of the Cocentration of Cations in Aqueous Phases on the Li^+-Selectivity of 1. The competitive ion transport of alkali metal ions (Li^+, Na^+, and K^+) by **1** against their concentration gradient was examined by changing the concentration of cations in both aqueous solutions under a constant concentration (1.5×10^{-4} mol in 30 ml of chloroform) of polyether (**1**) and a constant pH gradient. The results are shown in Figs. 1,2, and 3. Table 1 shows the amounts of cation transported after 2 d and the selectivities. Under these conditions, no cation could be transported without a carrier. In the membrane system (0.15 M† LiOH+0.15 M NaOH+0.15 M KOH+0.175 MH_2SO_4, 15 ml/1.5×10^{-4} mol of **1**, 30 ml of chloroform/0.15 M LiOH+0.15 M NaOH+0.15 M KOH+ 0.275 M H_2SO_4, 15 ml), which initially contained a sufficient cation concentration in comparison with the magnitude of the pH gradient between the two aqueous phases, the selectivity for the lithium ion was much higher than in the system which had an initial concentration of 0.1 M for each cation. That is, the transport ratios, Li/Na and Li/K, reach 6.6 and >10 respectively in this system, and the amount of the lithium ion transported reaches 0.795 mmol after 2 d. On the other hand, when the initial concentration of each cation was 0.033 M and the magnitude of the initial pH gradient was the same as above, 82% of the lithium ion in the source phase was trans-

† 1 M=1 mol dm^{-3}.

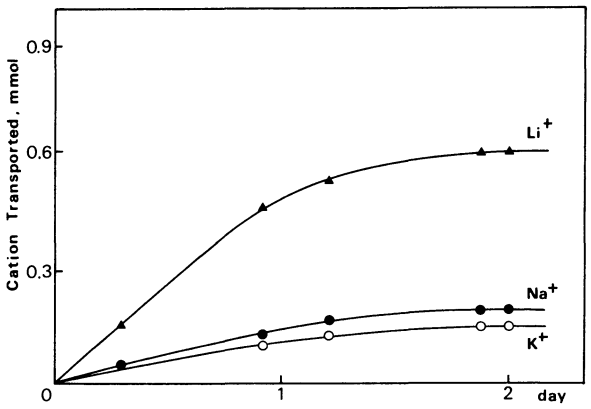


Fig. 1. Cation transport by (**1**) for lithium, sodium, and potassium ion species existing together. Initial transport conditions (25 °C) ; Source phase : 15 ml of 0.1M LiOH+0.1 M NaOH+0.1 M KOH+0.1 M H_2SO_4 aqueous solution, Chloroform membrane : 30 ml of chloroform containing 1.5×10^{-4} mole of (**1**), Receiving phase : 15 ml of 0.1 M LiOH+0.1 M NaOH+0.1 M KOH+0.2 M H_2SO_4 aqueous solution.

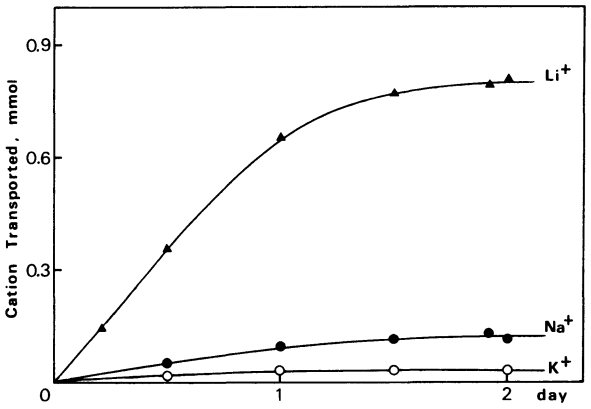


Fig. 2. Cation transport by (**1**) for lithium, sodium, and potassium ion species existing together. Initial transport conditions (25 °C); Sourcephase: 15 ml of 0.15 M LiOH+0.15 M NaOH+0.15 M KOH+0.175 M H_2SO_4 aqueous solution, Chloroform membrane: 30 ml of chloroform containing 1.5×10^{-4} mole of (**1**), Receiving phase: 15 ml of 0.15 M LiOH+0.15 M NaOH+0.15 M KOH+0.275 M H_2SO_4 aqueous solution.

ported by **1** after 2 d, although the selectivity (Li/Na) became fairly low. In this system, both sodium and potassium ions were transported gradually with the time, as is shown in Fig. 3, making a sigmoidal shape. This could be attributed to the excessive pH gradient, which is not exhausted by the transport of the lithium ion, between the two aqueous phases. Interestingly, this trend is in line with the results observed in the case of the potassium ion-selective polyether, 1-[2-[2-(8-quinolyloxy)-ethoxy]ethoxy]-2[2-[2-(*o*-carboxyphenoxy)ethoxy]ethoxy]-4(or 5)-*t*-butylbenzene, as has been reported recently.[7] These results mean that the selectivity for a cation can be changed greatly by changing the concentration of cations in the aqueous phases under a constant pH gradient. Therefore, it is suggested that the lithium ion can be separated and concentrated with a high selectivity from other alkali ions against their concentration gradient when adequate transport conditions are chosen in the system.

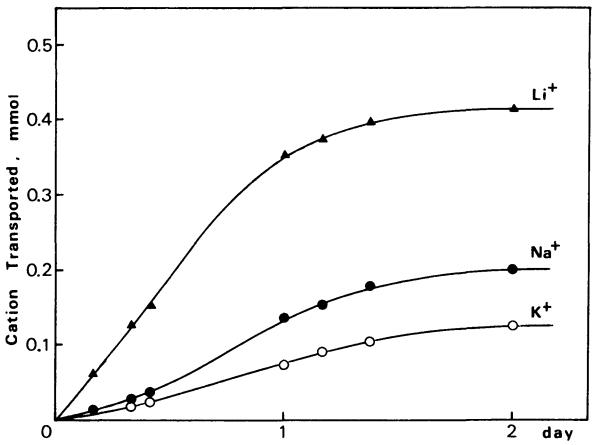


Fig. 3. Cation transport by (**1**) lithium, sodium, and potassium ion species existing together. Initial transport conditions (25 °C); Source phase: 15 ml of 0.033 M LiOH+0.033 M NaOH+0.033 M KOH aqueous solution, Chloroform membrane : 30 ml of chloroform containing 1.5×10^{-4} mole of (**1**), Receiving phase : 15 ml of 0.033 M LiOH+0.033 M NaOH+0.033 M KOH+0.1 M H_2SO_4 aqueous solution.

Table 1. Influence of initial cation concentration on the amounts of cation transported by (**1**)

Initial conc. of each cation*	Cation transported after 2 d (mmol)			Selectivity	
	Li	Na	K	Li/Na	Li/K
0.033 M	0.410	0.205	0.125	2.0	3.3
0.10 M	0.615	0.180	0.120	3.4	5.1
0.15 M	0.795	0.120	0.030	6.6	$\gg$10

* Other conditions: see the footnotes in Figures 1,2, and 3 respectively.

Effects of the Kind of Oxyalkylene Chain on the Selectivity. As has been described above, we have found that the noncyclic polyether (**1**), with both *o*-carboxyphenyl and 8-quinolyl terminal groups, exhibits the ability of the selective uphill transport of the lithium ion. Then, what structure of the noncyclic polyethers which exhibit lithium ion-selectivity is essentially required? In order to clarify this question, firstly, the effects of the kind of oxyalkylene chain on the selectivity were examined.

Some noncyclic polyethers which contain oxyethylene, oxytrimethylene, and/or oxytetramethylene chains were prepared and used as carriers in the cation transport through liquid membranes. The results are shown in Table 2. In Table 2, polyether (**1**) which contains two oxytrimethylene chains, exhibits the best selectivity for the lithium ion between them. The selectivity is lowered when the oxyalkylene chain

TABLE 2. INFLUENCE OF KINDS OF ALKYLENE CHAIN ON THE CATION-SELECTIVE TRANSPORT

Polyether	Cations transported after 2 d (%)				Selectivity		
	Li	Na	K	Total	Li/Na	Li/K	Na/K
(**1**)	41	12	8	61	3.4	5.1	1.5
(**9**)	34	17	11	62	2.0	3.1	1.5
(**10**)	36	16	11	63	2.2	3.3	1.5
(**11**)	28	21	13	62	1.3	2.1	1.6

Initial transport conditions (25 °C):

(Source phase)	(Chloroform membrane)	(Receiving phase)
0.1 M LiOH		0.1 M LiOH
0.1 M NaOH	Polyether	0.1 M NaOH
0.1 M KOH	1.5×10^{-4} mol	0.1 M KOH
0.1 M H_2SO_4	$CHCl_3$ 30 ml	0.2 M H_2SO_4
15 ml		15 ml

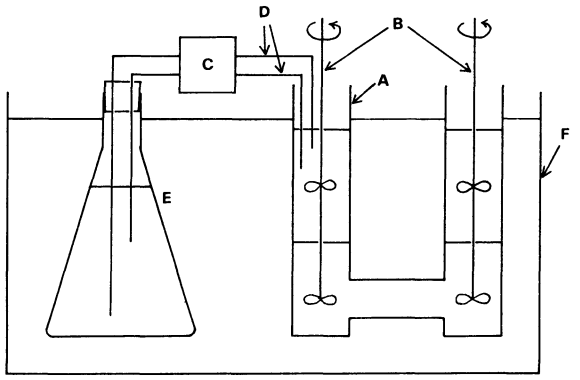


Fig. 4. Apparatus for measuring cation transport ; (A) U-type glass tube, (B) glass stirrer (200 min^{-1}.), (C) circulating pump, (D) polypropylene tube (diameter 2 mm) for circulating aqueous solution in the source phase, (E) 100-ml Erlenmeyer flask, (F) water bath controlled temperature (25 °C).

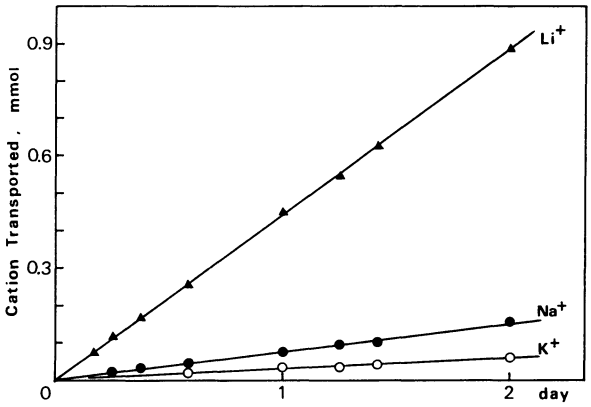


Fig. 5. Cation transport by (**2**) for lithium, sodium, and potassium ion species existing together. Initial transport conditions (25 °C) ; Source phase : 115 ml of 0.1 M LiOH+0.1 M NaOH+0.1 M KOH+0.1 M H_2SO_4 aqueous solution, Chloroform membrane : 30 ml of chloroform containing 1.5×10^{-4} mole of (**2**), Receiving phase : 15 ml of 0.05 M H_2SO_4 aqueous solution.

of polyether is either longer or shorter than oxytrimethylene. The structural significance of the oxytrimethylene-chain unit is noted for the appearance of a high selectivity for the lithium ion.

Effects of Terminal Groups on the Selectivity. Next, the effects of the kind of terminal groups on the selectivity were examined using polyethers containing other substituent groups in place of the 8-quinolyl terminal group of **1**. The other groups of **1** are not changed because the two trimethylene groups are important for the appearance of the high selectivity for the lithium ion and the other terminal group, the *o*-carboxyphenyl group, is required for cation-catching. In this study, as is shown in Fig. 4, a large amount of the solution in the source phase is circulated to keep the concentration of the cations constant, and the receiving phase contains only 15 ml of the 0.05 M sulfuric acid solution. Under these transport conditions, the amounts of each cation transported increased linearly with the running time for 2 d at least. Figure 5 summarizes the results obtained in the case of polyehter (**2**), while Table 3 shows the results of the transport rates (μmol/hr), which were calculated from the linear slopes of the amounts of each cation transported *vs.* the running time, and the selectivities of polyethers, (**1**)—(**8**) and (**12**). The values of the selectivities of **1** in Table 3 are a little different from those in Table 2 because of the different transport conditions. The values in Tables 1 and 2 were calculated from the amounts of the cation transported after 2 d, whereas the values in Table 3 were calculated from the transport rates of the cations. Here, it may be noted that the selectivity ratios, Li/Na and Li/K, change greatly with the change in the position of the substituent group introduced to the quinoline skelton. Polyether (**2**), which contains the 2-methyl-8-quinolyl group, gives a selectivity for the lithium ion superior to the (**1**) and (**3**) polyethers, whereas the (**3**) polyether which contains the 7-(1-propenyl)-8-quinolyl group,[8] gives a worse selectivity for the lithium ion than **1**. It is suggested that the structure of the terminal group and the position of the group introduced into the terminal group are important in order to increase the selectivity for the lithium ion. Furthermore, although there is little difference of selectivity for the lithium ion between **1** and the polyethers, (**4**) and (**5**), the significance of the heteroatom on the terminal

TABLE 3. INFLUENCE OF SUBSTITUENTS OF THE CARRIERS ON THE CATION-SELECTIVE TRANSPORT

Polyether	Transport rate (μ mol/hr)			Selectivity		
	Li	Na	K	Li/Na	Li/K	Na/K
(**1**)	20	6.2	3.4	3.2	5.9	1.8
(**2**)	18	3.1	1.3	5.8	14	2.5
(**3**)	18	6.9	5.6	2.6	3.2	1.2
(**4**)	19	6.3	5.3	3.0	3.6	1.2
(**5**)	19	6.1	5.0	3.1	3.8	1.2
(**6**)	19	6.9	5.0	2.8	3.8	1.4
(**7**)	19	5.3	4.1	3.6	4.7	1.3
(**8**)	10	3.4	2.2	2.9	4.6	1.6
(**12**)	13	11	10	1.2	1.3	1.1

Initial transport conditions (25 °C):

(Source phase)	(Chloroform membrane)	(Receiving phase)
0.1 M LiOH 0.1 M NaOH 0.1 M KOH 0.1 M H_2SO_4 115 ml	Polyether 1.5×10^{-4} mol $CHCl_3$ 30 ml	0.05 M H_2SO_4 15 ml

group may be presumed from the enhancement of the selectivity in the case of **7** containing the *o*-ethoxyphenyl terminal group compared with that of **6** containing the phenyl group.[9] In the case of **8**, which contains an ethyl terminal group, the selectivity is not much different from that in the case of the polyethers containing a phenyl or naphthyl group, but the transport rates of each cation using **8** as a carrier decrease apparently in spite of stirring mechanically at 200 min^{-1} in every case, in comparison with those in the case of the polyethers containing aromatic substituents. The transport rates may depend on the difference in hydrophobicity between them. Thus, no large difference in selectivities between polyethers, (**4**)—(**6**) and (**8**), is observed. These results suggest that the more important factor affecting the selectivities for a cation is the introduction of the oxytrimethylene chain, as is shown in Table 2, rather than the kinds of terminal group. By the way, polyether (**12**), with the 2-hydroxy-1,3-propanediyl group, with which 8-quinolyloxy and *t*-butyl-*o*-phenyleneoxy groups are bound, exhibits a much lower selectivity for the lithium ion than **1**. The cause of this will be discussed later.

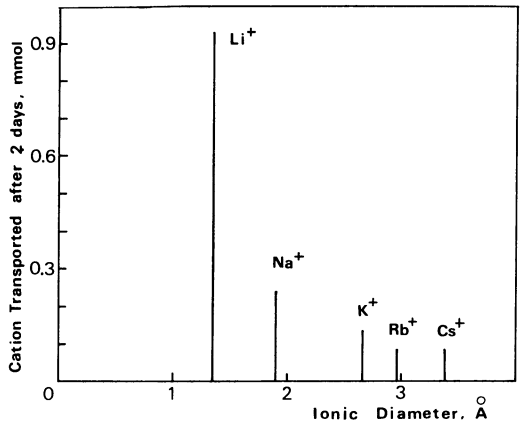


Fig. 6. Dependence of ionic diameter on the amounts of cation transported by (**1**) after 2 d. Initial transport conditions (25 °C) ; Source phase : 115 ml of 0.1 M LiOH+0.1 M NaOH+0.1 M KOH+0.1 M RbOH+0.1 M CsOH+0.2 M H_2SO_4 aqueous solution, Chloroform membrane : 30 ml of chloroform containing 1.5×10^{-4} mole of (**1**), Receiving phase : 15 ml of 0.05 M H_2SO_4 aqueous solution.

Structures of the Polyethers with Li^+-Selective Transport. From the results obtained, the structural significance of noncyclic polyethers may be pointed out. How can these polyethers exhibit Li^+-selective transport through liquid membranes?

Figure 6 shows the results of cation transport by **1** for five alkali metal ion species existing together in the source phese. Apparently, the smaller the ionic diameter, the larger the transport rates: $Li^+ \gg Na^+ > K^+ > Rb^+ \approx Cs^+$. Although the ionic diameter of a naked lithium ion is the smallest (1.32 Å) among alkali metal ions, its hydrated diameter (total hydration number =25) is the largest (6.80 Å) among them. The uptake of hydrated lithium ions by the polyethers does not occur, probably because the proton signal assigned to water does not appear in the NMR spectrum of Li-salt of **1** in $CDCl_3$. Furthermore, if the hydrated lithium ion can be transported, it can not be explained why the transport rates decrease in the order of the naked ionic diameter from the smallest Li^+ to the largest Cs^+. Additionally, in the case of the polyether containing the *p*-carboxyphenyl terminal group substituted for the *o*-carboxyphenyl one, its alkali salt can not be soluble in chloroform and can not be mobile through liquid membranes.[10] This means that the hydrated lithium ion is insoluble in chloroform. Therefore, it is reasonable to consider that the naked lithium ion becomes incorporated into the polyether carrier by means of the electrostatic interaction between ether-oxygens of the polyether and the lithium ion in a manner similar to cyclic polyethers, the so-called crown ethers.[11]

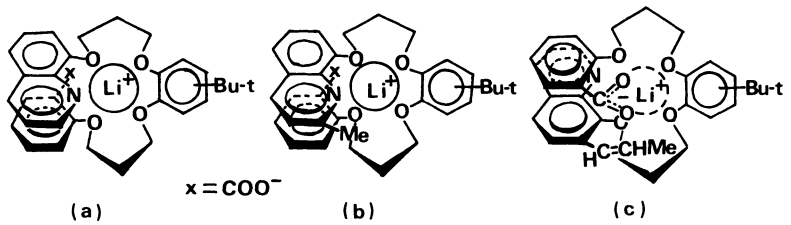


Fig. 7. Pseudocyclic structures Li-salts of polyethers on the basis of the CPK model; (a) Li—(**1**), (b) Li—(**2**), (c) Li—(**3**).

Here, if one looks at the molecular models of the carboxylate salt of the polyether with the lithium ion, it can be understood that these polyethers can transport the lithium ion selectively. As is shown in Fig. 7, the polyether (**1**) can form a pseudocyclic structure (a), the cavity of which has a diameter of 1.4—1.6 Å, and then the terminal aromatic rings overlap one another plainly to form a stacking structure,[12] when both ether-oxygen and nitrogen atoms are spatially directed to the inside. This indicates that the lithium ion best fits the size of the cavity formed. The other compounds with two oxytrimethylene chains, (**2**)—(**8**), also form the size of cavity which the lithium ion best fits among alkali metal ions. The stacking structure between terminal aromatic rings is suggested on the basis of the CPK-model building when the lithium ion becomes incorporated into the cavity of the polyethers.

The NMR spectra of polyether (**1**)-cation salts have been measured in order to get information concerning the stacking structure. Figure 8 shows the NMR spectra of the polyether (**1**), its Li^+ salt, and its K^+ salt. Especially notable is the proton at the 2-position of the quinolyl group; the proton (δ=8.96 ppm) in the case of Li^+ salt shifts to a higher magnetic field than that (δ=9.09 ppm) of the free polyether, while the proton (δ=9.08 ppm) in the case of the K^+ salt shifts hardly at all. It is presumed that the shift to the higher magnetic field in the case of Li^+ salt is to be attributed to the shielding effect (ring-current effect) of the aromatic rings on account of the stacking structure between them. If the nitrogen atom on the quinolyl group participates in the coordination to cations, the proton at the 2-position of the quinolyl group should shift to the lower magnetic field rather than that of free polyether (**1**). On the other hand, the size of the potassium ion is large, so that the terminal aromatic rings can not completely overlap each other. This can be confirmed from the CPK-model building.

The (**2**) polyether exhibits the most excellent selectivity for the lithium ion among the polyethers, whereas the (**3**) polyether exhibits a worse selectivity for it than even **1**. The difference in selectivity among the polyethers, (**1**)—(**3**), can not be explained by their lipophilicity because it increases in the following order: **1**<**2**<**3**. The difference in selectivity between **2** and **3** was also inferred on the basis of the CPK-model building (Fig. 7-b and 7-c). The CPK model indicates that the methyl moiety of **2** fills a space of the hydrophobic exterior which the (**1**) polyether forms around the cavity when aromatic terminal groups are stacked parallel to each other, playing a

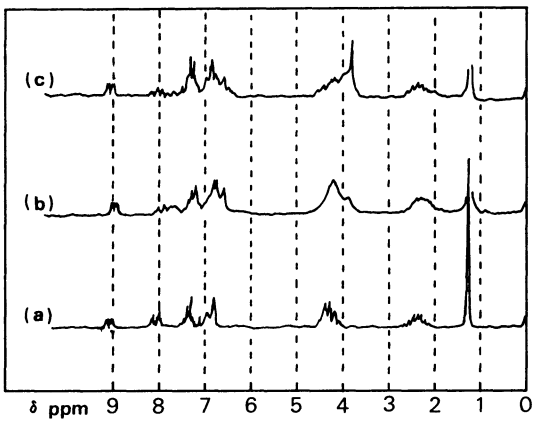


Fig. 8. NMR spectrum of (**1**) and its alkali salts ; (a) (**1**), (b) the Li salt, (c) the K salt.

part in the hydrophobic wall around the cavity (see, Fig. 7-b), whereas the 1-propenyl moiety of **3** can not act as a hydrophobic wall around the cavity, unlike the methyl moiety of **2**, but 1-propenyl and carboxylato groups on the two terminal aromatics could, rather, collide with each other when the complex with the lithium ion forms,to interfere a little with the favorable structure for the lithium ion (Fig. 7-c).

The small difference in selectivity for the lithium ion between **1** and **4** is not always reflected by the participation of the nitrogen atom,[9] which may be suggested from the CPK-model building, in the uptake of the lithium ion. On the contrary, the difference in selectivity dependent on the length of the oxyalkylene chain is reflected by the size of the cavity formed on the basis of the CPK-model building. The selective transport for the lithium ion by **12** is greatly lowered compared with that by **1**. It is presumed that the ability to wrap favorably around the lithium ion is decreased because the hydrophilic OH group on the trimethylene chain tends to be oriented inside the cavity in a nonpolar solvent (liquid membranes), resulting in the deformation of the cavity. From these considerations, we can reach the conclusion that the essential point in the structure of a noncyclic polyether for exhibiting lithium ion-selective transport is to contain the 1,2-bis(3-oxytrimethyleneoxy)phenyl group.

The schematic mechanism of cation transport by **1** as an example is proposed in Fig. 9. Thus, when the structure of the polyether can enoughly satisfy every process as follows: i) a selective uptake of cations at the boundary between phases (a) and (b), ii) solubility into the chloroform liquid membrane (b) and mobility

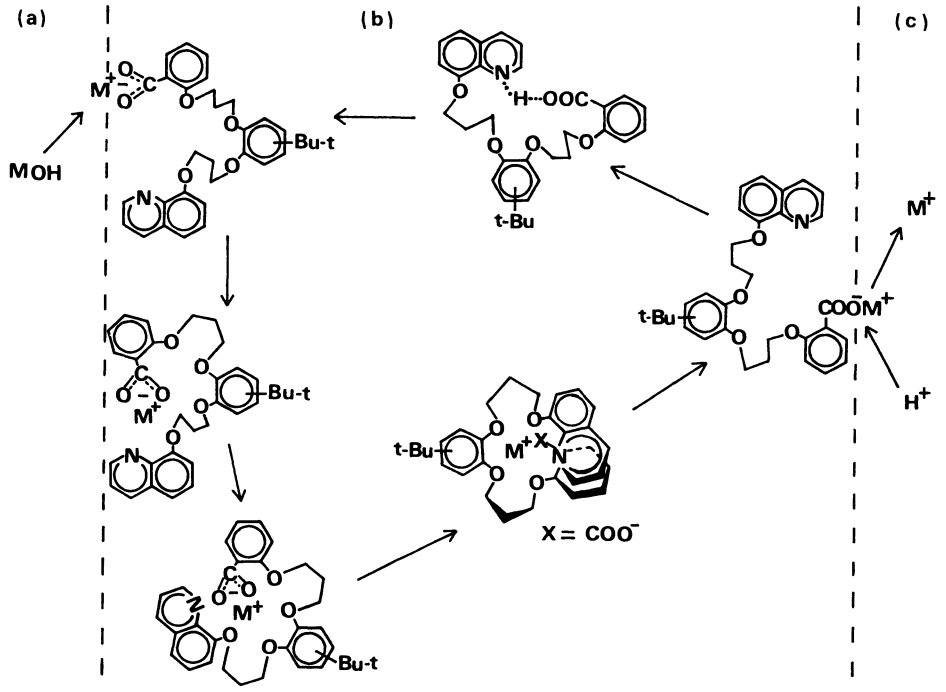


Fig. 9. Posturated cation transport sheme; (a) Source phase, (b) Chloroform membrane, (c) Receiving phase.

through it, and a smooth and rapid release of cations at the boundary between phases (b) and (c), the cation transport by the polyether is considered to proceed most effectively and selectively.

Experimental

General. The IR spectra were recorded with a JASCO A-3 Infrared spectrophotometer. The ^{1}HNMR (60 MHz) spectra were recorded with a Varian EM-360 spectrometer. The chemical shifts for $CDCl_3$ solutions are reported from internal tetramethylsilane.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-(8-quinolyloxy)propoxy]-4-(or 5)-t-butylbenzene (1). *Method 1*: Under a nitrogen atmosphere, to a solution of 33.2 g (0.2 mol) of 4-*t*-butylcatechol in 150 ml of DMF was added 55.2 g of powdered potassium carbonate, after which the reaction mixture was stirred at 70 °C for 2 h. Then, 40 g (0.21 mol) of 3-chloro-1-propanol and a small amount of KI were added to it, and the mixture was stirred at 70 °C for 24 h. The solvent was evaporated under reduced pressure, and the residue was added to an aqueous hydrochloric acid solution to neutralize it and then extracted with chloroform. The chloroform extract was washed with water, dried with anhydrous magnesium sulfate, and evaporated to give an oily residue. The residue was purified by Kugelrohr distillation at 190 °C (0.3 mmHg[††]) to give 43 g (76%) of 1,2-bis(3-hydroxypropoxy)-4-*t*-butylbenzene as a colorless liquid.

To the solution of 31.7 g of 1,2-bis(3-hydroxypropoxy)4-*t*-butylbenzene and 30 g of pyridine in 150 ml of benzene was added dropwise 20 g of thionyl chloride. After refluxing for 10 h, the benzene solution was washed twice with water, then with diluted aqueous K_2CO_3 and with water. After the solution had been dried with anhydrous $MgSO_4$, the benzene was removed and the residue was purified by Kugelrohr distillation at 186 °C (1.3 mmHg) to give 27 g (76%) of 1,2-bis(3-chloropropoxy)-4-*t*-butylbenzene as a colorless liquid.

The reaction mixture of 3.4 g (0.02 mol) of ethyl salicylate and 2.3 g (0.02 mol) of *t*-BuOK in 50 ml of DMF was stirred until it became homogeneous. To the solution was then added 15 g (0.047 mol) of 1,2-bis(3-chloropropoxy)-4-*t*-butylbenzene, and the mixture was stirred at 70 °C for 42 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with benzene. The benzene layer was washed with water three times and dried with anhydrous $MgSO_4$. After the solvent and the excess reactants had been removed under reduced pressure, the residue was submitted to column chromatography on activated alumina (Wako gel, 300 mesh) with a chloroform eluent to give 5.1 g (57%) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-(3-chloropropoxy)-4(or 5)-*t*-butylbenzene as a colorless liquid.

The reaction mixture of 2.0 g of 8-quinolinol and 0.30 g of NaH in 30 ml of DMF was stirred until it became homogeneous. To the solution was then added 4.8 g (0.011 mol) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-(3-chloropropoxy)-4(or 5)-*t*-butylbenzene, and the mixture was stirred at 70 °C for 48 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with benzene. The benzene layer was washed with water three times and dried with $MgSO_4$. After the solvent had been evaporated, the residue was submitted to column chromatography on activated alumina (Wako gel, 300 mesh) with a chloroform eluent to give 3.7 g (62%) of 1-[3-(*o*-ethoxycarbonylphenoxy)-propoxy]-2-[3-(8-quinolyloxy)propoxy]-4(or 5)-*t*-butylbenzene. This ethyl ester (2.8 g) and 1 g of KOH in 30 ml of ethanol were refluxed under stirring overnight. After the ethanol had been evaporated, water was added to the residue, and the solution was slightly acidified with glacial acetic acid and extracted with chloroform two times. The chloroform layer was washed with water two times and dried with $MgSO_4$. After the removal of chloroform, the residue was submitted to column chromatography on silica gel (Wako gel, 300 mesh)

[††] 1 mmHg≈133.322 Pa.

with a chloroform eluent to give 2.1 g (79%) of **1** as a pale yellow glassy solid. ^{1}H NMR ($CDCl_3$) δ=1.27 (9H, s, $C(CH_3)_3$), 2.0—2.8 (4H, m, $OCH_2C\underline{H}_2CH_2O$), 4.1—4.7 (8H, m, $OC\underline{H}_2$-$CH_2C\underline{H}_2O$), 6.8—7.7 (10H, m, aromatic), 8.1—8.4 (2H, m, aromatic), 9.09 (1H, m, aromatic), *ca.* 8—9 (1H, broad, COOH); IR(KBr): 3280 and 2500 (COOH), 1705 (C=O), 1600 and 1580 cm^{-1} (aromatic C=C). Found: C 72.03, H 6.51, N 2.55%. Calcd for $C_{32}H_{35}NO_6$: C 72.57, H 6.66, N 2.64%.

Method 2: The reaction mixture of 33 g (0.2 mol) of ethyl salicylate and 5 g (0.2 mol) of NaH in 150 ml of DMF was stirred until it became homogeneous. To the solution was added 40 g of 2-(3-chloropropoxy)tetrahydropyran, which had been obtained quantitatively by the reaction of 3-chloro-1-propanol with 3,4-dihydro-2*H*-pyran, and the mixture was stirred at 70 °C for 24 h. After it was cooled to room temperature, the reaction mixture was poured into water and extracted with benzene. The benzene layer was washed with water and dried with $MgSO_4$. After the benzene had been removed, 100 ml of ethanol and a few drops of conc. HCl were added to the residue, and the solution was stirred at room temperature overnight. After the removal of the solvent, water was added to the residue, and the solution was extracted with chloroform. The chloroform layer was washed with water and dried with $MgSO_4$. After the removal of the chloroform, the residue was purified by Kugelrohr distillation at 180 °C (0.5 mmHg) to give 36.0 g (80%) of ethyl 2-(3-hydroxypropoxy)benzoate. To the reaction mixture of 33 g (0.15 mol) of ethyl 2-(3-hydroxypropoxy)benzoate and 15 g of pyridine in 300 ml of benzene was then added 20 g of thionyl chloride, drop by drop, and then the mixture was refluxed under stirring for 17 h. After cooling to room temperature, the solution was washed with water three times, then with diluted aqueous K_2CO_3 and with water, and dried with $MgSO_4$. After the removal of the benzene, the residue was purified by Kugelrohr distillation at 150 °C (0.4 mmHg) to give 30 g (83%) of ethyl 2-(3-chloropropoxy)benzoate.

The reaction mixture of 50 g (0.3 mol) of 4-*t*-butylcatechol and 6.0 g (0.054 mol) of *t*-BuOK in 150 ml of DMF was stirred under a nitrogen atmosphere until it became homogeneous. To the solution was added 13 g (0.054 mol) of ethyl 2-(3-chloropropoxy)benzoate, and the mixture was stirred at 70 °C for 48 h. After cooling to room temperature, 200 ml of benzene was added to the solution, and it was washed with water three times and dried with $MgSO_4$. After the removal of the benzene, the excess *t*-butylcatechol was removed from the residue at 130 °C under reduced pressure (0.5 mmHg). The residue was submitted to column chromatography on activated alumina with a chloroform eluent to give 14.5 g (76%) of 2-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-4(or 5)-*t*-butylphenol (**13**) as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ=1.30 (9H, s, $C(CH_3)_3$), 1.37 (3H, t (7.2 Hz), $OCH_2C\underline{H}_3$), 2.0—2.6 (2H, m, $OCH_2C\underline{H}_2CH_2O$), 4.05—4.60 (4H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 4.35 (2H, q (7.2 Hz), $OC\underline{H}_2CH_3$), *ca.* 5.7 (1H, broad, OH), 6.8—8.0 (7H, m, aromatic); IR (neat): 3440 (OH), 1720 (C=O), 1600 and 1580 cm^{-1} (aromatic C=C). Found: C 71.28, H 7.65%. Calcd for $C_{22}H_{28}O_5$: C 70.94, H 7.58%.

The mixture of 36 g (0.25 mol) of 8-quinolinol and 28 g (0.25 mol) of *t*-BuOK in 70 ml of DMSO was stirred until it became homogeneous. To the solution 24 g (0.25 mol) of 3-chloro-1-propanol was added, and the mixture was stirred at 70 °C for 38 h. The solution was then poured into 500 ml of water, and the solid, which was precipitated in water, was separated from the solution by filtration, washed with water three times, and dried under a vacuum to give 33 g (66%) of 3-(8-quinolyloxy)-1-propanol. To the solution of 23 g (0.11 mol) of 3-(8-quinolyloxy)-1-propanol in 100 ml of benzene was added 16 g (0.13 mol) of thionyl chloride, drop by drop, after which the solution was refluxed for 5 h under stirring. After cooling to room temperature, diluted aqueous K_2CO_3 was slowly added to the solution until it became slightly basic. The benzene layer was washed with water two times and dried with $MgSO_4$. After the removal of the benzene, the crude product was purified by recrystallization from hexane to give 17 g (68%) of 1-chloro-3-(8-quinolyloxy)propane as a white solid; mp 68—69 °C.

The reaction mixture of 7.3 g (0.02 mol) of **13** and 2.2 g (0.02 mol) of *t*-BuOK in 50 ml of DMSO was stirred until it became homogeneous. To the solution was then added 4.4 g (0.02 mol) of 1-chloro-3-(8-quinolyloxy)propane and a small amount of KI, and the mixture was stirred at 70 °C for 4 d. Then, benzene and water were added to the solution, and the benzene layer was washed with water and dried with $MgSO_4$. After the removal of the benzene, the residue was submitted to column chromatography on activated alumina with a chloroform eluent to give 9.4 g (85%) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-[3-(8-quinolyloxy)propoxy]-4(or 5)-*t*-butylbenzene as a pale yellow liquid. The polyether (**1**) was obtained in a manner similar to that described in Method 1.

The polyethers, (**2**)—(**8**) and (**10**), were obtained by the reaction of **13** with the corresponding 3-substituted 1-chloropropane in a manner similar to that described in Method 2.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-(2-methyl-8-quinolyloxy)-propoxy]-4(or 5)-t-butylbenzene (2). The above procedure was followed, using **13** and 1-chloro-3-(2-methyl-8-quinolyloxy)propane; a pale yellow glassy solid. ^{1}H NMR ($CDCl_3$) δ=1.27 (9H, s, $C(CH_3)_3$), 2.0—2.7 (4H, m, OCH_2-$C\underline{H}_2CH_2O$), 2.77 (3H, s, CH_3-Ar), 4.05—4.65 (8H, m, $OC\underline{H}_2$-$CH_2C\underline{H}_2O$), 6.8—7.6 (10H, m, aromatic), 7.9—8.3 (2H, m, aromatic), *ca.* 8.9 (1H, broad, COOH); IR (KBr): 3280 and 2550 (COOH), 1710 (C=O), 1605, 1580, and 1575 cm^{-1} (aromatic C=C). Found: C 72.26, H 6.81, N 2.49%. Calcd for $C_{33}H_{37}NO_6$: C 72.91, H 6.86, N 2.57%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-[7-(1-propenyl)-8-quinolyloxy]propoxy]-4(or 5)-t-butylbenzene (3). The above procedure was followed, using **13** and 1-chloro-3-[7-(1-propenyl)-8-quinolyloxy]propane, which had been obtained by the reaction of 7-allyl-8-quinolinol with 3-chloro-1-propanol, followed by treatment with thionyl chloride. 7-Allyl-8-quinolinol was obtained in a good yield by the Claisen rearrangement of 8-(allyloxy)quinoline. Polyether (**3**): a pale yellow glassy solid. ^{1}H NMR ($CDCl_3$) δ=1.32 (9H, s, C (CH_3)$_3$), 1.78 (3H, d, $C\underline{H}_3$-CH=CH-Ar), 2.0—2.6 (4H, m, $OCH_2C\underline{H}_2CH_2O$), 4.0—4.6 (8H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 6.0—6.6 (1H, m, CH_3-C$\underline{H}$=CH-Ar), 6.7—7.8 (10H, m, aromatic and CH_3-CH=C$\underline{H}$-Ar), 8.10 (2H, m, aromatic), 8.87 (1H, m, aromatic), *ca.* 8.8 (1H, broad, COOH); IR (KBr): 3270 and 2450 (COOH), 1725 and 1700 (C=O), 1645 (CH=CH), 1600 and 1580 cm^{-1} (aromatic C=C). Found: C 73.07, H 6.71, N 2.38%. Calcd for $C_{35}H_{39}NO_6$: C 73.79, H 6.90, N 2.46%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-(1-naphthyloxy)propoxy]-4(or 5)-t-butylbenzene (4). The above procedure was followed, using **13** and 1-chloro-3-(1-naphthyloxy)propane, which had been obtained by the reaction of 1-naphthol with 1,3-dichloropropane: colorless liquid. ^{1}H NMR ($CDCl_3$) δ=1.28 (9H, s, C (CH_3)$_3$), 2.0—2.7 (4H, m, OCH_2-$C\underline{H}_2CH_2O$), 4.0—4.55 (8H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 6.7—8.5 (14H, m, aromatic), *ca.* 9—10 (1H, broad, COOH); IR (neat): 3300 (COOH), 1740 and 1700 (C=O), 1630, 1605, and 1580 cm^{-1} (aromatic C=C). Found: C 75.40, H 6.72%. Calcd for $C_{33}H_{36}O_6$: C 74.98, H 6.86%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-(2-naphthyloxy)propoxy]-4(or 5)-t-butylbenzene (5). The above procedure was followed, using **13** and 1-chloro-3-(2-naphthyloxy)propane: colorless liquid. ^{1}H NMR ($CDCl_3$) δ=1.31 (9H, s, $C(CH_3)_3$), 2.0—2.6 (4H, m, $OCH_2C\underline{H}_2CH_2O$), 4.05—4.55 (8H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 6.83—7.97 (13H, m, aromatic),

8.22 (1H, m, aromatic), *ca.* 9—10 (1H, broad, COOH); IR (neat): 3300 (COOH), 1740 and 1700 (C=O), 1630, 1600, and 1580 cm^{-1} (aromatic C=C). Found: C 74.41, H 6.95%. Calcd. for $C_{33}H_{36}O_6$: C 74.98, H 6.86%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-(3-phenoxypropoxy)-4(or 5)-t-butylbenzene (6). The above procedure was followed using **13** and 1-chloro-3-phenoxypropane: colorless liquid. ^1H NMR ($CDCl_3$) δ=1.30(9H, s, $C(CH_3)_3$), 2.0—2.6 (4H, m, $OCH_2C\underline{H}_2CH_2O$), 3.95—4.65 (8H, m, $OC\underline{H}_2CH_2$-$C\underline{H}_2O$), 6.7—7.7 (1H, m, aromatic), 8.05—8.30 (1H, m, aromatic), *ca.* 9—10 (1H, broad, COOH); IR (neat): 3290 (COOH), 1740 and 1695 (C=O), 1605 and 1590 cm^{-1} (aromatic C=C). Found: C 73.56, H 7.03%. Calcd for $C_{29}H_{34}O_6$: 72.78, H 7.16%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-(o-ethoxyphenoxy)propoxy]-4(or 5)-t-butylbenzene (7). The above procedure was followed, using **13** and 1-chloro-3-(*o*-ethoxyphenoxy)-propane which was obtained by the reaction of *o*-ethoxyphenol with 1,3-dichloropropnane: pale yellow liquid. ^1H NMR ($CDCl_3$) δ=1.30 (9H, s, $C(CH_3)_3$), 1.40 (3H, t, OCH_2-$C\underline{H}_3$), 2.0—2.6 (4H, m, $OCH_2C\underline{H}_2CH_2O$), 4.06 (2H, q, $OC\underline{H}_2CH_3$), 4.1—4.7 (8H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 6.93 (4H, s, aromatic), 6.8—7.8 (6H, m, aromatic), 8.22 (1H, m, aromatic), *ca.* 9—10 (1H, broad, COOH); IR (neat): 3300 (COOH), 1740 and 1700 (C=O), 1605 and 1580 cm^{-1} (aromatic C=C). Found: C 70.73, H 7.02%. Calcd for $C_{31}H_{38}O_7$: C 71.26, H 7.33 %.

1-[3-(o-Carboxyphenoxy)propoxy]-2-(3-ethoxypropoxy)-4(or 5)-t-butylbenzene (8). The above procedure was followed, using **13** and 1-chloro-3-ethoxypropane, which had been obtained by the reaction of 3-ethoxypropionic acid with $LiAlH_4$ following chlorination: colorless liquid. ^1H NMR ($CDCl_3$) δ=1.17 (3H, t, $OCH_2C\underline{H}_3$), 1.31 (9H, s, $C(CH_3)_3$), 1.75—2.65 (4H, m, $OCH_2C\underline{H}_2CH_2O$), 3.47 (2H, q, $OC\underline{H}_2CH_3$), 3.59 (2H, t, $OCH_2CH_2C\underline{H}_2O$-$CH_2CH_3$), 3.95—4.70 (6H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$), 6.87—7.80 (6H, m, aromatic), 8.22 (1H, m, aromatic), *ca.* 9 (1H, broad, COOH); IR (neat): 3290 (COOH), 1740 and 1700 (C=O), 1605 and 1580 cm^{-1} (aromatic C=C). Found: C 70.30, H 7.63%. Calcd for $C_{25}H_{34}O_6$: C 69.74, H 7.96%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[4-(8-quinolyloxy)butoxy]-4(or 5)-t-butylbenzene (10). The above procedure was followed, using **13** and 1-chloro-4-(8-quinolyloxy)butane, which had been obtained by the reaction of 8-quinolinol with 4-chloro-1-butanol, following chlorination: a pale yellow glassy solid. ^1H NMR ($CDCl_3$) δ=1.28 (9H, s, $C(CH_3)_3$), 1.9—2.5 (6H, m, $OCH_2C\underline{H}_2CH_2O$ and $OCH_2C\underline{H}_2C\underline{H}_2$-$CH_2O$), 3.85—4.65 (8H, m, $OC\underline{H}_2CH_2C\underline{H}_2O$ and $OC\underline{H}_2$-$CH_2CH_2C\underline{H}_2O$), 6.85—7.65 (10H, m, aromatic), 8.0—8.3 (2H, m, aromatic), 9.00 (1H, m, aromatic), *ca.* 8—9 (1H, broad, COOH); IR (KBr): 3290 and 2500 (COOH), 1710 (C=O), 1600 and 1580 cm^{-1} (aromatic C=C) Found: C 72.11, H 7.05, N 2.43%. Calcd for $C_{33}H_{37}NO_6$: 72.91, H 6.86, N 2.58%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[2-(8-quinolyloxy)ethoxy]-4(or 5)-t-butylbenzene (9). The reaction mixture of 3.7 g (0.01 mol) of **13** and 1.2 g of *t*-BuOK in 50 ml of DMSO was stirred until it became homogeneous. To the solution was then added 3.0 g of 2-(2-chloroethoxy)tetrahydropyran, and the mixture was stirred at 70 °C for 90 h. The solution was then poured into water and extracted with benzene. The benzene layer was washed with water three times and dried with $MgSO_4$. After the removal of the benzene, 50 ml of EtOH and a few drops of conc. HCl were added to the residue and the mixture was stirred overnight at room temperature. After the removal of the ethanol, the residue was extracted with chloroform, washed with water, and dried with $MgSO_4$. After the removal of the chloroform, the residue was submitted to column chromatography on activated alumina with $CHCl_3$–EtOH (9:1) eluents to give 2.9 g (70%) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-(2-hydroxyethoxy)-4(or 5)-*t*-butylbenzene as a colorless liqued.

To the solution of 2.8 g of 1-[3-(*o*-ethoxycarbonylphenoxy)-propoxy]-2-(2-hydroxyethoxy)-4(or 5)-*t*-butylbenzene and 0.60 g of pyridine in 30 ml of benzene was added 0.9 g of thionyl chloride, and the mixture was refluxed overnight. The benzene layer was washed with water and then with aqueous K_2CO_3, and dried with $MgSO_4$. After the removal of the benzene, the residue was submitted to column chromatography on activated alumina with a chloroform eluent to give 2.3 g (78%) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-(2-chloroethoxy)-4(or 5)-*t*-butylbenzene as a colorless liquid.

The reaction mixture of 1.0 g of 8-quinolinol and 0.65 g of *t*-BuOK in 15 ml of DMSO was stirred until it became homogeneous. To the solution was then added 2.3 g of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxyl-2-(2-chloroethoxy)-4(or 5)-*t*-butylbenzene, and the mixture was stirred at 70 °C for 4 h. After it had cooled to room temperature, 100 ml of benzene was added to the solution, and it was washed with water three times and dried with $MgSO_4$. After the removal of the benzene, the residue was submitted to column chromatography on activated alumina with a chloroform eluent to give 1.9 g (66%) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-[2-(8-quinolyloxy]ethoxy]-4(or 5)-*t*-butylbenzene as a pale yellow liquid. The solution of 1.1 g of this ethyl ester and 0.5 g of KOH in 30 ml of ethanol was refluxed overnight. After the removal of the ethanol, water was poured into the residue, and the solution was slightly acidified with glacial acetic acid and extracted with chloroform two times. The chloroform layer was washed with water two times and dried with $MgSO_4$. After the removal of the chloroform, the residue was submitted to column chromatography on silica gel (300 mesh) with a chloroform eluent to give 0.8 g (80%) of **9**: a pale yellow glassy solid. ^1H NMR ($CDCl_3$) δ=1.28 (9H, s, $C(CH_3)_3$), 2.0—2.5 (2H, m, $OCH_2C\underline{H}_2CH_2O$), 4.25 (2H, t, $OC\underline{H}_2CH_2CH_2O$-$C_6H_4$(*o*-COOH)), 4.37 (2H, t, $OCH_2CH_2C\underline{H}_2O$-$C_6H_4$(*o*-COOH)), 4.63 (4H, s, $OC\underline{H}_2C\underline{H}_2O$), 6.8—7.65 (10H, m, aromatic), 8.0—8.3 (2H, m, aromatic), 8.3 (1H, broad, COOH), 9.03 (1H, m, aromatic); IR (KBr): 3260 and 2500 (COOH), 1705 (C=O), 1600 and 1580 cm^{-1} (atomatic C=C). Found: C 71.88, H 6.62, N 2.85%. Calcd for $C_{31}H_{33}NO_6$: C 72.21, H 6.45, N 2.71%.

1-[2-(o-Carboxyphenoxy)ethoxy]-2-[2-(8-quinolyloxy)ethoxy]-4(or 5)-t-butylbenzene (11). A procedure similar to that described above (Method 1 for **1**) was used for the preparation of **11**: a pale yellow glassy solid. ^1H NMR ($CDCl_3$) δ= 1.30 (9H, s, $C(CH_3)_3$), 4.43 (4H, s, $OC\underline{H}_2C\underline{H}_2O$-quinolyl), 4.65 (4H, m, $OC\underline{H}_2C\underline{H}_2O$-$C_6H_4$(*o*-COOH)), 6.7—7.7 (10H, m, aromatic), 7.9—8.3 (2H, m, aromatic), 9.07 (1H, m, aromatic), 10.07 (1H, broad, COOH); IR (KBr): 3280 and 2500 (COOH), 1730 and 1710 (C=O), 1605 and 1580 cm^{-1} (aromatic C=C). Found: C 71.88, H 6.49, N 2.76%. Calcd for $C_{30}H_{31}NO_6$: C 71.98, H 6.24, N 2.80%.

1-[3-(o-Carboxyphenoxy)propoxy]-2-[3-(8-quinolyloxy)-2-hydroxypropoxy]-4(or 5)-t-butylbenzene (12). The reaction mixture of 7.4 g 0.02 mol) of **13** and 2.3 g (0.02 mol) of *t*-BuOK in 30 ml of benzene was stirred at room temperature until it became homogeneous. After the removal of the benzene, 24 g of epichlorohydrin was added to the residue, and then the mixture was stirred at 70 °C for 19 h. After cooling to room temperature, the mixture was poured into water and extracted with benzene. The benzene layer was washed with water three times and dried with $MgSO_4$. After the removal of the benzene and excess epichlorohydrin under a vacuum, 7.9 g (93%) of the crude product, 1-[3-(*o*-ethoxycarbonylphenoxy)-propoxy]-2-glycidyl-4(or 5)-*t*-butylbenzene, was obtained. This product was used for the following reaction without further purification.

After the reaction mixture of 3.0 g (0.02 mol) of 8-quinolinol and 2.0 g (0.018 mol) of *t*-BuOK in 50 ml of dioxane had been stirred at 70 °C for 2 h, 7.5 g (0.018 mol) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-glycidyl-4(or 5)-*t*-butylbenzene was added to it, and the mixture was stirred at 70 °C for 46 h. Then, after the removal of the dioxane, to the residue was added water and the solution was slightly acidified with glacial acetic acid and extracted with benzene. The benzene layer was washed with water three times and dried with $MgSO_4$. After the removal of the benzene, the residue was submitted to column chromatography on activated alumina with a chloroform eluent to give 5.6 g (53%) of 1-[3-(*o*-ethoxycarbonylphenoxy)propoxy]-2-[3-(8-quinolyloxy)-2-hydroxypropoxy]-4(or 5)-*t*-butylbenzene as a pale yellow liquid. The solution of 2.0 g of this ethyl ester and 1.0 g of KOH in 50 ml of ethanol was refluxed overnight. After the removal of the ethanol, water was poured into the residue, and the solution was slightly acidified with glacial acetic acid and extracted with chloroform. The chloroform layer was washed with water two times and dried with $MgSO_4$. After the removal of the chloroform, the residue was submitted to column chromatography on silica gel (300 mesh) with chloroform–ethanol (9:1) eluents to give 1.1 g (58%) of **12**: a pale yellow glassy solid. ^{1}H NMR ($CDCl_3$) δ=1.26 (9H, s, $C(CH_3)_3$), 2.0—2.6 (2H, m, $OCH_2C\underline{H}_2CH_2O$), 4.0—4.7 (9H, m, $OC\underline{H}_2$-$CH_2C\underline{H}_2O$ and $OC\underline{H}_2C\underline{H}(OH)C\underline{H}_2O$), 6.8—7.7 (12H, m, aromatic, $OCH_2CH(O\underline{H})CH_2O$, and $COO\underline{H}$), 7.94—8.40 (2H, m, aromatic), 9.06 (1H, m, aromatic); IR (KBr): 3450 (OH), 3290 and 2500 (COOH), 1720 (C=O), 1605 and 1580 cm^{-1} (aromatic C=C). Found: C 71.09, H 6.31, N 2.77%. Calcd for $C_{32}H_{35}HO_7$: C 70.44, H 6.47, N 2.57%.

General Procedure of Cation Transport. Reagents: Chloroform (extra-pure grade) was used without further purification. Each aqueous solution which was used in either the source or receiving phase was prepared by the dilution of one normal alkali hydroxide and/or one normal acid.

Procedure: A U-type glass tube as previously reported[7] was used for measuring the transport of the alkali-metal ions. In the first case (*cf.* Table 1 and Table 2), the same volumes of an aqueous solution which initially contained the same amounts of alkali-metal ions were used as both aqueous phases. First, 30 ml of chloroform containing 1.5×10^{-4} mol of a carrier was placed in the tube. Two kinds of the aqueous solution used for the source phase and the receiving phase were subsequently poured into both sides. The tube was then placed in a water bath whose temperature was kept at 25±0.2 °C. Each phase was agitated at 200 min^{-1} mechanically with a pair of glass stirrers.

In the second case (*cf.* Table 3), a large amount of the aqueous solution (115 ml) was used for the source phase, while 15 ml of a 0.05 M sulfuric acid solution was used for the receiving phase. As is shown in Fig. 4, the solution for the source phase was circulated by means of a circulating pump (circulating velocity, 2.5 ml/ min.). Under these conditions, the concentration of each cation in the receiving phase was confirmed to increase linearly with the running time (less than 2 d), and the apparent transport rates of cations were calculated.

The transport of alkali-metal ions was initiated by the addition of the aqueous solutions. At each time point, 50 μl of the solution was withdrawn from each aqueous phase, and the concentration of the cation was adjusted by using a measuring flask and determined by means of a Shimadzu AA-646 atomic absorption spectrometer. The transport of cations in the blank systems was negligible. The detailed conditions are shown in the tables.

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8) During the reaction of 3-chloro-1-propanol with 7-allyl-8-quinolinol, the 7-allyl group on the quinoline ring changed to a 7-propenyl one as a result of the base used.

9) B. Tümmler, G. Maass, F. Vögtle, H. Sieger, U. Heimann, and E. Weber, *J. Amer. Chem. Soc.*, **101**, 2588 (1979).

10) H. Kuboniwa, K. Yamaguchi, A. Hirao, S. Nakahama, and N. Yamazaki, *Chem. Lett.*, **1982**, 1937.

11) Also in natural noncyclic polyethers, *e.g.*, monensin and nigericin, the periphery of the complex consists of lipophilic regions making the complex *exo*-lipophilic and thus soluble in lipophilic media: M. Dobler, "Ionophores and Their Structures," John Wiley&Sons, New York (1981), Chap. 7, pp. 77—120.

12) In the complex of 1,11-bis(2-methyl-8-quinolyloxy)-3,6,9-trioxaundecane with RbI, the polyether has been reported by X-ray structure analysis to display a herical configuration with both heterocycles stacked parallel to each other at 3.4 Å: G. Weber and W. Saenger, *Acta Crystallogr, Sect. B*, **35**, 1346 (1979).