Registry No. 1 (Z = R = R′ = H), 62-53-3; 1 (Z = 2-Me, R = R′ = H), 95-53-4; 1 (Z = 2,6-Me_2, R = R′ = H), 87-62-7; 1 (Z = 4-Me, R = R′ = H), 106-49-0; 1 (Z = 4-Cl, R = R′ = H), 106-47-8; 1 (Z = 4-MeO, R = R′ = H), 104-94-9; 1 (Z = 2-CH, R = CH, R′ = H), 120-72-9; 1 (Z = H, R = R′ = Me), 121-69-7; 1 (Z = 2-Me-3-NH_2, R = R′ = H), 823-40-5; **3a**, 2987-53-3; **3b**, 104-96-1; **3c**, 100305-95-1; **3d**, 75794-20-6; **3e**, 120578-20-3; **3f**, 29690-20-8; **3g**, 29690-21-9; **3h**, 1658-03-3; **3i**, 40015-10-9; **3j**, 2388-51-4; **3k**, 13920-91-7; **3l**, 3463-02-3; **3m**, 119361-05-6; **3n**, 102093-65-2; $AlCl_3$, 7446-70-0; NH_4Br, 41591-55-3; $ZrCl_4$, 10026-11-6; $TiCl_4$, 7550-45-0; $FeCl_3$, 7705-08-0; $ZnCl_2$, 7646-85-7; NH_4I, 59917-23-6.

New Type of Ionophores for Lithium Ion: N-Pivot Lariat Ethers Based on Monoaza-14-crown-4

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Liquid membrane transport is one of the important separation techniques for useful substances. Macrocyclic polyethers are successfully used as the carriers for alkali metal cations in such systems.[1] The efficiency and the selectivity in the transport are dominated by molecular recognition of the cation size by a carrier. Concerning lithium ion, 14-crown-4 ethers are known to show a high selectivity.[2] However, the efficiency of liquid membrane transport based on the complexing ability is expected to be insufficient because 14-crown-4 possesses only four coordination atoms. To compensate for the weak complexing ability, proton-ionizable crown ethers were developed and gave improved results.[3-6] In this case, however, the selectivity was not necessarily coincident with the selectivity expected from the structure of the macrocyclic ring used as the constituent.[6] The driving force for recognition seems to be rather dependent on the nature of the ionizable moiety. As another promising approach to raise the complexing ability, derivatization to lariat ether by introducing an electron-donating side arm to the crown ring should be considered.[7] Recently, the combination of lipophilic monoazacrown ether and picric acid was found to cooperatively work as an effective ionophore in the active transport system,[8] and the selectivity was attained by the discrimination of the cation size using the macrocyclic ring in this case. This transport system enabled the use of a carrier with a relatively lower complexing ability such as *N*-octylmonoaza-15-crown-5 (log $K(Na^+)$ = 3.08, in MeOH, at 25 °C).

Scheme I. Synthesis of Monoaza-crown Ethers

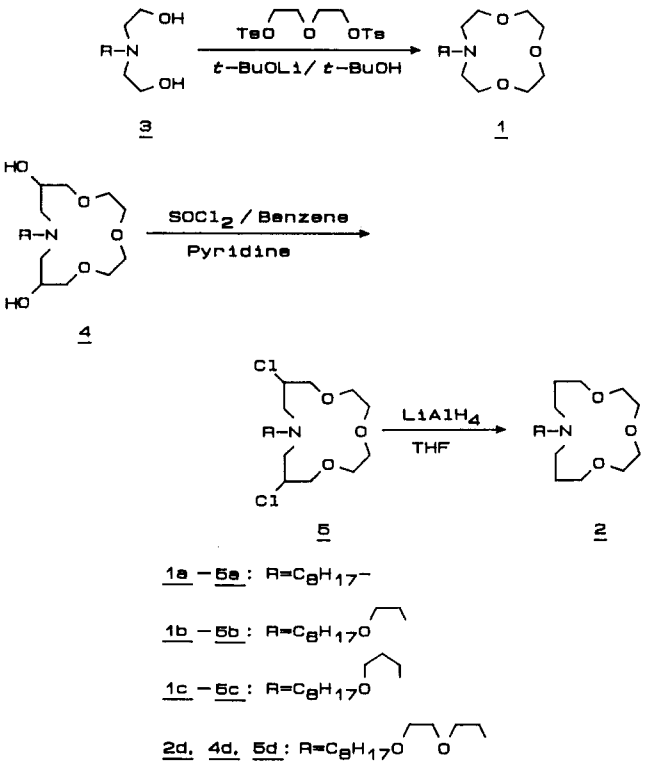

Table I. Competitive Passive Transport[a] Data toward Li^+, Na^+, and K^+

	transport velocity, 10^6 mol/h			selectivity	
ionophore no.	Li^+	Na^+	K^+	Li^+/Na^+	Li^+/K^+
1a	5.78	0.70	0.18	8.3	32
1b	5.44	6.71	1.78	0.8	3.1
1c	3.75	0.59	0.16	6.4	24
2a	1.35	0.21	0.030	6.3	45
2b	7.18	0.30	0.074	24	97
2c	2.77	0.14	0.020	20	136
2d	4.39	1.76	0.27	2.5	16

[a] Transport conditions: aqueous phase 1 (10 mL), [LiCl] = [NaCl] = [KCl] = [Me_4NOH] = 0.1 M; organic phase (CH_2Cl_2, 20 mL), ionophore and picric acid, 5×10^{-5} mol; aqueous phase 2 (10 mL), [HCl] = 0.1 M, 25 °C.

We now describe that novel N-pivot lariat ethers based on the 14-crown-4 ring are effective carriers for Li^+ in liquid membrane transport.

N-Substituted monoaza-12-crown-4 ethers **1** were prepared by the reaction of N-substituted diethanolamine **3** and diethylene glycol ditosylate according to a conventional procedure. On the other hand, N-substituted monoaza-14-crown-4 ethers **2** were synthesized by chlorination of the corresponding dihydroxy-14-crown-4[9] **4** with thionyl chloride, followed by reduction with $LiAlH_4$ in THF as shown in Scheme I. The structures were ascertained by IR, NMR, MS, and elemental analyses.

Transport experiments were carried out in a U-type cell under the conditions described in the footnotes in Table I. The results are also summarized in Table I.

As for **1a** and **2a**, the transport by **1a** is rather faster than that by **2a**, though the Li^+ selectivity is about the same. The introduction of the electron-donating side arm to the azacrown ethers, however, gave a different trend

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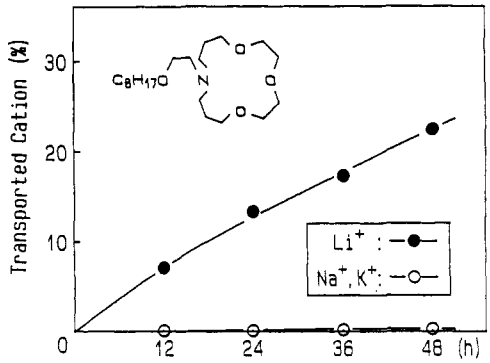

Figure 1. Competitive active transport of Li^+, Na^+, and K^+. Transport conditions: aqueous phase 1 (10 mL), [LiCl] = [NaCl] = [KCl] = [Me_4NOH] = 0.1 M; organic phase (CH_2Cl_2, 20 mL), ionophore and picric acid, 5×10^{-5} mol; aqueous phase 2 (10 mL), [LiCl] = [NaCl] = [KCl] = [HCl] = 0.1 M, 25 °C.

between these two types of crowns. A remarkable increase of the total cations transported was observed in **1b** based on 12-crown-4, but the selectivity was lost. It should be noted that **2b** based on 14-crown-4 showed a higher selectivity toward Li^+ over Na^+ and K^+ in addition to a higher transport velocity than **2a**.

These results may be explained by considering the fitness of sizes of the crown cavity and the cation. Since the cavity size of the 12-crown-4 ring is small for all alkali metal cations, the electron-donating side arm of **1b** seems to coordinate toward these cations in a similar manner. Its high symmetry suggests that all hetero atoms can effectively contribute to the complexation toward the spherical cation to give a high complexing ability. The complexing ability of N-pivot lariat ethers based on 15-crown-5 and 18-crown-6 toward Na^+ was reported to be dominated by the number of total hetero atoms in both the side arm and the ring.[10] The higher complexing ability of **1b** toward larger cations resulted in low selectivity toward Li^+. On the other hand, the cavity size of 14-crown-4 is suitable for Li^+ but is small for Na^+ and K^+. This means that the side arm of **2b** should be effective in complexation toward Li^+ compared with Na^+ and K^+.

Introduction of a trimethylene moiety to the side arm on monoaza-14-crown-4 (**2c**) also improved Li^+ selectivity, though its transport velocity was rather lower than that by **2b**. Elongation of the side arm by adding an oxyethylene unit to the structure of **2b** (**2d**) resulted in increasing affinity toward larger cations.

An active transport system is advantageous compared with a passive transport system because of the effectiveness of the separation.[1] In this transport system (phase 2: [HCl] = [LiCl] = [NaCl] = [KCl] = 0.1 M), compound **2b** was also found to be an efficient carrier for Li^+ over Na^+ and K^+ (Figure 1).[8]

The efficiency for protons of this ionophore (**2b**) is not so high as that of lipophilic monoaza-15-crown-5 or -18-crown-6 possibly because of the lower complexing ability. It is noted that the leak of the picrate moiety into the acidic phase could hardly be detected (<0.1%) as long as the receiving phase was kept acidic (pH < 2). This type of ionophore can be regarded as the equivalent of the ionizable carriers[3-6] because the lipophilic anion scarcely entered the receiving phase.

The solvent-extraction method is convenient for estimating the complexing ability of crown ethers toward all alkali metal cations. The data are summarized in Table II.

Table II. Extraction[a] Data toward Alkali Metal Picrate

compd no.	Li^+	Na^+	K^+	Rb^+	Cs^+
1a	18	3.4	1.3	1.6	1.0
1b	23	27	12	7.9	7.7
2a	4.8	0	1.6	3.3	1.9
2b	32	1.9	2.1	2.7	2.2
2d	35	19	3.3	3.6	3.6

[a] Extraction conditions: organic phase (CH_2Cl_2, 10 mL); aqueous phase (10 mL); [MOH] = 5×10^{-2} M; [extractant] = 2.5×10^{-3} M; [picric acid] = 5×10^{-4} M; 22 °C; 9 h.

II. The extractability of **2a** with a 14-crown-4 ring was rather low compared to **1a** with a 12-crown-4 ring. The poor transport velocity of **2a** can be attributed to its low extractability of cations in the uptake process. The trend in selectivity in the solvent extractions agrees well with that observed in the transport experiments. For Li^+, **2b** showed an excellent extractability and the highest selectivity.

Experimental Section

^1H NMR spectra were taken at 100 MHz on a JEOL JNM-PS 100 spectrometer, with tetramethylsilane as the internal standard. IR and UV spectra were obtained on a Hitachi 260-10 spectrometer and a Hitachi U-2000 spectrophotometer, respectively. Mass spectra were measured with a Hitachi RMU-6E mass spectrometer at an ionization potential of 70 eV. Dihydroxymonoaza-14-crown-4 ethers were prepared by the literature procedure.[9]

Synthesis of Monoaza-12-crown-4 Ethers 1. General Procedure. N-Substituted diethanolamine **3** (0.004 mol) and lithium metal (70 mg, 0.01 mol) were dissolved in *tert*-butyl alcohol (60 mL), and diethylene glycol ditosylate (1.82 g, 0.0044 mol) in 6 mL of dioxane was added in drops to the solution over a period of 2 h with stirring by continuing the gentle reflux. After the addition, the mixture was refluxed for another 25 h. After the solvent was evaporated, water (100 mL) was added to the residue and extracted with dichloromethane (100 mL + 20 mL). The dichloromethane solution was dried over $MgSO_4$ and concentrated to give a brown viscous oil. The crude product was purified by Kugelrohr distillation (for **1a** and **1b**) or by chromatography over alumina (3:97 dioxane–benzene) (for **1c**).

10-Octyl-1,4,7-trioxa-10-azacyclododecane (1a): colorless oil; yield 38%; bp 115 °C (0.05 Torr) (Kugelrohr); IR (neat) 2925, 2850, 1465, 1360, 1130 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (t, 3 H), 1.1–1.6 (m, 12 H), 2.4–2.8 (m, 6 H), 3.6–3.8 (m, 12 H); MS, *m/e* (relative intensity) 287 (M^+, 10), 188 (100), 142 (29), 100 (50), 56 (14).

Anal. Calcd for $C_{16}H_{33}O_3N$: C, 66.86; H, 11.57; N, 4.87. Found: C, 66.75; H, 11.60; N, 4.80.

10-[2-(Octyloxy)ethyl]-1,4,7-trioxa-10-azacyclododecane (1b): colorless oil; yield 43%; bp 125 °C (0.07 Torr) (Kugelrohr); IR (neat) 2940, 2860, 1465, 1360, 1120 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (t, 3 H), 1.1–1.7 (m, 12 H), 2.7–2.9 (m, 6 H), 3.3–3.8 (m, 16 H); MS, *m/e* (relative intensity) 331 (M^+, 1), 188 (100), 158 (6), 100 (13), 56 (7).

Anal. Calcd for $C_{18}H_{37}O_4N$: C, 65.22; H, 11.25; N, 4.23. Found: C, 64.93; H, 11.17; N, 4.16.

10-[3-(Octyloxy)propyl]-1,4,7-trioxa-10-azacyclododecane (1c): colorless oil; yield 51%; IR (neat) 2940, 2870, 1465, 1360, 1120 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (t, 3 H), 1.2–1.9 (m, 14 H), 2.5–2.8 (m, 6 H), 3.3–3.9 (m, 16 H); MS, *m/e* (relative intensity) 345 (M^+, 12), 232 (32), 200 (47), 188 (100), 100 (62), 44 (37).

Anal. Calcd for $C_{19}H_{39}O_4N$: C, 66.05; H, 11.38; N, 4.05. Found: C, 66.14; H, 11.38; N, 4.06.

11-Octyl-1,4,7-trioxa-11-azacyclotetradecane (2a). To a stirred solution of 9,13-dihydroxy-11-octyl-1,4,7-trioxa-11-azacyclotetradecane (**4a**) (3.48 g, 0.01 mol) in benzene (30 mL) and a few drops of pyridine was added thionyl chloride (2.62 g, 0.022 mol) over a period of 5 min, the temperature being kept below 10 °C in an ice bath. The reaction temperature was gradually raised, and the mixture was refluxed for 16 h. After the solvent was evaporated, 5% Na_2CO_3 aqueous solution (300 mL) was added to the residue and extracted with dichloromethane (300 mL). The organic layer was washed with water (150 mL) and concentrated

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to give a brown viscous liquid. The crude product was distilled under reduced pressure in a Kugelrohr apparatus [150 °C (0.05 Torr)] to give a slightly yellow oil, 9,13-dichloro-11-octyl-1,4,7-trioxa-11-azacyclotetradecane (**5a**) (3.34 g, 87%). This compound was used as the starting material of the next step without further purification.

To a stirred suspension of $LiAlH_4$ (0.25 g, 0.0065 mol) in THF (25 mL) was added **5a** (1.00 g, 0.0026 mol) in THF (5 mL) in drops at room temperature, and then the mixture was refluxed for 26 h. After cooling, a small portion of water was added to the mixture. Insoluble matter was removed by filtration and concentrated to give a yellow viscous liquid. The crude product was purified by a Kugelrohr distillation [150 °C (0.08 Torr)] to give a colorless oil (0.59 g, 72%): IR (neat) 2920, 2850, 1460, 1355, 1120 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.1–1.5 (m, 12 H), 1.6–1.9 (m, 4 H), 2.2–2.6 (m, 6 H), 3.5–3.9 (m, 12 H); MS, *m/e* (relative intensity) 315 (M^+, 9), 216 (100), 158 (14), 128 (22), 58 (50).

Anal. Calcd for $C_{18}H_{37}O_3N$: C, 68.53; H, 11.82; N, 4.44. Found: C, 68.15; H, 11.72; N, 4.51.

11-[2-(Octyloxy)ethyl]-1,4,7-trioxa-11-azacyclotetradecane (2b). The synthetic procedure was almost the same as that used for **2a**. 9,13-Dichloro-11-[2-(octyloxy)ethyl]-1,4,7-trioxa-11-azacyclotetradecane (**5b**) was purified by chromatography over a short alumina column (10:90 dioxane–benzene) (92%). Compound **5b** was used for the next step without further purification: colorless oil; yield 73%; bp 150 °C (0.1 Torr) (Kugelrohr); IR (neat) 2920, 2850, 1460, 1350, 1120 cm^{-1}; NMR ($CDCl_3$) δ 0.84 (t, 3 H), 1.2–1.6 (m, 12 H), 1.6–1.9 (m, 4 H), 2.4–2.6 (t, 4 H), 3.2–3.8 (m, 18 H); MS, *m/e* (relative intensity) 359 (M^+, 1.4), 216 (100), 128 (6), 58 (39), 43 (6).

Anal. Calcd for $C_{20}H_{41}O_4N$: C, 66.81; H, 11.49; N, 3.90. Found: C, 66.80; H, 11.60; N, 3.97.

11-[3-(Octyloxy)propyl]-1,4,7-trioxa-11-azacyclotetradecane (2c). The synthetic procedure was almost the same as that used for **2a**. The intermediate **5c** was purified by chromatography over a short alumina column (5:95 dioxane–benzene) (59%). Compound **5c** was used for the next step without further purification: colorless oil; yield 63%; bp 155 °C (0.06 Torr) (Kugelrohr); IR (neat) 2930, 2860, 1465, 1360, 1120 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (t, 3 H), 1.1–1.6 (m, 12 H), 1.6–1.9 (m, 6 H), 2.2–2.7 (m, 6 H), 3.3–3.9 (m, 16 H); MS, *m/e* (relative intensity) 373 (M^+, 12), 260 (41), 216 (100), 128 (31), 58 (82).

Anal. Calcd for $C_{21}H_{43}O_4N$: C, 67.52; H, 11.60; N, 3.75. Found: C, 67.23; H, 11.55; N, 3.80.

11-[2-[2-(Octyloxy)ethoxy]ethyl]-1,4,7-trioxa-11-azacyclotetradecane (2d). The synthetic procedure was almost the same as that used for **2a**. The intermediate **5d** was purified by chromatography over a short alumina column (10:90 dioxane–benzene) (72%). Compound **5d** was used for the next step without further purification: colorless oil; yield 73%; bp 170 °C (0.06 Torr) (Kugelrohr); IR (neat) 2925, 2860, 1460, 1350, 1290, 1245, 1120, 980, 930 cm^{-1}; NMR ($CDCl_3$) δ 0.94 (t, 3 H), 1.2–1.6 (m, 12 H), 1.6–1.9 (m, 4 H), 2.5–2.8 (m, 4 H), 3.4–3.9 (m, 22 H); MS, *m/e* (relative intensity) 403 (M^+, 1), 284 (1), 230 (3), 217 (15), 216 (100), 186 (4), 158 (4), 128 (11), 58 (26).

Anal. Calcd for $C_{22}H_{45}O_5N$: C, 65.47; H, 11.24; N, 3.47. Found: C, 65.08; H, 11.29; N, 3.53.

Liquid Membrane Transport. Transport experiments were carried out in a U-type cell at 25 °C. The details for transport conditions are summarized in the footnotes of Table I and the caption of Figure 1. In the case of passive transport, the receiving phase was sampled from six different cells after 6, 12, 18, 24, 36, and 48 h and analyzed for cation concentration by using a Nippon Jarrell-Ash AA-8500 atomic absorption spectrometer. The value reported in Table I was the mean of six samples. The deviations from the mean were less than ±10%.

Solvent Extraction.[11] A mixture of an aqueous solution (10 mL) of alkali metal hydroxide (5×10^{-2} M) and picric acid (5×10^{-4} M) and a dichloromethane solution (10 mL) of an appropriate extractant (2.5×10^{-3} M) was shaken at 22 °C for 9 h. The extractability was obtained from the calculation based on the absorption of picrate anion in the aqueous phase at 354 nm in the UV spectrum.

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Registry No. **1a**, 120547-32-2; **1b**, 120547-33-3; **1c**, 120547-34-4; **2a**, 120547-36-6; **2b**, 120547-41-3; **2c**, 120547-42-4; **2d**, 120547-44-6; **3a**, 15520-05-5; **3b**, 65308-72-7; **3c**, 91374-49-1; **4a**, 117021-77-9; **4b**, 120547-37-7; **4c**, 120547-38-8; **4d**, 120547-43-5; **5a**, 120547-35-5; **5b**, 120547-39-9; **5c**, 120547-40-2; **5d**, 120577-48-2; $TsO(CH_2)_2O(CH_2)_2OTs$, 7460-82-4; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7.

A Simplified Synthetic Route to Polyaza Macrocycles

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Polyaza macrocycles have received considerable attention in recent years largely because of the cation and anion binding properties of the polyaza cavity.[1-3] Many of the synthetic routes to these systems use high dilution techniques[4] or template syntheses,[5] but the most popular involves the cyclization of the sodium salt of a linear tosylamide with a tosylated diol, as reported by Richman and Atkins.[6] More recently,[7] several large-ring macrocyclic diamines have been synthesized using Cs_2CO_3 to deprotonate the ditosylamide in DMF followed by slow addition of a dibromoalkane. Excellent yields were reported for 17–28-membered rings but low yields and incomplete reactions reported for 11–12-membered rings and for synthesis of the larger rings using Li_2CO_3, Na_2CO_3, or K_2CO_3 for deprotonation.[7] A comparison of yields for the cyclization of a 28-membered diamino macrocycle using cesium carbonate for deprotonation versus preforming the sodium salt, i.e., the Richman–Atkins approach, suggests that a combined ion-pair/template effect may be operative, giving Cs^+ a significant advantage over the smaller Na^+ for this size ring closure. With this background and the knowledge that K_2CO_3 has been used successfully to deprotonate tosylamides in DMF,[8-11] we decided to reinvestigate the use of K_2CO_3 to deprotonate and perhaps aid in the cyclization of 9–15-membered ring polyazamacrocycles. We report here the preparation of a series of previously known tri-, tetra-, and pentaaza macrocycles plus two previously unreported triazabenzo macrocycles.

Koyama and Yoshino[8] have previously reported the synthesis of **2**, **3**, and **4** using K_2CO_3 in DMF under high-

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