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Li^+-Selective Transport by Acyclic Neutral Carriers Having Benzoquinolyl Units

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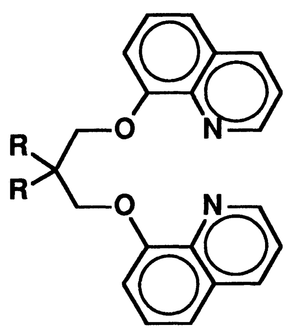
1,2-Bis(benzoquinolyloxy)ethane, which has been prepared as a carrier in alkali cation transport through liquid membranes, exhibits high Li^+-selectivity. From a systematic investigation, we found the length of the ethylene chain linking the two benzoquinolyl units is crucial for Li^+-selective transport.

We have previously reported several kinds of acyclic carriers for alkali and alkaline earth metal ions.[1–4] One is a group of neutral polyethers containing 8-quinolyl units, which are applicable for Li^+-selective electrodes.[3b] Investigation of structural effects has shown that introducing a trimethylene unit into a polyether chain is effective in enhancing Li^+-selectivity.[1,3,5] Two oxygen atoms in 1,3-position as in carriers **1** are essentially important to coordinate to Li^+.[3a,c] Here we report another type of neutral polyethers having benzoquinolyl (BQ) units with oxygen and nitrogen atoms in a 1,3-position. We studied the effects of substitution of quinolyl group to benzoquinolyl group and alkyl chain length on Li^+-selective carrier performance.

Carriers, $\mathbf{2_n}$ (n=2-6), were synthesized from the corresponding α,ω-dibromide and sodium salt of 10-hydroxybenzoquinoline in DMF. They were purified by column chromatography (silica or alumina gel, hexane-AcOEt), followed by recrystallization from $CHCl_3$-hexane when necessary.[6] Carrier **3** was also prepared in the same way using 1-chloro-3-(8-quinolyloxy)propane[1] as a starting material.

Transport experiments of alkali metal ions were carried out using a conventional U-type glass tube[7] at 25±0.2°C as reported previously.[3a] The initial transport conditions were shown in the footnote of Table 1. The amount of each cation transported into the receiving phase was determined by atomic absorption analysis.

The amounts of the transported cations after 2 days are summarized in Table 1. As seen in the table, the transport ability of polyethers $\mathbf{2_n}$ largely depended on the chain length between two BQ units. Carrier $\mathbf{2_2}$ transported a large amount of Li^+ with high selectivity 84 for Na^+, comparable to carriers **1**.[3a] Based on these results, we believe $\mathbf{2_2}$ binds Li^+ via intramolecular complexation as previously reported for **1**.[3a,c]



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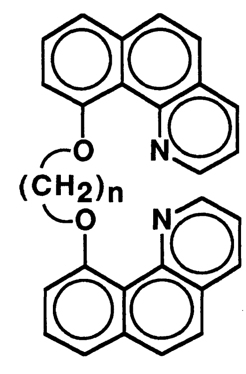

$\mathbf{2_n}$ (n=2-6)

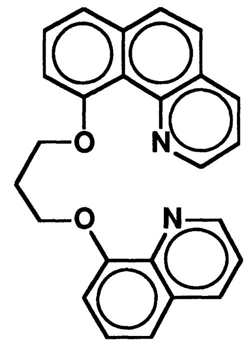

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Table 1. Alkali Ion Transport through $CHCl_3$ Membranes by Acyclic Carriers[a)]

Carrier	Alkali ion transported after 2 days (x10 μmol)			Selectivity	
	Li	Na	K	Li/Na	Li/K
$\mathbf{2_2}$	1120	13.3	4.1	84.1	274
$\mathbf{2_3}$	13.5	2.0	0.8	6.9	16.9
$\mathbf{2_4}$	2.5	4.0	2.5	0.63	1.0
$\mathbf{2_5}$	1.9	1.3	0.8	1.4	2.3
$\mathbf{2_6}$	0.3	4.9	2.4	0.06	0.1
3	113	2.1	1.3	54.9	90.0
No carrier	0	≈2	≈1	-	-

a) Initial transport conditions (25 °C):[3a)] Source phase; 1 M LiCl, 1 M NaSCN, 1 M KSCN 15 ml / liquid membrane; carrier 0.15 mmol in 30 ml $CHCl_3$ / receiving phase; H_2O 15 ml.

Carrier $\mathbf{2_3}$ transports fewer cations, in sharp contrast with $\mathbf{2_2}$. A CPK model investigation of $\mathbf{2_3}$ showed the distance between two oxygens closer than $\mathbf{2_2}$ and more steric hindrance between terminal groups, not allowing to complex a cation intramolecularly. Carrier **3**, which seems to have much space for a cation than $\mathbf{2_3}$, was prepared to compare the effect of the terminal group and its improved transport ability supports the above discussion. On the other hand, carriers having longer alkyl chains, $\mathbf{2_4}$-$\mathbf{2_6}$, could avoid steric hindrance between BQ units but were too flexible to catch and form an intramolecular complex with an alkali metal ion.

In conclusion, an ionophore composed of two benzoquinolyloxy groups linked by an ethylene chain was shown to be an effective Li^+-selective carrier. Crystallographic studies of the $\mathbf{2_2}$-Li^+ complex are under way.

References

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6) All new compounds gave the expected ^1H NMR and IR spectra. Their melting points and/or precise mass data are as follows. $\mathbf{2_2}$: mp 190.9-191.5 °C, M^+ 416.1486 (Calcd for $C_{28}H_{20}O_2N_2$ 416.1524), $\mathbf{2_3}$: mp 160.3-160.9 °C, M^+ 430.1647 (Calcd for $C_{29}H_{22}O_2N_2$ 430.1680), $\mathbf{2_4}$: mp 173.3-174.0 °C, M^+ 444.1788 (Calcd for $C_{30}H_{24}O_2N_2$ 444.1836), $\mathbf{2_5}$: oil, M^+ 458.1961 (Calcd for $C_{31}H_{26}O_2N_2$ 458.1993), $\mathbf{2_6}$: mp 123.6-123.9 °C, M^+ 472.2111 (Calcd for $C_{32}H_{28}O_2N_2$ 472.2149), **3**: oil, M^+ 380.1515 (Calcd for $C_{25}H_{20}O_2N_2$ 380.1524).
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