

## Ionic recognition by proton-ionizable lariat ethers and their polymers

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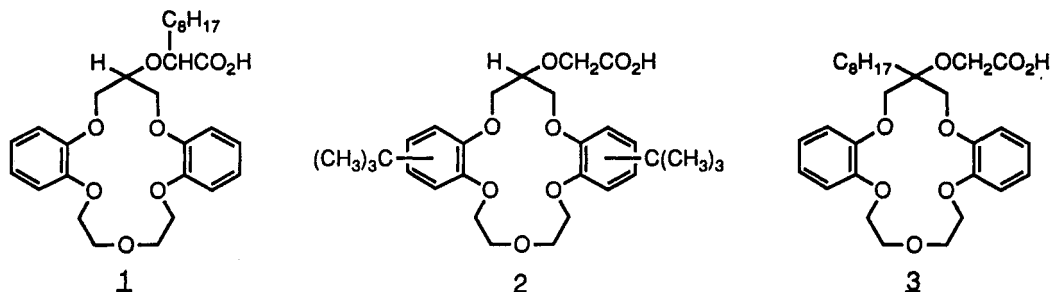
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### Abstract

To probe the influence of structural variation within dibenzo-16-crown-5-oxyacetic acids upon the selectivity of alkali metal cation separations by solvent extraction and liquid membrane transport processes, studies have now been conducted in homogeneous solution by NMR spectroscopy and titration calorimetry and in the solid state. Condensation polymerization of such proton-ionizable lariat ethers with formaldehyde produces a new class of ion-exchange resins which contain cyclic polyether binding sites as well as ion-exchange site for metal ion complexation.

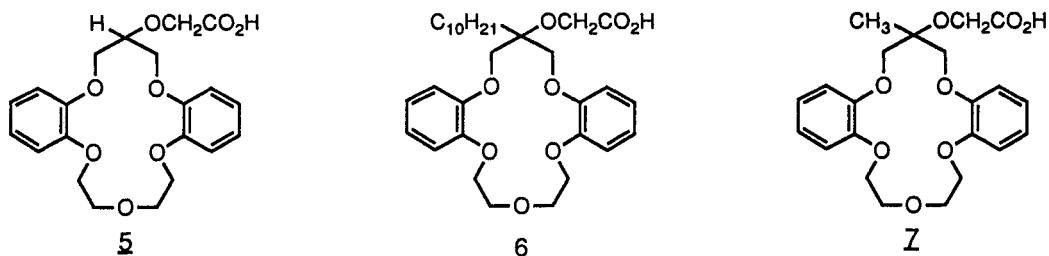
Proton-ionizable lariat (ref. 1) ethers are crown ethers which possess a pendent acidic group (eg. carboxylic acid, sulfonic acid, phosphonic acid). Compared with neutral crown ethers and lariat ethers, proton-ionizable lariat ethers have an important advantage that the transfer of a metal ion into an organic medium in a separation process does not require concomitant transport of an aqueous phase anion (refs. 2 and 3). This factor is of immense importance for potential practical applications in which hard, hydrophilic aqueous phase anions, such as chloride, nitrate or sulfate, would be involved.

The reaction of bisphenols with epichlorohydrin and metal hydroxides in aqueous solvents provides a convenient synthesis of dibenzocrown ethers containing a three-carbon bridge with a hydroxyl group on the center carbon (ref. 4). Such dibenzocrown ether alcohols may be transformed into lariat ether carboxylic acids, such as 1-3 (refs. 5-7). Lipophilic groups are incorporated into these proton-ionizable lariat ethers to prevent loss of the crown ether carboxylate from the organic layer into a contacting highly alkaline aqueous phase during solvent extraction (ref. 8).



In studies of the influence of structural variation within proton-ionizable lariat ethers upon the selectivity of competitive solvent extraction of alkali metal and alkaline earth cations (ref. 3), the effect of varying the lipophilic group attachment site was probed. Thus compounds 1-3 are structural isomers which possess a common dibenzo-16-crown-5-oxyacetic acid unit. The lipophilic group is attached to the side arm, the benzo groups, and a polyether ring carbon in lariat ether carboxylic acids 1-3, respectively. Although all three ligands exhibit sodium selectivity for competitive solvent extractions of the five alkali metal cations from aqueous solution into chloroform (as would be predicted for a 16-crown-5 ring), the sodium selectivity of 3 was much higher than those observed for structural isomers 1 and 2 (ref. 9). It was proposed that when the lipophilic

octyl group in **3** is directed away from the polar polyether ring the pendent carboxylic acid function is oriented directly over the crown ether ring (ref. 9). Thus the enhanced sodium selectivity of **3** is attributed to preorganization of the binding site (ref. 10).



To provide experimental support for this contention, solid state structures for dibenzo-16-crown-5-oxyacetic acids **5** and **6** have now been determined. As shown in Figure 1, the carboxylic acid group in **5** points away from polyether ring; whereas in **6**, it is positioned over the crown ether cavity.

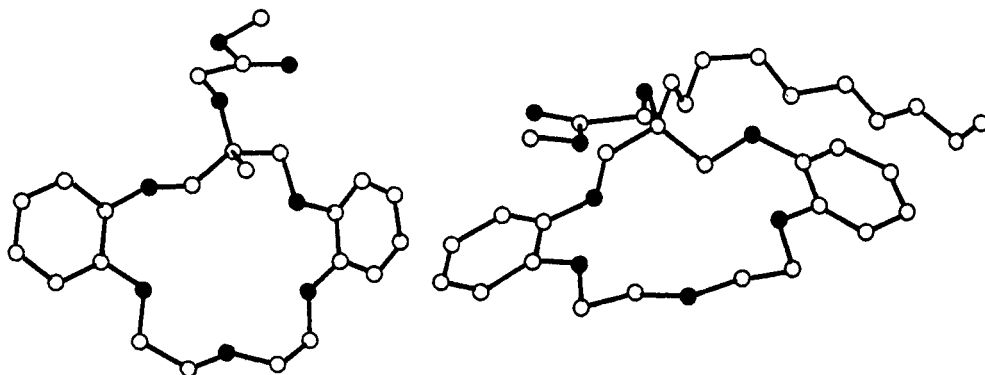


Figure 1. Ball and stick drawings for solid-state structures of dibenzo-16-crown-5-oxyacetic acids **5** (left) and **6** (right). Hydrogens are omitted except for those of the carboxylic acid group and the methine hydrogen in **5**.

Pre-orientation of the binding side for *sym*-(*R*)dibenzo-16-crown-5-oxyacetic acids and derivatives in homogeneous solution has also been studied by NMR spectroscopy. A portion of the PMR spectrum for *sym*(methyl)dibenzo-16-crown-5-oxyacetic acid (**7**) is shown in Figure 2. Noteworthy is the AB pattern for the diastereotopic methylene protons on the three-carbon bridge which shown a lack of interconversion of these protons on the NMR time scale. By a combination of decoupling, HOMO COSY, HETERO COSY and NOE experiments, the spectral assignments shown in structure **8** were deduced. The NOE experiments also demonstrated that the carboxylic acid group was located over the polyether cavity.

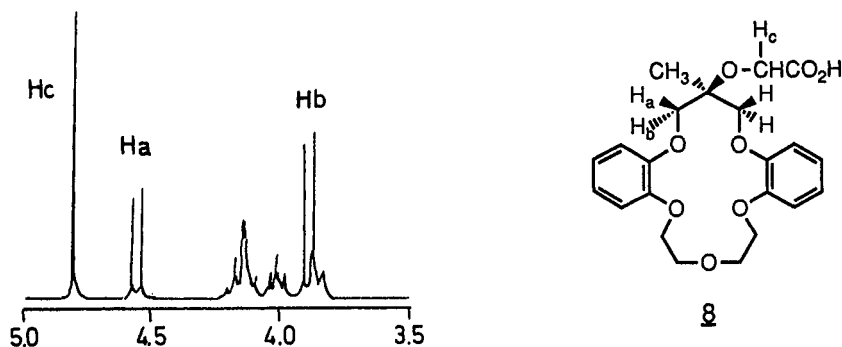
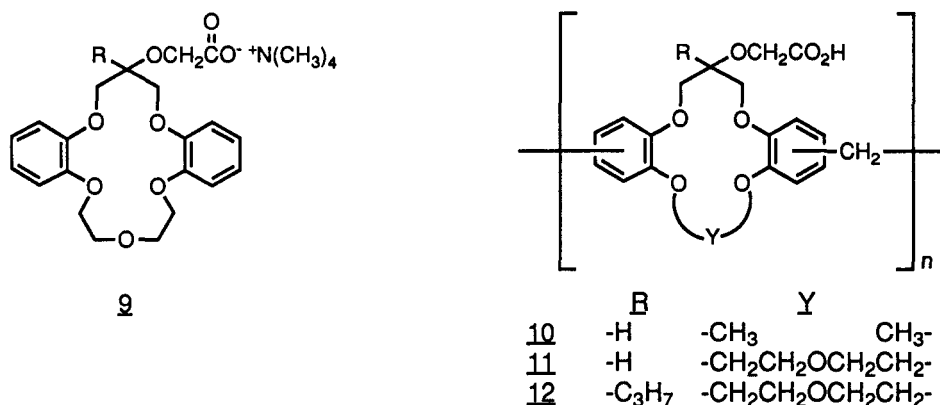


Figure 2. Proton magnetic resonance spectrum of *sym*(methyl)dibenzo-16-crown-5-oxyacetic acid (**7**) in chloroform-d.

Solution conformations of *sym*-(alkyl)dibenzo-16-crown-5-oxyacetic acids were further probed by NMR with *syn*-(decyl)dibenzo-16-crown-5-oxyacetic acid (**6**). The

chemical shift difference between the diastereotopic Ha and Hb hydrogens of the methylene groups of three-carbon bridge,  $\Delta\nu(\text{HaHb})$ , was utilized as a measure of conformational flexibility. The  $\Delta\nu(\text{HaHb})$  value for **6** in chloroform-d was found to decrease from 217 Hz at 258 °K to 185 Hz at 328 °K. Thus conformational rigidity is diminished at higher temperatures. The  $\Delta\nu(\text{HaHb})$  value for **6** is also strongly influenced by the identity of the solvent. For variation of the deuterated NMR solvent from benzene to chloroform to acetone to acetonitrile to dimethyl sulfoxide at room temperature, the  $\Delta\nu(\text{HaHb})$  values were 244, 205, 134, 127 and 87 Hz, respectively. This trend may be readily rationalized by considering a competition between intramolecular and intermolecular hydrogen bonding of the carboxylic acid function. With the carboxylic acid group oriented over the crown ether cavity, it is well positioned for intramolecular hydrogen bonding with an ethereal oxygen. Such intramolecular hydrogen bonding should increase the conformational rigidity. In benzene, where intermolecular hydrogen bonding of the carboxylic acid function with the solvent should be minimal, such intramolecular hydrogen bonding should be at a maximum. At the other extreme, dimethyl sulfoxide is a hydrogen bond-accepting solvent which would reduce the level of intramolecular hydrogen bonding of the carboxylic acid group. In agreement, the  $\Delta\nu(\text{HaHb})$  value for **5** is a maximum in benzene and decreases steadily as the hydrogen bond-accepting nature of the solvent is increased to reach a minimum with dimethyl sulfoxide.



The influence of a geminal alkyl group on complexation of individual alkali metal cation species by sym-(alkyl)dibenzo-16-crown-5-oxyacetic acids in homogeneous solution was also investigated. Association constants for complexation of alkali metal cations by tetramethylammonium crown ether carboxylates **9** in 90 % methanol-10 % water were determined by titration calorimetry. Results are recorded in Table 1.

TABLE 1. Association constants for complexation of alkali metal cations by tetramethylammonium sym-dibenzo-16-crown-5-oxyacetates **9** in 90 % methanol-10 % water.

R	log K			
	Na	K	Rb	Cs
hydrogen	3.69±0.15	3.27±0.14	2.63±0.07	2.43±0.09
methyl	4.69±0.07	3.56±0.07	3.22±0.24	2.35±0.08
ethyl	4.47±0.08	3.60±0.10	2.92±0.12	2.18±0.10
butyl	4.46±0.06	3.43±0.06	2.85±0.14	2.11±0.12
hexyl	4.50±0.01	3.47±0.06	2.73±0.08	2.01±0.03
octyl	4.40±0.06	3.42±0.04	2.87±0.15	2.34±0.21
decyl	4.41±0.01	3.31±0.03	2.90±0.25	2.32±0.01

In all cases insufficiency heat was generated with lithium for calculation of the association constant. For **9** with R = H, the association constant for sodium is largest, as would be predicted for the 16-crown-5 ring size. When a methyl group is introduced on the ring carbon geminal to the carboxylate containing side arm, the association constants for sodium, potassium, and rubidium increase, while that

for cesium remains unchanged. It is noteworthy that the increase in log K is much larger for sodium than for potassium and rubidium. Thus the methyl group not only gives overall binding enhancement for appropriate-sized alkali metal cations, but also increases the sodium selectivity. Replacement of R = methyl with ethyl causes only minor alteration in the association constants and for the series of 9 with R = ethyl, butyl, hexyl, octyl and decyl, the association constants are essentially the same. Thus the enhanced sodium selectivity of sym-(alkyl)dibenzo-16-crown-5-oxyacetic acids relative to sym-dibenzo-16-crown-5-oxyacetic acid (5) occurs for both small and extended alkyl groups.

By polymerization or immobilization on solid supports, crown ethers may be adapted to continuous separation processes. Condensation polymers 10-12 were formed by refluxing the corresponding acyclic or cyclic polyether monomers with formaldehyde in formic acid (ref. 11). The precipitated polymer was washed, dried, and ground to a powder (finer than 100 mesh). For batch competitive sorption of alkali metal cations from shaken aqueous solutions, it was found that metal ion sorption was rapid (85 % of the equilibrium sorption was achieved in five minutes) in contrast with the reported slow metal salt sorption by resins formed from neutral crown ether resins. Stripping of the sorbed metal ions was readily accomplished by shaking for 30 seconds with 0.10 M HCl.

The acyclic polyether carboxylic acid resin 10 exhibited similar lithium sorption selectivity to that of a commercial poly(methacrylic) acid resin. This indicates that metal ion sorption occurs primarily at the ion-exchange site in 10. On the other hand, sodium and lithium were sorbed equally well by crown ether carboxylic acid resin 11. The enhanced sodium sorption demonstrates the importance of the cyclic polyether binding site in the resin. Crown ether carboxylic acid resin 12 exhibits good sodium sorption selectivity. The geminal propyl group in 12 orients the carboxylic acid group over the crown ether cavity which pre-organizes the binding site. This is the first instance in which conformational positioning of an ion-exchange group in a resin has shown an important influence on metal ion recognition.

#### Acknowledgements

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