

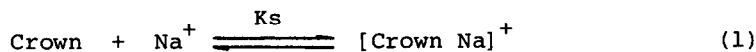
THE EFFECT OF SIDEARM HETEROATOMS AND A QUATERNARY METHYL GROUP  
 AT THE PIVOT POSITION IN LARIAT ETHERS

Yohji Nakatsuji, Tetsuya Nakamura, Mitsuo Okahara,\*  
 Dennis M. Dishong# and George W. Gokel\*#

(Department of Applied Chemistry, Faculty of Engineering, Osaka University,  
 Yamada-oka 2-1, Suita, Osaka, Japan 565 and #Department of Chemistry,  
 University of Maryland, College Park, Maryland 20742, USA)

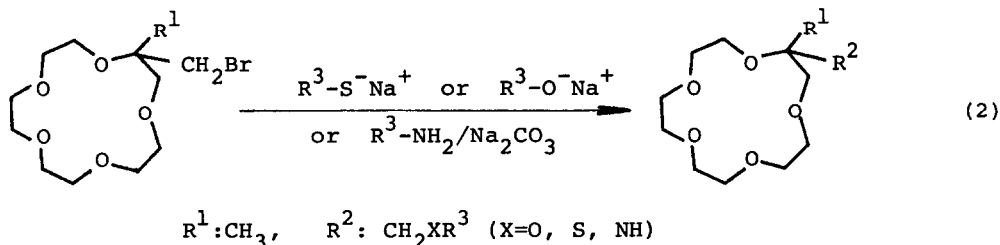
Summary: A methyl group geminal to the "pivot" carbon in hydroxy-methyl-derived lariat ethers dramatically enhances the binding afforded a complexed cation by the sidearm.

A number of recent papers detail the preparation of macrocyclic polyethers attached to sundry sidearms.<sup>1-4</sup> We have previously shown that when a donor group is present in the sidearm, at a distance appropriate to afford additional Lewis base interactions with a complexed cation, complexing ability is considerably enhanced.<sup>5-7</sup> In polar, aqueous methanol solution, these differences are apparently minimized as reflected in binding constants (Ks) for equation 1.<sup>8</sup>



We have now found that the effect of a methyl group on the carbon bearing the sidearm is to conformationally lock the arm, apparently holding it over the crown macroring and thereby shifting the complexation equilibrium (equation 1) to the right.

We have previously reported the facile synthesis of 2-bromomethyl-2-methyl-15-crown-5 by intramolecular bromoalkoxylation of tetraethylene glycol mono-2-methylallyl ether (generated *in situ*).<sup>4</sup> Formation of the  $\alpha$ -methyl-lariat ethers is accomplished according to equation 2. A number of sidearms have been added to this parent methyl-lariat in an effect to assess the methyl group's effect on the sodium and potassium binding constants (methanol solution).



An examination of Corey-Pauling-Koltun molecular models suggests that the effect of the methyl group on sidearm conformation should be significant. When all of the ring oxygens are turned inward as required for cation complexation, the sidearm is normally restricted in its rotation by two methylene groups, one vicinal and the other removed by a single oxygen. This interaction does not appear inconsequential in the nonmethyl-lariats,<sup>5,8</sup> but when a geminal methyl group is present, it seems clear that an additional "gearing" interaction between the sidechain methylene and the quaternary methyl group should restrict rotation even further.

There has been considerable interest in oxygen-lariat type molecules with "inert" alkyl sidechains as potential tethers to polymer backbones.<sup>1,9</sup> It appears that considerable additional advantage may be gained by resorting to the methyl-lariats in these applications.

Table: Binding Data for Lariat Ethers<sup>a</sup>

Compound No.	R <sup>1</sup>	R <sup>2</sup>	Log Ks (MeOH) <sup>c</sup>	
			Na <sup>+</sup>	K <sup>+</sup>
1	H	H	3.27	3.60
2	CH <sub>3</sub>	CH <sub>2</sub> Br	2.86	2.70
3 <sup>b</sup>	H	CH <sub>2</sub> OCH <sub>3</sub>	3.03	3.27
4	CH <sub>3</sub>	CH <sub>2</sub> O-n-C <sub>6</sub> H <sub>13</sub>	3.57	3.35
5	CH <sub>3</sub>	CH <sub>2</sub> S-n-C <sub>6</sub> H <sub>13</sub>	3.08	2.98
6	CH <sub>3</sub>	CH <sub>2</sub> NH-n-C <sub>6</sub> H <sub>13</sub>	3.08	2.94
7 <sup>b</sup>	H	CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	3.05	3.32
8	CH <sub>3</sub>	CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	3.87	3.42
9 <sup>b</sup>	H	CH <sub>2</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub>	3.13	3.72
10	CH <sub>3</sub>	CH <sub>2</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>2</sub> CH <sub>3</sub>	3.89	3.98
11	CH <sub>3</sub>	CH <sub>2</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> CH <sub>3</sub>	3.87	4.00

- All new compounds had IR, NMR, and combustion analyses in accordance with the assigned structures.
- These were prepared as previously described.<sup>5</sup>
- Log Ks values were determined by ion selective electrode measurements.

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