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Dimerization behavior of substituted dibenzo-14-crown-4 alcohols studied by NMR spectroscopy

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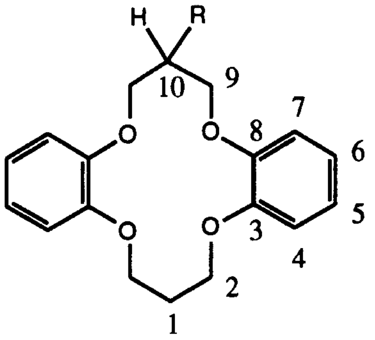
Dibenzo-14-crown-4 alcohols are shown to aggregate in chloroform by the formation of hydrogen-bonded dimers. Structural variations between crown ether alcohols significantly affect the degree of dimerization. This self-association is of relevance for understanding the complexation and extractive properties of these and related macrocycles.

To understand metal-ion recognition by an ionophore requires an understanding of the initial state of the ionophore as well as its final complexed state. In low-polarity environments, such as those found in solvent extraction and liquid membranes, the initial state of an ionophore frequently involves self-association promoted especially by hydrogen bonding, dipole-dipole interactions, and hydration.[1,2] Self-association essentially represents a competitive effect that must be taken into account when evaluating measures of complexation strength and when interpreting distribution and transport data. In addition, to the extent that conformations of free ligands may be altered by intermolecular interactions, self-association may well be expected to influence ligand preorganization.

Lariat ethers have proven to be an important class of ionophores because of the strong degree of control of ion-binding properties afforded by sidearm structural modifications.[3–6] Sidearm function has also been linked to self-association phenomena, but the focus has been directed toward aqueous solutions of lariat ethers modified to have surfactant properties.[7] Scant attention has been devoted to self-association of lariat ethers in low-polarity media relevant to solvent extraction and liquid membranes, and the evidence for self-association in this case has so far been essentially negative under select conditions.[8] Yet the litany of evidence regarding the behavior of simple alcohols and carboxylic acids in solution would imply that lariat ethers bearing these functionalities would be highly likely to aggregate in low-polarity solvents.[9,10] Thus, it is our thought that this aspect of lariat ethers deserves further consideration.

The synthesis, structure, alkali metal ion binding, and solvent-extraction chemistry of *sym*-dibenzo-14-crown-4 ethers bearing carboxylic acid and alcohol sidearms have been reported.[11–23] In this paper, we specifically focus on the self-association behavior of lariat ether alcohols (**1–3**)[11,22,28] based on the *sym*-dibenzo-14-crown-4 (DB14C4) frame:



1 $R = \overset{11}{C}H_2\overset{12}{C}H_2OH$
2 $R = O\overset{11}{C}H_2\overset{12}{C}H_2OH$
3 $R = OH$

Although various techniques have been used for studying hydrogen bonding in solution,[9] NMR offers several distinct advantages and has become an important tool in this regard.[10,24] Formation of a hydrogen bond causes a large change in the shielding of a proton donor by lowering the effective electron

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density, resulting in a shift of the resonance signal to lower fields. In the case of alcohol functionalities, the NMR resonance of the hydroxyl proton is easily observed, and a number of self-associating alcohol systems have been so characterized.[10]

The temperature and concentration dependencies of the chemical shifts of the proton resonances in **1** are shown in Table 1. As the temperature increases from −40 to 50 °C, the hydroxyl proton resonance is shifted progressively upfield. For the same temperature gradient, the chemical shifts of the other protons change only slightly. Upfield shifts of the hydroxyl proton are also observed when the solution concentration of **1** is decreased from 600 to 3 mM however, the magnitude of the observed shifts is less than that observed in the variable-temperature experiment. These same trends were observed for compounds **2** and **3**.

In the concentration range investigated (3–600 mM), the chemical-shift behavior could be modeled by considering only dimer formation as given by the equation,

$$\mathrm{LOH}+\mathrm{LOH}\rightleftharpoons(\mathrm{LOH})_2 \qquad (1)$$

The presence of a single resonance for each proton indicated fast exchange between the monomer LOH and the dimer $(\mathrm{LOH})_2$. Thus, the observed chemical shifts, δ_{obs}, are weighted averages of the chemical shifts of the monomer, δ_{M}, and of the dimer, δ_{D}, according to the equation:[25]

$$\delta_{\mathrm{obs}}=X_{\mathrm{M}}\delta_{\mathrm{M}}+X_{\mathrm{D}}\delta_{\mathrm{D}} \qquad (2)$$

where X_{M} and X_{D} are the mole fractions of the monomer and the dimer, respectively. These in turn are related to the dimerization constant, K_{D}, by the relationship:

$$K_{\mathrm{D}}=[(\mathrm{LOH})_2]/[\mathrm{LOH}]^2 \qquad (3)$$

The dependence of δ_{obs} on the total alcohol concentration, C, can be derived from eqns. (2) and (3):[25]

$$\delta_{\mathrm{obs}}=\delta_{\mathrm{M}}+(\delta_{\mathrm{D}}-\delta_{\mathrm{M}})[(1+8K_{\mathrm{D}}C)^{1/2}-1]/[(1+8K_{\mathrm{D}}C)^{1/2}+1] \qquad (4)$$

The parameters K_{D}, δ_{M}, and δ_{D}, as obtained by non-linear least squares regression using the program MINSQ,[26] are listed in Table 2.

To provide information on the types of interactions possible in these systems, the mixing experiments summarized in Table 3 were performed. Chloroform solutions containing *sym*-dibenzo-14-crown-4-ethanol (**1**) or *sym*-hydroxydibenzo-14-crown-4 (**3**) at 3 mM were prepared and then made 50 mM in dibenzo-14-crown-4, *sym*-methoxydibenzo-14-crown-4 ($\mathrm{DB14C4OCH_3}$), or *t*-butanol. Changes in the chemical shift of the hydroxyl protons of **1** and **3** defined as $\Delta\delta=\delta_{\mathrm{observed}}-\delta_{\mathrm{M}}$

Table 1 Proton chemical shifts (δ, ppm) of *sym*-dibenzo-14-crown-4-ethanol (**1**) in $\mathrm{CDCl_3}$ under conditions of varying temperature and concentration[a]

	δ (−40 °C)	δ (20 °C)	δ (50 °C)	$\Delta\delta_{\mathrm{T}}$[b]	δ (600 mM)	δ (3 mM)	$\Delta\delta_{\mathrm{C}}$[c]
$\mathrm{H_1}$	2.25	2.20	2.18	0.07	2.18	2.20	−0.02
$\mathrm{H_2}$	4.13	4.15	4.16	−0.03	4.13	4.15	−0.01
$\mathrm{H_{9a}}$	4.05	4.13	4.14	−0.09	4.07	4.13	−0.06
$\mathrm{H_{9e}}$	4.00	4.02	4.04	−0.04	4.01	4.02	−0.01
$\mathrm{H_{10}}$	2.54	2.45	2.44	0.10	2.44	2.45	−0.01
$\mathrm{H_{11}}$	1.71	1.74	1.75	−0.04	1.71	1.74	−0.03
$\mathrm{H_{12}}$	3.74	3.77	3.77	−0.03	3.72	3.77	−0.05
OH	3.41	2.23	1.99	1.42	2.98	2.22	0.75

[a] Proton chemical shifts were measured using a Bruker MSL-400 NMR spectrometer at 400.13 MHz. Solvent was dried and stored over molecular sieves before use. Samples were dried under vacuum prior to use. All sample preparations were performed under an Argon atmosphere.

[b] $\Delta\delta_{\mathrm{T}}$ is the observed change in the chemical shift for a 50 mM solution of **1** over the temperature range −40 to 50 °C.

[c] $\Delta\delta_{\mathrm{C}}$ is the observed change in the chemical shift over the concentration range 3 to 600 mM at 20 °C.

Table 2 Hydroxyl proton chemical shifts of monomer (δ_{M}) and dimer (δ_{D}), calculated total change in chemical shift ($\Delta\delta_{(\mathrm{D-M})}$), and dimerization constant (K_{D}) in $\mathrm{CDCl_3}$ at 20 °C.[a]

Alcohol	δ_{M}	δ_{D}	$\Delta\delta_{(\mathrm{D-M})}$	K_{D} ($\mathrm{L\,mol^{-1}}$)
$\mathrm{DB14C4CH_2CH_2OH}$ (**1**)	2.11	5.91(11)	3.80	0.27(01)
$\mathrm{DB14C4OCH_2CH_2OH}$ (**2**)	2.38	3.56(11)	1.28	0.95(14)
DB14C4OH (**3**)	2.95	4.09(02)	1.14	3.20(12)

[a] Refinement of δ_{M}, δ_{D}, and K_{D} was carried out by regression analysis using eqn. (4). Estimated standard deviations are indicated in parentheses; values of δ_{M} were precise to ±0.002 or less.

Table 3 Changes of chemical shifts ($\Delta\delta$, ppm) of hydroxyl protons in *sym*-dibenzo-14-crown-4 alcohols **1** and **3** in $CDCl_3$ at 25 °C.[a]

Alcohol (3 mM)	$\Delta\delta$ DB14C4 (50 mM)	$\Delta\delta$ DB14C4OCH$_3$ (50 mM)	$\Delta\delta$ t-C_4H_9OH (50 mM)
DB14C4CH$_2$CH$_2$OH (**1**)	None	None	0.03[b]
DB14C4OH (**3**)	None	None	0.25

[a] $\Delta\delta$ is the change in chemical shift of the indicated alcohol upon addition of DB14C4, DB14C4OCH$_3$, or t-C_4H_9OH.
[b] 40 °C.

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were then recorded. Since compounds **1**–**3** exist predominantly as monomers at 3 mM (Table 2), $\Delta\delta$ may be attributed to hydrogen bonding with the added compound.

The results given in Tables 1 and 2 demonstrate the importance of dimerization of the lariat alcohols **1**–**3** in chloroform at moderate concentrations. Furthermore, the alcohol chemical shifts clearly implicate the involvement of hydrogen bonding in the observed self-association. As given by the equilibrium constants K_D, the strength of the interaction varies significantly and follows the order **3**>**2**>**1**.

As shown in Table 3, intermolecular hydrogen bonding between the hydroxyl protons of **1** and **3** and ether oxygen atoms either in the macrocyclic ring of DB14C4 or sidearm of DB14C4OCH$_3$ occurs negligibly under the present conditions. On the other hand, **1** and **3** strongly interact with *t*-butanol. In applying these results to the interpretation of the self-association data in Table 2, it may be concluded that alcohols **1**–**3** do not dimerize via a single alcohol-to-ether hydrogen bond. Rather, a reciprocal alcohol-to-ether arrangement involving two hydrogen bonds or an alcohol-to-alcohol interaction is implied. The strong interaction of either **1** or **3** with *t*-butanol points to an important alcohol-to-alcohol group interaction, and we thus favor this explanation for the self-association of alcohols **1**–**3**.

Three principal effects may be expected to influence the strength and extent of hydrogen bonding, including steric, inductive, and conformational effects. Since the most sterically hindered alcohol, **3**, has the highest value of K_D, steric effects appear relatively unimportant. On the other hand, both **2** and **3** have an ether functionality at the position β to the hydroxyl group; a β ether functionality is not present in **1**. The electron-withdrawing effect of these substituents can be expected to increase the acidity of the hydroxyl proton, making it a stronger hydrogen-bond donor.[27] Additionally, sidearm conformation including the effect of intramolecular hydrogen bonding may be significant. Recent results[28] have shown that the sidearm of **1** prefers a pseudo-equatorial configuration (*anti* to the ring C–O bond), whereas the sidearms of **2** and **3** prefer the pseudo-axial (*gauche*) configuration. On the basis of these considerations, the pseudo-equatorial sidearm of **1** is unfavorably oriented to engage in intramolecular hydrogen bonding with the ring ether oxygen atoms. On the other hand, although the sidearm of **2** has conformational mobility, the OH group can engage in intramolecular hydrogen bonding to either the ether oxygen atom of the sidearm or to ring oxygen atoms. Finally, the OH group of **3** in the pseudo-axial configuration is well preorganized to hydrogen bond to the closest ring oxygen atoms (O–O distance 2.80 Å[16]). Recalling the 'cooperative effect' principle of hydrogen bonding,[29] the expected strengthening effect of existing intramolecular O–H···O hydrogen bonds on intermolecular hydrogen bonding, in addition to the inductive effects, provides a rationale for the observed order of K_D values.

Since chloroform is a popular extraction solvent, the present results have direct relevance to the interpretation of extraction data for protogenic classes of lariat ethers. As pointed out by others,[16] water interactions may also be important. Further experiments are underway in a effort to investigate the thermodynamics and structure of intra- and intermolecular hydrogen bonding of lariat ethers in solution.

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