Current Research:

Our primary research thrust in recent years has been directed toward developing an understanding of how thermal motion affects the structures and stabilities of supramolecular complexes. These complexes, which are bound by non-covalent intermolecular forces, have been shown in experiments conducted by the Atwood group and others to yield materials having unusual properties. For example, a specially prepared crystal form of the calix[4]arene macrocycle—calix[4]arene is a cup-shaped molecule that can trap a small molecule within its cavity—sorbs atmospheric gases even though it is without the well-defined pore structure found in zeolites or metal-organic frameworks (MOFs). These crystals furthermore exhibit selectivity: carbon dioxide is preferentially retained when the crystals are exposed to a mixture of carbon dioxide and molecular hydrogen. The Atwood group also has shown that a similar macrocycle, pyrogallol[4]arene, when reacted with solutions of transition metal salts, often yields metal-seamed capsules, which could serve as micro-reactors or as vessels for selectively transporting drug molecules to tumor or infection sites. The challenge here will be to devise capsules with larger and larger interior volumes, but meeting this challenge requires that we understand the dynamics of the capsules themselves as well as the dynamics of the sequestered guest species. The latter consideration is significant because NMR is conventionally used to investigate the guest, and the mobility of the guest on the NMR time scale affects the number of resonances observed.

As an example of this work, a snapshot is shown below of a zinc-seamed pyrogallol[4]arene dimer capsule with exo pyridine ligands and a sequestered protonated pyridine molecule (two orientations are depicted).

![Snapshot of a zinc-seamed pyrogallol[4]arene dimer capsule](image)

We also are investigating the dynamics of the macrocycles themselves. Formation of dimeric capsules requires that the macrocycles adopt a cone conformation, but there is no guarantee that the synthesis of the macrocycles yields exclusively (or even primarily) the desired conformer. Thus, by identifying the conditions under which a non-cone conformer will transition to the cone conformer, we will assist in the development of more efficient syntheses of these systems.
In addition to the work carried out in collaboration with the Atwood and Deakyne groups (the latter group focusing on structural characterizations and energetics determined from electronic structure calculations), we have joined the Deakyne group in examining various species of interest to the Jurisson group, species that have been shown to complex radionuclides such as technetium and rhenium. One of our contributions to this research program is an investigation of the effect of explicit solvent molecules on molecular conformation. The solvent environment can play a very significant role, for example, in determining the orientation of amino acid side chains that are involved in substrate binding.

Recent Representative Publications: