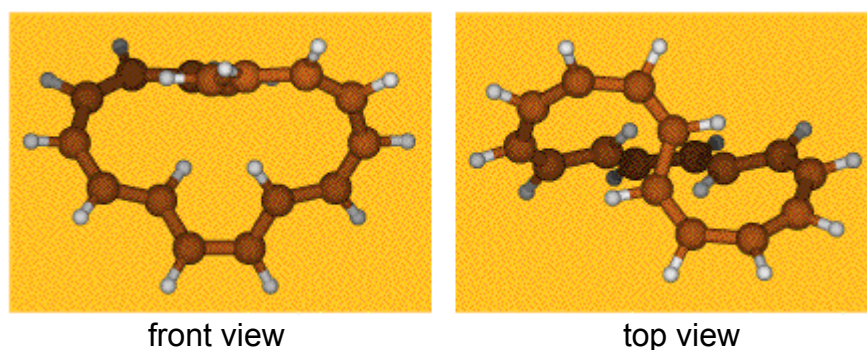


Research Interests

Recent work in the Castro-Karney research group revolves around various aspects of annulene chemistry. Annulenes have been subject to intense study by experimentalists and theoreticians for several decades, by virtue of what we can learn from them about concepts such as structure, aromaticity, delocalization, bonding, and magnetic properties. Work in our group lies primarily in the two areas summarized below.

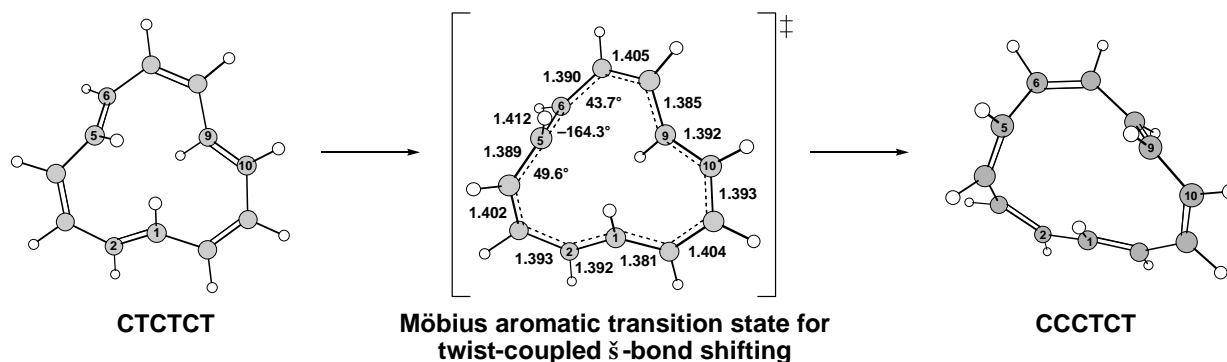
Möbius Annulenes and Aromaticity

Based on a 1964 prediction by Heilbronner regarding the π -electron energy of $[4n]$ annulenes with Möbius topology, we and others have searched for such systems that exhibit a high degree of aromaticity, based on geometric (Δr) and magnetic (NICS and magnetic susceptibility exaltation) criteria. One hypothetical $[16]$ annulene isomer we located (shown below) has a very high degree of bond-length equalization and a large negative nucleus-independent chemical shift (NICS), both indicative of strong aromaticity.



Mechanisms of Dynamic Processes in Annulenes

Annulenes undergo a variety of dynamic processes, including conformation change, valence isomerization, planar bond shifting, and configuration change. Much of our work involves the use of quantum chemical calculations to determine the precise mechanisms and barriers for these processes. One fascinating example is configuration change in $[12]$ annulene (shown below), proposed in 1971 by Oth and Schröder to explain some experimental observations. We found that the key step in this process is "twist-coupled bond shifting", via a Möbius-topology transition state. This transition state is highly aromatic, as expected for a strongly bond-equalized Möbius $[4n]$ annulene.



Recent Publications

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3. C. Castro*, W. L. Karney*, C. M. McShane, and R. P. Pemberton, "[10]Annulene: Bond Shifting and Conformational Mechanisms for Automerization," *J. Org. Chem.* **2006**, *71*, 3001-3006.
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