A New Strategy for the Synthesis of Small, Strained Cyclophanes

Graham J. Bodwell
Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, Canada
E-mail: gbodwell@mun.ca

Small, strained cyclophanes are especially interesting because of the deviation of various structural features from ideality and the unusual spectroscopic and physical properties that emerge. Of course, the strained nature of such systems renders them challenging synthetic targets and the level of challenge tends to increase with the level of strain in the cyclophane. There is currently only one general synthetic strategy for accessing the more highly strained cyclophanes, *i.e.* the conversion of a bridged pre-arene with low strain to the corresponding bridged arene (cyclophane) with high strain. The success of this approach is rooted in the gain of aromatic stabilization energy (ASE) that accompanies the conversion of the pre-arene to the arene, which serves to offset the strain that accumulates at the same time.

We report here early results of work aimed at the development of a new strategy for the synthesis of small, highly strained cyclophanes. It is a three-stage process, which commences with an existing small cyclophane. The first step is to functionalize the aromatic system at a position adjacent to one of the bridgeheads. This is followed by synthetic manipulation that leads to the formation of a new ring linking the arene to the benzylic position. Finally, the new ring is aromatized to afford a new cyclophane, which has both a larger aromatic system and a shorter bridge. In essence, the bridge is being used as food for the growth of the aromatic system. The gain of ASE again plays a role in offsetting the increase in strain in the final step.