

MOBIUS ANNULENE CATIONS

Since Heilbronner¹ proposed the Möbius annulene in 1964, organic chemists have been fascinated with this structure and many have tried to synthesize an example. I have written many blog posts (1, 2, 3, 4, 5) related to computed Möbius compounds. Now, Herges and Grimme and co-workers have looked at cationic Möbius annulenes.

For the [9]annulene cation,² a variety of DFT methods, along with SCS-MP2 and CCSSD(T) computations suggest that the lowest energy Hückel (**1h**) and Möbius (**1m**) structures, shown in Figure 1, are very close in energy. In fact, the best estimate (CCSD(T)/CBS) is that they differ by only 0.04 kcal mol⁻¹. Laser flash photolysis of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene suggest however that only the Hückel structure is formed, and that its short lifetime is due to rapid electrocyclic ring closure.

In a follow-up study, Herges has examined the larger annulene cations, specifically [13]-, [17]- and [21]-annulenes.³ The Möbius form of [13]-annulene cation (**2m**) is predicted to be 11.0 kcal mol⁻¹ lower in energy than the Hückel (**2h**) form at B3LYP/6-311+G**. The structures of these two cations are shown in Figure 1. The Möbius cation **2m** is likely aromatic, having NICS(0) = -8.95. Electrocyclic ring

closure of **2m** requires passing through a barrier of at least 20 kcal mol⁻¹, suggesting that **2m** is a realistic target for preparation and characterization.

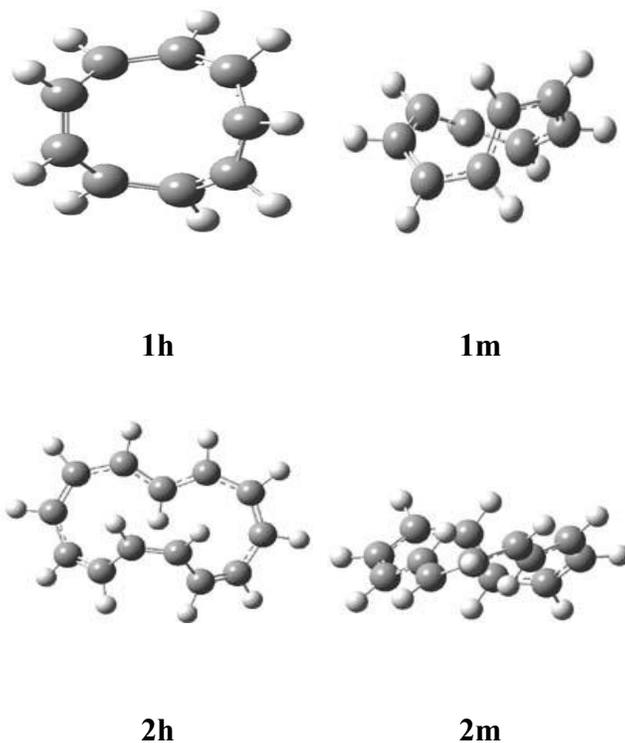


Figure 1. Optimized structures of **1** (CCSD(T)/cc-pVTZ)² and **2** (B3LYP/6-311+G**)³.

The energy difference between the Möbius and Hückel structures of the larger annulenes is very dependent on computational method, but in all cases the difference is small. Thus, Herges concludes that [13]-annulene cation should be the sole target of synthetic effort toward identification of a Möbius annulene.

Experimental studies are eagerly awaited!

Source: <http://comporgchem.com/blog/?p=932>