

MOBIUS AROMATICITY

Rzepa has published another study of Möbius aromaticity.¹ Here he examines the [14]annulene **1** using the topological method (AIM) and NICS. The B3LYP/6-31G(d) optimized structures of **1**, the transition state **3** and product of the 8- e^- electrocyclization **2** are shown in Figure 1.

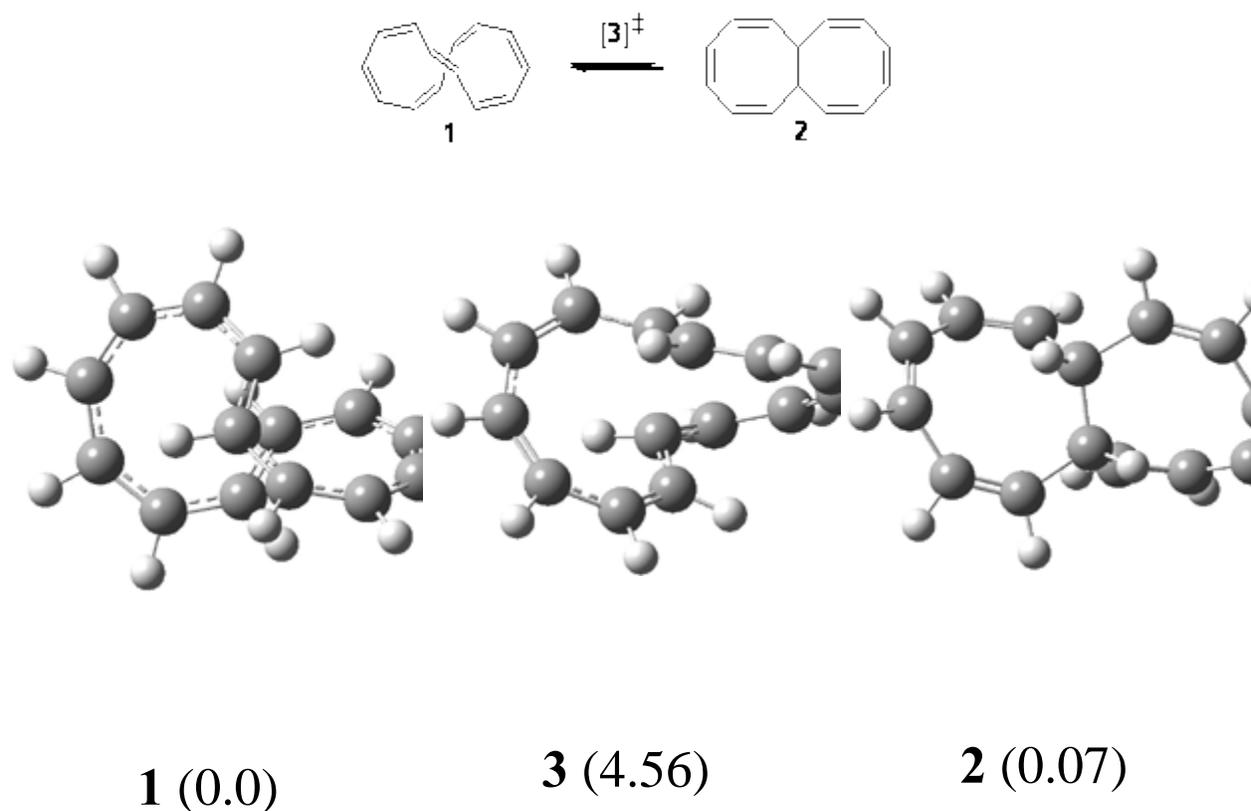
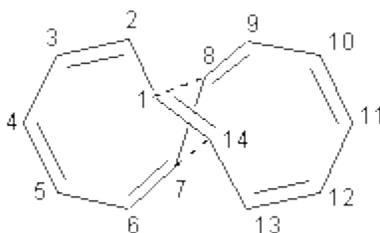


Figure 1. B3LYP/6-31G(d) optimized structures and relative energies (kcal mol⁻¹) of 1-3.¹

The topological analysis of **1** reveals a number of interesting features of the density. First, there are two bond critical points that connect the carbon atoms that cross over each other in the lemniscate structure **1** (these bond paths are drawn as the dashed lines in Scheme 1, connecting C₁ to C₈ and C₇ to C₁₄). These bond critical points have a much smaller electron density than for a typical C-C bond. With these added bond critical points come additional ring points, but not the anticipated 3 ring critical points. There is a ring critical point for the quasi-four member ring (C₁-C₁₄-C₇-C₈-C₁), but the expected ring point for each of the two 8-member ring bifurcate into two separate ring critical points sandwiching a cage critical point!

Scheme 1



Rzepa argues that the weak bonding interaction across the lemniscates is evidence for Möbius homoaromaticity in each half of **1**. The NICS value at the central ring critical point is -18.6 ppm, reflective of overall Möbius aromaticity. But the NICS values at the 8-member ring ring critical points of -8.6 ppm and the cage critical points (-7.9 ppm) provide support for the Möbius homoaromaticity.

Transition state **3** corresponds to motion along the bond path of those weak bonds along either C₁-C₈ or C₇-C₁₄. This leads to forming the two fused eight-member rings of **2**. An interesting thing to note is that there is only one transition state connecting **1** and **2** – even though one might think of the electrocyclization occurring in either the left or right ring. (Rzepa discusses this in a nice *J. Chem. Ed.* article.²) This transition state **3** is stabilized by Möbius aromaticity.

As an aside, Rzepa has once again made great use of the web in supplying a great deal of information through the web-enhanced object in the paper. As in the past, ACS continues to put this behind the subscriber firewall instead of considering it to be supporting material, which it most certainly is and should therefore be available to all.

Source: <http://comporgchem.com/blog/?p=95>