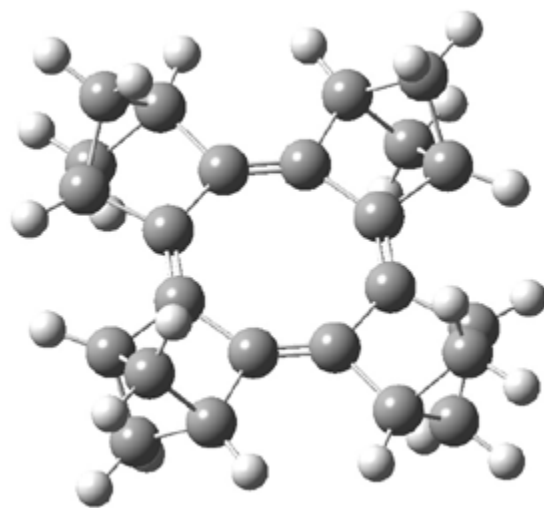
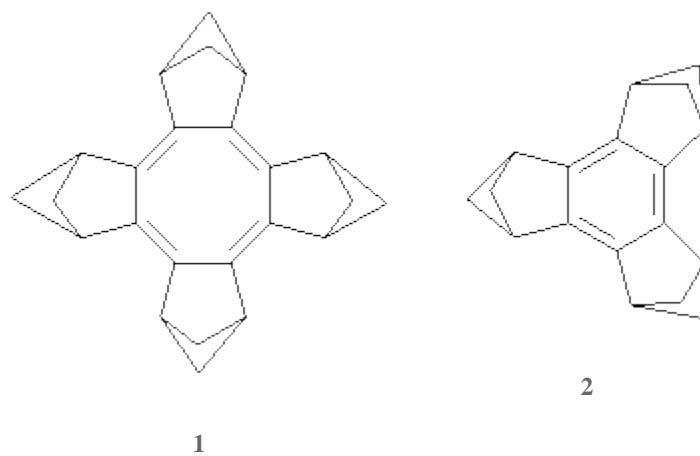


A PLANAR CYCLOOCTATETRAENE

The planar substituted cyclooctatetraene **1** has been prepared and characterized.¹ The B3LYP/6-31G (d) optimized geometry is shown in Figure 1.



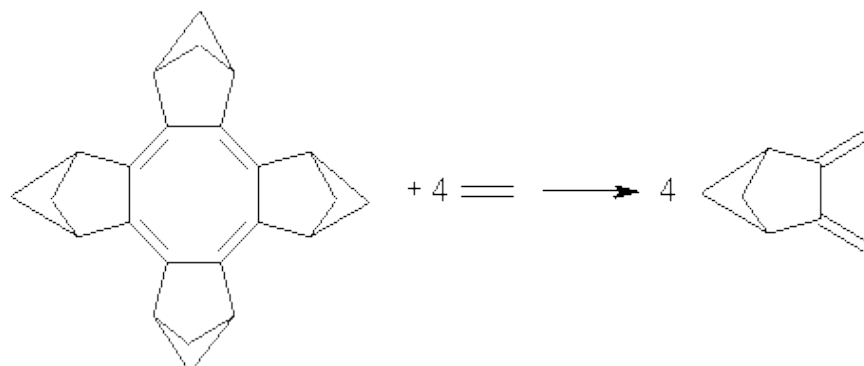
1

Figure 1. B3LYP/6-31G(d) optimized geometry of **1**.

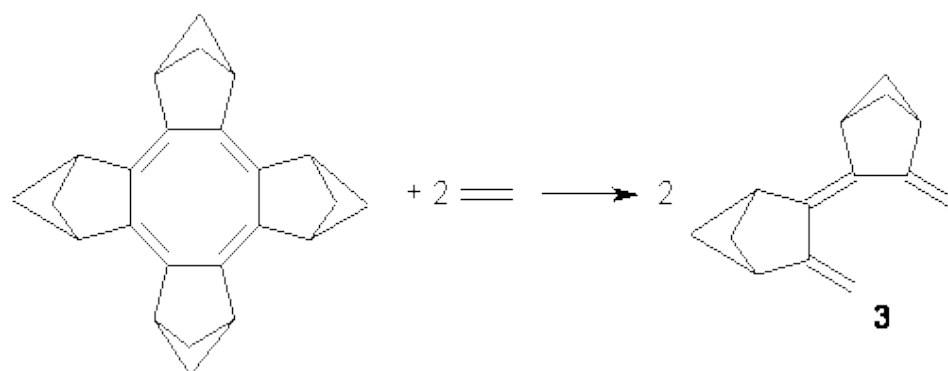
The ^1H NMR spectrum of **1** shows the bridgehead proton has only a small upfield shift ($\Delta\delta = 0.18\text{ppm}$) relative that of **2**. This suggests that both molecules have similar degrees of aromaticity/antiaromaticity, and since both molecules display large bond alternation ($\Delta R = 0.169 \text{ \AA}$ in **1** and 0.089 \AA in **2**) one can argue that both paratropic and diatropic ring currents are attenuated in both molecules. However, the NICS value of **1** is 10.6 ppm , indicative of considerable antiaromatic character, though this NICS value is much reduced from that in planar cyclooctatetraene constrained to the ring geometry of **1** (22.1 ppm). Rabinowitz and Komatsu argue that large HOMO-LUMO gap of **1** is responsible for the reduced antiaromatic character of **1**.

Though not discussed in their paper, the aromatic stabilization (destabilization) energy of **1** can be computed. I took two approaches, shown in Reactions 1 and 2. The energies of the two reactions are $-13.8 \text{ kcal mol}^{-1}$ for Reaction 1 and $-3.4 \text{ kcal mol}^{-1}$ for Reaction 2. The large exothermicity of Reaction 1 reflects the strain of packing the four bicyclo moieties near each other, forcing the neighboring bridgehead hydrogens to be directed right at each other. The strain is better compensated in Reaction 2 by using **3** as the reference. Since **3** is of C_2 symmetry, some strain relief remains a contributor to the overall reaction energy. Thus it appears that if **1** is antiaromatic, it manifests in little energetic consequence.

Reaction 1



Reaction 2



Source: <http://comporgchem.com/blog/?p=105>