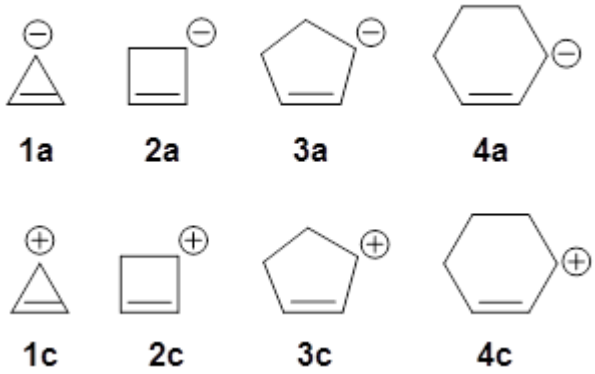
IS THE CYCLOPROPENYL ANION ANTIAROMATIC?

The concept of antiaromaticity is an outgrowth of the well-entrenched notion or aromaticity. While 4*n*+2 π-electron systems are aromatic, 4*n* π-electron systems should be antiaromatic. That should mean that antiaromatic systems are unstable. The cyclopropenyl anion **1a** has 4 π-electrons and should be antiaromatic. Kass has provided computational results that strongly indicate it is *not antiaromatic*![1]

Let's first look at the 3-cyclopropenyl cation **1c**. Kass has computed (at both G3 and W1) the hydride affinity of **1c-4c**. The hydride affinities of the latter three compounds plotted against the C=C-C^+ angle is linear. The hydride affinity of **1c** however falls way below the line, indicative of **1c**being very stable – it is aromatic having just 2 π-electrons.



A similar plot of the deprotonation enthalpies leading to **1a-4d** vs. C=C-C$^-$ angle is linear including*all four compounds*. If **1a** where antiaromatic, one would anticipate that the deprotonation energy to form **1a** would be much greater than expected simply from the effect of the smaller angle. Kass suggests that this indicates that **1a** is not antiaromatic, but just a regular run-of-the-mill (very) reactive anion.

A hint at what's going on is provided by the geometry of the lowest energy structure of **1a**, shown in Figure 1. The molecule is non-planar, having C_s symmetry. A truly antiaromatic structure should be planar, really of D_{3h} symmetry. The distortion from this symmetry reduces the antiaromatic character, in the same way that cyclobutadiene is not a perfect square and that cyclooctatraene is tub-shaped and not planar. So perhaps it is more fair to say that **1a** has a distorted structure to avoid antiaromaticity, and that the idealized D_{3h} structure, does not exist because of its antiaromatic character.

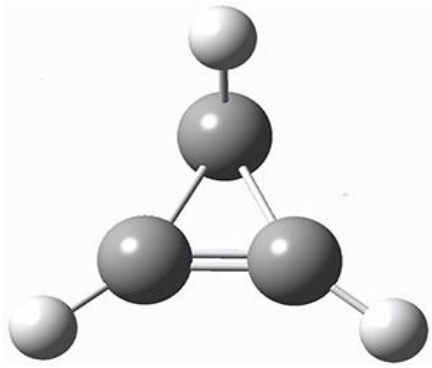


Figure 1. G3 optimized geometry of **1a**.

Source: http://comporgchem.com/blog/?p=2987