

## REFLECTIONS ON WHETHER CERTAIN MOLECULES SHOULD BE CLASSIFIED AS NON-AROMATIC OR ANTI-AROMATIC

In Chem. 360 lecture on January 29, 2003, I spent some time talking about **anti-aromaticity**. Molecules are classified as anti-aromatic if (like aromatic compounds) they are cyclic, planar systems of  $sp^2$ -hybridized atoms but (unlike aromatic compounds) they have  $(4n)$   $\pi$ -electrons. Thus, systems with 4, 8, 12, etc.  $\pi$ -electrons would be anti-aromatic, in contrast to those with 2, 6, 10, etc., which are aromatic.

I need to introduce some molecular orbital theory in order to proceed. On p. 610 of the text, the energy levels of the six MOs for benzene are shown (Fig. 14.2a); these six MOs were created by taking "linear combinations" of the six p atomic orbitals, one per carbon. Note that three of these MOs are bonding and three are anti-bonding. With six  $\pi$ -electrons to distribute, the bonding orbitals are filled and the anti-bonding orbitals are avoided. Similarly, cyclopentadienide ion (Fig. 14.2b) has its six  $\pi$ -electrons filling its three bonding orbitals.

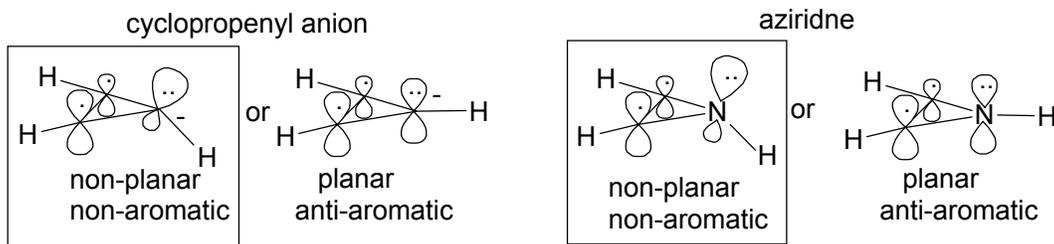
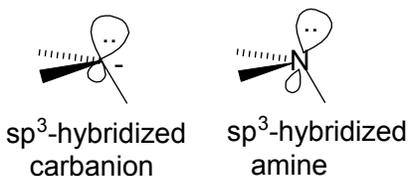
For the latter system, removing a pair of  $\pi$ -electrons creates the cyclopentadienyl cation. Two of the four  $\pi$ -electrons go into the lowest bonding orbital. What should be done with the other two? As we learned in Chem. 350, Hund's rules require that "whenever possible" electrons go into separate orbitals with parallel (unpaired) spins. Because the two higher bonding orbitals are degenerate (i.e., of equal energy), Hund's rules put one electron into each as shown in Fig. 14.2c; the prediction is that  $C_5H_5^+$  is a diradical with two unpaired spins.

To avoid such a situation, some molecules undergo a geometrical distortion that relieves the degeneracy of the two MOs; one orbital goes to lower energy, the other to higher energy. If this were to occur for  $C_5H_5^+$ , the four  $\pi$ -electrons could be placed, paired, in two bonding orbitals: two in the original lowest orbital and two in the lower energy of the orbitals that had been degenerate. For some molecules, the cost of such distortion is so great that the diradical character persists. The evidence suggests that cyclopentadienyl cation retains its regular pentagonal geometry and is, in fact, an anti-aromatic compound with two unpaired electrons.

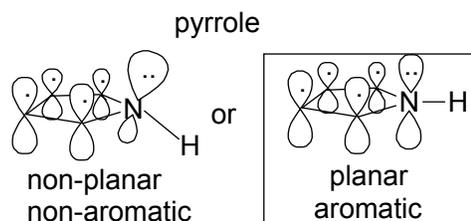
The other anti-aromatic compound that I showed in class was the cycloheptatrienyl anion, a species with eight  $\pi$ -electrons. I mumbled a bit about what might be the best way to think about this molecule, and I promised that I'd return to you either with some insight or some further muddling. Any confusion is perpetuated by Bruice who, in the answer to Problem 14.7, calls this anion anti-aromatic, but in the answer to Problem 14.20 calls azepine (the seven-membered heterocycle with NH in place of a CH) non-aromatic because the nitrogen is  $sp^3$ -hybridized. Similarly,  $C_3H_3^-$  is called anti-aromatic (Problem 14.9) whereas aziridine (its nitrogen analog) is called non-aromatic (Problem 20, again).

I asked Dr. Bartmess to search his vast data base of organic anions to provide an

answer here. Based on calculations and experimental data, it seems certain that both  $C_3H_3^-$  and  $C_2H_3N$  are non-aromatic. Carbanions and amines are usually  $sp^3$  hybridized, as shown to the right. There would have to be a good reason for either of them to go  $sp^2$ . Such a reason is not provided by the "promise" of anti-aromaticity, so almost certainly these three-membered ring species are non-planar and non-aromatic.



In a molecule like pyrrole, however, it makes all the sense in the world for the nitrogen to go from  $sp^3$  to  $sp^2$  so that the electron pair on nitrogen is in a p-orbital that becomes part of the aromatic sextet (a Hückel number).

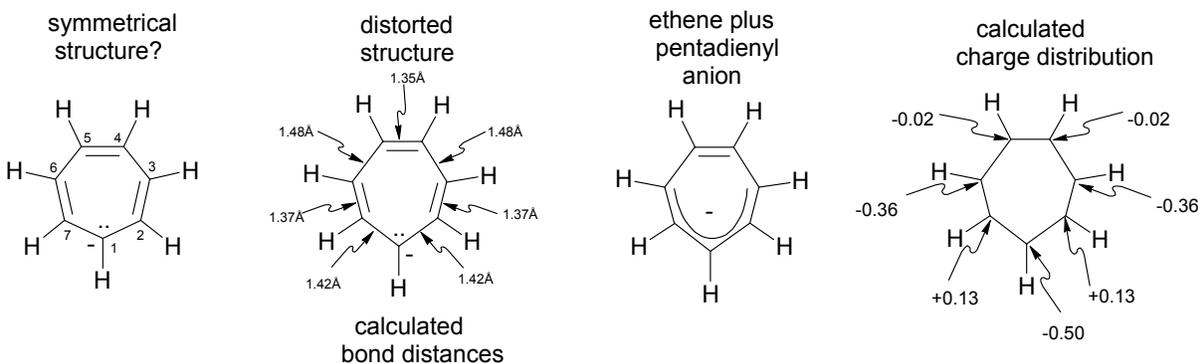


We come now to  $C_7H_7^-$ , cycloheptatrienyl anion. If it stayed as a regular heptagon, it would be anti-aromatic because it has eight  $\pi$ -electrons. (In terms of the molecular orbital energies, it has three bonding MOs, which can hold six electrons; the seventh and eighth electron go, separately, into a pair of degenerate anti-bonding orbitals with parallel spins.) One way that it could avoid this situation is for the carbanionic carbon to be  $sp^3$  hybridized. Like cyclopropenyl anion, it would be non-aromatic. But refusing to leave good enough alone, the ambitious and persistent Dr. Bartmess did some calculations on this molecule. His results (which may or may not be spurious) are both fascinating and confusing.

According to his calculations, all fourteen atoms are coplanar but the ring is not the regular heptagon (shown on the next page). Instead of being symmetrical about a point, it is symmetrical about a line (or a plane) that passes through the carbanionic center and the midpoint of the  $C_5-C_4$  bond. Note that the  $C_5-C_4$  bond is very much a typical  $C=C$  with a distance of  $1.35\text{\AA}$ . It is flanked by two  $C-C$  bonds at  $1.48\text{\AA}$ , reminiscent of the  $sp^2-sp^2$  carbon-carbon single bond in 1,3-butadiene (Table 7.2, p. 304). Next come a pair of bonds ( $1.37\text{\AA}$ ) that are only slightly longer than a typical  $C=C$ . And finally there is a pair of bonds ( $1.42\text{\AA}$ ) whose lengths are about halfway between  $C-C$  and  $C=C$ .

According to further calculations on this structure, it seems that the best way to describe it is as a pentadienyl anion bridged by an ethene group, as shown in the following picture. And when calculations are done on the distribution of the negative charge, 50%

is at C<sub>1</sub> and 36% at each of C<sub>3</sub> and C<sub>6</sub>. This sums to 122%, but then there is about 13% of a positive charge at each of C<sub>2</sub> and C<sub>7</sub> and just 2% of a negative charge at C<sub>4</sub> and C<sub>5</sub>, making the overall charge -1.00. In other words, there is essentially no charge at the ethene portion (C<sub>4</sub>-C<sub>5</sub>) and there is negative charge at the first, third, and fifth carbons (C<sub>6</sub>, C<sub>1</sub>, and C<sub>3</sub>) of the pentadienyl portion.



Calculations are all very well, but the significance of a planar molecule with one  $\pi$ -system (ethene) apparently insulated from another (pentadienyl anion) is mysterious, at least to me. So I think that if I were to ask you on an exam to decide whether the cycloheptatrienyl anion is (a) aromatic, (b) anti-aromatic, or (c) non-aromatic, you would be justified in giving any of the following answers:

It is (b) anti-aromatic because it has eight  $\pi$ -electrons (a  $4n$  number) in a cyclic coplanar system of  $sp^2$  hybridized atoms.

It is (c) non-aromatic because one of the ring atoms is  $sp^2$ -hybridized (even though Dr. Bartmess's calculation says otherwise), just as is the nitrogen in azepine.

It is (c) non-aromatic because Dr. Bartmess's calculations of bond-distance and charge are consistent with non-interacting  $\pi$  systems, even though the system is planar.

The only answer that is clearly incorrect is (a) aromatic!

They (whoever "they" may be) say that a professor doesn't *really* understand a subject until he or she can explain it to a beginning student. I think that your organic chemistry professor has failed this test of understanding!