# Exercise 4.6
# Pi Molecular Orbital Energy Level Diagrams: Frost Circles

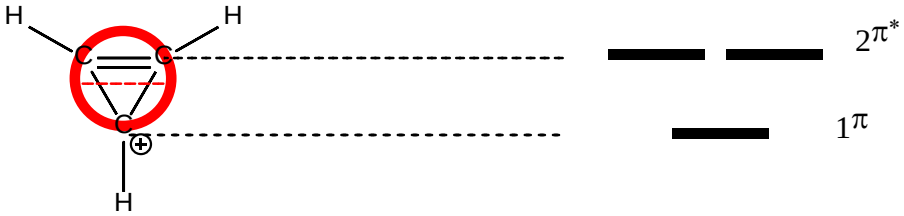
The examples in Exercise 4.4 were all molecules containing a chain of trigonal planar (or linear) atoms which formed an acyclic[1] pi system. In such cases, every $\pi$ MO has a different energy. When a pi system is branched or cyclic, that is no longer the case.

## Cyclic Pi Systems

For a pi system to be cyclic, every atom in the ring must be either planar or linear in geometry. A ring containing one or more tetrahedral atoms is *not* a cyclic pi system.

The relative energies of the $\pi$ MOs in a cyclic pi system can be predicted using an easy empirical trick called a Frost circle. To draw a Frost circle, draw a circle. *(shown below in red)* At the very bottom of the circle, draw one atom of the pi system. Then draw the rest of the molecule so that the other atoms in the pi system are touching the circle.

Every point where an atom in the pi system touches the circle corresponds to one energy level:



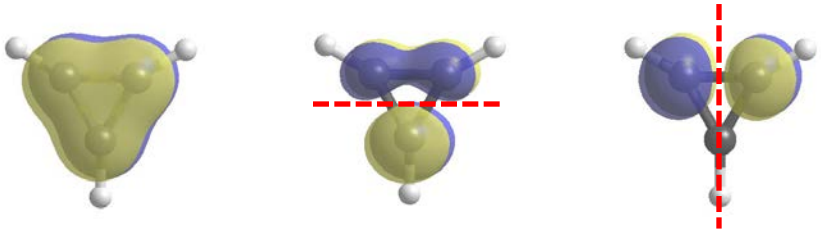

A horizontal line passing through the center of the circle has also been drawn in red. All energy levels derived from points below this line correspond to bonding MOs; all energy levels derived from points above this line correspond to antibonding MOs; all energy levels derived from points along this line correspond to nonbonding MOs.

For cyclic pi systems, it is easiest to use the Frost circle to predict the energy levels first *then* draw the orbitals using the same process as always. Draw the lowest energy combination ("most bonding") first then the highest energy combination ("most antibonding") then use nodes to help you draw the remaining orbitals. In cases where there are two $\pi$ MOs with the same energy, the nodes must be as different as possible.

e.g. If there is one node, one $\pi$ MO will have it vertical and the other will have it horizontal.

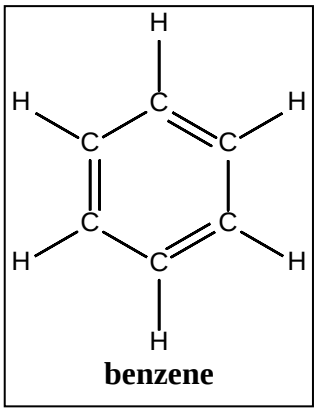
e.g. If there are two nodes, one $\pi$ MO will have them + and the other will have them ×.

For the cyclopropenyl cation ($C_3H_3^+$), the three $\pi$ MOs are shown below.



| $1\pi$ | $2\pi^*$ | $2\pi^*$ |
|---|---|---|
| 0 ⊥ nodes | 1 horizontal node | 1 vertical node |

[1] "acyclic" = "not cyclic"



**benzene**

1.

(a) Construct a pi molecular orbital energy level diagram for benzene.
Fill in the electrons. Label the HOMO and LUMO.
Draw a picture of each $\pi$ MO.

(b) The $C - C$ bond order in benzene is 1.5. Justify this using Lewis diagrams.

(c) The $C - C$ bond order in benzene is 1.5. Justify this using MO theory.