

## Answers to Exercise 4.6

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

1.

(a)

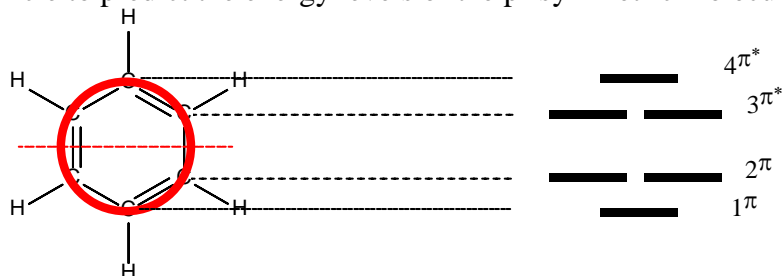
$C_6H_6$  has 30 valence electrons, four from each C and one from each H.

Grouping the AOs by symmetry and energy gives:

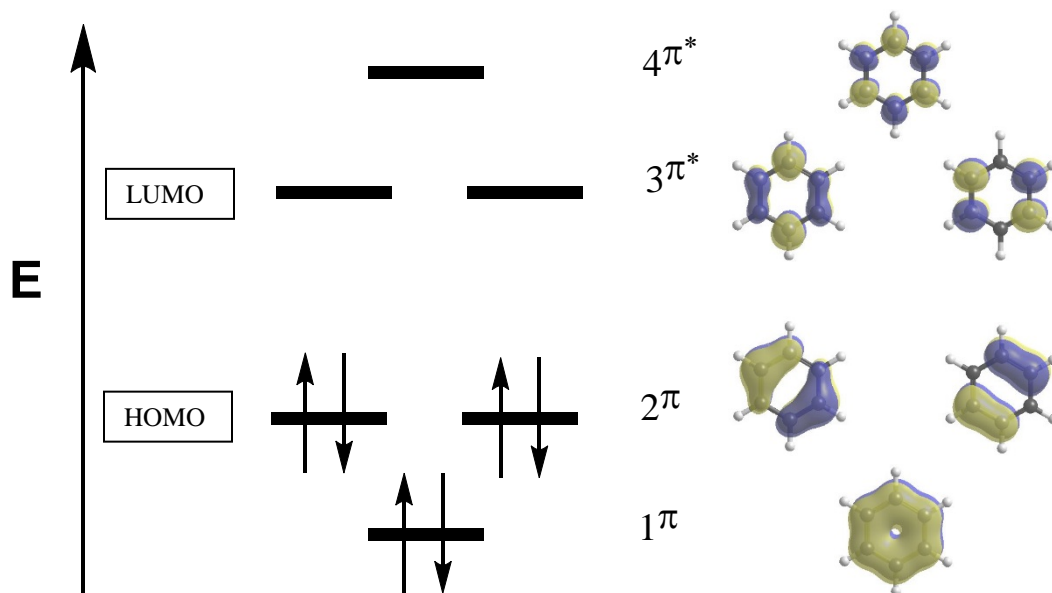
- **six pi-symmetric  $2p_z$  orbitals: one from each C,**
- **twenty four sigma-symmetric orbitals: six  $2s(C)$ , six  $2p_x(C)$ , six  $2p_y(C)$ , and six  $1s(H)$ .**

We count twenty four electrons in sigma-symmetric MOs and six electrons in pi-symmetric MOs.

We can use a Frost circle to predict the energy levels of the pi-symmetric molecular orbitals:

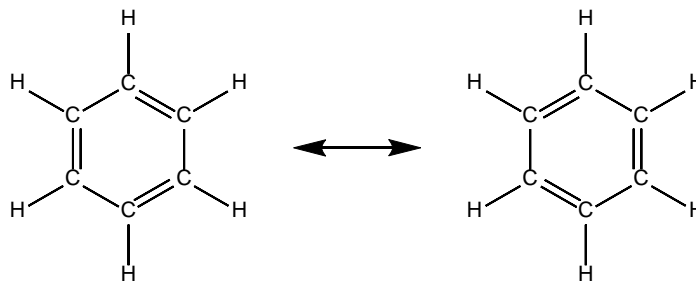


The molecular orbital energy level diagram for  $C_6H_6$  therefore looks like:



*Your pictures of the  $2\pi$  and  $3\pi^*$  orbitals may not look exactly the same as the ones pictured here, but they must have the same number of nodes with the lobes symmetrically distributed (i.e. node down the middle of the molecule not off to the side). Also, the nodes must be different in the two MOs. (e.g. in the  $2\pi$  orbitals shown, one node is / and the other is \; it would also be fine to have a horizontal node in one orbital and a vertical node in the other). As always, phase must be opposite on either side of a node.*

(b)



For each  $C - C$  bond in benzene, the bond order is  $\frac{1+2}{2} = 1.5$ .

*In one resonance diagram, the  $C - C$  bond is shown as a single bond (bond order = 1).*

*In the other resonance diagram, the same  $C - C$  bond is shown as a double bond (bond order = 2).*

*Therefore, the actual  $C - C$  bond order is the average of those two values.*

(c) The **pi bond order** for the  $C - C$  bonds in benzene can be calculated from the pi molecular orbital energy level diagram:

- There are six electrons in pi bonding molecular orbitals (and no electrons in pi antibonding molecular orbitals).
- Those electrons are shared over six  $C - C$  bonds.
- Therefore, the pi bond order for the  $C - C$  bonds is  $\frac{6-0}{6} = 0.5$

To the pi bond order of 0.5, we **add a sigma bond order of 1** to calculate the total  $C - C$  bond order of 1.5.