

# 1 Cognitive reasoning in the chemical sciences 6.3

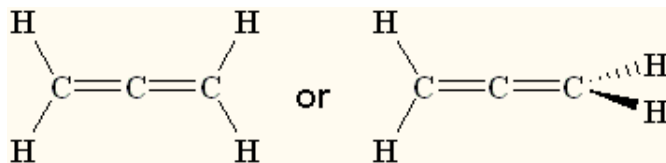
## 1.1 $\pi$ MOs

### 1. Rules for making MO diagrams:

- In a minimal basis set MO diagram, the number of MOs equals the number of AOs.
- When two orbitals combine, they combine to make two new orbitals. The original orbitals combine to make the lowest and highest energy combinations possible.
- Orbitals which are initially close in energy interact stronger than orbitals which are initially far apart in energy. When two orbitals of different energy combine, the resultant low energy combination resembles more the initially lower energy orbital; the resultant high energy combination resembles more the initially high energy orbital. Two orbitals of equal initial energy combine to make two new orbitals with equal contributions from the two starting orbitals equally.

### 2. Constructing $\pi$ MO diagrams. These rules can be used to generate $\pi$ MO diagrams.

- Please first draw the Lewis structures and the localized hybridized  $\sigma$  and  $\pi$  bands for the following molecules:
    - ethylene,  $C_2H_4$
    - dinitrogen,  $N_2$
    - butadiene,  $CH_2CHCHCH_2$
    - formic acid,  $HCO_2H$
    - the carbonate ion,  $CO_3^{2-}$ .
  - Please, now, find the most constructive and destructive interference  $\pi$  orbital combinations possible for each of the above molecules/ions.
  - Based on your answer above, please derive the  $\pi$  MO diagrams for each of the above molecules/ions.
3. **Allene**,  $CH_2CCH_2$ , is a Chem 2070 favorite. In this exercise, we put a new spin on this classic problem. As is traditionally done, we speculate that allene should be found in one of two shapes, see below. The new spin is the use of the  $\pi$  MO diagram to determine which geometry is the correct one. To do so we assume that the *outside planar and interior linear carbon atoms are respectively  $sp^2$  and  $sp$  hybridized*. We then deduce the most constructive and destructive orbitals and finally draw  $\pi$  MO diagrams for the two possible allene geometries.



Please now answer the following questions:

- What is the  $\pi$  MO diagram bond order?
- Which allene shape has more  $\pi$  bonds?
- Which allene shape has lower energy?
- In which shape is allene found in nature?