

Exercise 4.4

Pi Molecular Orbital Energy Level Diagrams: Planar Molecules

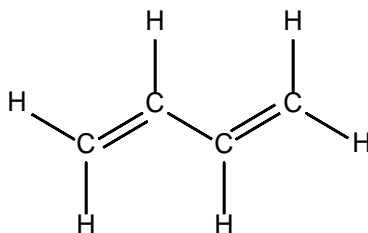
Sigma-Pi Separation

Every time we generate MOs or a molecular orbital energy level diagram, we separate the AOs according to symmetry before combining any of them to make MOs. Once separated, the two sets of orbitals are never recombined; although they can be presented on the same energy level diagram (as was done in all examples so far). This means that a molecular orbital energy level diagram is really two overlapping diagrams: one for the σ MOs and one for the π MOs. In many cases, the most difficult part of generating the diagram is deciding how to rank σ MOs vs π MOs that are clearly close in energy.

Conveniently, as planar molecules get larger and more complex, it becomes more probable that the most interesting MOs (the HOMO and LUMO) will be π MOs. For this reason, chemists will often focus on the π MOs and generate a pi molecular orbital energy level diagram (a diagram which only shows the energy levels of the π MOs). It is important to be aware that this type of diagram may miss an important nonbonding σ MO, but if we suspect that such an MO is likely to exist, we can use modeling software to generate the full molecular orbital energy level diagram for that particular molecule.

Pi Molecular Orbital Energy Level Diagram for 1,3-Butadiene

Typically, we only draw pi molecular orbital energy level diagrams for molecules with more than one atom contributing to the pi system. For example, 1,3-butadiene has four consecutive trigonal planar carbon atoms, so there are four atoms contributing to its pi system:

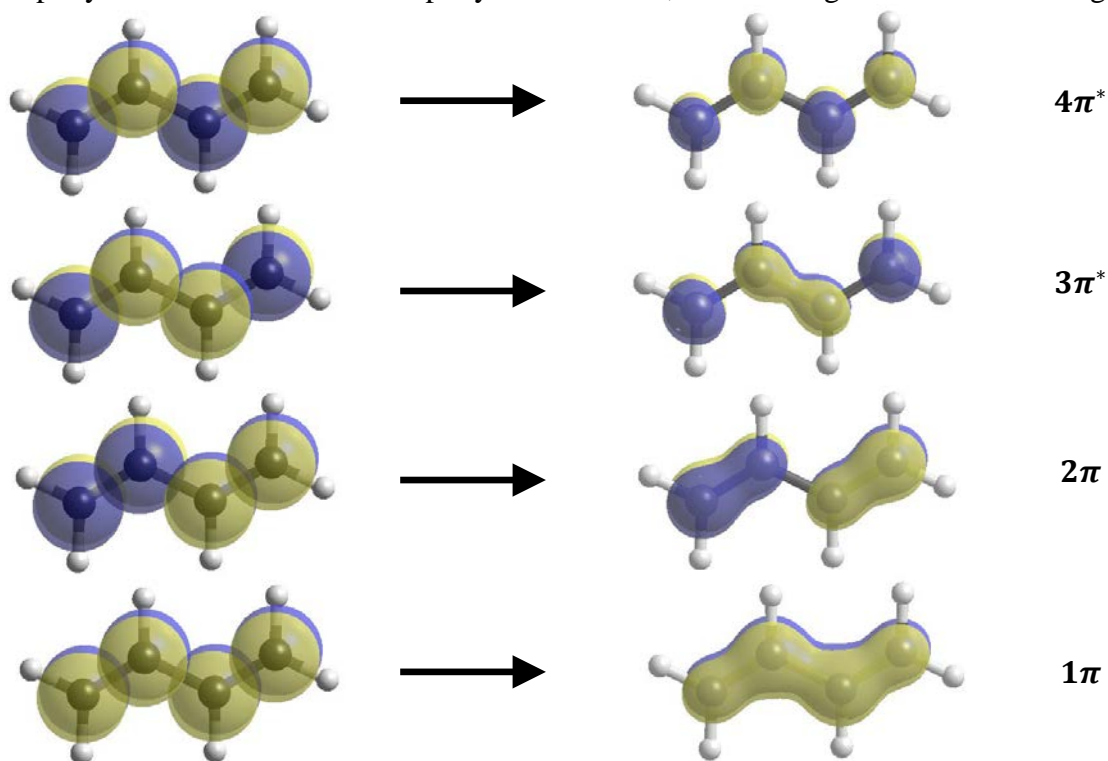


First, write electron configurations for carbon and hydrogen: $1s^2 2s^2 2p^2$ for C and $1s^1$ for H. This tells us that the valence shell for each C is $n = 2$, so their valence AOs are the $2s$ and $2p$ orbitals. The valence shell for each H is $n = 1$, so their valence AOs are the $1s$ orbitals. It also tells us that C_4H_6 has 22 valence electrons, four from each C and one from each H. Grouping the valence AOs by symmetry and energy gives:

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

We are very happy that we only have to predict shapes and energies of the four π MOs! ☺

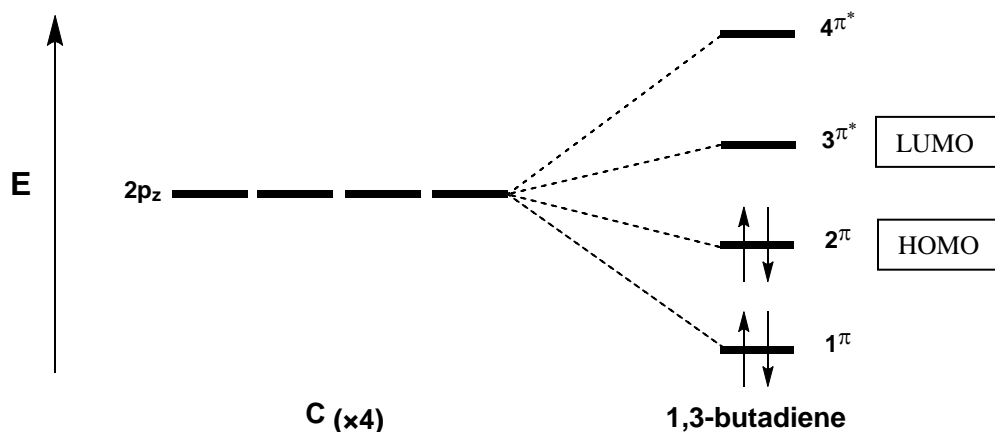
The group of pi-symmetric AOs makes four pi-symmetric MOs, two bonding and two antibonding:



We know that there are four electrons in π MOs because the Lewis diagram shows us that there are two double bonds. In larger molecules like this one:

- every single bond corresponds to two electrons in σ MOs,
- every double bond corresponds to two electrons in σ MOs and two electrons in π MOs,
- every triple bond corresponds to two electrons in σ MOs, two electrons in one set of π MOs (one pi system) and two electrons in another set of π MOs (another pi system),
- lone pair electrons can be in either σ MOs or π MOs; they are addressed in Exercise 4.5.

The resulting pi molecular orbital energy level diagram looks like this:



It would not be unusual to just see the 1,3-butadiene column; as the molecules get larger, it becomes tedious to draw all the atomic orbital energies.

1.

- (a) Construct a pi molecular orbital energy level diagram for the allyl cation ($C_3H_5^+$). Label the HOMO and LUMO.

Hint: You drew pictures of all the π MOs in question 2 of Exercise 4.3.

- (b) Based on your pi molecular orbital energy level diagram and on the pictures of the π MOs (from Exercise 4.3), what can you conclude about how the allyl cation is most likely to react?

2.

(a) Construct a pi molecular orbital energy level diagram for ethene ($H_2C = CH_2$). Label the HOMO and LUMO.

(b) Construct a pi molecular orbital energy level diagram for ethyne ($H - C \equiv C - H$). Label the HOMO and LUMO.

(c) How and why do the pi molecular orbital energy levels for ethene and ethyne differ?