An Introduction to π-Molecular Orbital Theory for Organic Chemistry

The forms and energies of the π-MOs of conjugated π-systems can give us special insight into resonance, aromaticity, and reactivity in a way that complements and extends the simple Lewis structure models we normally work with.

Let's begin by remembering how π-bonds are formed... Two p-orbitals, shown schematically below, overlap to make two new orbitals, π and π*. Add these to the diagram below.
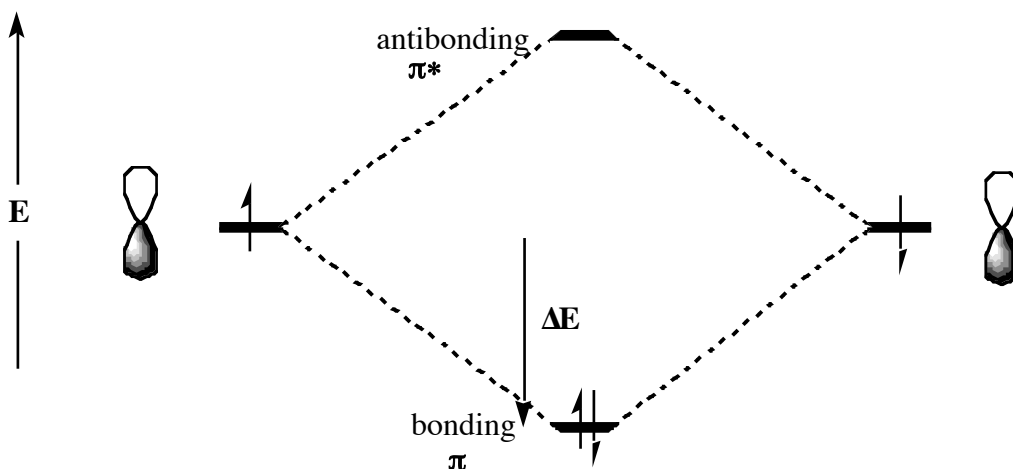
(Recall that the shading shows the relative phases of the wavefunctions — the two halves of each p-orbital are out-of-phase, meaning that *when* one part is a wave "peak", the other is a wave "trough".)

Bonding is good because 2 e⁻s (and thus the total energy of the molecule) go down in energy — by a lot.

We learned how to construct the (approximate) π-MOs of 1,3-butadiene by uniting the orbitals of two localized π-bonds. Finding the π-MOs of longer conjugated π-systems is not quite that simple, but if we learn a few simple rules, it's not too difficult.

Here are a few rules for determining the π-MO energy level pattern and the relative phases of the p-orbitals that contribute to each delocalized π-MO in linear π-systems —

**1** *n* p-orbitals overlap to make *n* molecular orbitals.

(a) If *n* is even, we have a simple polyene. Half the π-MOs are bonding, the other half are antibonding. Assuming the molecule is overall neutral, there are two electrons in each bonding π-MO, and none in the antibonding.

(b) If *n* is odd, we have a delocalized radical, anion, or cation. One π-MO is *non-bonding*. The others are bonding and antibonding — the same number of each. If the molecule is overall neutral, it is a radical, and the unpaired electron occupies the non-bonding MO. If the molecule is an ion, the NBMO is either doubly occupied or empty.

2 The lowest-E orbital is entirely bonding, i.e. all the p-orbitals are in-phase, and there are zero nodes between p-orbitals. The number of nodes increases as the π-MO energy increases — each π-MO has one more node than the one below it.

3 The p-orbital phases in each π-MO are such that the orbital is either symmetric (S) or antisymmetric (A) with respect to the center of the chain. The symmetries of the π-MOs alternate as one goes up in energy.

Examples —
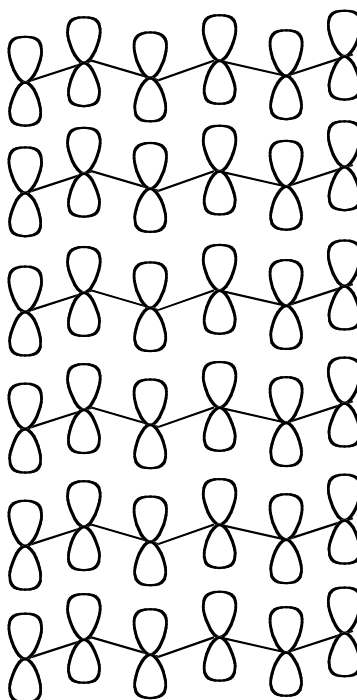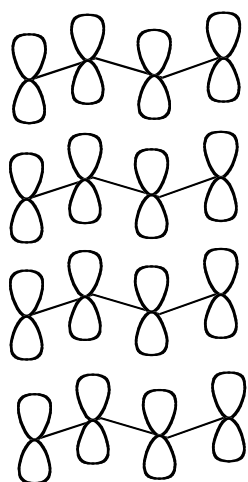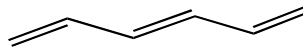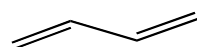
Now for some π-systems with odd numbers of p-orbitals.

A theorem that can be derived within the framework of simple π-MO theory says that for neutral odd-membered system like these, each atom has a charge of zero (just as we would expect based on our usual Lewis structure model).

So where are the charges in the delocalized ions that correspond to the π-systems above?

Does this have any relationship to the charge positions we predict by drawing resonance structures?

Simple cyclic π-systems follow the same general principles, but the π-MOs above the lowest-E one come in degenerate (equal-energy) pairs. Each member of a degenerate pair has the same number of nodes, but the nodes are situated to make the orbitals orthogonal (in the quantum mechanical sense, which means zero net overlap).

Let's look at the π-MO patterns of cyclobutadiene and benzene to start —