*Lecture outline*

Diels-Alder Reaction

How do substituents affect the energies and p-orbital coefficients of the HOMO and LUMO of the reactants? We can get some additional insight into this by doing Hückel calculations to see how electron-donating and electron-withdrawing substituents affect the frontier orbitals.

Add the HOMO and LUMO energies below, then identify the most important HOMO-LUMO interaction. Next, find the p-orbital coefficients at the reaction sites in these orbitals.
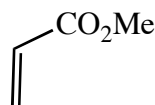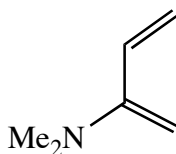
Aromatic transition state theory.

An alternative approach that is more easily extended to other classes of pericyclic reactions is *aromatic transition state theory*. We'll start by applying this to cycloadditions.

Sketch the p-orbital arrays of benzene and of the Diels-Alder transition state. It's important to remember that this is an entirely different approach from frontier orbital theory — we're not drawing π-MOs, only *array of interacting atomic orbitals*. Keep this in mind as you now shade the orbitals to create as many in-phase interactions as possible.

An array of interacting orbitals with no phase changes is called a Hückel array. Just like in cyclic π-systems, if such a transition state orbital array contains **4n+2** π-electrons, it is stabilized by aromaticity; if it contains **4n** π-electrons, it is destabilized by *anti*aromaticity.

How does this idea apply to other cycloadditions, e.g., 2 + 2, 4 + 4, 4 + 6, etc? (Of course, we don't get quite as much insight into the nuances of the reaction as we do from frontier orbital theory, but this is a very easy way to identify favorable and unfavorable processes.)

One advantage of aromatic transition state theory is that it can easily be extended to pericyclic reactions other than cycloadditions. Two additional classes of pericyclic reactions are electrocyclic processes and sigmatropic shifts.

Electrocyclic reactions — a 6-e⁻ ring closure and 4-e⁻ ring opening —

Sigmatropic rearrangements — a [1,5] sigmatropic shift and a [3,3] sigmatropic shift —

CH₃

CH₃