

Molecular Orbitals, Stereoelectronic Effects, and Aromatic Substitution

Section Agenda

- 1) Pop Quiz
- 2) Random First Day Housekeeping
- 3) Handout: MOs, Stereoelectronic Effects, and Aromatic Substitution
- 4) Handout: In-Section Problem Set
- 5) Handout: In-Section Solution Set

Molecular Orbitals

- Be familiar with the MO “rules” discussed in the slides to lecture 1. There are a number of concepts that are critically important and some common themes to identify which make their digestion much easier.
- A molecular orbital (MO) results from a linear combination of atomic orbitals (LCAO). More specifically, the wavefunction for a molecular orbital, Ψ , is yielded by adding and subtracting fractions of the wavefunctions, ψ , of overlapping AO's. (Recall, wavefunctions, ψ/Ψ , are used to predict the position and velocity of an electron, and that a 3D plot of ψ^2 (the probability density) is what we are making when we “draw an orbital”).

There are a number of consequences to MO's being simple linear combinations:

1) Conservation of AOs in MOs

First, because electron density must be conserved (two electrons will not interfere (add/subtract) to yield fewer than two electrons), the number of molecular orbitals ($\sigma, \pi, n, \sigma^*, \pi^*$) in a system is equal to the number of atomic orbitals (s, p, sp^n , etc.) that contribute to the system.

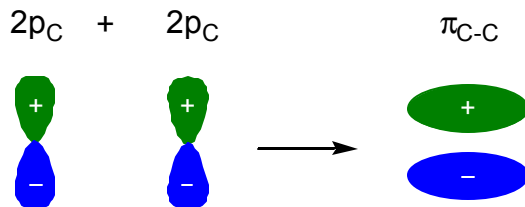
- Recall from general chemistry that on any particular atom, n unhybridized atomic orbitals (s, p, d, etc.) can hybridize to form n hybridized orbitals (e.g., $1 s + 3 p \rightarrow 4 sp^3$).

2) Wavesigns, Constructive Interference, Destructive Interference

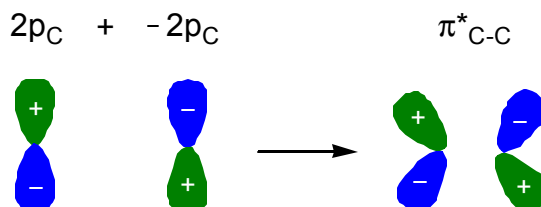
What is meant by “adding” and “subtracting” wavefunctions is that the electrons (which have wave character) can interfere constructively and destructively.

- When they interfere constructively along the bond axis, Ψ^2 is largest between the bonded atoms, resulting in higher electron density in these regions, and thus, more bonding character. Recall that the positively charged nuclei are both attracted to this electron density and shielded from each other by it—electrons are the glue that hold nuclei together in molecules.
- When the atomic orbitals interfere destructively along the bond center, the function Ψ^2 has greatest magnitude behind the bonded atoms. The result is that any electron density in these regions attracts the nuclei away from the bonding center (hence, “antibond”).
- Regions where there is perfect destructive interference ($\Psi^2 = 0$) are called “nodes.” There is no electron density at these locations in space (there is zero probability of an electron being at these locations).

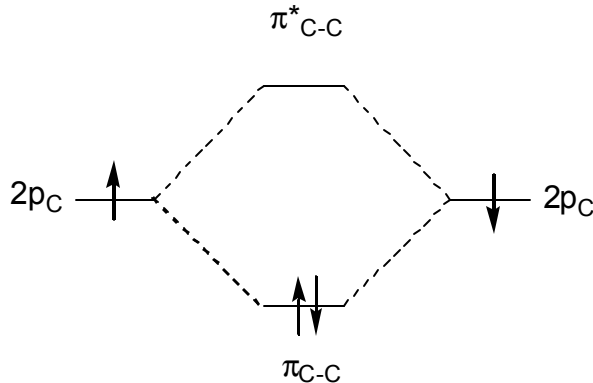
- For simplicity, we indicate wavesign by either coloring the lobes of orbitals or writing “+” or “-” inside of the lobes. In the case of drawing +/-, these designations have absolutely nothing to do with charge—they only indicate the phase of the wave.
- When orbitals with matching wavesigns overlap, the wavefunctions interfere constructively and a bonding interaction results.



- When orbitals with mismatched wavesign overlap, the wavefunctions interfere destructively and an antibonding interaction results.



- When two orbitals interact to form two new molecular orbitals, both constructive and destructive interference occur to give one new bonding and one new antibonding orbital.



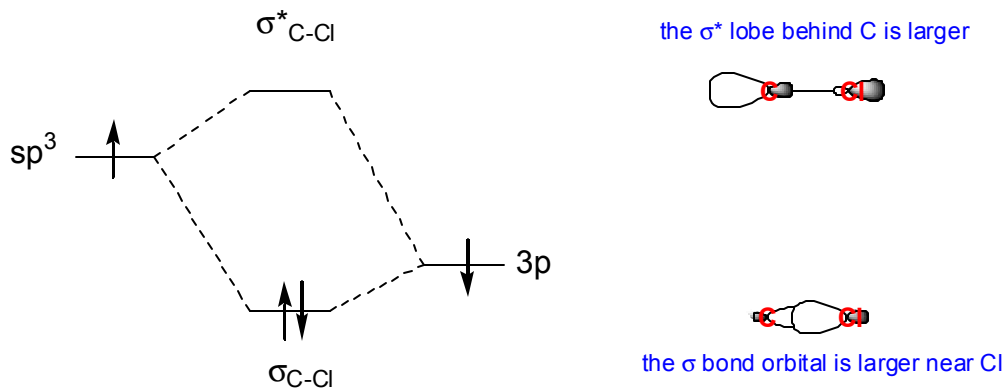
3) Orbital Character

We have discussed that two atomic orbitals can blend to form two molecular orbitals, and that both the bonding and antibonding orbitals must have coefficients whose squares add to 1. However, this does not mean that the contribution of each atomic orbital will be equal to each molecular orbital.

The consequence is that if AO_1 contributes more than AO_2 to the bonding molecular orbital, then AO_1 will contribute less than AO_2 to the antibonding molecular orbital. Thus:

- MO (bonding) will have more AO_1 “character”
- MO* (antibonding) will have more AO_2 “character”

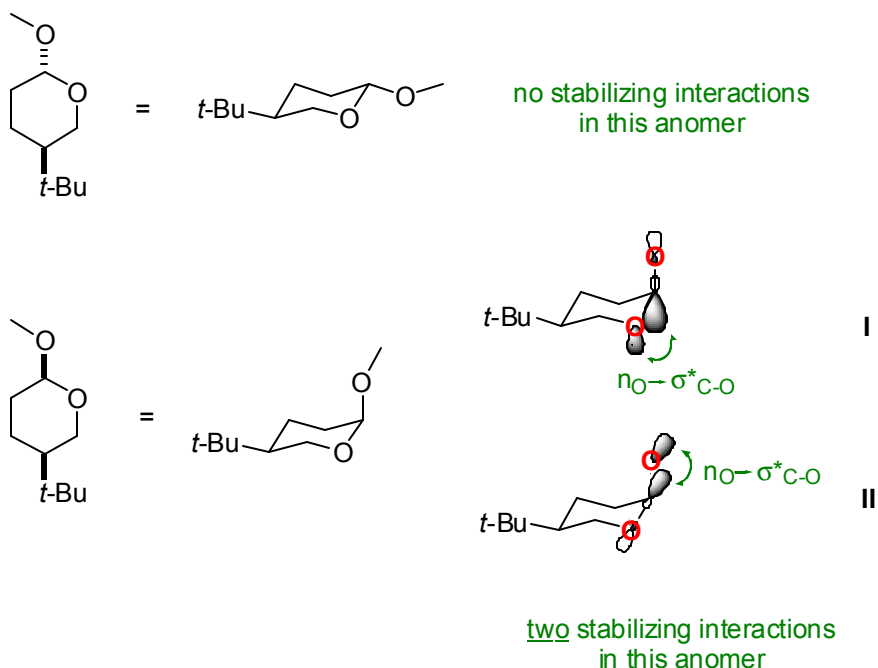
The AO that is lower-in-energy will contribute more character to the bonding MO, while the AO higher-in-energy will contribute more character to the antibonding AO. The result is that we can predict how a bond will be polarized:



- We know that by an electronegativity/Lewis bonding model, the C-Cl bond is polarized with more electron density near Cl. The molecular orbital explanation would be that the chlorine's 3p atomic orbital is more stable than the sp^3 orbital. Consequently, the 3p contributes more character to the bonding MO. Thus, when you fill the bonding MO, you expect more electron density closer to the Cl atom.
- Since the bonding MO has more probability density near Cl, the antibonding MO will have more probability density near C.

Stereoelectronic Effects

- The general principle behind understanding stereoelectronic effects is not hard—if you can donate electron density from a filled orbital into an unfilled orbital, this interaction will be stabilizing (it will lower the potential energy of the molecule). Orbital interactions are not always easy to see, so to help yourself, you should be careful about how you draw your Lewis structures.
- Example: The Anomeric Effect

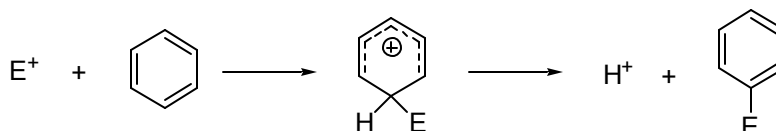


- Recall: Often a *t*-Bu group is used to “lock” a cyclohexane ring. It will occupy an equatorial position—there is a large energy cost to its assuming an axial position by conformational change of the ring (“ring flipping”).
- The geometry of the molecule must allow for any interacting orbitals to overlap in space. You cannot have an interaction (e.g. resonance stabilization of electron density) when your electron pushing does not correspond to real orbital overlap.
- It is important to practice drawing complete and correct 3D Lewis structures to catch these interactions.

General Reactions of Aromatic Compounds

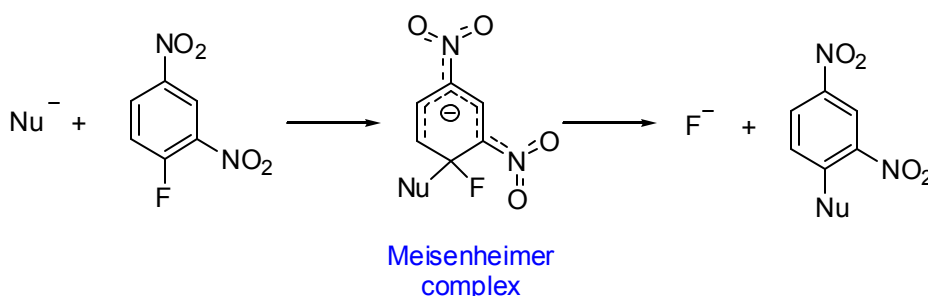
Electrophilic Aromatic Substitution

- Aromatic compounds tend to undergo substitution reactions as opposed to addition reactions. The simple reason for this is that the resonance energy gained as a result of breaking the aromatic π system is not compensated for by the extra stabilization associated with replacing a π bond from the aromatic substrate with a stronger σ bond. The case is reversed for alkenes, where addition is the norm and substitution is less common.



Nucleophilic Aromatic Substitution

- While aromatic compounds tend to react with electrophiles instead of nucleophiles, there are examples where reactions with nucleophiles are observed:



- Anytime you're working a problem and see an aromatic ring with a substituent that can act as a leaving group (typically a halogen) and one or more strong electron withdrawing groups (typically nitro, $-\text{NO}_2$) *ortho* and *para* to the leaving group, immediately ask yourself “does nucleophilic aromatic substitution play a role?”