Course: Chem 345	Lecturer: Prof. Gellman
Day: Friday	Date: 4/29/15
Notes Taken By: Cassie Jarus	Total # of Pages: 5

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Recall: (Dr. MacDonald = lecturer today)

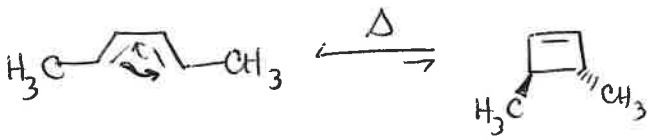
Chp. 27: All problems are recommended, but some towards the end are tricky

- Pericyclic Reactions ⇒ These reactions feature a concerted mechanism with a cyclic array of partial bonding at the TS (transition state).

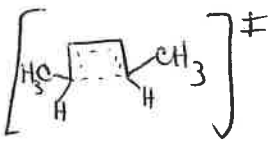
ie. Diels-Alder cycloaddition:

- Electrocyclic Reactions (to start with)
  - * Definition: unimolecular reactions that result in "trading" a π bond for a σ bond or vice versa

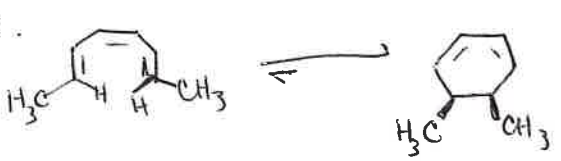
ie.



trans



ie.



cis

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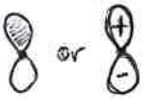
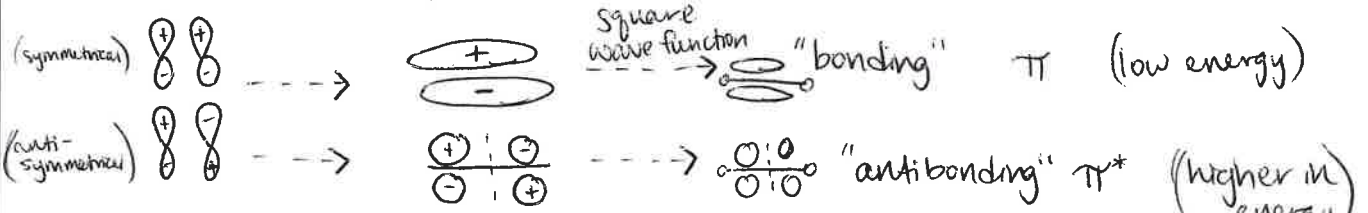
* Problem:
  - = curved arrows do not explain the stereospecificity of reactions
    - ↳ must look @ p-orbitals to understand

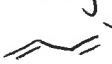
* Prelude:

p-orbital

 ⇒ the region of space is described by a wave function (ie. probability of finding an e- w/in this region is the square of the wave function)

* Two ways to combine p orbitals from adjacent atoms

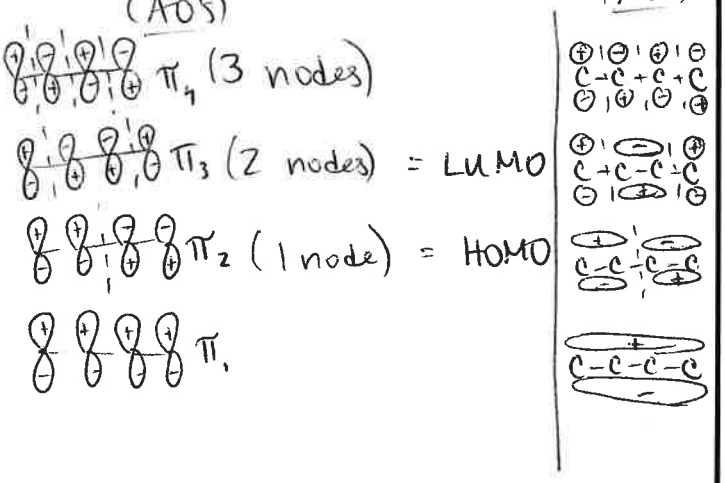


- Apply to larger π systems (ie. )

4 Carbon → 4 x C2P

4 C 2P orbitals

E↑



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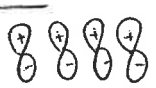
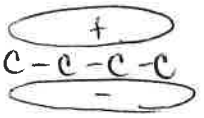
* All of this allows us to assign a feature of π MO's that was previously invisible

- Consider:

π_1  or  ⇒ symmetric (MO sign orientation identical for two ends)

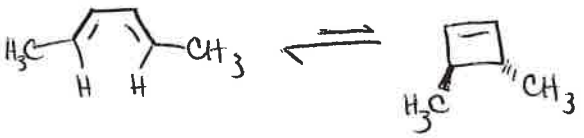
π_2  or  ⇒ anti symmetric (signs of end not same)

(assign π_3 + π_4 yourself...)

- Note:

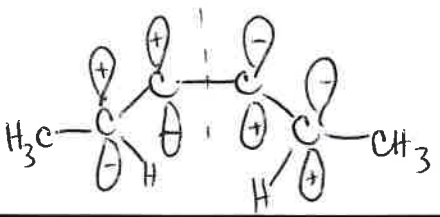
1) Every π MO in any organic molecule is either symmetric or anti-symmetric
2) For a given conjugated alkene (π system), S vs. A alternates as we move up the energy state

* Recall:



How do we explain stereochem?

⇒ Draw HOMO on top of molecule



π_2 = HOMO

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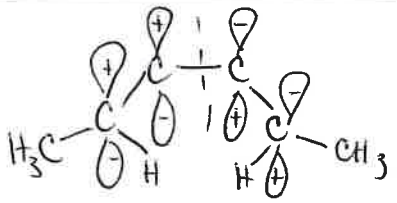
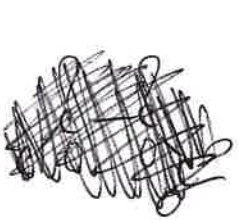
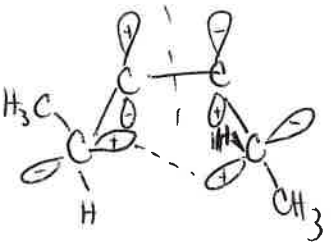


π_2 = HOMO

if ends rotate in the same direction = "conrotatory"

if ends rotate in opposite direction = "disrotatory"

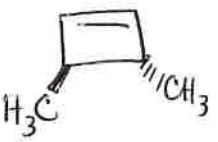




= both ends rotate ↷ (can also rotate both ↖ for conrotatory)

↳ conrotatory

= leads to bonding interaction



"conrotatory ring closure" allowed

= how get trans stereochemistry

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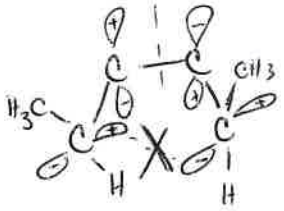

= one rotates ↷ + other ↶

↳ disrotatory

= leads to antibonding

↓

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disrotatory ring closure forbidden