Course Chem 345 Lecturer Gellman
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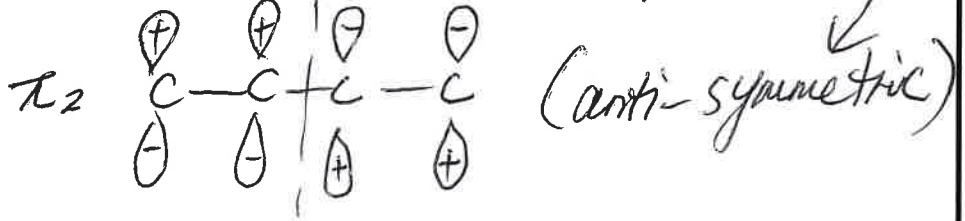
Exam #3 on Wed. → usual rooms.
office hour today after class
Review tomorrow, 5pm, B371
Recall: Trying to understand stereospecificity of electrocyclic rxns, e.g.,

E, E

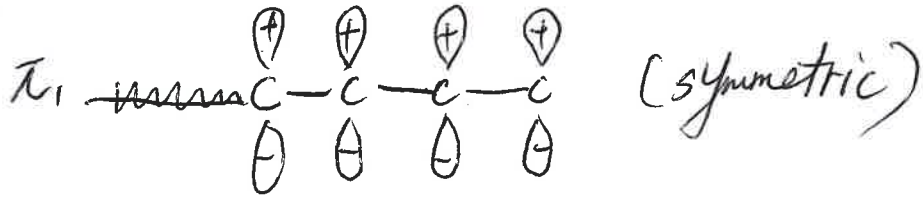
trans

Curved arrows do not offer insight...

Focus on π M.O. symmetry. Conjugated diene
⇒ 4 π M.O.'s



E↑



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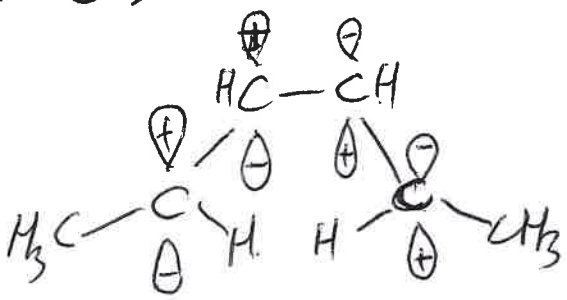
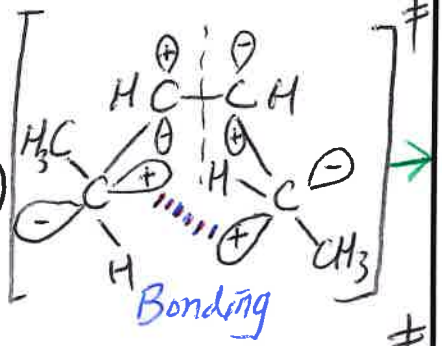
Diene, π_2 (HOMO)

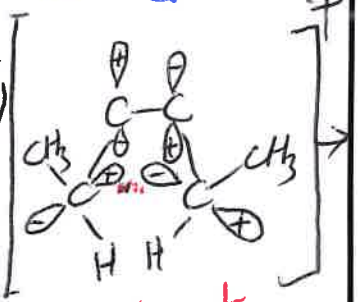


Conrotation ("same direction")



Bonding

disrotation ("opposite directions")



Antibonding

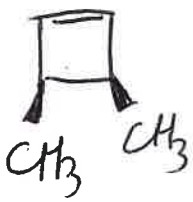
Cont. from Conrotation

conrotation "allowed"

~~this~~

---

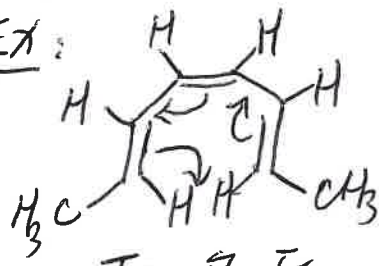
cont. from disrotation



disrotation "forbidden"

MO symmetry analysis extends to larger polyenes / larger rings.

Ex:



E, Z, E

cis

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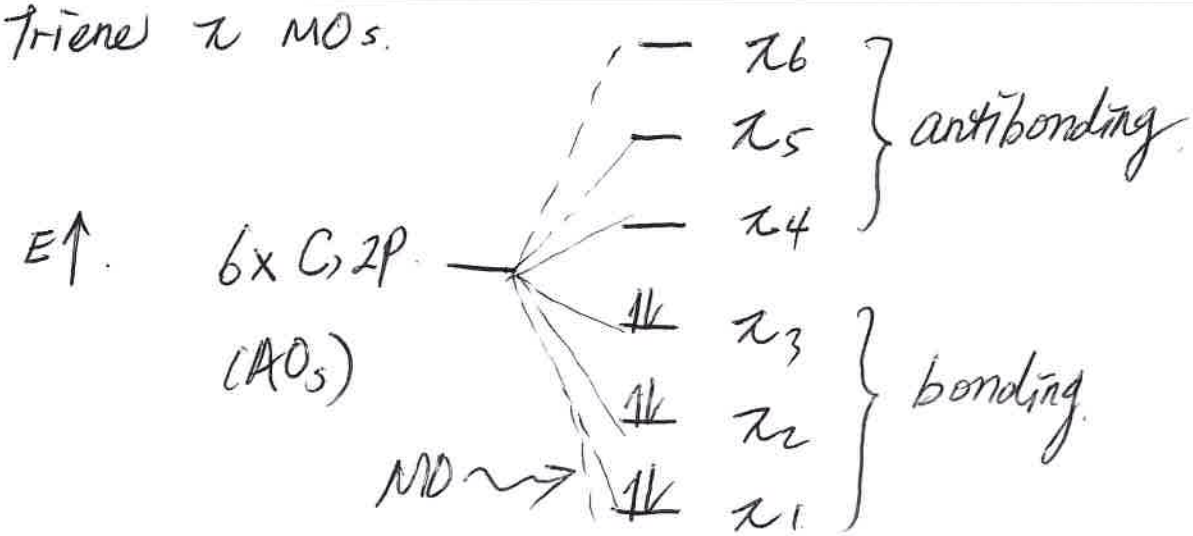
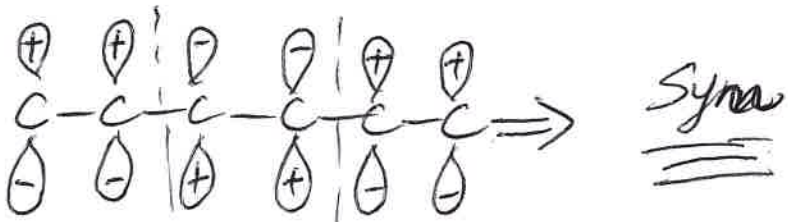
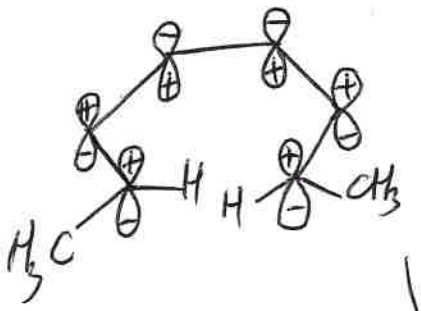
Triene π MOs.



∴ π_3 = MO →



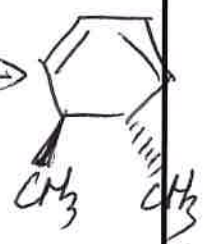


SM

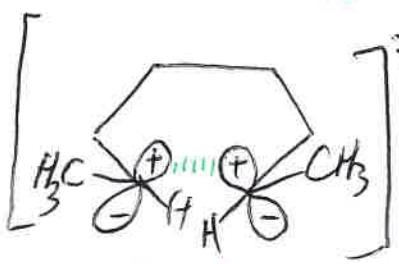
conrot.

antibonding

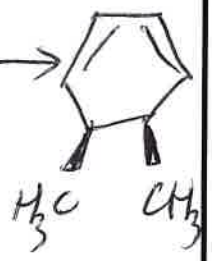
"forbidden"



disrot.



bonding



"allowed"

These rxns can be induced by light, but stereospecificity changes!

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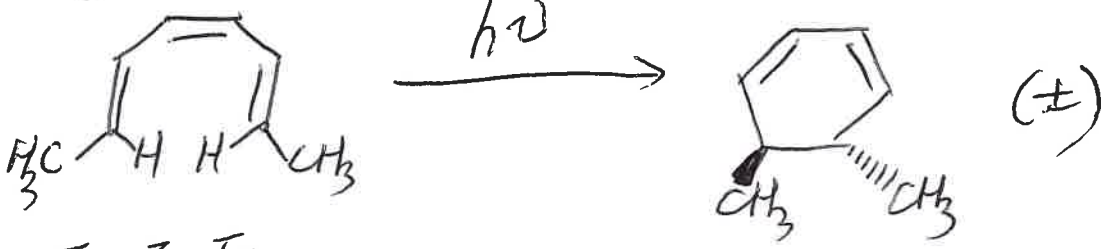
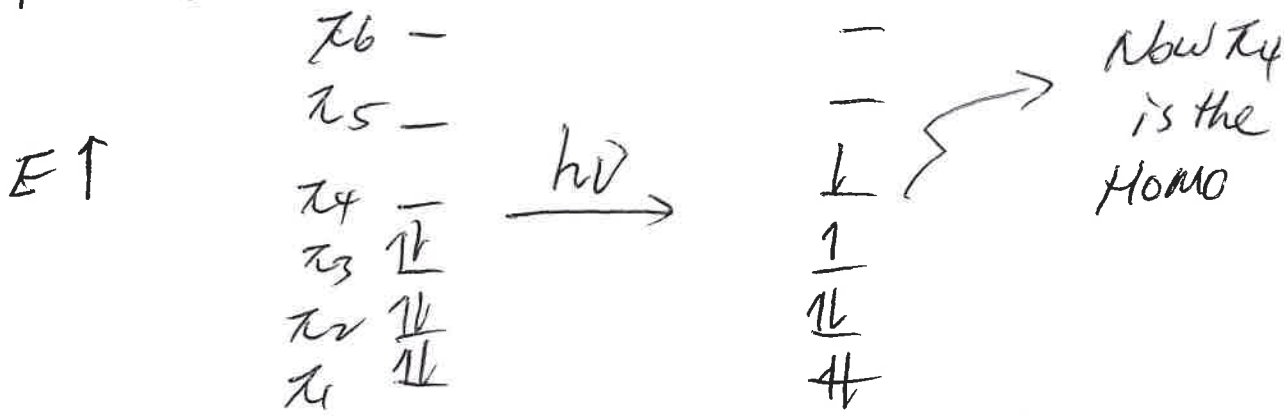
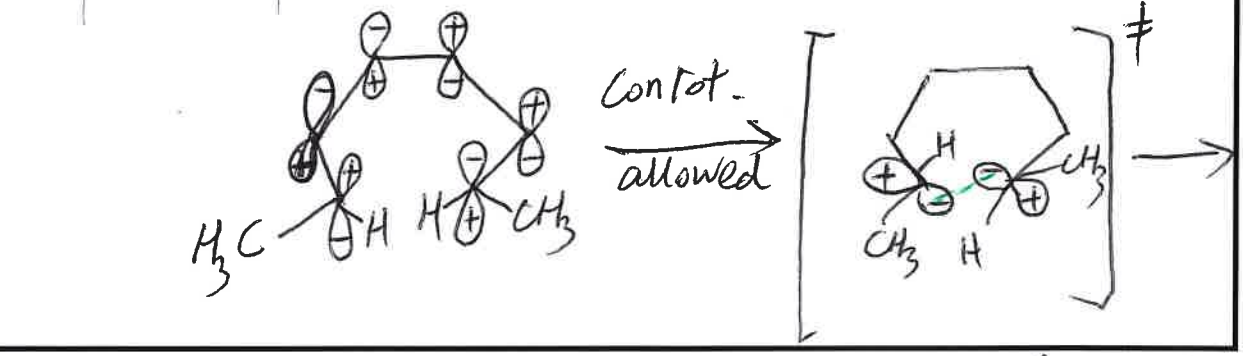
E.g. ← "light"



E, Z, E

Absorption of a photon leads to electronic excited state





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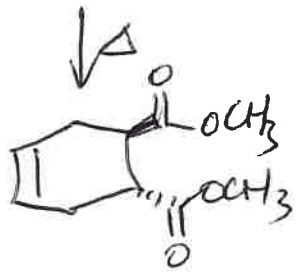
You fill in disrotatory pathway.
("forbidden")

Second class of pericyclic rxns, cycloaddition rxns.
(ex = Diels-Alder)

Systematic classification of cycloadditions: focus on # π e⁻'s from each partner involved in the rxn.



trans

Diels-Alder rxn = [4+2] cycloaddition
↓ ↓
diene dienophile