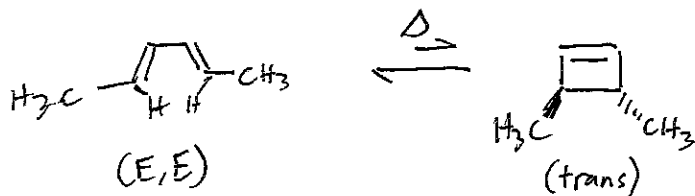


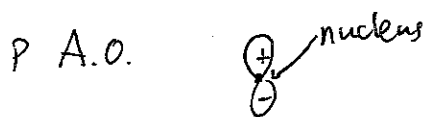
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Exam #3 This wednesday (usual locations) → through ch. 23.

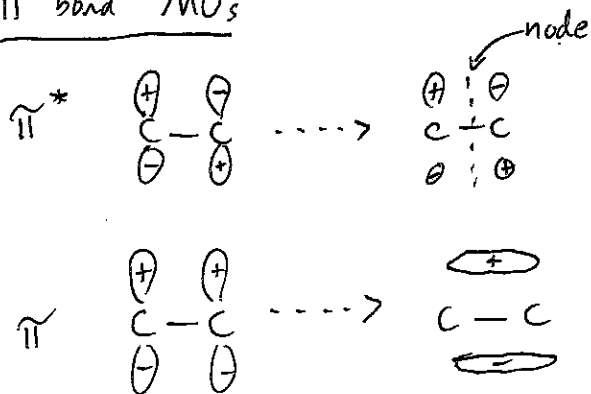
Recall: Trying to understand stereochemistry of electrocyclic reactions, e.g.



New view of p/ π orbitals involving sign of wavefunction...

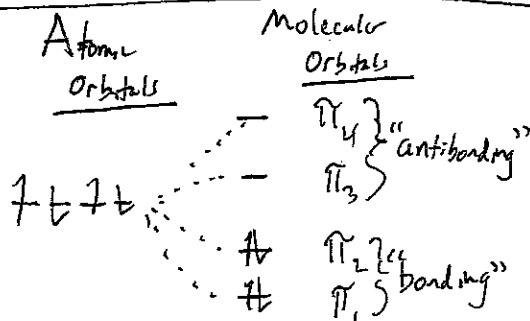


π band MOs

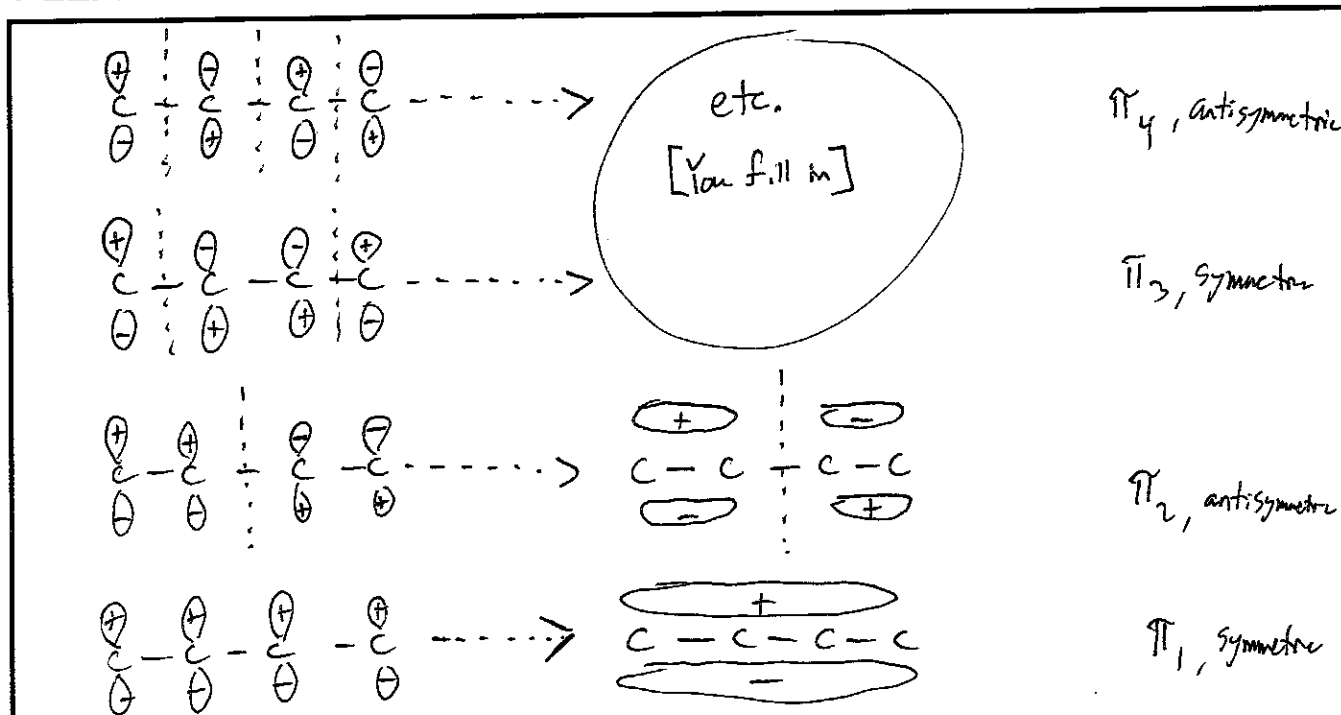


Conjugated Diene MOs

Combine 4 carbon 2p orbitals (atomic orbitals)
 Create 4 π molecular orbitals



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Note:

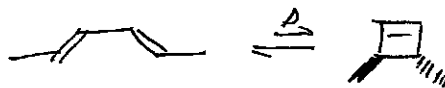
→ π_1 is symmetric, because the signs are identical at the ends of the π system.

→ π_2 is antisymmetric, " " " " opposite " " " " .

In general, all π MOs are either symmetric or antisymmetric.

And, for any π system, the sym/antisym alternates as we move up in energy.

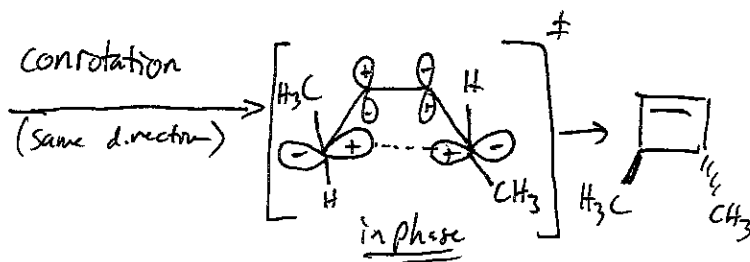
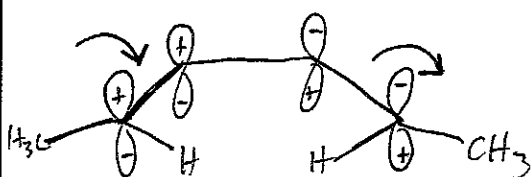
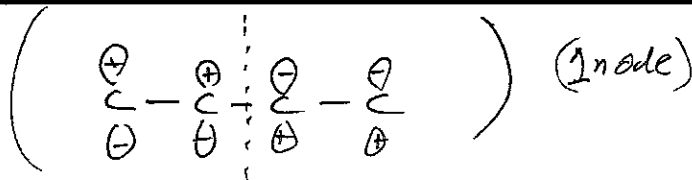
For electrocyclic reaction, consider the HOMO (highest occupied molecular orbital) to understand stereochemistry.



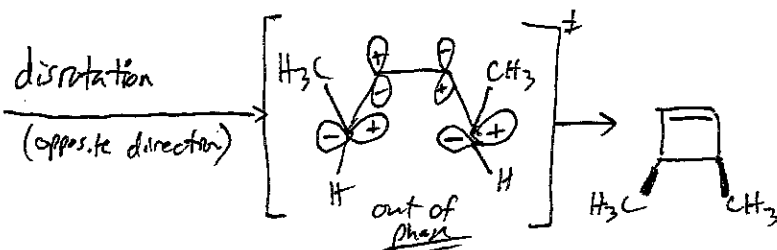
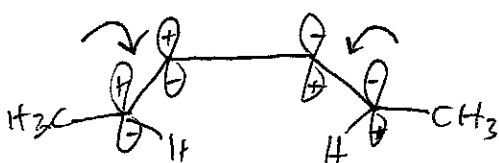
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In this case, $HOMO \equiv \psi_2$.

Superimpose HOMO on the
 reactant:



vs.



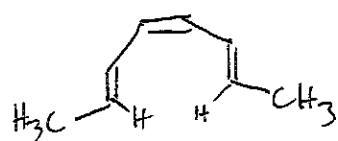
So why is the top one favored? The building σ bond is a bonding orbital (in phase) for conrotation, but antibonding (out of phase) for disrotation.

The top process is ~~the~~ an "allowed" transformation, whereas the bottom is "forbidden"

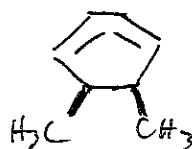
MO symmetry rationalizes/predicts many electrocyclic and other pericyclic reaction outcomes! This is a generally-applicable model.

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Ex:



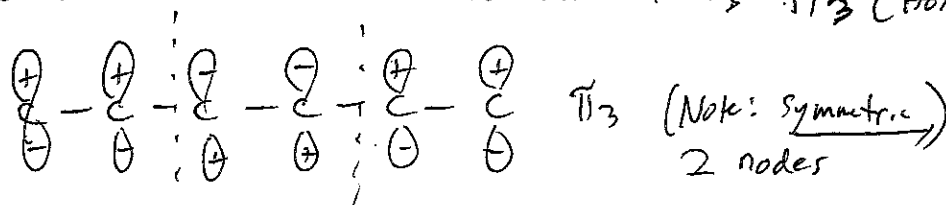
(E, Z, E)



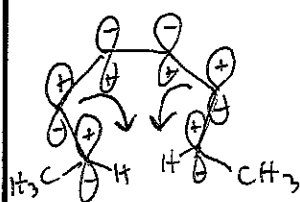
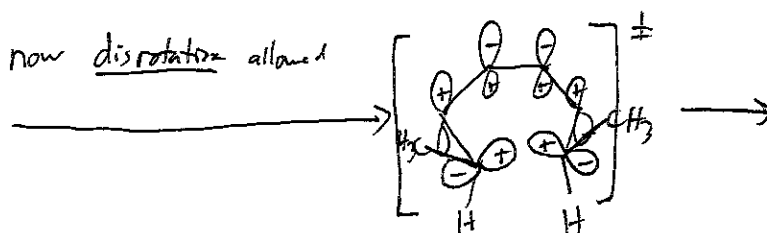
↑↑↑↑↑↑
 6 x C, 2 p orbitals
AOs

— π_6
 — π_5
 — π_4
↑ π_3 HOMO
 ↑ π_2
 ↑ π_1
MOs

So the relevant orbital to look at is π_3 (HOMO)



Now consider the HOMO in the context of the triene:

now disrotatory allowed

Signs match,
 bonding interaction

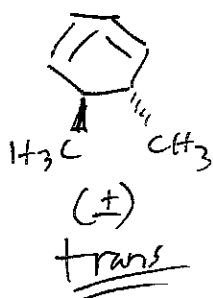
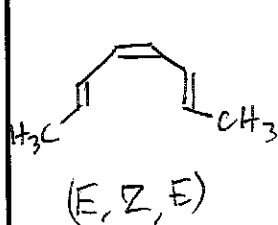


[You fill in the forbidden conrotator].

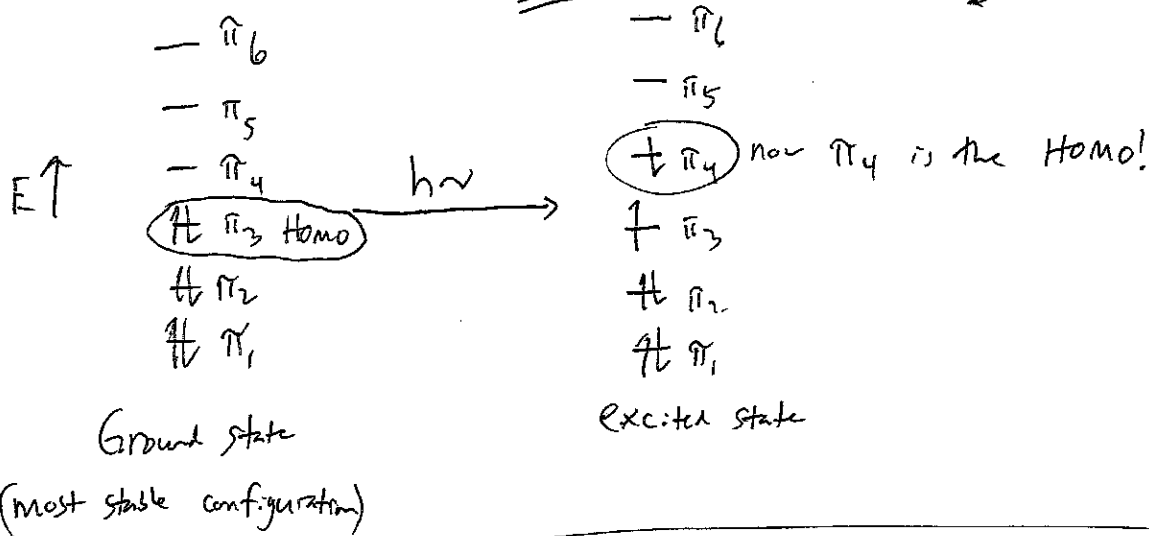
So far, these are all "thermal" reactions \rightarrow promoted by heating. However, in many cases, photochemical versions are possible — but w/ different stereochem outcome.

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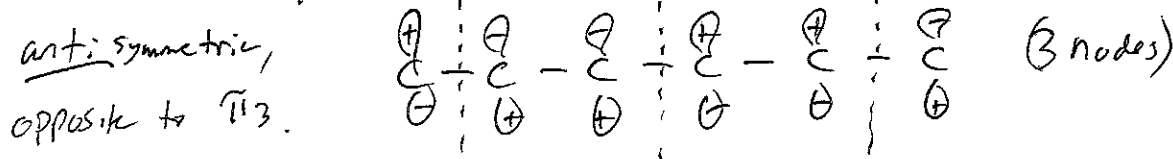
e.g.



MO symmetry analysis explains this behavior. Consider the 6 MOs for this triene starting material.



Since symmetric/antisymmetric alternates w/ each MO, our new HOMO is now



So in the photochemical regime, the hexatriene ring closure

will now be conrotationally-allowed, disrotationally-forbidden, which is opposite

the thermal regime.

This theory accommodates the observation that thermal and photochemical regimes give divergent stereochemical outcomes.