How to determine whether a pericyclic reaction in a particular mode (e.g. conrotatory vs disrotatory in Electrocyclic reaction, suprafacial shift in sigmatropic shift and S, S mode in cycloaddition reaction) is thermally or photochemically allowed

Dewar's Aromatic Transition state theory:

- The theory says that if a T.S. is found to be aromatic in a particular mode, then that mode of pericyclic process is thermally allowed.
- If the T.S. happens to be anti-aromatic, then that mode of pericyclic process will be photochemically (light) allowed.

Steps to determine the nature of TS:

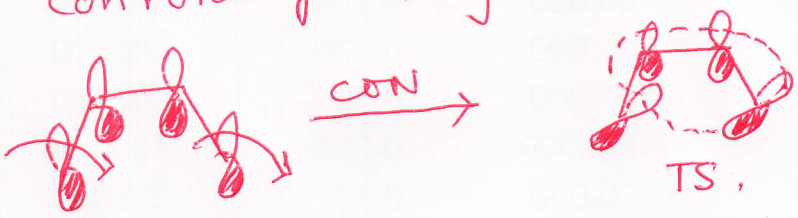
- Draw the T.S. for a particular process
- Count the number of electrons participating in the reaction (n).
- Determine the number of antibonding interactions in the T.S.
- Determine whether the T.S. is a Hucked or Möbius system.
- If no. of antibonding interactions = 0 or even, the system is Hucked;
- For $n = 2, 6, \ldots$ and if $= 1, 3, 5, \ldots$ the system is Möbius and the system is Hucked,

the T.S. will then be aromatic and the process ~~with~~ under consideration will be thermally allowed. for $n = 4, 8$, etc, and the system is Hucked, then the T.S. will be antiaromatic and the process under consideration will occur with light.

- If $n = 4, 8, \ldots$ are the system is Möbius, then the TS. will be aromatic and the process will be thermally allowed (carried out by heat). For $n = 2, 6 \ldots$ and the system is Möbius, the TS. will be antiaromatic and the process under consideration will be carried out by light.

Example:

Conrotatory ring closure of 1,3-butadiene.

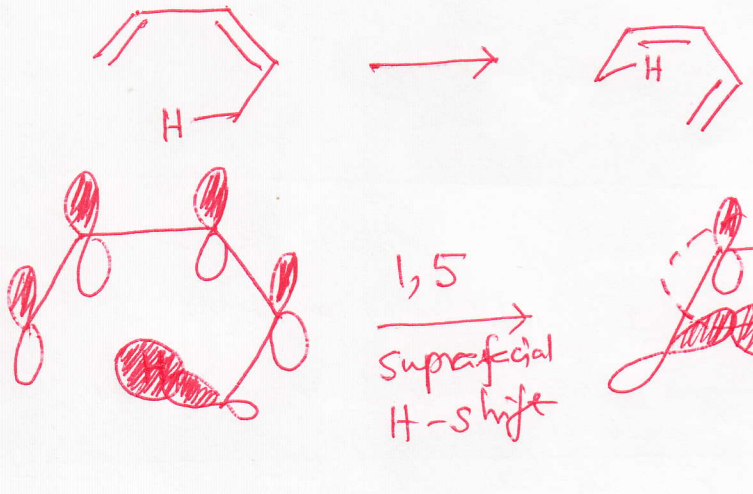


Take any type of MO. (for simplicity, all in-phase atomic orbitals are considered).

- No of antibonding interactions = 1
- So it is a Möbius system
- number electrons participating = 4
- So TS. is aromatic
- So CON - rotatory pross will take place thermally (that is by heat).

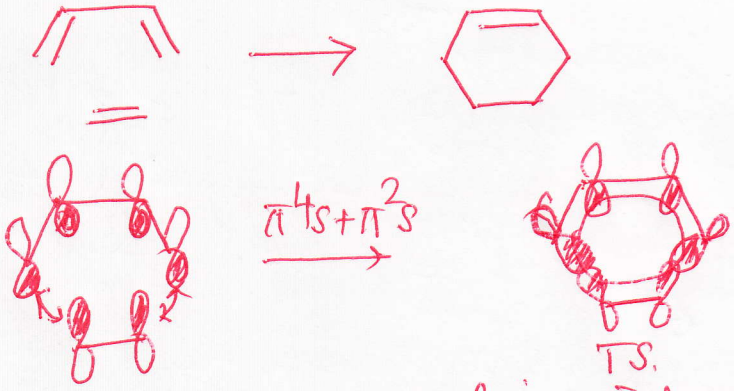
- You can do similar analysis for CON or DIS rotatory ring closure of 1,3,5-hexatriene.

1,5- suprafacial migration of H.



- No. of antibonding interaction = 0
- So it is a Huckel system
- No. of electrons participating = 6
- So TS is aromatic
- So 1,5- suprafacial H-shift is thermally allowed

$\pi^4s + \pi^2s$ cycloaddition



- no. of antibonding interactions = 0
- So it is a Huckel system
- no. of electrons participating = 6
- So TS is aromatic
- So S,S addition will occur with heat.
