How to determine whether a pericyclic reaction in a particular mode (e.g. con vs dis in electrocyclic, or supra-supra or supra-antara addition in case of cycloaddition) using Frontier Molecular Orbital Theory.

- Consider the interaction of Highest Occupied Molecular Orbital of one component (HOMO) with the Lowest Unoccupied Molecular Orbital of the other component (LUMO).
- If there is matching of phases of the orbitals, in a particular process under consideration, then that process will be thermally allowed. Otherwise, it will happen under light.

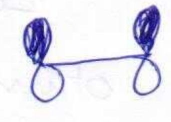
- As such, there is no restriction in selecting the HOMO or LUMO of each component. The result will be the same irrespective of your choice of HOMO or LUMO of a particular component. For example, in a [4+2] cycloaddition, if you chose the HOMO of the 4e-component, then chose the LUMO of the 2e-component or vice-versa.
- However, if one of the component is electron-rich and the other component is electron-deficient then take HOMO of the electron rich component and LUMO of the electron-deficient component.

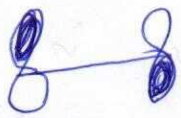
Example:

Qn. Is $\pi^2 s + \pi^2 s$ process thermally allowed?

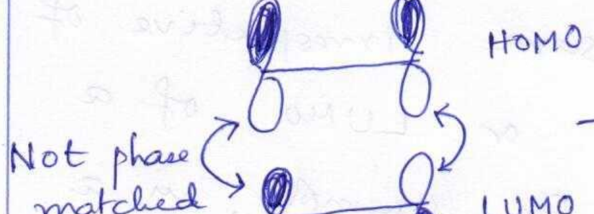
Ans. The reaction under consideration is dimerization of two ethylenes.

A B

Process: Consider HOMO of $\underline{\underline{A}}$ 

Consider LUMO of $\underline{\underline{B}}$ 

Now consider S, S addition of $\underline{\underline{A}}$ and $\underline{\underline{B}}$ (remember S, S addition means supra supra addition).

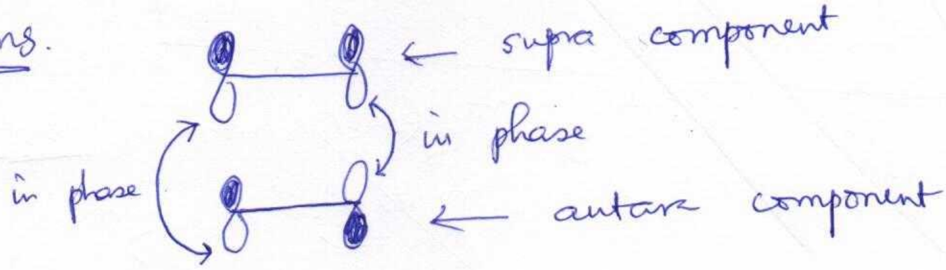


Because of mismatch of phase as shown, this process, i.e. $\pi^2 s + \pi^2 s$ is thermally forbidden.

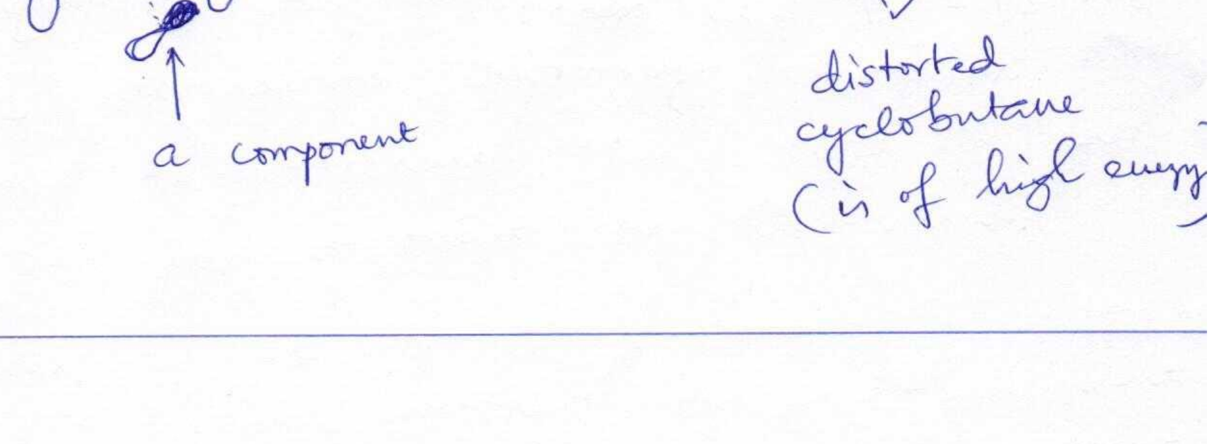
This process will occur photochemically

Qn. Is $\pi^2 s + \pi^2 a$ thermally allowed ?

Ans.

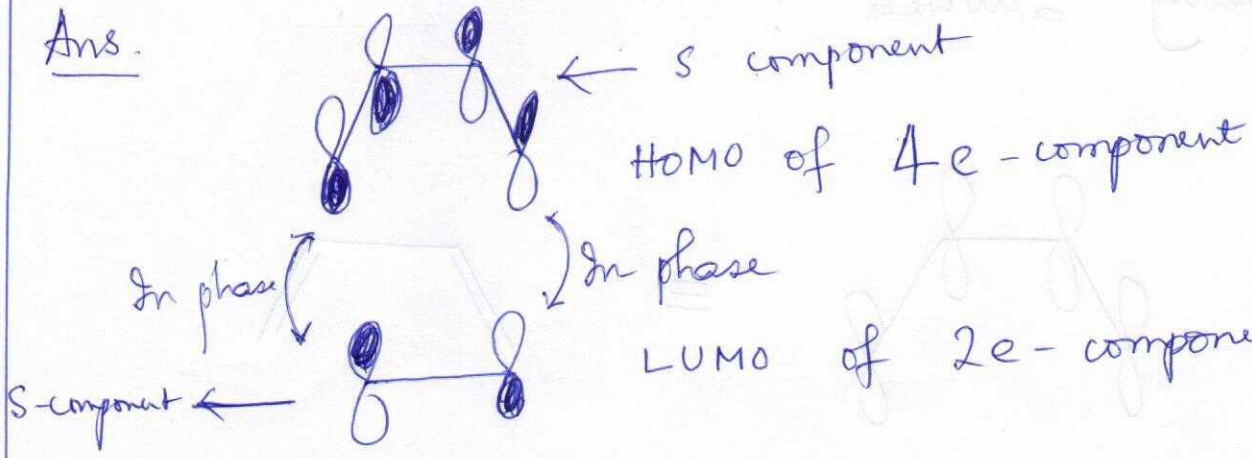


Because of phase matching at both ends, the process is thermally allowed. Thus $\pi^2 s + \pi^2 a$ is a thermally allowed process. However, because of the difficulty to geometrically access the overlap in the left side, the process is difficult from geometric point of view. The only way these overlaps can occur is through the distorted geometry as shown below;



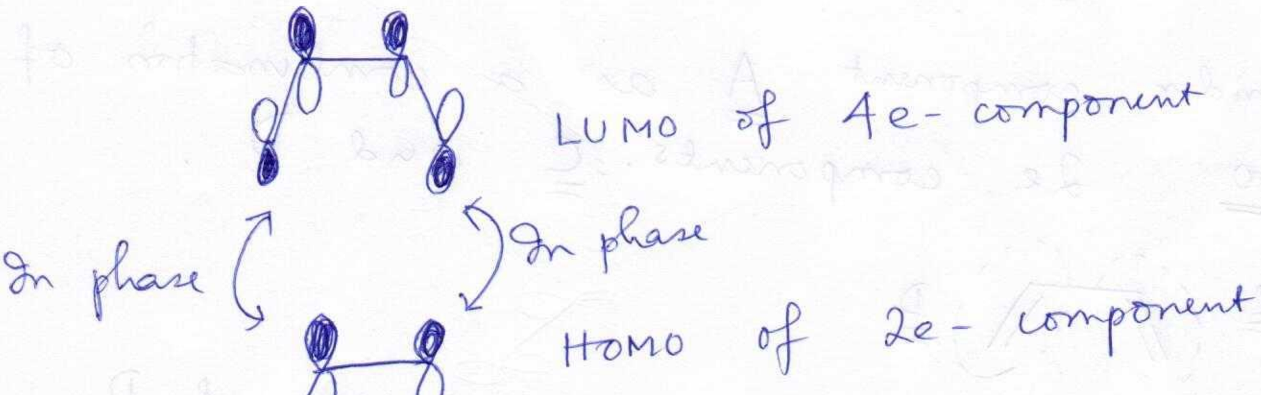
Is $\pi 4s + \pi 2s$ thermally allowed?

Ans.



The process is therefore thermally allowed.

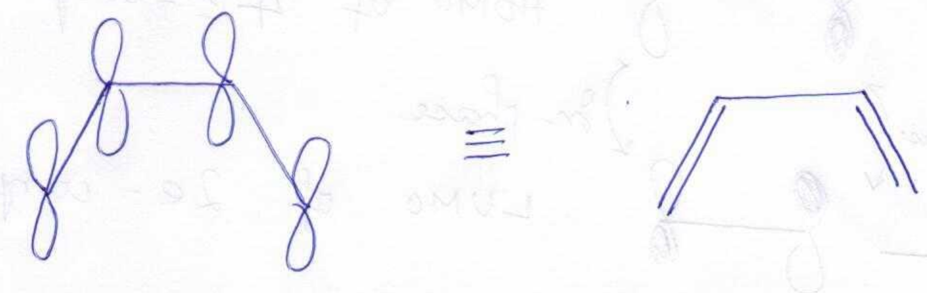
OR



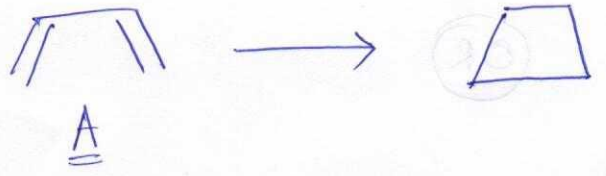
So the process is thermally allowed.

Qn Is conrotatory ring closing for a $4\pi e$ - system thermally allowed ?

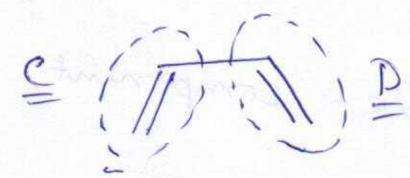
Ans.



The rxn. under consideration is



Consider component A as a combination of two 2e components. C and D.

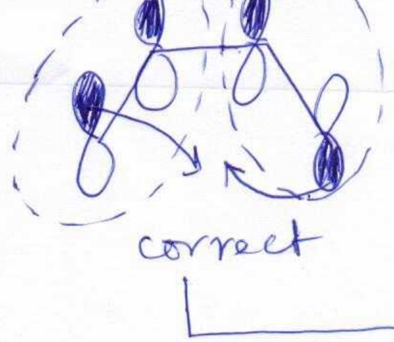


Draw HOMO of C and LUMO of D.
While drawing, take care of the matching scenario at the two inner carbons as shown.

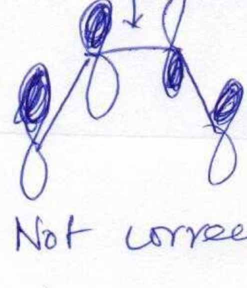
matching

(mismatch)

HOMO



LUMO and not



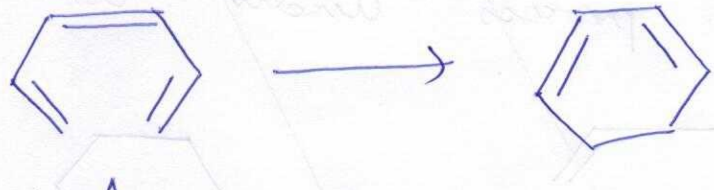
correct

Not correct

Controtatory motion will give matching of phases of the terminal orbitals. So the process is thermally allo

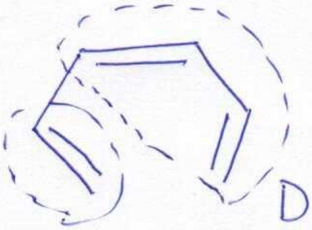
Qn. Is disrotatory ring closing process for a $6\pi e$-system thermally allowed?

Ans.



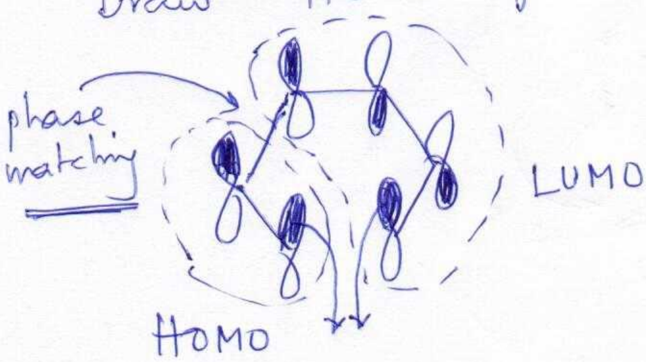
A

Consider A as having two components C and D



C D

Draw HOMO of C and LUMO of D.



→ Disrotatory process produces phase matching scenario.

So the process is thermally allowed.

Try with LUMO of C and HOMO of D