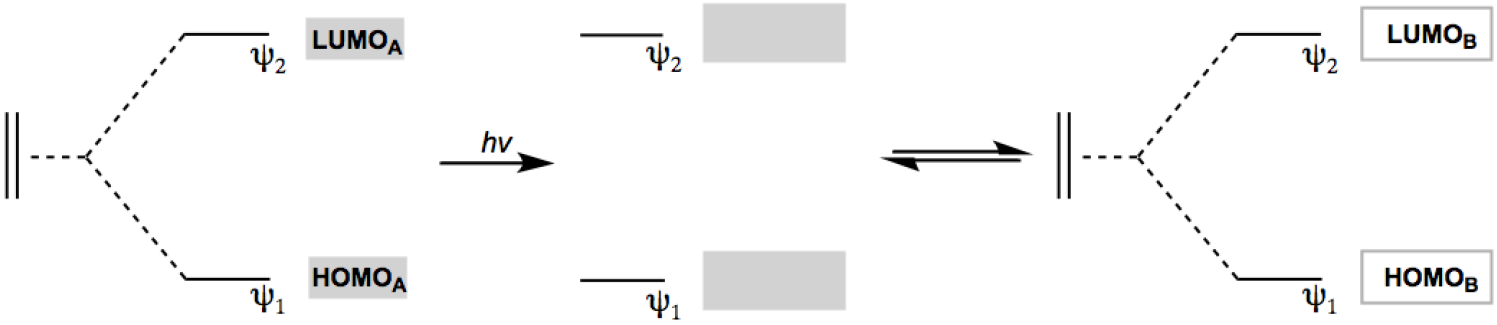
CONCEPT: PHOTOCHEMICAL CYCLOADDITION REACTIONS

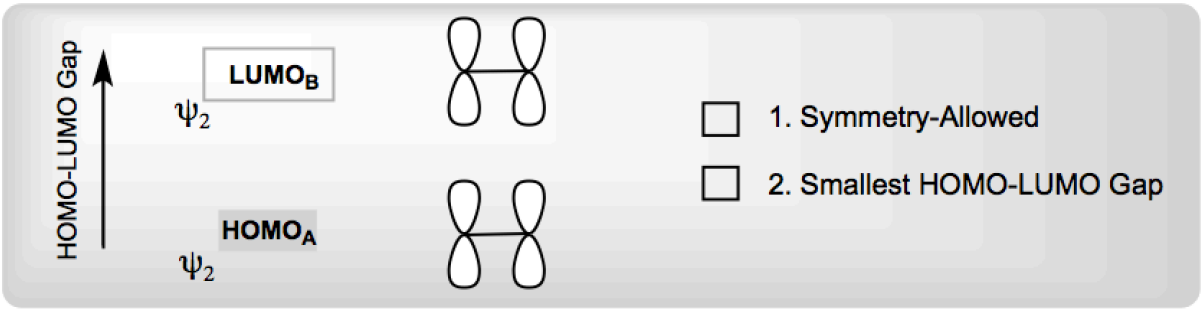
● Pericyclic reactions in which _____ ***π-bonds*** are destroyed after a _____-*activated* cyclic mechanism

● In cycloaddition, $HOMO_A$ must fill $LUMO_B$.

□ According to FMOT, bonding interaction is ***strongest*** when orbital *symmetry* and *energy* match closely.

□ Light excites ground-state electrons to a _____ energy state ($\psi \rightarrow \psi^*$). HOMO / LUMO orbitals change.





Cycloadditions Summary:

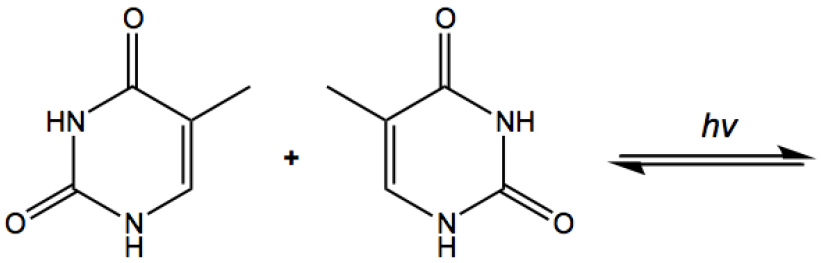
● Assuming only ***suprafacial*** interactions (*antrafacial* not possible on small rings):

Total π–electrons	Activator	ψ-orbital Difference
4n	Photochemical	Odd
4n + 2	Thermal	Even

PRACTICE:

a. Use FMOT to predict the mechanism and products for the following cycloaddition. If no product is favored, write "symmetry-disallowed" in place of the product.

$2\pi + 2\pi$ cycloaddition (thymine dimerization)



Thymine (T)

b. Use the cycloaddition summary rules to verify that you have come to the correct conclusion.