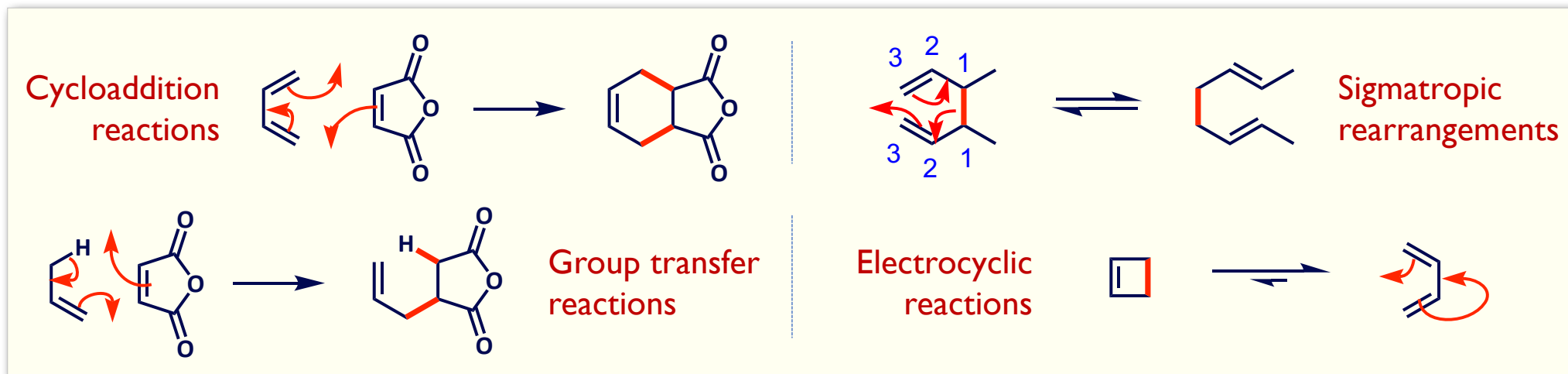


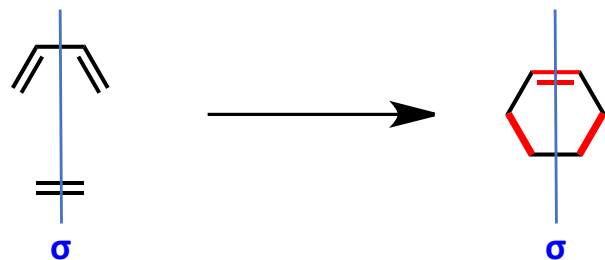
Recap of Lecture I

Pericyclic reactions have cyclic transition states in which all bond-forming and bond-breaking take place in a concerted manner without the formation of an intermediate



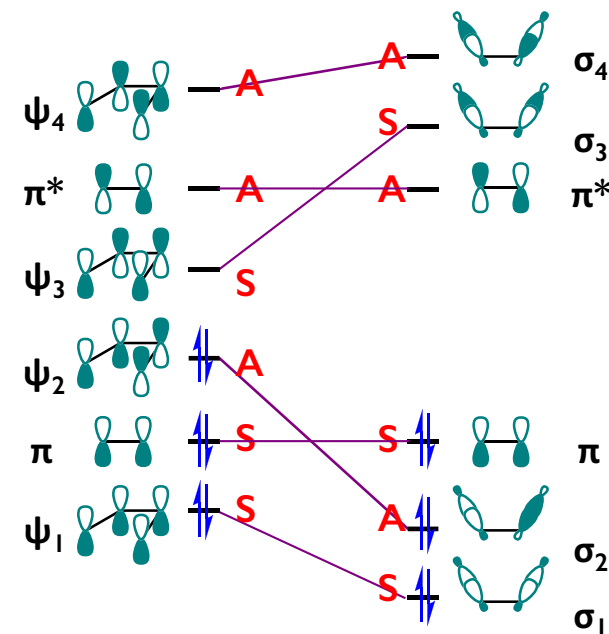
During a pericyclic reaction, the symmetry of the orbitals with respect to any symmetry operations of the molecule must be conserved in moving from the starting material(s) to product.

This allows us to decide whether a reaction is allowed or forbidden



For the Diels-Alder reaction, all interacting bonding orbitals in the diene/dienophile are correlated with new *bonding* orbitals in the product.

The reaction is thermally allowed.

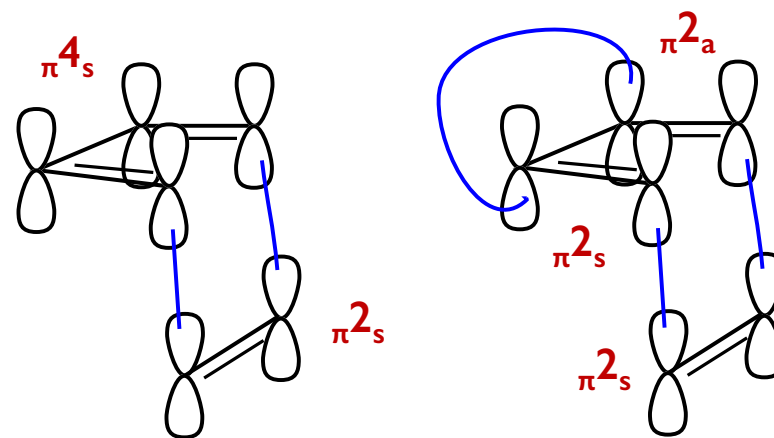
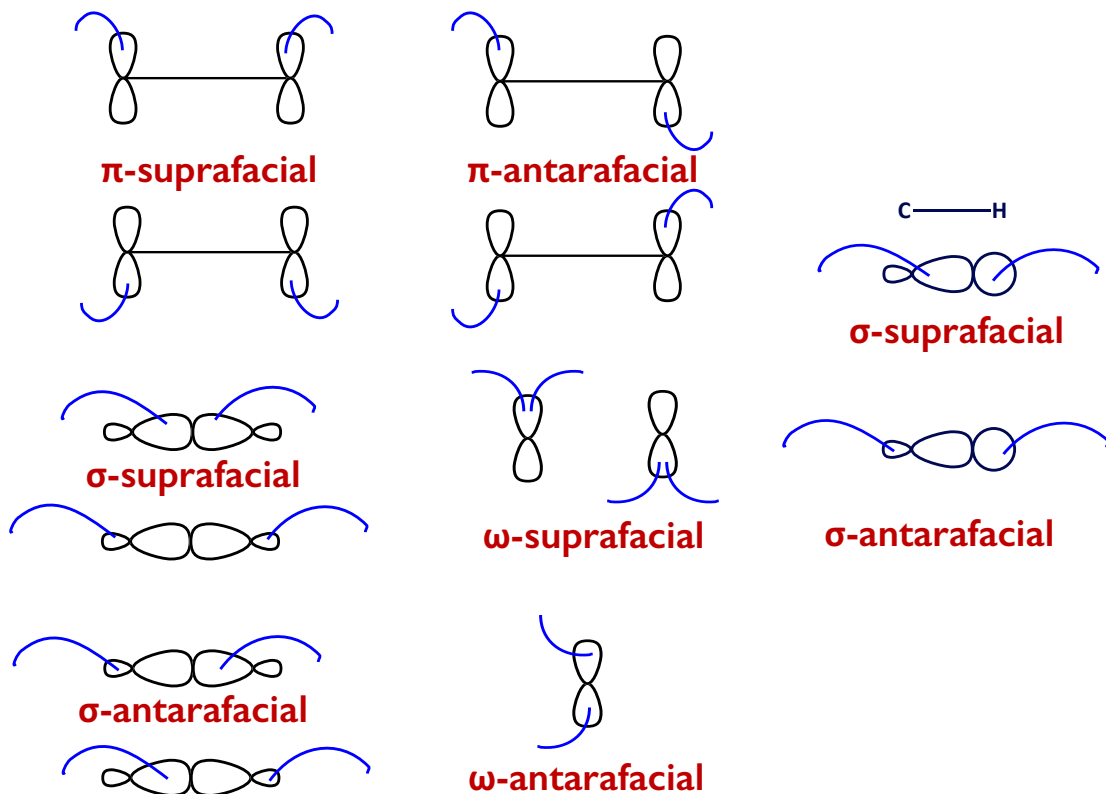


Recap of lecture 2

A ground state pericyclic reaction is symmetry allowed when the total number of $(4q + 2)_s$ and $(4r)_a$ components is odd (q and r must be integers).

A pericyclic change in the first electronically excited state (i.e. a photochemical reaction) is symmetry allowed when the total number of $(4q + 2)_s$ and $(4r)_a$ components is even.

's' = suprafacial ['same' faces of 'component']
 'a' = antarafacial ['opposite' faces of 'component']



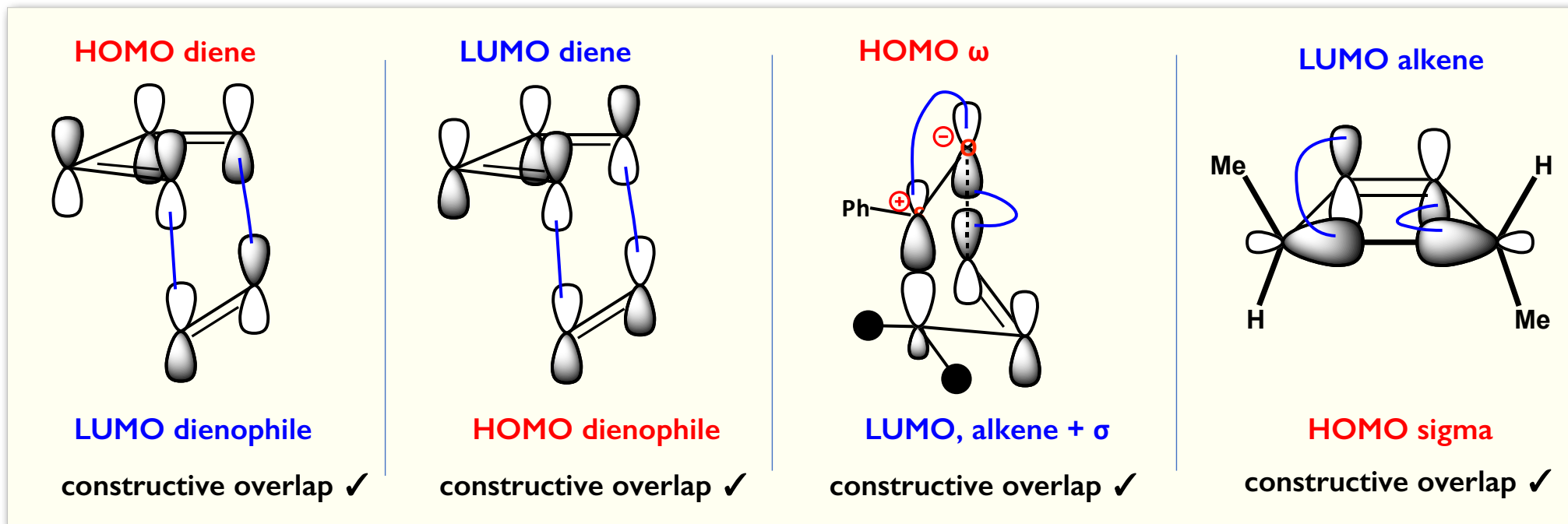
$$\begin{aligned}
 (4q + 2)_s &= 1 \\
 (4r)_a &= 0 \\
 \text{Total} &= 1 \\
 &\text{odd } \checkmark \\
 &\text{allowed}
 \end{aligned}$$

$$\begin{aligned}
 (4q + 2)_s &= 2 \\
 (4r)_a &= 0 \\
 \text{Total} &= 2 \\
 &\text{even } \times \\
 &\text{forbidden}
 \end{aligned}$$

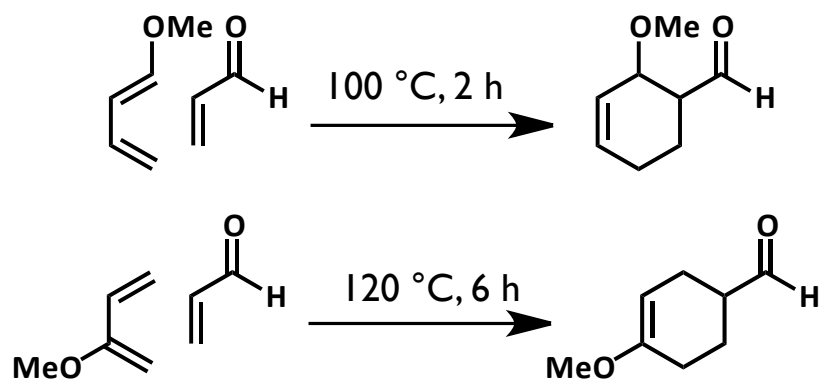
(1) identify components, arrange in 3D and draw overlap. (2) label as 's' or 'a'. (3) sum components according to W-H rule

Recap of lecture 3

- Frontier molecular orbitals offer an alternative method for rationalizing pericyclic reactions

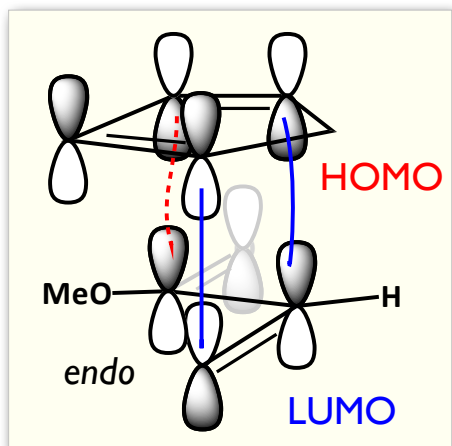


- Substituents on Diels-Alder reaction components influence reactivity and regiochemistry



EDG on the diene raises the energy of the HOMO
EWG on dienophile lowers energy of the LUMO
Diene HOMO and Dienophile LUMO best energy match
This can be rationalized by examining orbital coefficients for the Diene and Dienophile

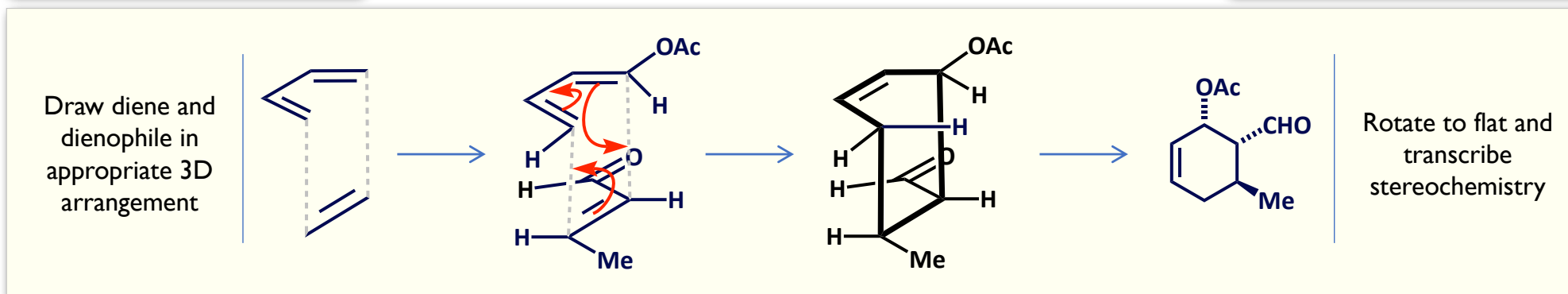
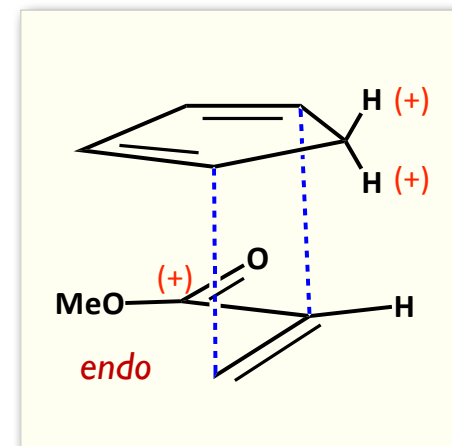
Recap of lecture 4



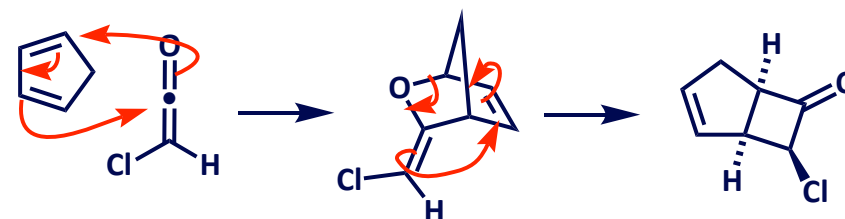
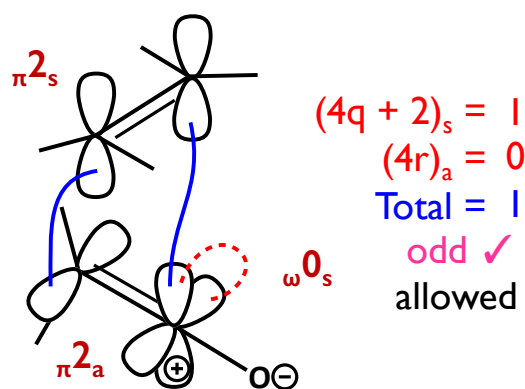
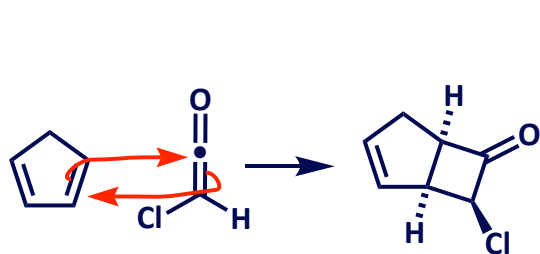
■ Secondary orbital overlap is a simple explanation for the kinetic preference for the *endo*-adduct in the Diels-Alder reaction

■ Electrostatic arguments have also been proposed as a reasonable explanation for 'endo'-selectivity

The Diels Alder reaction is stereospecific, and good 3D models are essential to elucidate stereochemistry



■ Ketenes and other cumulated systems readily undergo [2+2] cycloaddition reactions

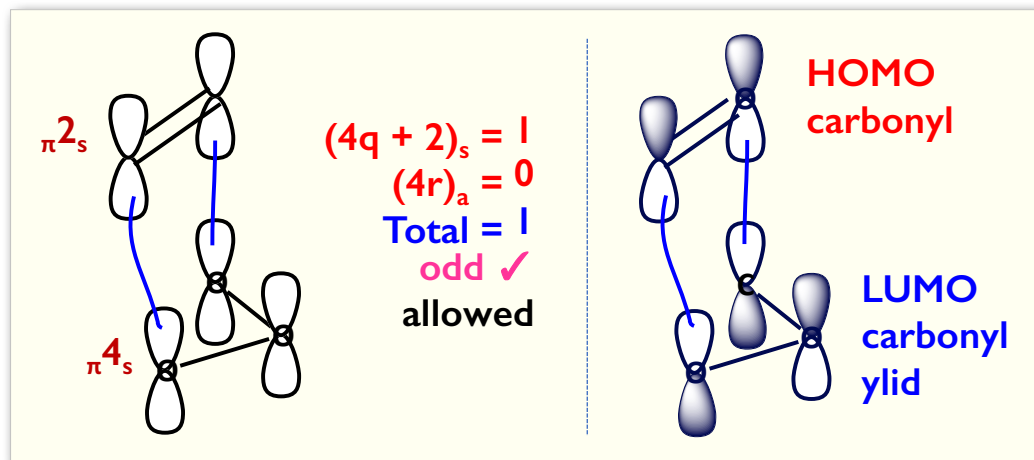
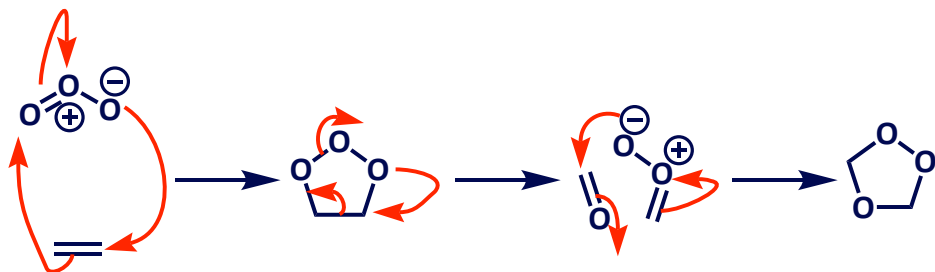


Treat ketene as a vinyl cation

Alternative mechanism: Diels-Alder then Claisen

Recap of lecture 5

■ Ozonolysis is a 1,3-dipolar cycloaddition followed by a series of other pericyclic reactions



■ All electrocyclic reactions are allowed, but their stereochemical outcome changes with heat or light

Thermal electrocyclic processes will be *conrotatory* if the total number of electrons is $4n$ and *disrotatory* if the total number of electrons is $(4n + 2)$.

This is reversed for photochemical reactions.

