

# Pericyclic Reactions

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## Molecular Orbitals of Polyenes:

You should be familiar with substitution, elimination, and addition reactions. In substitution reactions one electron rich group displaces another. In elimination reactions atoms are removed from a carbon backbone while in addition reactions atoms are added to a multiple bond. There is another class of chemical reactions wherein an array of conjugated bonds form new carbon-carbon bonds with stereocontrol. These reactions were once called "no-mechanism" reactions because they involved bond reorganization. These reactions are now appreciated as being concerted and stereocontrolled, and governed by orbital symmetry rules. We shall consider two types of these pericyclic reactions: cycloaddition and electrocyclic reactions.

Figure 1 shows two isolated p-atomic orbitals (AO) of equal energy. When the wave functions of these **two** orbitals are added to and subtracted from one another, **two** new molecular orbitals (MOs) are formed. Note the emphasis on two. The same number of MOs are formed from the same number of AOs. One MO ---namely  $\pi_1$ --- is bonding and lower in energy than the parent AOs while  $\pi_2^*$  is antibonding and higher energy than the p-AOs. These two MOs represent the pi-bond in ethylene. The two paired electrons of the  $\pi$ -bond are placed in the bonding MO, which is the Highest Occupied Molecular Orbital (HOMO). The antibonding MO is the Lowest Unoccupied Molecular Orbital (LUMO) and contains no electrons. The HOMO and LUMO are called frontier MOs (FMOs).

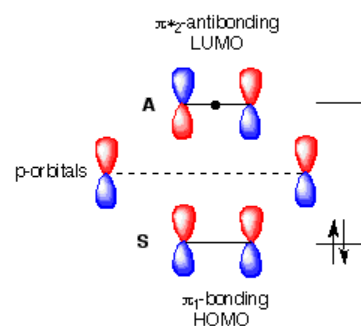


Fig.1

Notice that the HOMO has no node and it is symmetrical (S) with respect to a mirror plane orthogonal to the sigma bond while the LUMO has one node and it is antisymmetrical (A) in the mirror plane. Bear in mind that the red and blue lobes of the orbitals do not signify charge but rather the phase of the wave function.

In the case of ethylene one of the electrons in the HOMO can be promoted to the LUMO orbital having the same spin (Fig. 2). This process occurs with electromagnetic energy just to the high energy side of the ultraviolet range (UV, ~200 - 400 nm). This excited state LUMO (a singlet, paired electrons) involves the absorption of energy. When the electron returns to the ground state (HOMO) energy is emitted. Higher homologs of ethylene such as 1,3-butadiene, 1,3,5-hexatriene, 1,3,5,7-octatetraene, etc. can be treated in a similar way.

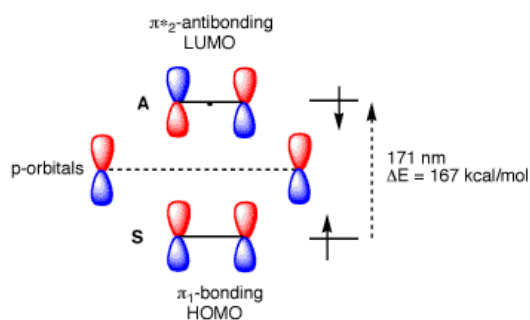


Fig. 2

When the wave functions of two bonding MOs of ethylene are combined, two new MOs are formed (Fig. 3). One of these will be lower in energy than the ethylene MOs, the other higher. The lower one will have S symmetry while the higher one will have A symmetry, hence the single node. Likewise, the two non-bonding MOs of ethylene (A), can be brought together to form a LUMO having constructive overlap between C<sub>2</sub> and C<sub>3</sub> and lower energy than either of the LUMOs of ethylene. Non-constructive overlap gives the non-bonding A MO of butadiene having three nodes. The HOMO-LUMO energy gap in 1,3-butadiene is therefore lower in energy than it is ethylene. This method of building MOs is called Perturbational Theory. It can be used to construct the MOs of higher polyenes.

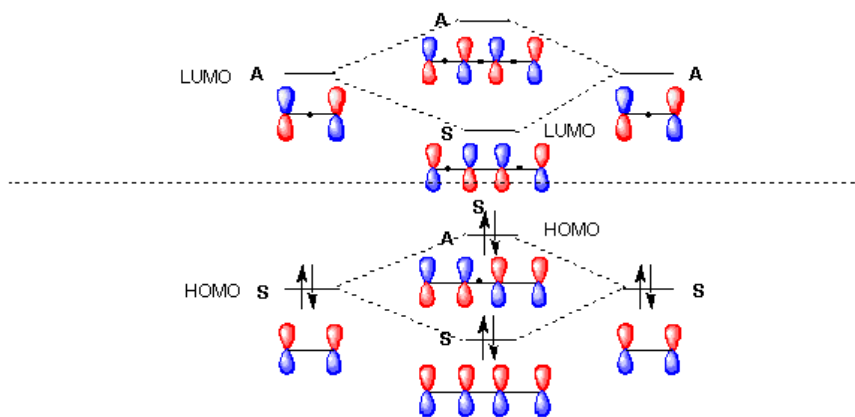


Fig.3

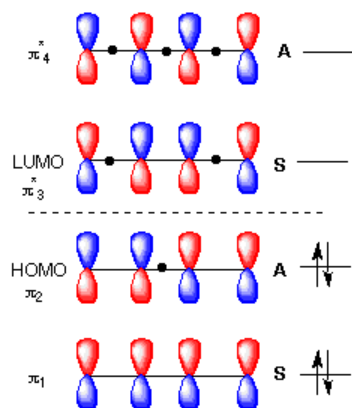


Fig. 4

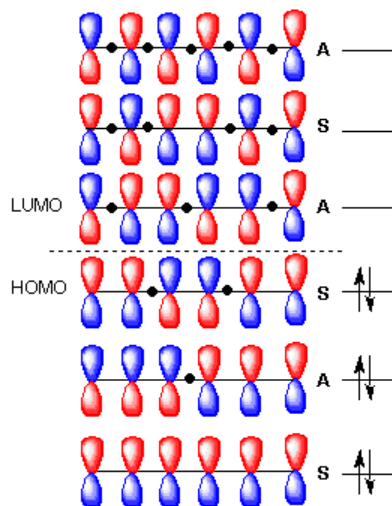


Fig. 5

For 1,3-butadiene there are four MOs, two bonding and two antibonding (Fig. 4). Each successive, higher energy MO has an additional node. The HOMO is  $\pi_2$  while the LUMO is  $\pi_3^*$ . The energy gap between the HOMO and the LUMO is 131 kcal/mol (214 nm), less than that for ethylene. Promotion of a bonding HOMO electron to the LUMO is effected by UV light. It is called a  $\pi \rightarrow \pi^*$  transition. The 16 orbitals in Fig. 4 are all shown as the same size. In fact, they are of different sizes. The terminal orbitals in the HOMO and LUMO are larger than their respective internal orbitals. Nonetheless, treating all of these orbitals as the same size will suffice for our needs. One last example is 1,3,5-hexatriene (Fig. 5). There are three bonding and three antibonding MOs.

The HOMO-LUMO gap ( $\pi \rightarrow \pi^*$  transition) in the hexatriene has dropped to 109 kcal/mol (258 nm) and the wavelength of absorption has increased. Note that the symmetry of the FMOs for each successive longer polyene alternates **S****A**, **S****A****S****A**, and **S****A****S****A****S****A**, etc. The HOMO of ethylene (Fig.1) and the HOMO of 1,3,5-hexatriene are both **S** while their LUMOs are **A**. This situation is the opposite of that observed for 1,4-butadiene where the HOMO is **A** and the LUMO is **S**. What about 1,3,5,7-octatetraene? It is the same as 1,3-butadiene. Try it. Thus, every other polyene has the same HOMO-LUMO phasing. One group obeys the  $4n + 2$  rule while the other one satisfies  $4n$ , where  $n = 0, 1, 2, 3$ , etc.

$n = 0, 1, 2, 3$ , etc.	HOMO	LUMO
$4n + 2$	S	A
$4n$	A	S

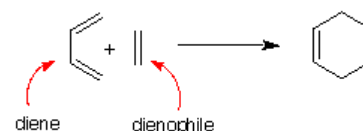
It also follows that the terminal orbitals of any **S**-MO must mirror one another because the whole MO as a whole does so. Likewise, an **A**-MO has terminal orbitals that do not match.

Pericyclic reactions require the proper matching of the symmetry of the HOMO and LUMO of reacting components. Let's begin with cycloaddition reactions.

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### Cycloaddition Reactions:

The Diels-Alder Reaction (DAR), reported in 1928 by Otto Diels and Kurt Alder, is a thermal, concerted, suprafacial, [4+2] cycloaddition. The prototypical DAR is illustrated in Fig. 6. While 1,3-butadiene is a viable diene in the reaction, ethylene itself is a poor dienophile (dienophobe?). Generally, a deactivated dienophile is employed in the DAR. By concerted is meant that both sigma bonds are formed at



the same time but not necessarily at the same rate and certainly not stepwise. Suprafacial means that the new sigma bonds are formed on the same face of each reactant, the diene and the dienophile. The opposite of suprafacial is antarafacial. The term [4+2] refers to a 4-electron conjugated system reacting with a 2-electron system.

Figure 7 shows the MOs of 1,3-butadiene and ethylene and their respective, relative energies. As noted earlier, the HOMO-LUMO energy gap is greater in ethylene than in butadiene. For the two compounds to react, a HOMO of one must react with the LUMO of the other with conservation of orbital symmetry. There are two seemingly isoenergetic possibilities. The SS and the AA reaction (green arrows), both of which react suprafacially and conserve symmetry. Both energy gaps are equal and too large for reaction to occur readily.

One way to reduce the HOMO-LUMO energy gap is to lower the LUMO of one reactant. This is accomplished by using an "ethylene" that has an electron-withdrawing group (EWG) attached to it (Fig. 8). Acrylate esters,  $\alpha,\beta$ -unsaturated ketones and  $\alpha,\beta$ -unsaturated nitriles are typical dienophiles. These dienophiles absorb light in the UV range (~210-240 nm), which means that the HOMO-LUMO gap is reduced in energy to about the HOMO-LUMO gap in butadiene.

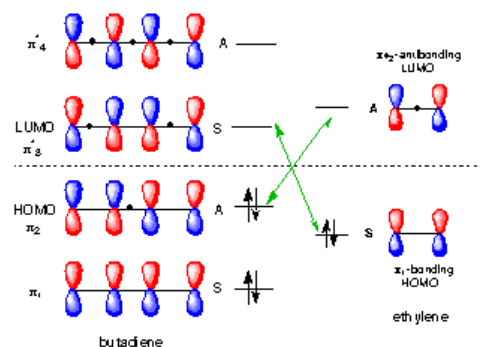


Fig. 7

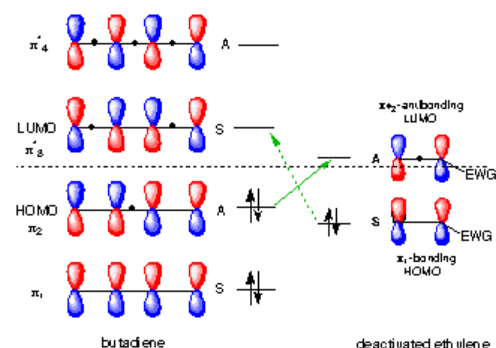


Fig. 8

You will have noticed that all of the MO diagrams constructed thus far have been formed from carbon AOs. Moreover, the energy of the bonding and antibonding MOs are distributed symmetrically above and below the energy of the carbon p-AO (dotted line). Because the EWG contains a heteroatom, whose AO is lower in energy than a carbon AO, the symmetry about the dotted line is lost. Now there are not two equal HOMO-LUMO gaps. It is the diene HOMO and the dienophile LUMO that have the lower energy gap. The deactivated ethylene of Fig. 8 is in reality a 4-electron system if you include the carbonyl group. The highest and lowest MOs have been omitted from the diagram.

What can be said about [2+2] cycloadditions? In a word...plenty. In Fig. 9 it is clear that the symmetry elements do not match between the HOMO and LUMO of ethylene for cycloaddition to occur in a concerted suprafacial-suprafacial mode (S and A). The formation of cyclobutane from two ethylenes cannot be a concerted, thermal reaction. Is there a way to make the reaction concerted? Clearly, if both reactants had the same symmetry, our problem would be solved.

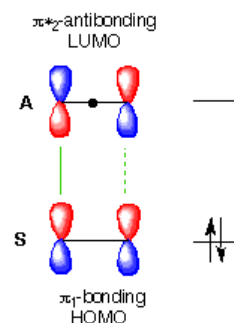


Fig. 9

The HOMO-LUMO gap, a.k.a. the  $\pi \rightarrow \pi^*$  transition, requires light of wave length 171 nm for excitation of ethylene (see Fig. 2). An electron is promoted from the bonding HOMO to the non-bonding LUMO. Now the HOMO (HOMO\*) has A symmetry. This excited state HOMO has the same symmetry as the ground state LUMO. Concerted cycloaddition occurs in the suprafacial-suprafacial mode. So we see that in the suprafacial-suprafacial mode the concerted [4 + 2]-cycloaddition is ground state (thermal) allowed and excited state (hv) forbidden, while the [2 + 2]-cycloaddition is just the opposite, ground state forbidden; excited state allowed. A general rule can be established for suprafacial-suprafacial cycloadditions. For  $i = 1, 2, 3 \dots$  and  $4i = m + n$ , or  $4i + 2 = m + n$  where  $m$  and  $n$  are even numbers, then the following Table applies. This Table can be generalized even more but this would take us beyond the scope of this exercise.

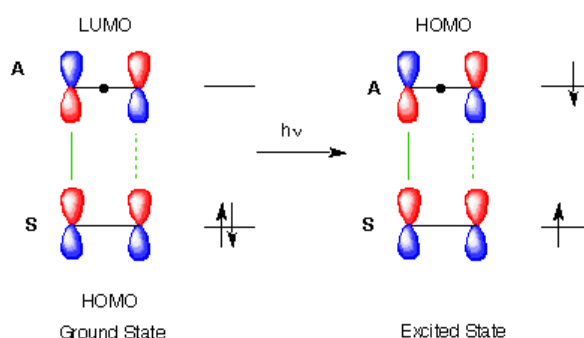


Fig. 10

m + n	Ground State (thermal)	Excited State (photochemical)
4i	forbidden	allowed {[2+2], [6+2], [4+4]...}
4i + 2	allowed {[4+2], [8+2], [6+4]...}	forbidden

In all the examples that have been discussed thus far, the number of orbitals and the number of electrons have been the same. Two and two for ethylene; four and four for 1,3-butadiene, etc. But this need not be the case. It is the electrons that count; the orbitals determine "allowedness".

Consider the reaction shown in Fig. 11 where butadiene reacts with the allyl cation. This is a [4 + 2]-cycloaddition in spite of the fact that the allyl cation has three orbitals (or does it?) and only two electrons. Fig. 12 reveals the **AA** symmetry of the reaction. The non-bonding (the same energy as that of a carbon p-AO) allyl cation LUMO has but two orbitals.

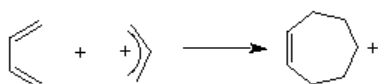


Fig. 11

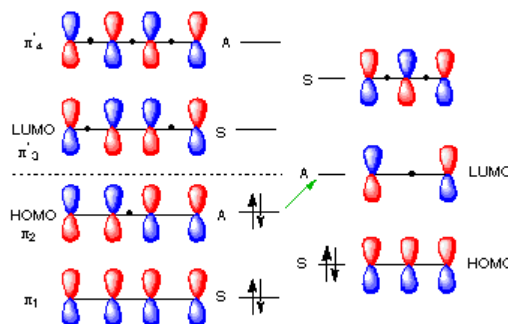


Fig. 12

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### Electrocyclic Reactions:

Conjugated polyenes can undergo stereocontrolled, unimolecular cyclizations under thermal and photochemically conditions. These reactions are known as electrocyclic reactions; they are controlled by orbital symmetry. Fig. 13 illustrates the prototypical reaction. For instance, 1,3,5-hexatriene affords 1,3-cyclohexadiene. Owing to ring strain in cyclobutene, this reaction gives 1,3-butadiene under thermal conditions, whereas the photochemical reaction can be tuned to drive the reaction in either direction. Most of these reactions are reversible; they are controlled by the HOMO in the ground state and the HOMO\* in the excited state.

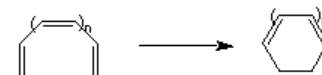


Fig. 13

To gain a better handle on the stereochemical issues involved, we need to consider some polyenes that have substituents. Figure 14 illustrates the relationship between (E,E)-2,4-hexadiene and its (E,Z)-stereoisomer to trans and cis-3,4-dimethylcyclobutene. The transformations of the (E,E)-isomer are exemplified in Fig. 15. The dotted arrows refer to endothermic processes. The HOMO of the diene in the ground state is MO  $\pi_2$  which has **A** (mirror plane) symmetry. In a thermal reaction, the terminal p-orbitals of the HOMO rotate about the dotted axes in a conrotatory (same direction) to give a bonding  $\sigma$ -bond (**S**) and a  $\pi^*$  ethylene (double bond, **A**). The cyclobutene as a whole, considering orbitals only, has **A** symmetry. As mentioned earlier, this reaction is thermodynamically unfavorable. The reverse reaction still occurs in the conrotatory mode. Note that this rotation places one methyl group on each side of the ring, a trans-dimethyl cyclobutene. When the diene is irradiated with UV light ( $\sim 225$  nm) an electron is promoted from the  $\pi_2$  HOMO to the  $\pi_3^*$  LUMO, which, because the MO is now occupied, becomes the HOMO (HOMO\*). This MO has **S** symmetry which requires disrotatory ring closure or ring opening. The ring closure produces cis-3,4-dimethylcyclobutene.

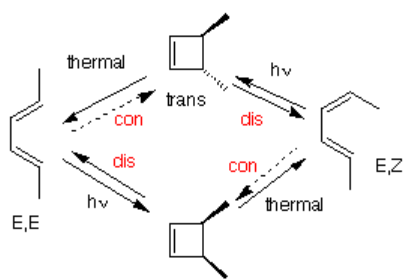


Fig. 14

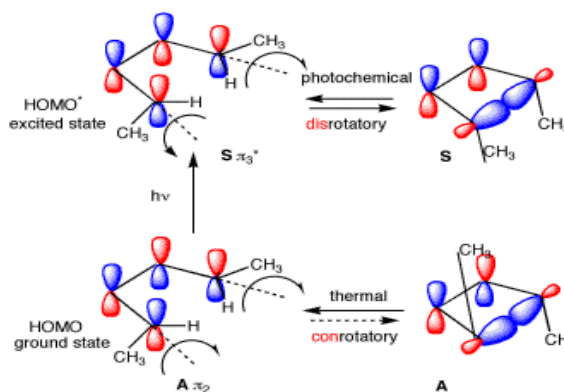


Fig. 15

Figure 16 differs from Fig. 15 in that we are now dealing with the (E,Z)- rather than the (E,E)-2,4-hexadiene. All operations are precisely the same except that cis-3,4-dimethylcyclobutene produces the (E,Z)-diene by a

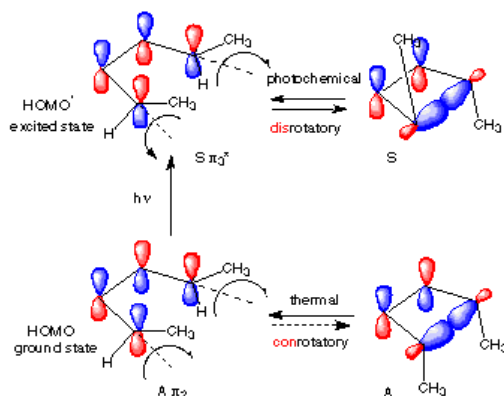


Fig. 16

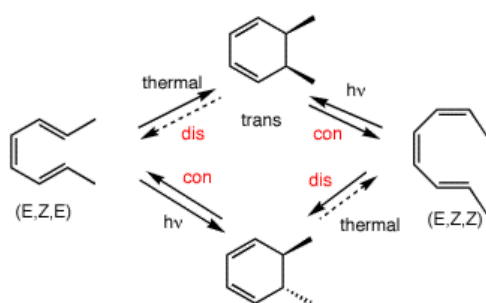


Fig. 17

The HOMO of the triene ( $\pi_3$ ) has **S** symmetry (Fig. 18). Here the terminal orbitals mirror one another, unlike the ground state HOMO of the hexadiene discussed above. Thus, the thermal reaction is now disrotatory while the photochemical reaction (**A** symmetry) is conrotatory. There is no need here to elaborate upon the fate of the (E,Z,Z)-triene except to state that the thermal reaction gives the trans-cyclohexadiene while the photochemical reaction gives the cis isomer. As with the cycloaddition reactions, a pattern arises which is contained in the following Table.

n=1,2,3...	thermal	photochemical
<b>4n</b>	con	dis
<b>4n+2</b>	dis	con

Are there any violations? "**There are none!**"

Woodward and Hoffmann, *The Conservation of Orbital Symmetry*.

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conrotatory opening, while the (E,Z)-diene/trans-3,4-dimethylcyclobutene photolysis proceeds by a disrotatory process. The following Table obtains.

	trans	cis
<b>E,E</b>	thermal	photochemical
<b>E,Z</b>	photochemical	thermal

Let's consider two trienes, --namely-- (2E,4Z,6E)-2,4,6-octatriene and (2E,4Z,6Z)-2,4,6-octatriene and their interconversion to trans and cis-5,6-dimethyl-1,3-cyclohexadiene (Fig. 17). In going from the acyclic triene to the cyclic diene a  $\sigma$ -bond is formed and a  $\pi$ -bond is broken. Because C-C  $\sigma$ -bonds are stronger than C-C  $\pi$ -bonds, the process is exothermic and driven toward the unstrained, cyclized product. Because the diene and triene have different UV maxima, irradiation of the diene at its absorption maximum (253 nm), drives the photochemical reaction toward the triene. absorption of UV light at the triene absorption maximum will drive the reaction in the opposite direction. The central bond of the triene must be of the (Z)-configuration to allow the terminal orbitals to be proximate to one another for reaction to take place.

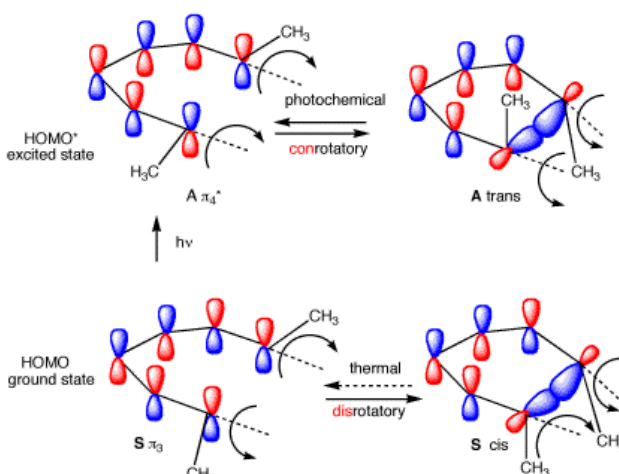


Fig. 18