LESSON IV

ANALYSIS OF PERICYCLIC REACTIONS BY CORRELATION DIAGRAM APPROACH

3.4.i) Symmetry properties of molecular orbitals

Molecular orbitals are classified according to their symmetry properties. The symmetry of these orbitals may be due to (1) mirror plane symmetry (m) and (2) two fold axis symmetry (C_2). If the molecular orbital has a mirror plane (m), perpendicular to the plane of the atoms which bi sects the molecular orbital into two halves, each of which is a mirror image of the other, it is said to have mirror plane symmetry or m-symmetry. On the other hand, if the molecular orbital has a symmetry about a two fold axis passing at right angles in the same plane, and through the centre of the frame work of the atoms forming the molecular orbitals, it is said to have a two fold axis (C_2) of symmetry. Whether the given molecule orbital has a two fold axis of symmetry or not can be readily ascertained by rotation of the molecular orbital through 180°. If the resultant molecular orbital is exactly identical with the original one, it is said to have a two fold axis of symmetry.

Let us examine the symmetry property of π-orbitals of ethylene in ground state and also in the excited state. The ground state bonding orbital (π) is symmetric (S) with respect to mirror plane (m) and anti-symmetric (A) with respect to the two fold rotation axis C_2. On the other hand, the anti-bonding orbital π^* of ethylene is anti-symmetric with respect to mirror plane symmetry and symmetric with respect to the two fold axis as shown below.
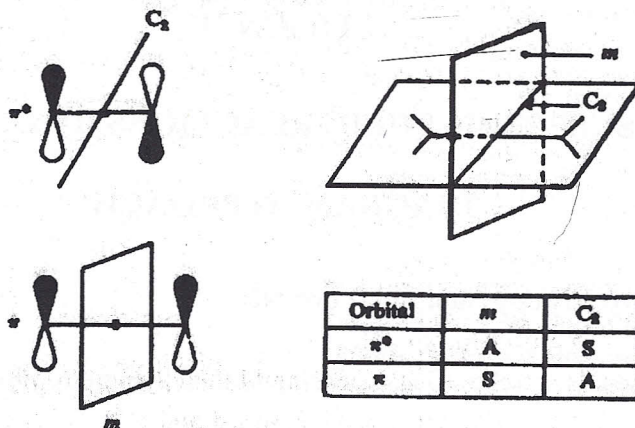
Orbital	m	C_2
π^*	A	S
π	S	A

A similar consideration leads to the following symmetry properties for the four π-molecular orbitals of 1,3-butadiene and six molecular π-orbitals of hexatriene.

Symmetry properties of π-molecular orbitals of 1,3-butadiene

Molecular orbital	Mirror plane symmetry (m)	Two-fold axis symmetry (C_2)
ψ_1	Symmetric	Antisymmetric
ψ_2	Antisymmetric	Symmetric
ψ_3	Symmetric	Antisymmetric
ψ_4	Antisymmetric	Symmetric

## Symmetry properties of the π-molecular orbitals of hexatriene

Molecular orbital	Mirror plane symmetry (m)	Two-fold axis symmetry (C_2)
ψ_1	Symmetric	Antisymmetric
ψ_2	Antisymmetric	Symmetric
ψ_3	Symmetric	Antisymmetric
ψ_4	Antisymmetric	Symmetric
ψ_5	Symmetric	Antisymmetric
ψ_6	Antisymmetric	Symmetric

Symmetry properties and nodes

In a linear conjugated π-system, the wave function φ_n has n-1 nodes. Further, it has also been noticed that whenever the value of (n-1) is zero or an even integer φ_n will be symmetric with respect to mirror plane symmetry and anti-symmetric with respect to two-fold axis symmetry. On the other hand, when n-1 is an add integer φ_n will have a two – fold symmetry but will be anti-symmetric with respect to the mirror plane symmetry.

Sigma orbital of a C-C covalent bond has a mirror plane symmetry, and since a rotation of 180° through its mid-point regenerates the same sigma orbital, it also has a C_2 symmetry. The σ^* orbital in anti-symmetric with respect to both 'm' and C_2.

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| Orbital	m	C_2
σ^*	A	A
σ	S	S
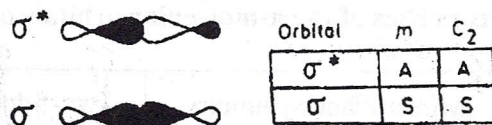
3.4.ii) Analysis of electro cyclic reactions by Correlation Diagram Approach

An electro cyclic reaction is a concerted and cyclic process in which reactant orbitals transform into product orbitals. The transition state of such reactions should be intermediate between the electronic ground states of starting material and product. Obviously the most stable transition state is the one which conserves the symmetry of the reactant orbitals in passing to product orbitals. In other words, a symmetric (S) orbital in the reactant must transform into a symmetric (S) orbital in the product and antisymmetric (A) orbital must transform into an antisymmetric (A) orbital. If the symmetries of the reactant and product orbitals are not the same, the reaction will not take place in a concerted manner.

Let us exemplify the above principle by analyzing cyclobutene-butadiene transformation. The ring opening (or ring closing) may be a disrotatory process in which the groups as saturated carbons rotate in opposite directions, or alternatively, it may be proceed (via) conrotation involving the rotation of the groups in the same direction. In the case of disrotatory ring opening, cyclobutene preserves a plane of symmetry (m), throughout the transformation while a two-fold (C_2) symmetry axis is maintained at all times in the conrotatory mode of ring opening.
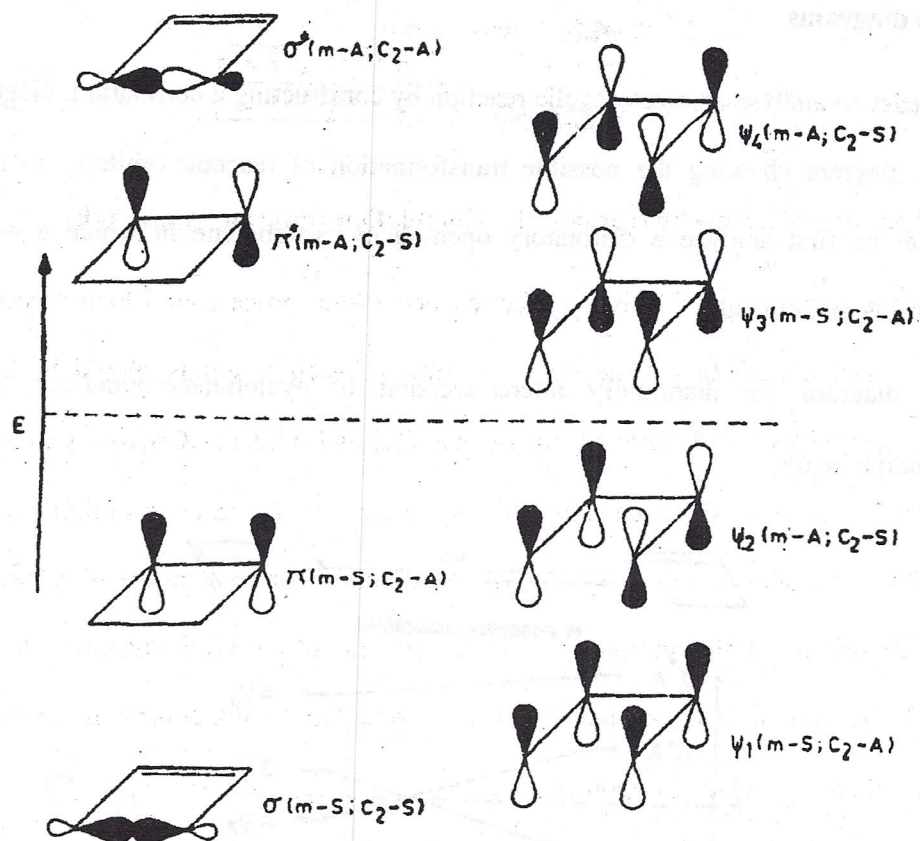
We are now set to analyze the above transformation in terms of the fundamental rule of conservation of orbital symmetry as proposed by wood ward and Hoffmann. The directly involved orbitals of the cyclobutene are σ and π and the related antibonding orbitals σ^* and π^*, these orbitals pass on to the four π molecular orbitals of butadiene viz ψ_1 ψ_2 ψ_3 ψ_4. All these orbitals are listed in the order of increasing energy in the above diagram along with their mirror plane and C_2 symmetry properties. In the ground state of cyclo butene and butadiene only σ π and ψ_1 ψ_2 are filled with electron pairs.

Correlation diagrams

It is easy to analyse an electrocyclic reaction by constructing a correlation diagram, which is simply a diagram showing the possible transformation of reactant orbitals to the product orbitals. Let us first analyze a disrotatory opening of cyclobutene in which a mirror plane symmetry (m) is maintained.

Correlation diagram for disrotatory interconversion of cyclobutene-butadiene system (m-symmetry maintained)
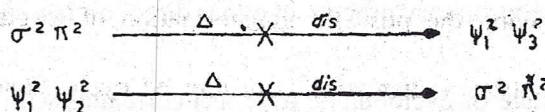

m symmetry maintained
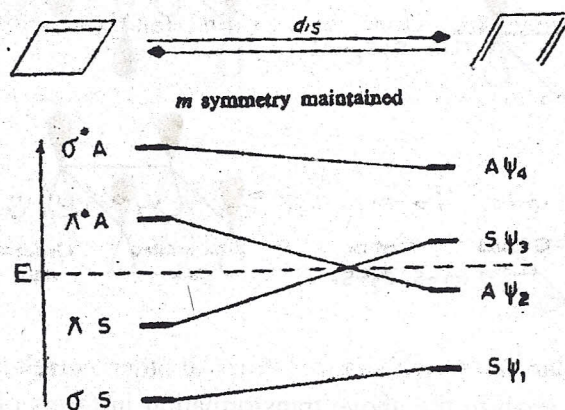
In constructing this correlation diagram we have to simply connect by lines the various orbitals of cyclo butene and butadiene keeping in view that there is correlation between orbitals of the same symmetry, having minimum energy differences. The following two conclusions can be immediately be drawn by a close inspection of such a diagram.
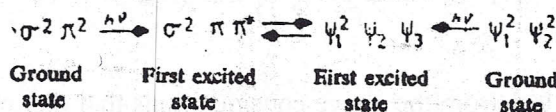
(a)   We expect a thermal transormation tc takes place only when the ground state orbitals of the reactants correlate with the ground state orbitals of the products. Although in the above diagram, the cyclobutene ground state orbital, σ, correlates with the butadiene ground state orbital, ψ_1, the π orbital of the former does not correlate with ψ_2 of latter. Instead it correlates with ψ_3

which is an excited state and an antibonding orbital. Thermal transformation of cyclobutene $\rightleftharpoons$ butediene system by disrotatory process is thus symmetry forbidden.

$$\sigma^2 \pi^2 \xrightarrow{\Delta} \cdot X \xrightarrow{dis} \psi_1^2 \psi_3^2$$

$$\psi_1^2 \psi_2^2 \xrightarrow{\Delta} X \xrightarrow{dis} \sigma^2 \overset{*}{\pi}^2$$

(b)   Irradiation of cyclo butene produces the first excited state in which an electron is promoted from π to π^* and in this case σ, π and π^* orbitals of cyclobutene correlate with ψ_1 ψ_2 ψ_3 orbitals of butadiene. In other words, the first excited state of cyclobutene correlates with the first excited state of butadiene and hence disrotatory ring opening (and ring closing_) is photochemically asymmetry allowed process

$$\sigma^2 \pi^2 \xrightarrow{h\nu} \sigma^2 \pi \pi^* \rightleftharpoons \psi_1^2 \psi_2 \psi_3 \xleftarrow{h\nu} \psi_1^2 \psi_2^2$$

| Ground | First excited | First excited | Ground |
| state | state | state | state |

Working on similar lines, we can construct another correlation diagram for the con-rotatory opening in which a C_2 symmetry is maintained through out the reaction.
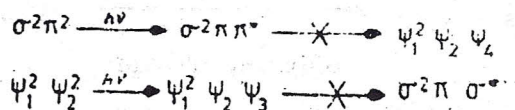

C_2 symmetry maintained
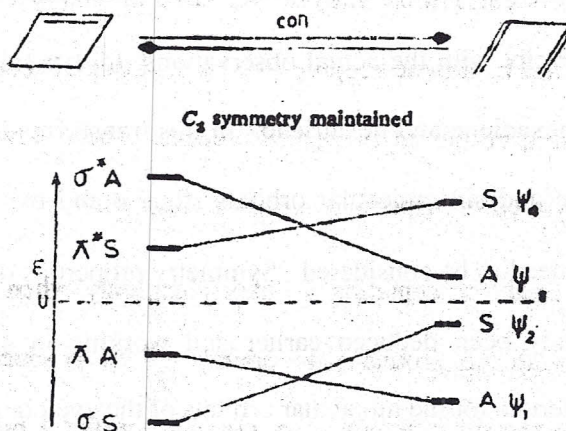
Two conclusion may be drawn from the above correlation diagram.

Since there is correlation between the ground state orbitals of cyclobutene and butadiene ($\sigma^2\pi^2 \leftrightarrows \psi_1^2\psi_2^2$) a thermal conrotatory process in either direction is a symmetry allowed process

The first excited state of cyclobutene ($\sigma^2\pi\ \pi^*$) correlates with the upper excited state ($\psi_1^2 \psi_2 \psi_4$) of butadiene thus making it a high energy symmetry forbidden process. Similarly the first excited state of butadiene ($\psi_1^2 \psi_2 \psi_3$) correlates with a high energy upper excited state ($\sigma^2\pi\ \sigma^*$) of cyclobutene. In other words, a photochemical conrotatory process in either direction is symmetry forbidden.

$$\sigma^2\pi^2 \xrightarrow{h\nu} \sigma^2\pi\pi^* \ \ -\!\!\times\!\!-\!\!\rightarrow \ \ \psi_1^2\ \psi_2\ \psi_4$$

$$\psi_1^2\ \psi_2^2 \xrightarrow{h\nu} \psi_1^2\ \psi_2\ \psi_3 \ \ -\!\!\times\!\!-\!\!\rightarrow \ \ \sigma^2\pi\ \sigma^*$$

Thus it becomes clear from the above considerations that thermal oopening of cyclobutene proceeds in a conrotatory process while photochemical interconversion involves a disrotatory mode. These generalisations are true for all the systems containing $4\ n\ \pi$ electrons where n = 0, 1, 2, etc. However for systems containing $(4n+2)\ \pi$ electrons theoretical prediction is entirely different and is in conformity with the actual observations. A typical system of this type is the interconversion of cyclohexadiene and hexatriene. In this transformation. Six molecular orbitals ($\psi_1 - \psi_6$) of heaxa triene and six molecular orbitals (four π and two σ) of cyclohexadiene are actually involved and so need to be considered. Symmetry properties of the six molecular orbitals of hexatriene have already been deduced earlier and working in similar lines, we have the following symmetry properties for the molecular orbitals of the cyclohexadiene.

## Symmetric properties of molecular orbitals of cyclohexadiene

	m	C_2
σ^*	A	A
π_4	A	S
π_3	S	A
π_2	A	S
π_1	S	A
σ	S	S

The correlation diagram for disrotatory pathway is constructed in the same way as in the case of cyclobutene-butadiene transformation.


m symmetry maintained
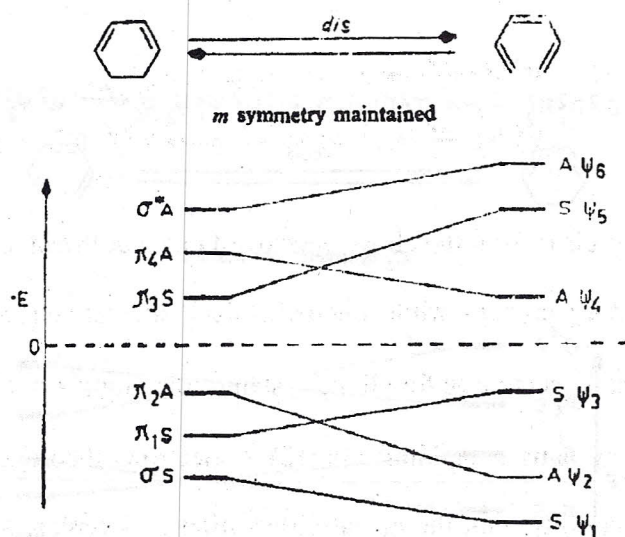
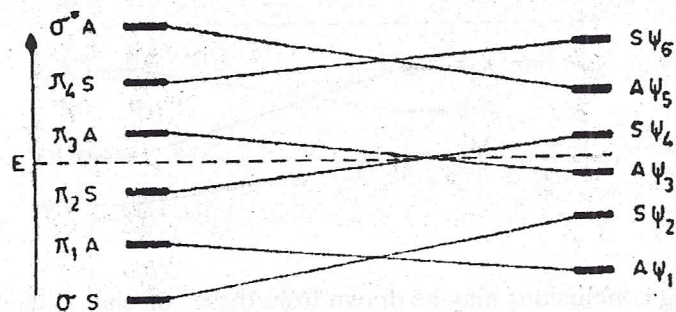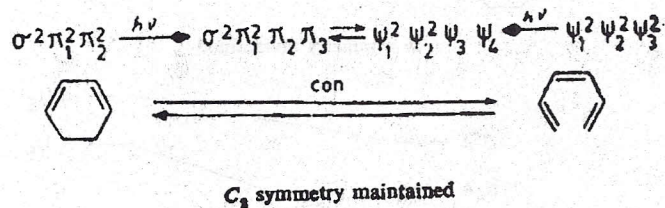The following conclusions may be drawn from these correlation diagrams.

(a)   In the disrotatory mode (m-symmetry) ground state bonding orbitals of cyclohexadiene correlate with the ground state bonding orbitals of hexatriene and so it is a thermally allowed process.

$$\sigma^2 \pi_1^2 \pi_2^2 \xrightarrow{\Delta \ . \ dis} \psi_1^2 \psi_2^2 \psi_3^2$$
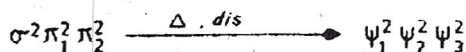
(b)   But in the conrotatory mode (C_2 symmetry) ground state bonding orbitals of cyclo hexadiene do not correlate with the ground state bonding orbitals of hexatriene (fig. below) since the presence of two electrons in ψ_4 is a very high energy process, a conrotatory mode is prohibited under the thermal conditions.

$$\sigma^2\,\pi_1^2\,\pi_2^2 \quad \xrightarrow{\quad \Delta \quad} \!\!\times\!\! \xrightarrow{\text{con}} \quad \psi_1^2\,\psi_2^2\,\psi_4^2$$
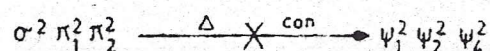
(c)   However if we promote an electron to π_3 orbital in cyclohexadiene (obviously by irradiation) then the orbitals of the reactant with C_2 symmetry correlate with the first excited state of the product.

$$\sigma^2\pi_1^2\pi_2^2 \xrightarrow{h\nu} \sigma^2\pi_1^2\,\pi_2\,\pi_3 \rightleftharpoons \psi_1^2\,\psi_2^2\,\psi_3\,\psi_4 \xleftarrow{h\nu} \psi_1^2\,\psi_2^2\psi_3^2$$

C_2 symmetry maintained

Therefore, photochemical interconversion is symmetry allowed in conrotatory pathway. These generalisations are true for all the systems containing $(4n + 2)$ π electrons, when $n = 0., 1, 2$ etc. Thus Woodward and Hoffmann rules for electrocyclic reactions may be summed up in the form of table

Number of π electrons	Thermal	Photochemical
4n	con	dis
4n + 2	dis	con

Woodword and Hoffman have further explained that under severe thermal conditions, symmetry forbidden reations may takes place but then they follow non-concentrated path and their energy of activation is 10-15 Kcal/mole higher than those of symmetry allowed reactions. It is because of this energy difference that most of the electrocyclic reactions follow Woodward and Hoffmann rules.

3.4.iii) Analysis of cycloaddition reactions by correlation diagram approach

In the construction of orbital correlation diagram, caution is exercised in choosing the symmetry elements. A symmetry element must bisect bond formed or broken in the process and symmetry element is useless if the orbitals involved in the reactions are all symmetric or all antisymmetric.

To illustrate the control of orbital symmetry on cycloaddition reactions, we choose the simplest example in which the two ethylene molecules approach each other vertically (π^2S+ π^2S) to the form of a molecule of cyclobutane. Such a system has vertical and horizontal planes of symmetry which are referred to as 1 and 2, respectively.
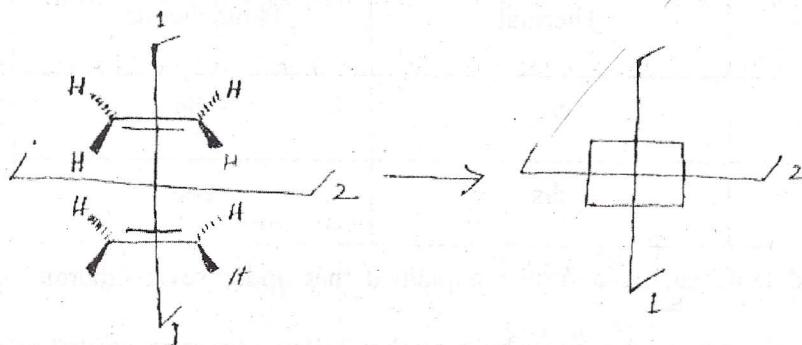
In the above transformation we are mainly concerned with the 4 π orbitals of the two ethylene molecules and the four σ orbitals of cyclo butane.
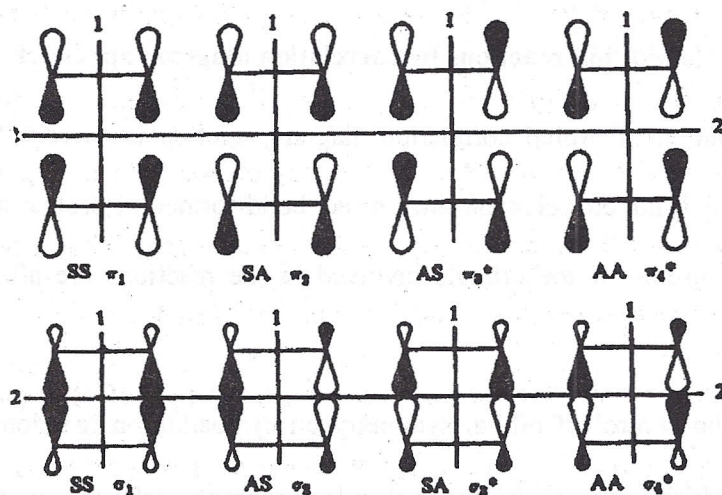
The shapes and symmetrical properties of these four π orbitals (π_1, π_2 bonding; π_3^*, π_4^* antibonding) and four σ orbitals (σ_1, σ_2 bonding; σ_3^*, σ_4^* antibonding) have been illustrated in the above fig. symmetry classifications (SS, SA, AS and AA) with respect to the plane of symmetry 1 are given first nd with respect to 2 next.

On the basis of the above information, a correlation diagram may be drawn in which the reactant and product orbitals of like symmetry having minimum energy differences are connected by lines.
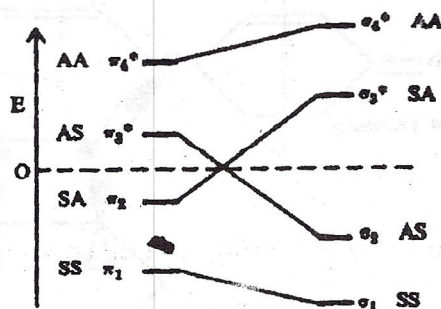

A close examination of the diagram leads us to the following two conclusions.

1.   The ground state orbitals of ethylene correlate with an excited states of cyclobutane, π_1^2, $\pi_2^2 \leftrightarrows \sigma_1^2$, σ_3^2*. Consequently, the combination of two ground state ethylene molecules cannot result in the formation of ground state cyclobutane while conserving the orbital symmetry. Hence the thermal process is symmetry-forbidden.

2.   As there is correlation between the first excited state of the ethylene system and cyclobutane π_1^2, $\pi_2 \pi_3* \leftrightarrows$ σ_1^2, $\sigma_2 \sigma_3*$, the photochemical process is symmetry-allowed.
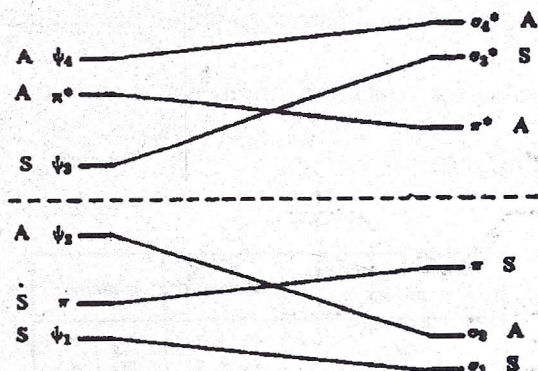
A similar correlated diagram may be constructed for the Diels Alder reaction which is $\pi^4s + \pi^2s$ cyclo addition reaction. In this case there is only a single vertical plane of symmetry bisecting carbon frame work of two reactants and the product.
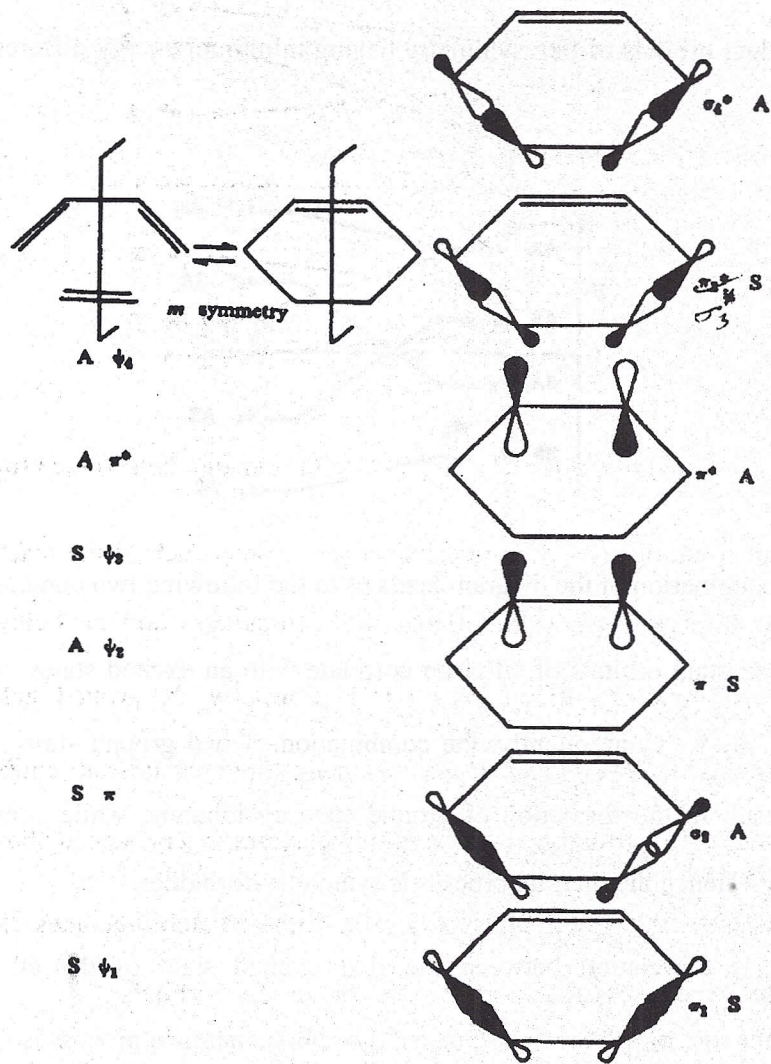
Butadiene and ethylene
π-MOs with symmetry
properties

Cyclohexene orbitals with
symmetry properties

Correlation an dia gram for $\pi 4S + \pi 2S$ cycloaddition and the reverse process.

In this transformation we have to consider six orbitals each of the reactants and products. The ground state orbitals of the reactants are $\psi_1 \psi_2$ (of Butadiene) and π (of ethylene) while ψ_3, π^* and ψ_4 are the corresponding antibonding orbitals. Similarly, the ground state orbitals of cyclo hexene are represented by σ_1, σ_2 and π; the remaining three orbitals are antibonding. All these orbitals and symmetry properties and the correlation diagram is represented above.

From the inspection of the above diagram it immediately becomes clear that there is a smooth transformation of the reactant orbitals into the product orbitals.

$$\psi_1^2 \pi^2 \psi_2^2 \rightleftharpoons \sigma_1^2 \sigma_2^2 \pi^2$$
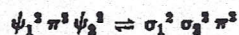
The Diels-Alder reaction ($\pi^4 s + \pi^2 s$ cyclo addition) is, therefore, a thermally allowed process. On the other hand, photochemical transformation is not possible as the first excited state of the reactant does not correlate with the first excited state of the product. Rather it correlates with the upper excited state of the product

$$\psi_1^2 \pi^2 \psi_2 \psi_3 \xrightarrow{\;\;\times\;\;} \sigma_1^2 \sigma_2^2 \pi \pi^*$$
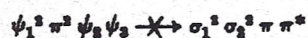
Hence there is symmetry-imposed barrier to photochemical reactions of $(\pi^4 s + \pi^2 s)$ type. The generalised selection rules for concerted (m+n) cyclo addition reactions are shown below where q is an integer including zero.

Number of electrons $m+n$	Δ allowed	hv allowed
$4q$	$m_s + n_a$ $m_a + n_s$	$m_s + n_s$ $m_a + n_a$
$4q + 2$	$m_s + n_s$ $m_a + n_a$	$m_s + n_a$ $m_a + n_s$

It should be noted that sometimes formal correlation diagrams cannot be drawn as in the case of concerted (4s + 2a) and (6s + 2a) cyclo addition, even though the former is forbidden and the latter allowed under thermal conditions.

Model Questions:

1. Write the shapes and symmetry properties of 6 molecular orbitals of cyclohexene.

2. Construct a correlation diagram for disrotatory inter conversion of cyclobutene – Butadiene system and predict whether the reaction is allowed thermally or photochemically.

3. Construct a correlation diagram for conrotatory inter conversion of cyclohexadiene – Hexatriene system and predict whether the reaction is allowed thermally or photochemically.

4. By constructing a correlation diagram predict whether $\pi^2 S + \pi^2 S$ cyclo addition reaction is allowed thermally or photochemically.

5. Construct a correlation diagram for Diels Alder reaction and predict whether the reaction is allowed thermally or photochemically.

Recommend books

1. Conservation of orbital symmetry by R.B. Woodward.

2. Pericyclic reactions by S.M. Mukherji.

3. Pericyclics and photochemistry by Mukherji.