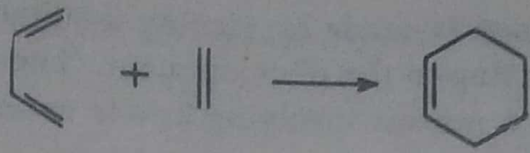
14.3 Cycloaddition Reactions: Correlation Diagram and FMO Method

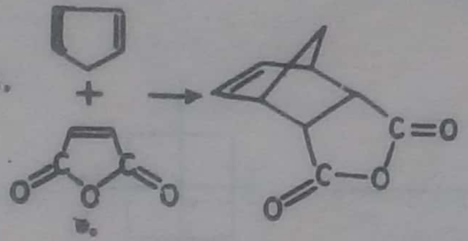
The most familiar example of a cycloaddition reaction is the Diels-Alder reaction which involves the formation of a cyclic compound from an alkene and a diene.

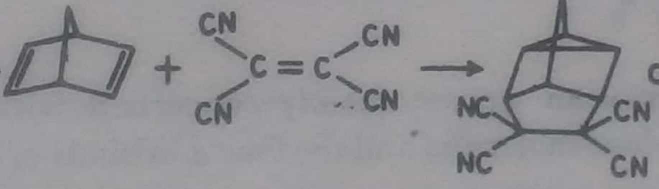


These reactions consist in the addition of a system of m π electrons to a system of n π electrons thereby forming a cyclic product They offer a versatile route to the synthesis of cyclic compounds with a high degree of stereo-selectivity under thermal and photochemical conditions. Depending upon the number of π electrons participating in the process, these reactions are termed $(m+n)$ or $(m+n+...)$ cycloaddition reactions.

1. 
2+2 Cycloaddition

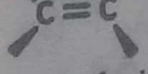
2. 
2+4 Cycloaddition

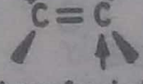
3. 
2+4 Cycloaddition

4. 
2+2+2 Cycloaddition

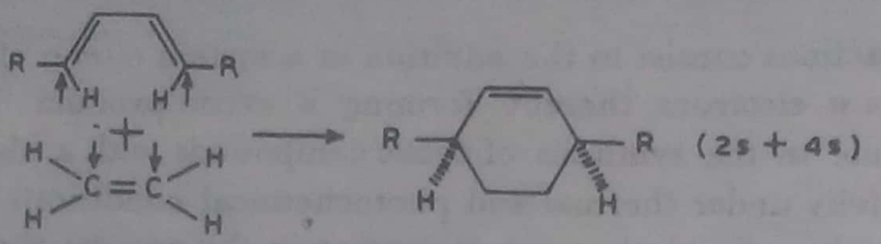
14.3.1 STEREOCHEMICAL MODES OF CYCLOADDITION: SUPRAFACIAL AND ANTARAFACIAL PROCESSES

Since in a typical cycloaddition reaction, there is addition of two systems containing double bonds, it is logical to expect the addition to occur on the same or the opposite side of the system. Furthermore, as both the π systems are undergoing addition, it is necessary to specify these modes of addition on each of them. These different modes have been termed *suprafacial* (on the same side) and *antarafacial* (on the opposite side).


suprafacial


antarafacial

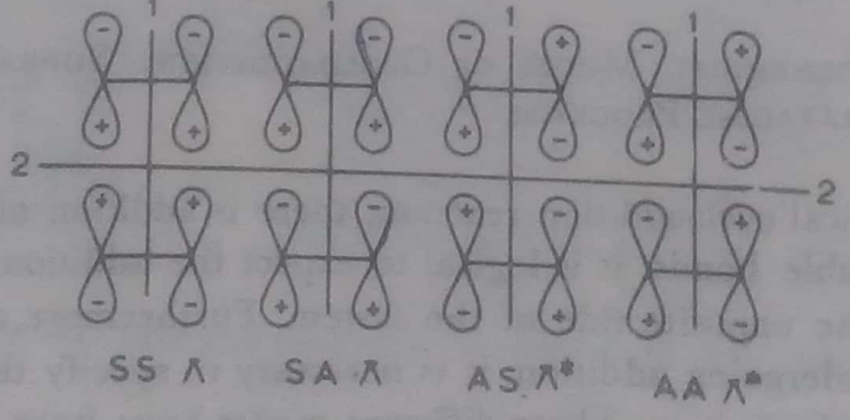
This specification is usually made by placing a suitable subscript (*s* or *a*) after the number referring to the pi component. The Diels-Alder reaction may be considered as a process involving $2s+4s$ cycloaddition.

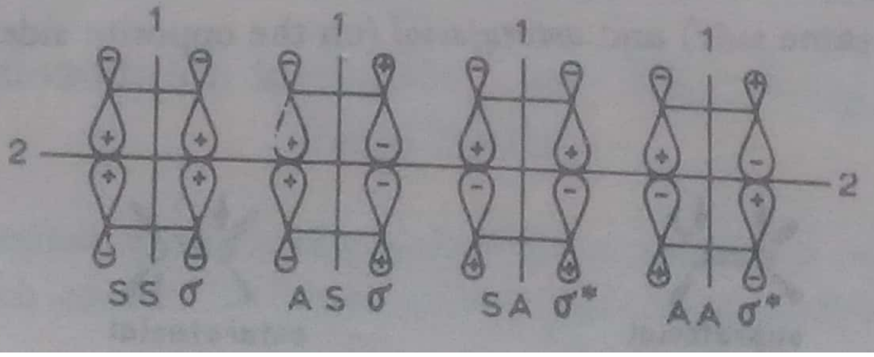


14.3.2 ORBITAL SYMMETRY IN CYCLOADDITION REACTION: CORRELATION DIAGRAMS

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 ($2s+2s$) to form a molecule of cyclobutane. Such a system has vertical and horizontal planes of symmetry which shall be referred to as 1 and 2, respectively.

In the above transformation we are mainly concerned with the four π orbitals of the two ethylene molecules and the four σ orbitals of cyclobutane.





The symmetry properties of the remaining orbitals remain unchanged during the reaction and need not be considered further. The shapes and symmetry properties of these four π orbitals (π, π bonding; π^*, π^* anti-bonding) and four σ orbitals (σ, σ bonding; σ^*, σ^* antibonding) are listed in Fig. 14.10. The symmetry classifications (*SS*, *SA*, *AS* and *AA*) are with respect firstly to plane of symmetry 1 and then to 2.

On the basis of the above information, a correlation diagram (Fig. 14.11) may be drawn in which the levels of like symmetry are connected by lines.

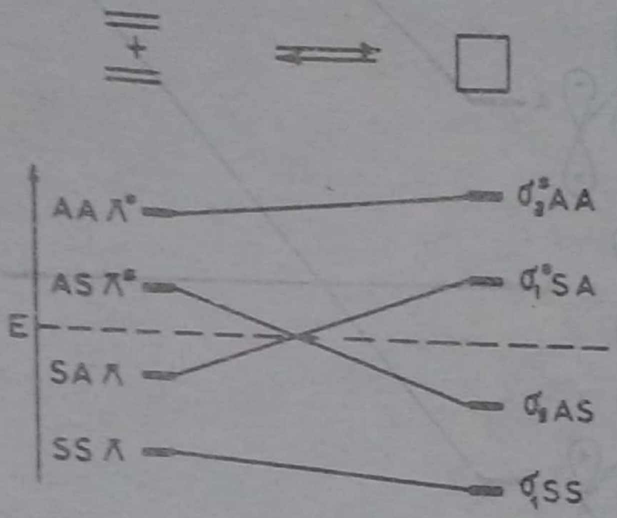


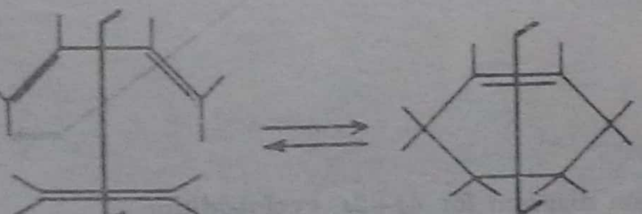
Fig. 14.11 Correlation diagram for cycloaddition and cycloreversion of ethylene-cyclobutane system

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

A. The ground state orbitals of ethylene correlate with an excited state of cyclobutane, $\pi^2\pi^2 \leftrightarrows \sigma_1^2\sigma_1^{*2}$. 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.*

B. As there is correlation between the first excited state of the ethylene system and cyclobutane, $\pi^2\pi\pi^* \leftrightarrows \sigma_1^2\sigma_2\sigma_1^*$, the photochemical process is *symmetry-allowed.*

A similar correlation diagram may be constructed for the Diels-Alder reaction which is a $4s+2s$ cycloaddition reaction. In this case there is only a single vertical plane of symmetry bisecting the carbon framework of two reactants and the product.



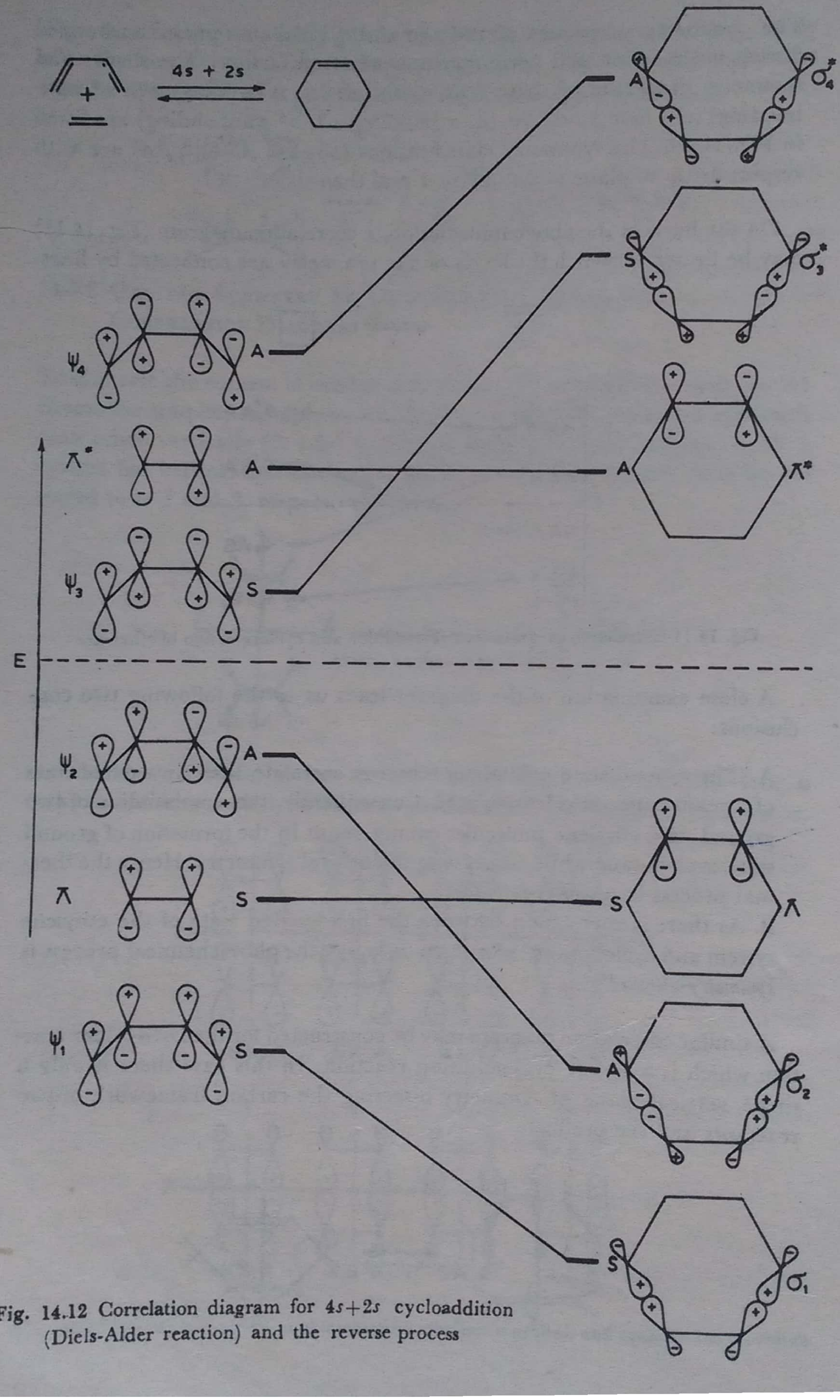


Fig. 14.12 Correlation diagram for $4s+2s$ cycloaddition (Diels-Alder reaction) and the reverse process

In this transformation, we have to consider six orbitals each of the reactants and the product. 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 cyclohexene are represented by σ_1, σ_2 and π; the remaining three orbitals are antibonding. All these orbitals along with their symmetry properties are shown in the correlation diagram (Fig. 14.12).

It becomes immediately clear from an inspection of the above diagram that there is a smooth transformation of the reactant orbitals into the product orbitals.

$$\psi_1^2\pi^2\psi_2^2 \longrightarrow \sigma_1^2\sigma_2^2\pi^2$$

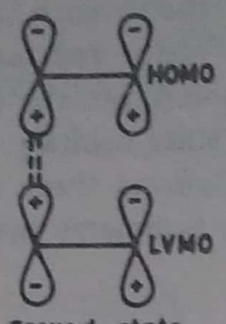
The Diels-Alder reaction ($4s+2s$ cycloaddition) is, therefore, a *thermally allowed process*. On the other hand, photochemical transformation is not possible as the first excited state of the reactant does not correlate with the first excited state of the product. Rather it correlates with the upper excited state of the product.

$$\psi_1^2\pi^2\psi_2\psi_3 \xrightarrow{\times} \sigma_1^2\sigma_2^2\pi\sigma_3^*$$

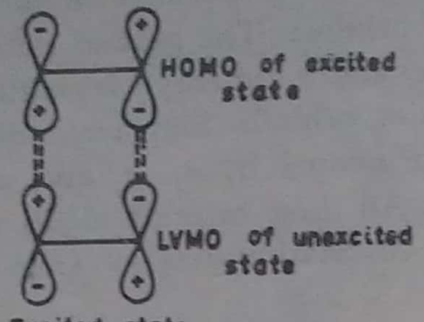
Hence there is a symmetry-imposed barrier to photochemical reaction of ($4s+2s$) type.

14.3.3 FRONTIER MOLECULAR ORBITAL (FMO) METHOD

An alternative approach to determine whether or not a cycloaddition reaction is allowed depends upon the symmetry properties of the *highest occupied molecular orbital* (HOMO) of one reactant and the *lowest vacant molecular orbital* (LVMO) of the other. A favourable interaction is possible only when the signs of the coefficients of HOMO and LVMO are the same. In the $2s+2s$ cycloaddition of ethylene to form cyclobutane, lobes of HOMO in one molecule and that of LVMO in the other do not have corresponding signs and hence the reaction is thermally forbidden. Irradiation of ethylene, however, promotes an electron to the antibonding orbital which now becomes HOMO and corresponds with the LVMO of the second unexcited ethylene molecule. As expected, the combination now proceeds smoothly.

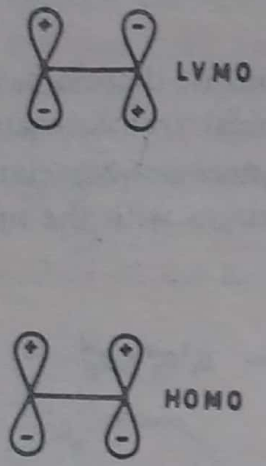


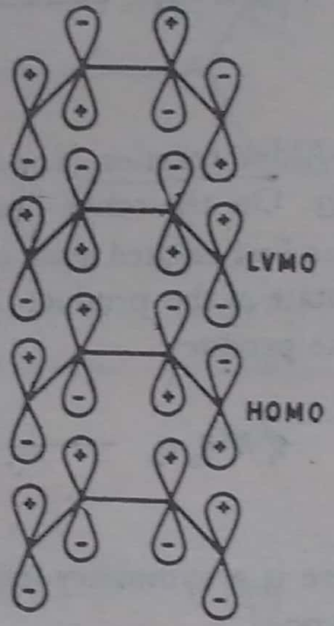
Ground state
(Δ forbidden)



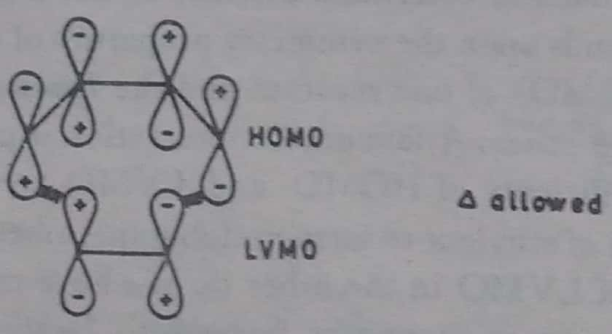
Excited state
(hν allowed)

The Diels-Alder reaction may also be analyzed by a similar consideration of the molecular orbitals of ethylene and butadiene.

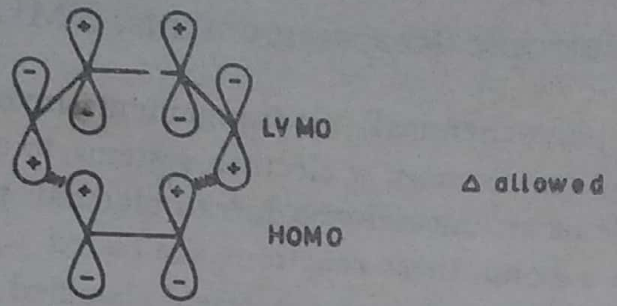




Since signs of the 1, 4-lobes of butadiene HOMO match those in the LVMO of ethylene, the addition is thermally allowed.



We reach a similar conclusion by considering the signs of butadiene LVMO and HOMO of ethylene.



No such correspondence is obtained by the irradiation of the reactants and consequently the Diels-Alder reaction is a photochemically forbidden process.

An interesting example of the role of frontier orbitals in determining the roduct is the Diels-Alder reaction of cyclopentadiene forming dicyclopentadiene. Invariably, the *endo* dimer is formed rather than the *exo*. This is due to the favourable secondary forces as a result of interaction of frontier orbitals of diene and dienophile components which lower the energy of the transition state. In the following figure (Fig. 14.13) orbitals involved in actual bonding are connected by full lines and the secondary interactions shown by broken lines. An inspection of the transition states reveals that these interactions are present in the *endo* transition state while they are absent in the *exo*. Thus, the *endo* transition state for this reaction is stabilized *vis-a-vis* the *exo* and, therefore, the *endo* attack should be favoured. However, in some cases steric factors may be of a greater magnitude than this effect.

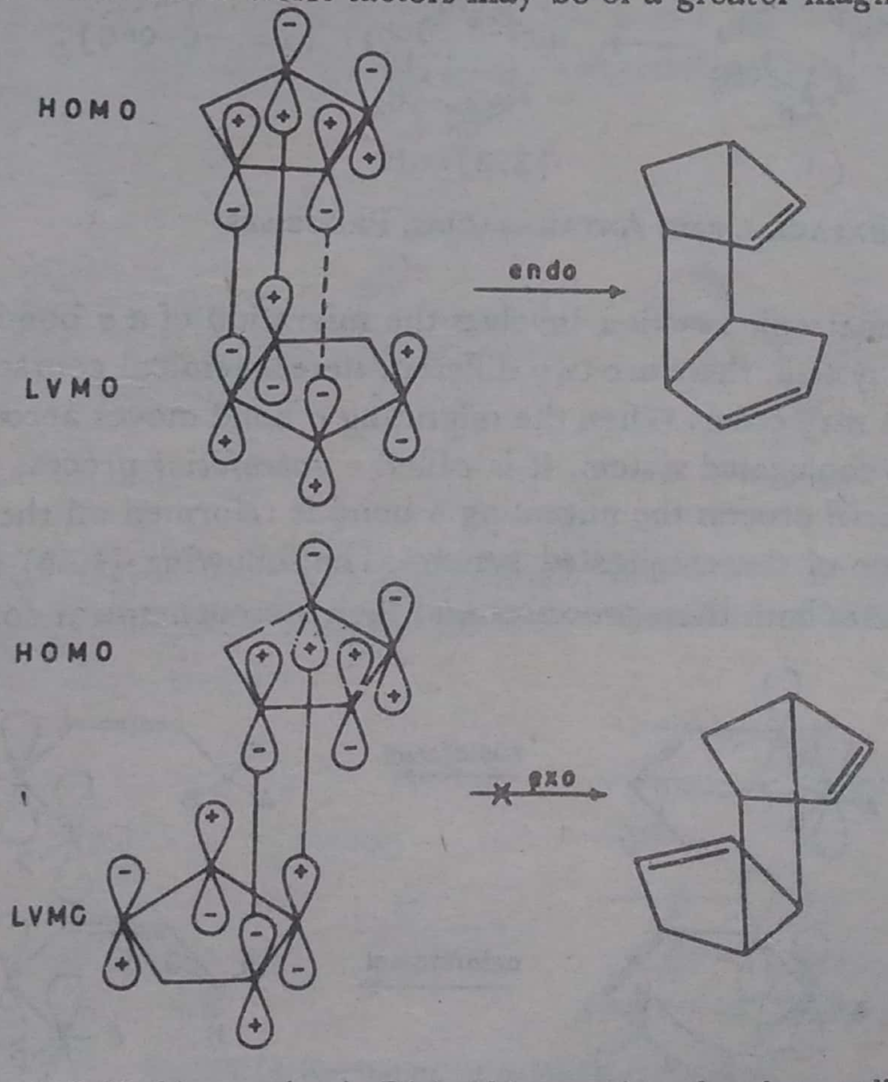


Fig. 14.13 Orbital interaction in Diels-Alder reaction of cyclopentadiene

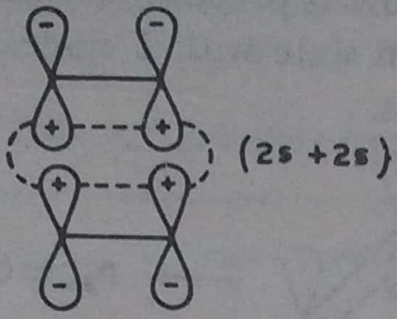
14.5 Applications of PMO Method to Pericyclic Reactions

There is yet another qualitative molecular orbital approach developed by M. J. S. Dewar which yields simple mnemonics to predict the same stereochemical variations in pericyclic reactions as do the other methods.

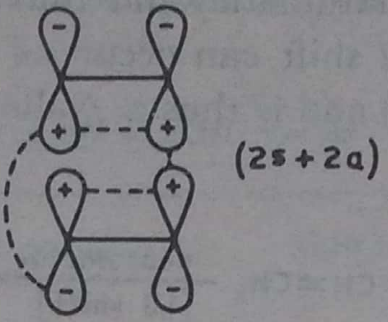
Huckel's rule of aromaticity states that a monocyclic planar conjugated system with $(4q+2)$ π electrons is *aromatic* and consequently stable in the ground state. A system with $(4q)$ π electrons is unstable and is referred to as *antiaromatic*. However, further calculations show that these rules are reversed by the presence of a node in the array of atomic orbitals. In other words, systems with $(4q+2)$ π electrons and a node are antiaromatic while systems with $(4q)$ π electrons and a node are aromatic and hence stable (in theory) in the ground state. Application of these rules to per-

B. Cycloaddition

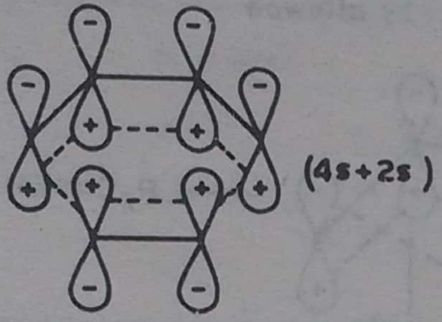
The transition-state for 2*s*+2*s* cycloaddition has 4 electrons with zero node, and is therefore antiaromatic, and hence the reaction is thermally forbidden.



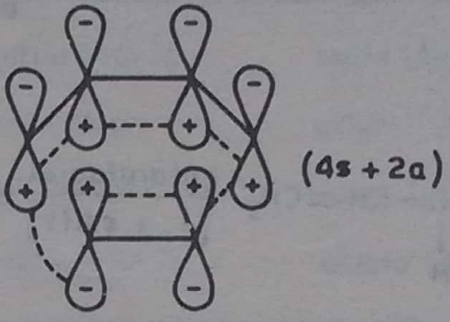
0 node, 4 electrons
antiaromatic, hν allowed



1 node, 4 electrons
aromatic, Δ allowed



0 node, 6 electrons
aromatic, Δ allowed



1 node, 6 electrons,
antiaromatic, hν allowed

Thus we come to the same conclusions as by other methods. The selection rules for cycloadditions are summarized in Table 14.8.

Table 14.8: Selection rules for cycloadditions and cycloreversions by PMO method

$m+n$ electrons	number of nodes	aromaticity	Δallowed	$h\nu$ allowed
$4q$	0 or even	antiaromatic	—	*supra-supra* *antara-antara*
$4q$	odd	aromatic	*supra-antara* *antara-supra*	—
$4q+2$	0 or even	aromatic	*supra-supra* *antara-antara*	—
$4q+2$	odd	antiaromatic	—	*supra-antara* *antara-supra*

q is an integer