(4n + 2) (4n̄ + 2) (4n)

2.7 HÜCKEL-MOBIUS (H-M) METHOD OR PMO (PERTURBATION MOLECULAR ORBITAL) METHOD

Another method for quickly assessing whether a given pericyclic process is allowed is to examine the cyclic array of orbitals at the transition state of the pericyclic reaction. This method was popularised by H. Zimmerman and M.J.S Dewar.

Hückel rule of aromaticity states that a monocyclic planar conjugated system is aromatic if it has $(4n + 2)$ π conjugated or delocalised electrons and consequently stable in ground state. Similarly monocyclic planar conjugated system is anti-aromatic if it has $(4n)$ π conjugated or delocalised electrons. This system is unstable in ground state. However further calculation shows that these rules are reversed by the presence of a node in the array of atomic orbitals. Thus system with $(4n + 2)$ π electrons and a node is antiaromatic while system with $(4n)$ π electrons and a node is aromatic.

Thus system has no node then:

$(4n + 2)\pi$ electrons → Aromatic → Stable in ground state

$(4n)\pi$ electrons → antiaromatic → unstable in ground state

Similarly system having a node then

$(4n)$ π electron → aromatic → stable in ground state

$(4n + 2)$ π electrons → antiaromatic → unstable in ground state.

If system has no node then it is called Hückel system and array is called Hückel array. Similarly if system has node then it is called Mobius system and array is called Mobius array. Application of these rules to pericyclic reactions led to the generalisation that thermal reactions take place via aromatic transition state [*i.e.* $(4n + 2)$ π electrons having no node or $(4n)$ π electrons having one node] where as photochemical reactions proceed via antiaromatic transition state [*i.e.* $(4n)$π electrons having no node or $(4n + 2)$ π electrons having one node].

A cyclic transition state is said to be aromatic or isoconjugated with corresponding aromatic system if the number of the conjugated atoms and that of the pi electrons involved are the same as in the corresponding aromatic system. Similarly, a cyclic transition-state is said to be antiaromatic or isoconjugated with the corresponding antiaromatic system if the number of conjugated atoms and that of the *pi* electrons involved are the same as in the corresponding antiaromatic system. We have only to consider a cyclic array of atomic obitals representing those orbitals which undergo change in the transition state and assign signs to the wave function in the best manner for overlap. Then the number of nodes in the array and number of electrons involved are counted.

Let us consider the following electrocyclic reaction (Fig. 13 and Fig. 14).

Cis-1, 3, 5-hexatriene ⇌ cyclohexadiene

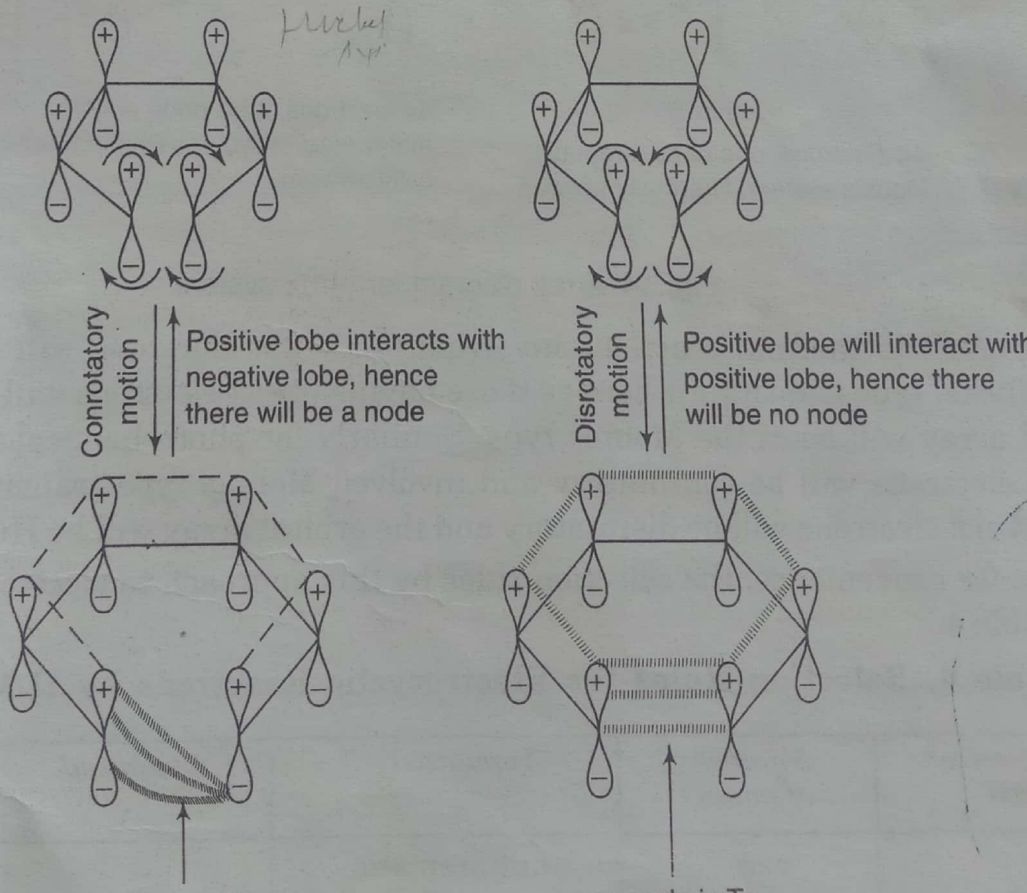

Fig. 13 Array diagram for (4n + 2)π system.

Similarly for

1,3-Butadiene ⇌ cyclobutene

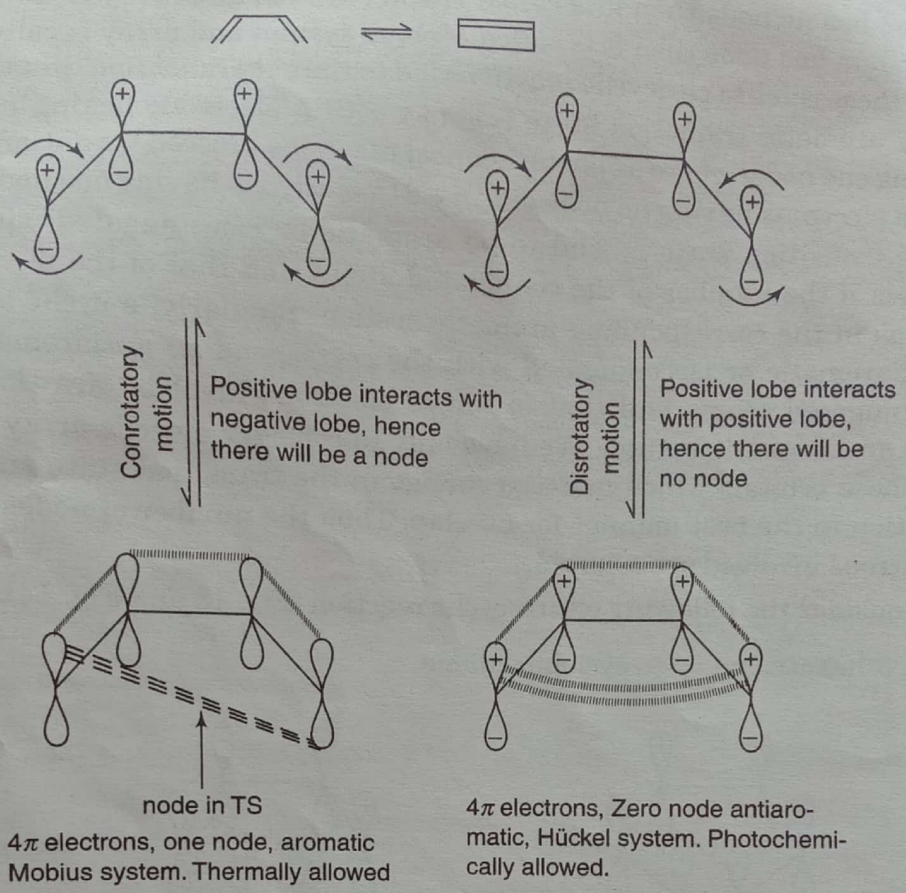

Fig. 14 Array diagram for (4n)π system.

Thus for the thermal reactions involving $(4n + 2)\pi$ electrons will be disrotatory and involved Hückel type transition where as those having $(4n)$ π electrons will be conrotatory and the orbital array will be of the Mobius type. Similarly for photochemical reactions involving $(4n + 2)$ π electrons will be conrotatory and involved Mobius type transition whereas those involving $(4n)$ π electrons will be disrotatory and the orbital array will be Hückel type.

Thus for convenience, the selection rules by this approach to electrocyclic reactions are given in Table 4.

Table 4. Selection Rules for Electrocyclic Reactions by H.M. Method

Array of π electrons involved	*Number of nodes*	*Aromaticity*	*Δ allowed*	*hν allowed*
$4n$	zero	antiaromatic	—	disrotatory
$4n$	one	aromatic	conrotatory	—
$(4n + 2)$	zero	aromatic	disrotatory	—
$(4n + 2)$	one	antiaromatic	—	conrotatory