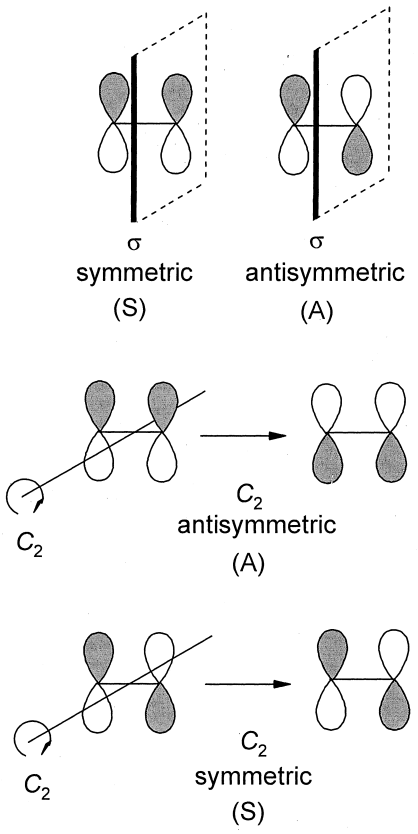


Figure 1.9 Symmetry properties of the MOs of ethylene.

1.4.5 Group Transfer Reactions:

These reactions are characterized by the transfer of a group or groups from one molecule to another molecule in a concerted manner.

All of the above types of pericyclic reactions can be considered in the broad category of cycloaddition reactions. However, it is advantageous to consider them individually for the sake of clarity.

1.5 Methods of Analyzing Pericyclic Reactions:

There are three common methods used for the analysis of pericyclic reactions.

1. The Orbital symmetry correlation method (developed by Woodward and Hoffmann and also by Longuet-Higgins and Abrahamson).

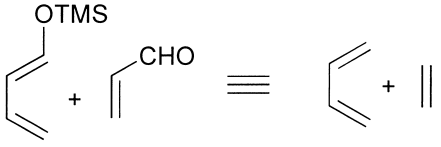
2. The frontier orbital method (developed initially by Woodward and Hoffmann and later by Fukui).
3. The transition state aromaticity method (developed by Dewar and Zimmerman).

1.5.1 Orbital Symmetry Correlation Method:[5]

In this method the MOs corresponding to the bonds being formed and broken during the reaction are considered. Their symmetry properties with respect to the elements of symmetry that are present throughout the course of the reaction are identified. Then a correlation diagram is drawn by matching the symmetry of the MOs of the starting material to that of the product MOs. While doing so attention is paid to the fact that the non-crossing rule is not violated, i.e., orbitals of the same symmetry must not cross in the correlation diagram. If the symmetry of the MOs of the starting material in the ground state electronic configuration is correlated with that of the product in the ground state, then the reaction is thermally symmetry allowed. On the other hand if the symmetry of the MOs of the starting material in the excited electronic state is correlated with that of the product, then the reaction is photochemically symmetry allowed. While constructing an orbital correlation diagram the following points need to be considered.

1. *Each reacting system must be reduced to its highest inherent symmetry by the removal of all substituents.*

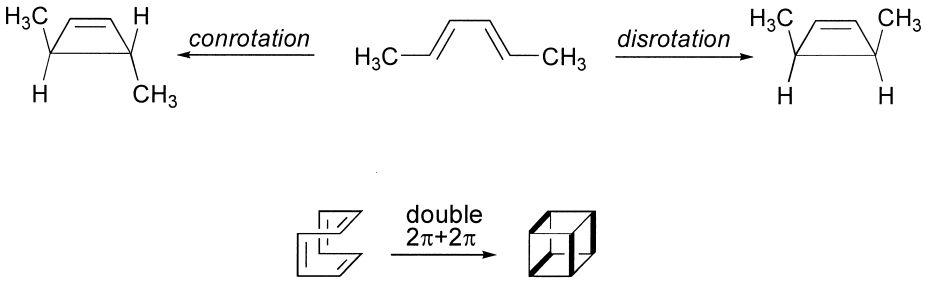
For example, while analyzing the cycloaddition reaction between 1-trimethylsilyloxybuta-1,3-diene and acrolein, the system is reduced to butadiene and ethylene (Scheme 1.1). Substituents affect only the electronic energy levels and coefficients of MOs and not the symmetry properties of the MOs.



Scheme 1.1 Reactant molecules reduced to their highest symmetry for a cyclo-addition reaction.

2. *Processes that are independent must be considered separately even if they occur in the same molecule.*

For example hexa-2,4-diene is capable of undergoing electrocyclic ring closure in two modes, namely the conrotatory and the disrotatory modes (Scheme 1.2). These two processes need to be considered as independent from the point of view of symmetry correlation. Similarly, consider the hypothetical double 2π+2π cycloaddition of cyclooctatetraene to cubane (the newly formed sigma bonds are indicated by thick lines). Each of the two cycloaddition processes has to be considered separately for the construction of the orbital correlation diagram. *If two independent processes are considered together for the construction of the orbital correlation diagram the outcome can be erroneous.*



Scheme 1.2 Processes that are independent occurring in the same molecule.

3. *The symmetry element used for the analysis must bisect the bonds that are made or broken during the reaction.*

For the 2π+2π cycloaddition of ethylene to cyclobutane in the suprafacial-suprafacial mode only the planes that bisect the π bonds and the newly formed sigma bonds in cyclobutene constitute symmetry planes (Figure 1.10). The two planes containing the ethylene units are not to be considered as symmetry elements for the cycloaddition process. Similarly, for the Diels-Alder reaction of butadiene with ethylene in the suprafacial-suprafacial mode the plane bisecting the two π systems alone is the symmetry element (Figure 1.10).

4. *The chosen symmetry element(s) should be present throughout the reaction i.e., through the entire process of starting material going to product through the transition state.*

5. *Orbitals of the same symmetry do not cross, as required by the non-crossing rule.*

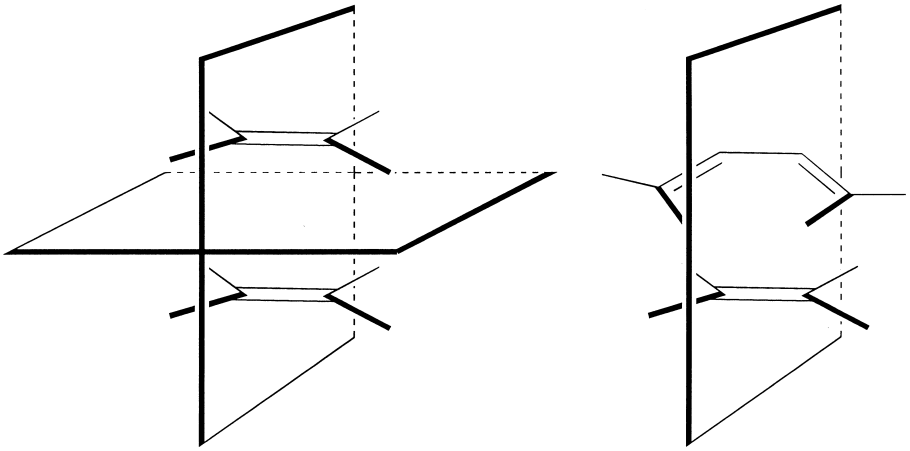


Figure 1.10 Symmetry planes for the [2+2] and [4+2] cycloaddition reactions in the suprafacial-suprafacial mode.

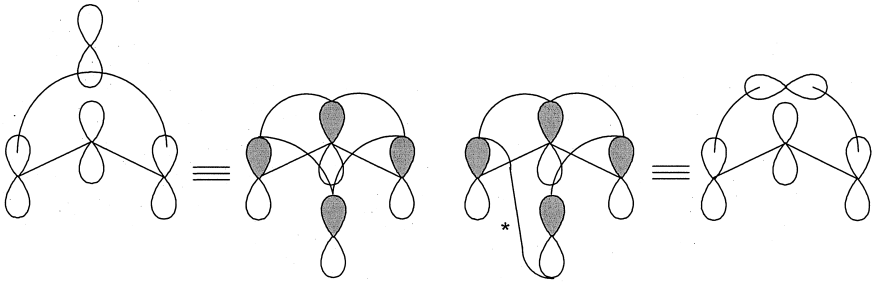
1.5.2 Frontier Orbital Method:[6]

Frontier orbitals of a system are comprised of the pair of the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). For example, the π MO of ethylene is the HOMO of ethylene and the π^* level is the LUMO in the ground state electronic configuration. In the case of the excited state of butadiene, π_3 is the HOMO and π_4 is the LUMO (Figure 1.6). Pericyclic reactions can be analyzed by the interaction of the HOMO and LUMO of the reacting systems. When two reacting systems are separated by an infinite distance their MOs are unperturbed by each other. When they approach sufficiently close to each other, their MOs begin to interact. MOs that are close in energy interact more strongly than others. The interaction of two filled MOs does not lead to any net stabilization of the system. It is the interaction of

one filled MO with an unfilled MO that leads to the net stabilization of the system. Hence it is the interaction of the HOMO of one of the reacting system with the LUMO of the other reacting system that is considered in this method of analysis. If the interaction of the two MOs is of the bonding type in the ground state electronic configuration, then we call the reaction thermally allowed. If the HOMO-LUMO interaction leads to anti-bonding interaction in the ground state electronic configuration then the reaction is thermally disallowed.

1.5.3 Transition State Aromaticity Method: [7]

In this method a cyclic pathway of the interacting orbitals of the reacting systems in the transition state is constructed. This is called the interaction diagram and it depicts sets of basis orbitals and not molecular orbitals. After the construction of the interaction diagram algebraic signs are assigned to the orbital lobes so as to minimize the number of phase inversions. The following examples illustrate the construction of orbital interaction diagrams for the [1,3] shift by suprafacial and antarafacial modes (Figure 1.11), for [2π+2π] and [4π+2π] cycloadditions by supra-supra and supra-antara modes (Figure 1.12). The star (*) indicates the phase inversion where the signs of the orbital lobes change along the interaction. (The term suprafacial implies that



[1,3] suprafacial shift

[1,3] suprafacial shift – 4e Hückel type antiaromatic transition state

[1,3] antarafacial shift – 4e Möbius type aromatic transition state

[1,3] antarafacial shift

Figure 1.11 Orbital interaction diagram for [1,3] suprafacial and antarafacial shifts.

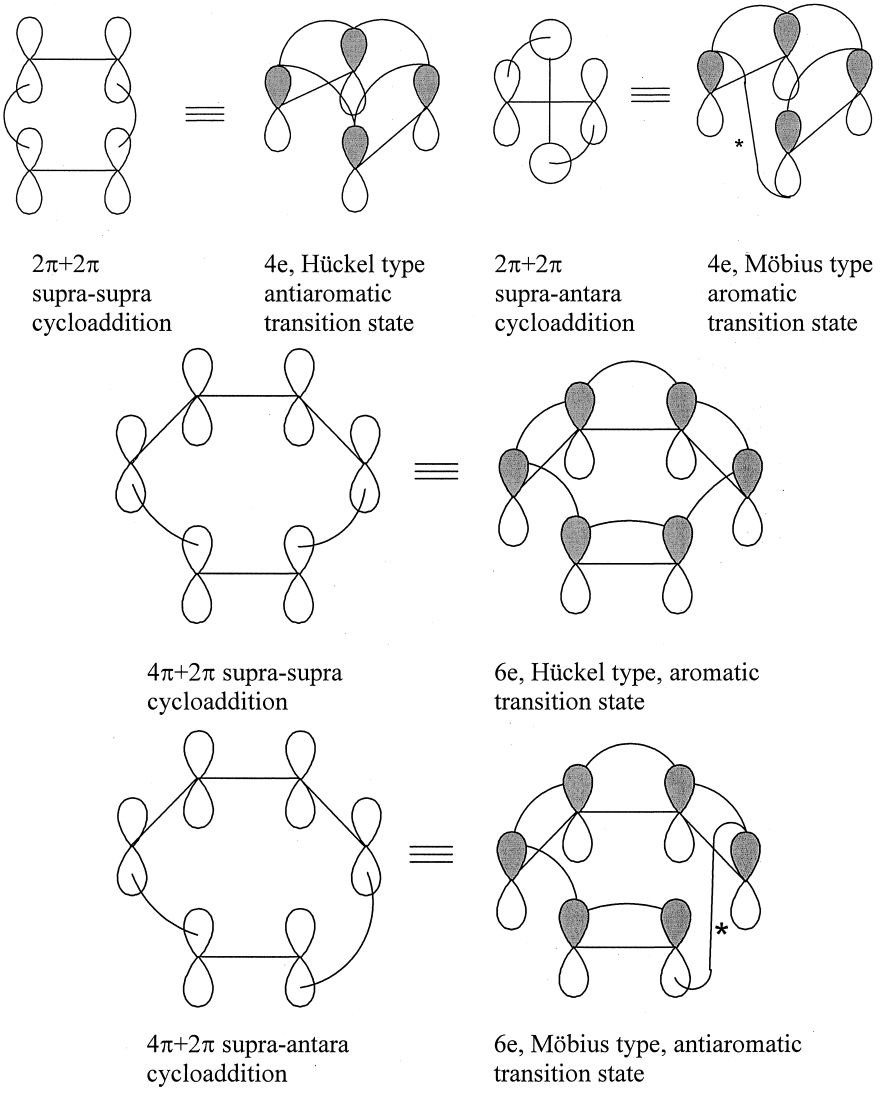


Figure 1.12 Orbital interaction diagrams for cycloaddition reactions.

with respect to a molecule the orbital lobes of that molecule interact from the same face. The term antarafacial implies that the lobes from opposite faces interact. For a detailed description of these terms, refer to Chapter 3, Sec. 3.3 for cycloaddition reactions and Chapter 4 for sigmatropic reactions). Those orbitals having zero phase inversions are classified as Hückel type rings. These have a continuous strip of a closed loop of orbitals without a twist in them. Those having one phase inversion are

classified as anti-Hückel type and they are like the Möbius strip with a twist in the closed loop of orbitals. The allowedness or the disallowedness of the reactions is predicted as follows. For Hückel ring systems with $4n+2$ electrons in the transition state the reaction is thermally allowed in the ground state. For $4n$ electron systems the reaction is thermally forbidden in the ground state. For an anti-Hückel system containing $4n$ electrons, the reaction is thermally allowed and for the $4n+2$ electron system the reaction is thermally forbidden in the ground state.

Table 1.1 Woodward-Hoffmann rules based on the transition state aromaticity method.

No. of phase inversion	Ring type	No. of electrons	Allowedness
zero	Hückel	4n+2 (aromatic) 4n (antiaromatic)	Thermally allowed Thermally forbidden
one	Möbius	4n (aromatic) 4n+2 (antiaromatic)	Thermally allowed Thermally forbidden

According to Dewar and Zimmerman the basic criterion for deciding whether a given process is allowed or forbidden depends upon the stabilization or destablilization of the cyclic transition state in comparison with the open chain system. The aromatic or the anti aromatic character of the ground state decides the stabilization or the destabilization of the systems, which in turn is decided by the number of electrons in the system.[8]

References:

1. For further reading on molecular orbital theory
   (a) A. Streitweiser Jr., *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, **1961**.
   (b) M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw Hill, New York, **1969**.
   (c) M. J. S. Dewar, R. C. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, **1975**.
   (d) W. T. Borden, *Modern Molecular Orbital Theory for Organic Chemists*, Prentice- Hall, Engelwood Cliffs, New Jersey, **1975**.
   (e) For a pictorial representation of molecular orbitals W. L. Jorgensen, L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, **1973**.
2. (a) T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 2nd Edition, Harper and Row, New York, **1981**, pp. 70 - 78.
   (b) M. J. Goldstein, R. Hoffmann, *J. Am. Chem. Soc.*, **1971**, *93*, 6193 - 6204.
3. For further reading on symmetry, operations, point groups etc.
   (a) H. H. Jaffe, M. Orchin, *Symmetry in Chemistry*, Wiley, New York, **1965**.
   (b) E. Heilbronner, J. D. Dunitz, *Reflections on Symmetry*, VCH, Weinheim, **1993**.
   (c) E. L. Eliel, S. H. Wilen, L. N. Molander, *Stereochemistry of Organic Compounds*, John Wiley, New York, **1994**, Chapter 4, pp. 71 - 99.
   (d) D. Nasipuri, *Stereochemistry of Organic Compounds*, 2nd Edition, Wiley Eastern, New Delhi, **1994**, Chapter 2, pp. 15 - 26.
4. (a) R. B. Woodward, R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, **1971** and Academic Press, New York, **1970**.
   (b) R. B. Woodward, R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **1969**, *8*, 781 - 853.
   (c) R. E. Lehr, A. P. Marchand, *Orbital Symmetry, A Problem-Solving Approach*, Academic Press, New York, **1972**.
   (d) A. P. Marchand, R. E. Lehr, (Eds.), *Pericyclic Reactions*, Academic Press, New York, Vol. 1 and 2, **1977**.
   (e) I. Fleming, *Pericyclic Reactions*, Oxford University Press, Oxford, **1999**.

(f) L. Gilchirst, R. C. Storr, *Organic Reactions and Orbital Symmetry*, 2nd Edition, Cambridge University Press, Cambridge, **1979**.

5. (a) R. Hoffmann, R. B. Woodward, *J. Am. Chem. Soc.*, **1965**, *87*, 2046 - 2048.
   (b) R. Hoffmann, R. B. Woodward, *Acc. Chem. Res.*, **1968**, 1, 17 - 22.
   (c) H. C. Longuet-Higgins, E. W. Abrahamson, *J. Am. Chem. Soc.*, **1965**, *87*, 2045 - 2046.
6. (a) I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, John Wiley, New York, **1976**, Chapter 2, pp. 5 - 32.
   (b) K. Fukui, *Acc. Chem. Res.*, **1971**, *4*, 57 - 64.
   (c) R. B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.*, **1965**, *87*, 395 - 397.
   (d) K. N. Houk in *Pericyclic Reactions*, A. P. Marchand, R. E. Lehr (Eds.), Academic Press, New York, **1977**, Vol. 1, Chapter 4, pp. 182 - 266.
7. (a) M. J. S. Dewar, *Angew. Chem. Int. Ed. Engl.*, **1971**, *10*, 761 - 870.
   (b) M. J. S. Dewar, *Tetrahedron Suppl.8*, **1966**, 75 - 92.
   (c) H. E. Zimmerman, *J. Am. Chem. Soc.*, **1966**, *88*, 1564 - 565.
   (d) H. E. Zimmerman in *Pericyclic Reactions*, A. P. Marchand, R. E. Lehr (Eds.), Academic Press, New York, **1977**, Vol.1, Chapter 2, pp. 53 -106.
8. (a) For a generalized selection rule for pericyclic reactions, known as the Odd-Even Rule see F. C. He, G. V. Pfiffer, *J. Chem. Edu.*, **1984**, *61*, 948 - 951.
   (b) For the analysis of pericyclic reactions using MO following method see H. E. Zimmerman, *Acc. Chem. Res.*, **1972**, *5*, 393 - 401.