

Frontier Orbitals Aromaticity: A Simple Approach to the Analysis of Pericyclic Reactions[†]

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Dedicated to Professor H. Firouzabadi, one of the founders of Ph.D. program in organic chemistry in Iran on the occasion of his 65th birthday and also his retirement.

A new and simple approach to the analysis of pericyclic reactions based on combination of the interaction of HOMO-LUMO molecular orbitals and Huckel-Mobius aromaticity concept in transition state is reported. This approach seems to be more powerful than the Woodward-Hoffmann approach which appears to be limited to reactions with sufficiently high symmetry, and the Huckel-Mobius that use the non-participating lowest basis set (Ψ_1). One important impact of the current approach is its capability in addressing the photochemical concerted reactions.

Keywords: Frontier orbitals aromaticity, Pericyclic reactions, Huckel-Mobius aromaticity, Aromaticity, Cycloaddition.

INTRODUCTION

An important class of concerted reactions is the pericyclic reactions [1,2]. Three major approaches have been developed for the complete mechanistic description of these reactions controlled by orbital symmetry: (i) orbital correlation diagrams, or conservation of orbital symmetry (ii) frontier orbital concept, and (iii) incipient aromatic of basic set molecular orbitals (MO) character in transition state.

The definitive rules developed by Woodward and Hoffmann [1-6] based on the conservation of orbital symmetry are of great interest to organic chemists. To predict whether a chemical reaction is symmetry allowed or disallowed, one requires knowledge of symmetry properties of the molecular orbital of the reactants and products and

also their relative energies to construct a MO correlation diagram. Although, this approach explains the presently known reactions and it has great predictive power on the hitherto unstudied reactions, the analysis of concerted reactions with this approach is very hard in complicated systems and therefore, it can not be practically applied to such systems. Moreover, the correlation diagram criteria are not employed in interpretation of sigmatropic reactions, in which the reaction path has no usable symmetry character.

There is another useful viewpoint of concerted reactions that is based on the frontier molecular orbitals (FMO) concept or HOMO-LUMO interaction [7-11]. It can be applied to various processes which has been mentioned and discussed by Woodward and Hoffmann. This approach presents an extremely simple and practical method to interpret or predict the course of thermal and photochemical concerted reactions.

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Nevertheless this method is general in character, it is particularly suitable for the interpretation of rather complicated reactions such as intramolecular rearrangements, to which the correlation diagram method is not always directly applicable. While superficially attractive, this approach is not really the transition state itself. It only applies to the early stages of the interaction orbitals [12]. On the other hand, it explains the possibility of the reaction based on MO of reactants without attention to the transition state.

The final approach is the aromaticity concept [13,14]. The analysis of concerted reactions by this approach consists of examining the array of orbitals that would be present in transition state and classifying the system as aromatic or antiaromatic. A stabilized aromatic transition state will lead to a low activation barrier, that is, an allowed reaction. An antiaromatic transition state that results in a high energy barrier corresponds to a forbidden reaction. The simplicity of applying this concept on concerted reactions is very important, but this approach focuses attention on the orbital symmetry of the basic set MO's (Ψ_1), that can not practically participate in reactions. In addition, the selection rule for cycloaddition reactions considers the interaction of the Ψ_1 's of the reactants that are both occupied.

As is clear from the explanations provided, the simple FMO method suffers from the lack of attention to the transition state, as an important concept in chemistry. Considering the fact that transition state has an important role on all the reactions, a question that may arise is: "could the two latter approaches be combined together to generate a new approach?" which able to the analysis of pericyclic reactions based on transition state.

In the present work, I wish to develop a new approach based on combination of FMO and Huckel-Mobius aromaticity concept, which it explains the property of pericyclic reactions based on both HOMO-LUMO interaction and the transition state concept. This new approach is called the Frontier Orbitals Aromaticity (FOA) throughout the paper.

RESULTS AND DISCUSSION

In Huckel's system (zero or even number of phase changes around the orbital array) if there is $4n+2$ electrons in a cyclic polyene, this compound will have aromatic and hence, stability. On the other hand, systems with $4n$ electrons are said

to be antiaromatic and therefore, unstable. Contrarily in Mobius system (odd number of phase changes) with $4n$ electrons would have aromatic stability, whereas those with $4n+2$ electrons would be antiaromatic [Scheme 1].



Scheme 1. Hypothetical π systems with Huckel (left) and Mobius (right) topology.

Having such general understanding of the current approach, let us first see how FOA concept is applied to the pericyclic reactions. The frontier orbitals are drawn as in the case of FMO. Then, those connection pathways would be accepted that result in the formation of aromatic or antiaromatic transition state, either Huckel or Mobius. It is noticed that the same-sign orbitals in this approach are not necessarily connected to each other anymore. Also, one has to be careful in accounting the number of sign inversion because it may occur both between two orbitals to be connected or two orbitals already been connected.

Let us now apply this approach to a number of pericyclic reactions. These reactions are investigated under thermal reaction conditions, first, and then corresponding photochemical reactions will be discussed.

A: Pericyclic reactions under thermal reaction conditions

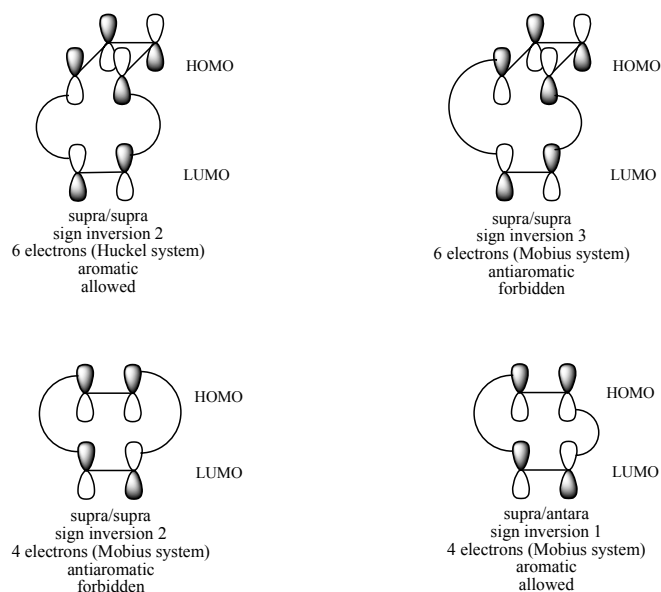
A-1: Cycloaddition reactions

As indicated in Scheme 2, in $4n+2$ systems, supra/supra interactions are thermally allowed while the fragments in $4n$ systems are connected to each other in supra/antara manner.

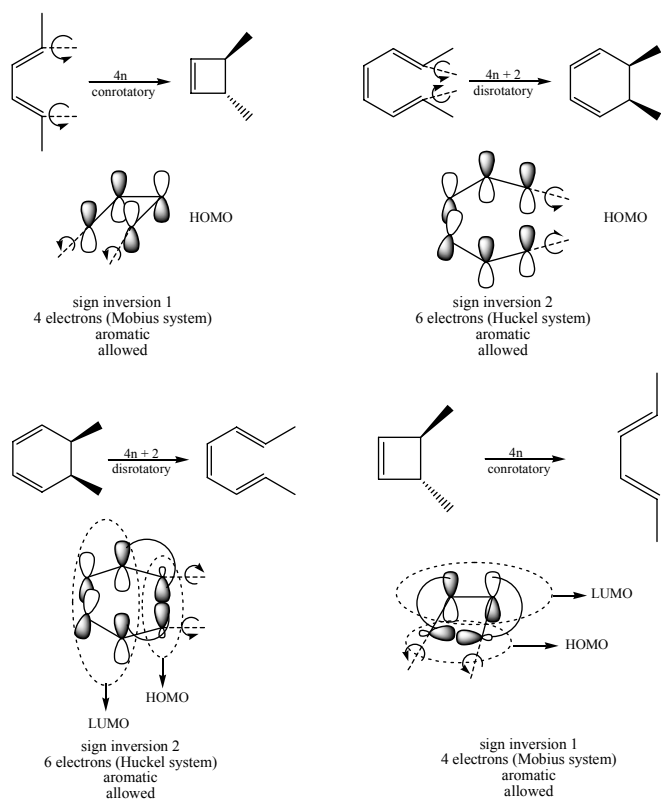
A-2: Electrocyclic reactions

The conrotatory cyclization of butadiene and its derivatives and disrotatory of hexatriene and its derivatives are allowed processes as compared to disrotatory cyclization of butadiene and its derivatives and conrotatory of hexatriene and its derivatives. These have been shown in Scheme 3.

Frontier Orbitals Aromaticity: A Simple Approach to the Analysis



Scheme 2. Investigation of cycloaddition reactions by the FOA method under thermal reaction conditions.

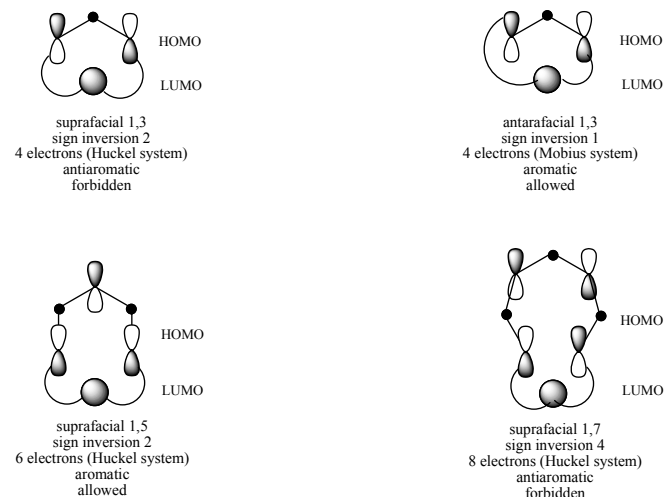


Scheme 3. Investigation of electrocyclic reactions by the FOA approach under thermal reaction conditions.

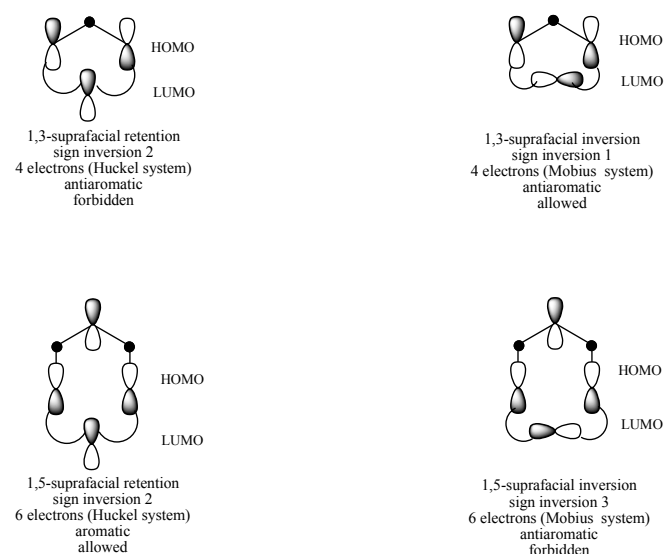
A-3: Sigmatropic reactions

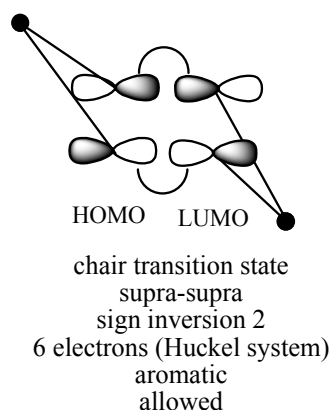
Example of sigmatropic shift of hydrogen, alkyl and allyl are illustrated in Scheme 4.

A-3-1: H-shift



A-3-2: Alkyl-shift [1, j]



A-3-3: Allyl-shift [3,3]

Scheme 4. Investigation of sigmatropic hydrogen, alkyl and allyl shift by the FOA approach under thermal reaction conditions.

A-5: Ene reactions

As shown in Scheme 6 an ene reaction take place between ethylene and propylene in supra/supra fashion.

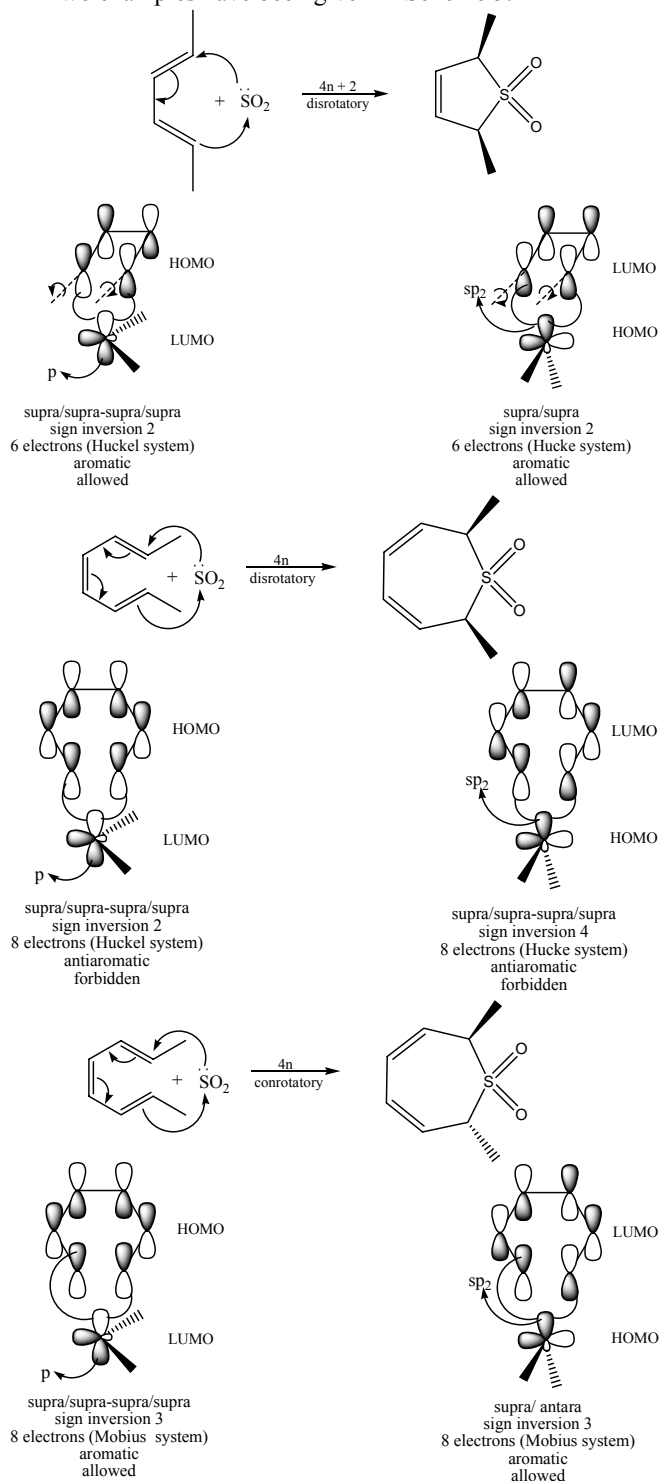
B: Pericyclic reactions under photochemical conditions

A number of pericyclic reactions take place photochemically, usually with consequences different from those of analogous thermal reactions. Light must therefore play some role other than that of merely providing energy to overcome an activation barrier. In contrast to the thermal reactions which prefer aromatic or stable transition state, photochemical reactions prefer antiaromatic or less stable transition state. This is the case because a controlling factor in photochemical processes is conversion of excited state reactants into ground state products. In other words, the photochemical reactions tend to lead to the conversion of the reactants into the antiaromatic transition states that correspond to forbidden thermal pericyclic reactions and so lead to corresponding products [15-17].

Since the photochemical pericyclic reactions prefer antiaromatic transition states, we can formulate the following rule: photochemical pericyclic reactions prefer Möbius geometric when $(4n+2)$ electrons are involved and Huckel geometric when $4n$ electrons are involved.

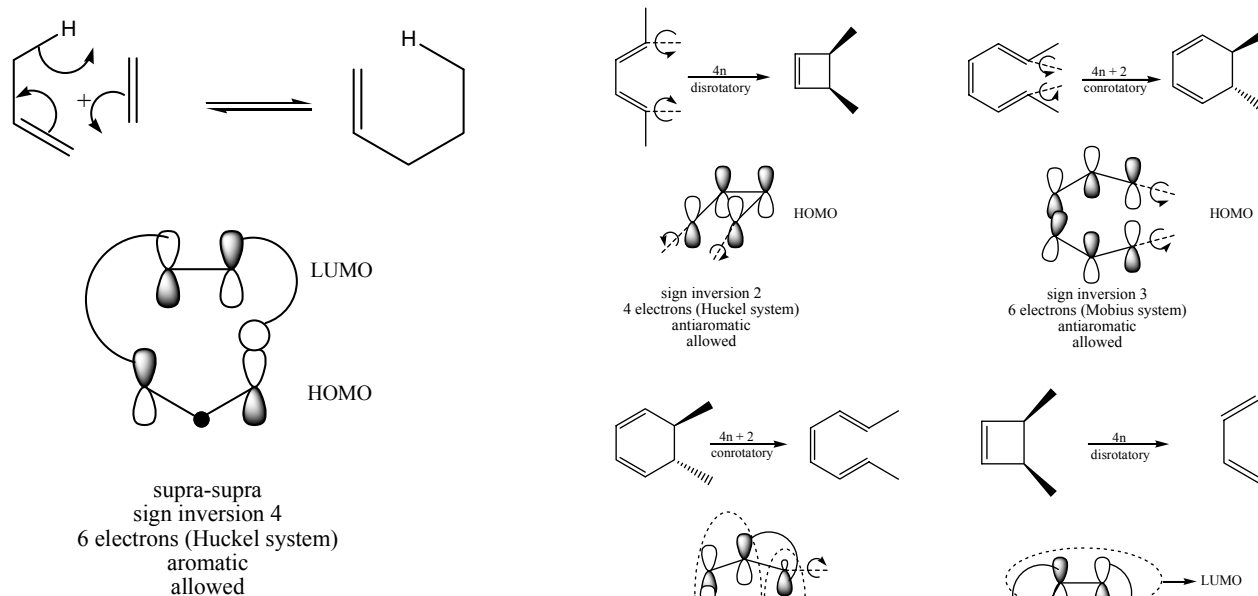
A-4: Chelotropic reactions

Two examples have been given in Scheme 5.



Scheme 5. Investigation of chelotropic reactions by the FOA approach under thermal reaction conditions.

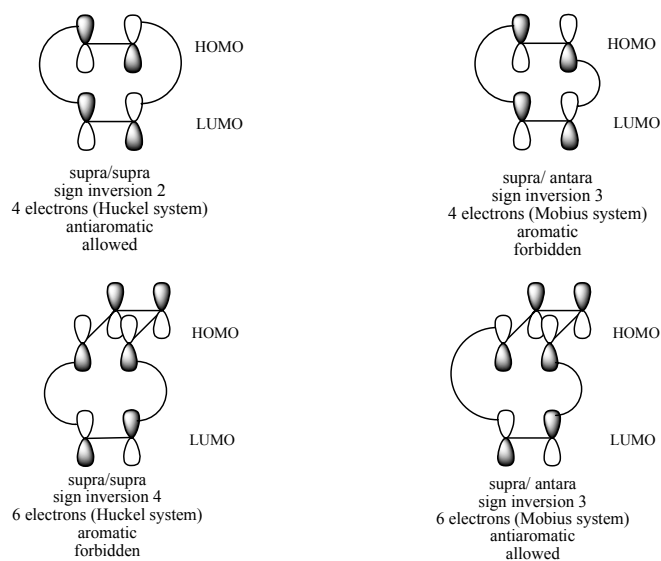
B-2: Electrocyclic reactions



Scheme 6. Investigation of ene reactions by the FOA approach under thermal reaction conditions.

Scheme 8. Investigation of electrocyclic reactions by the FOA approach under photochemical reaction conditions.

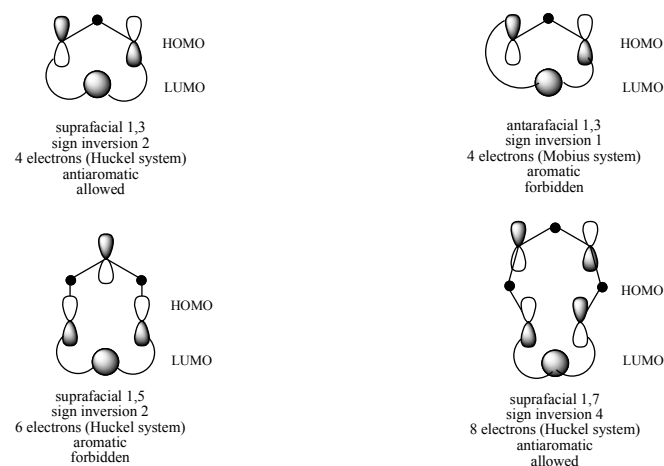
B-1: Cycloaddition reactions



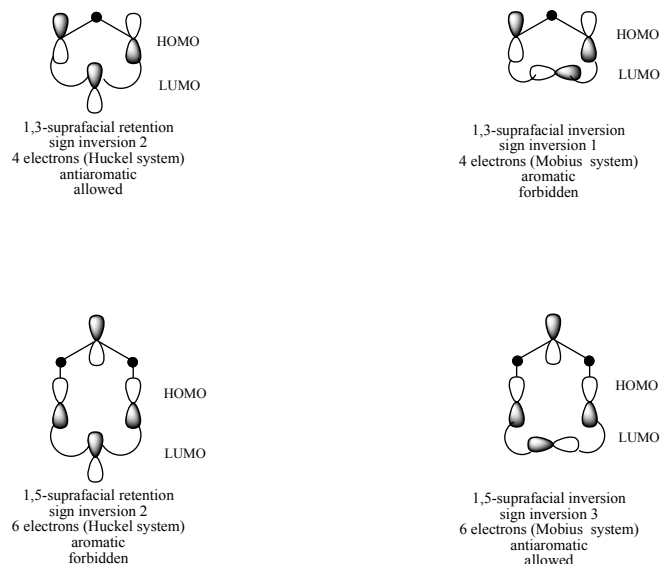
Scheme 7. Investigation of cycloaddition reactions by the FOA method under photochemical reaction conditions.

B-3: Sigmatropic rearrangements

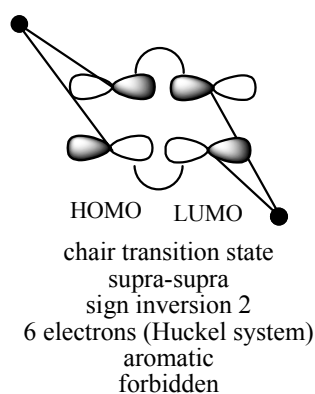
B-3-1: H-shift



B-3-2: Alkyl-shift [1, j]

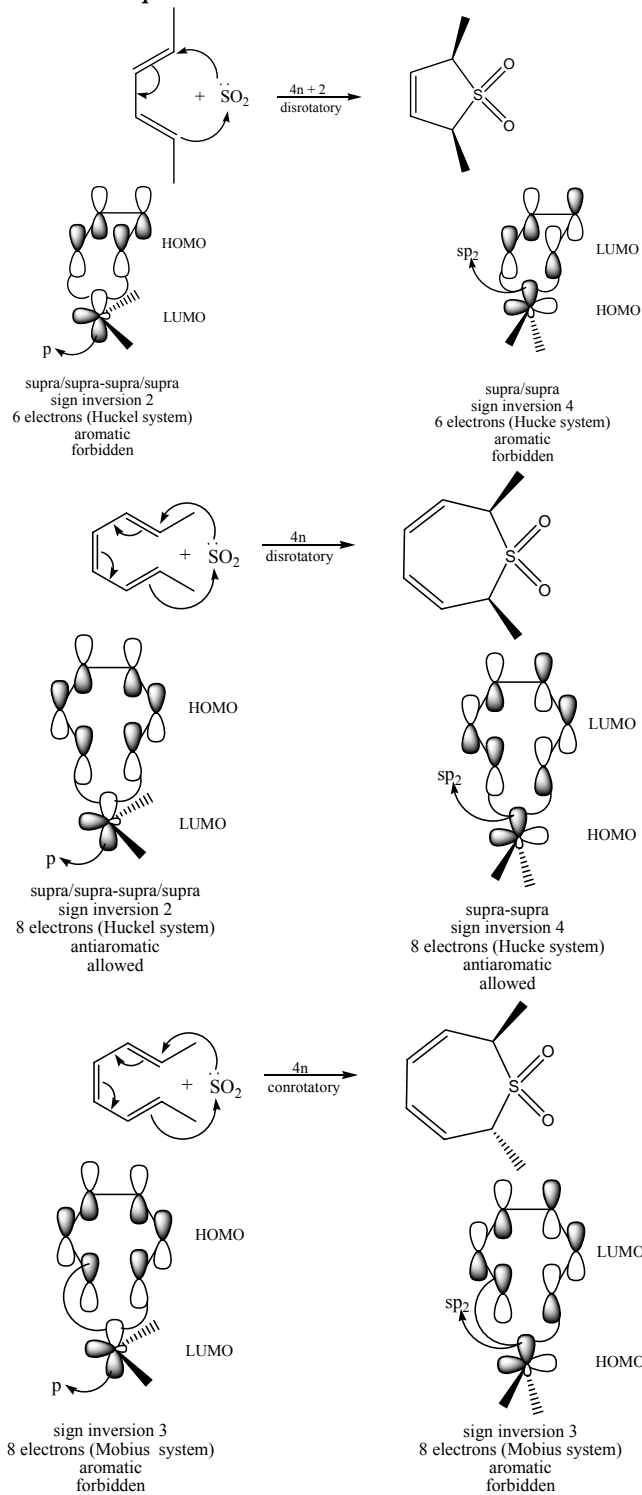


B-3-3: Allyl-shift [3,3]

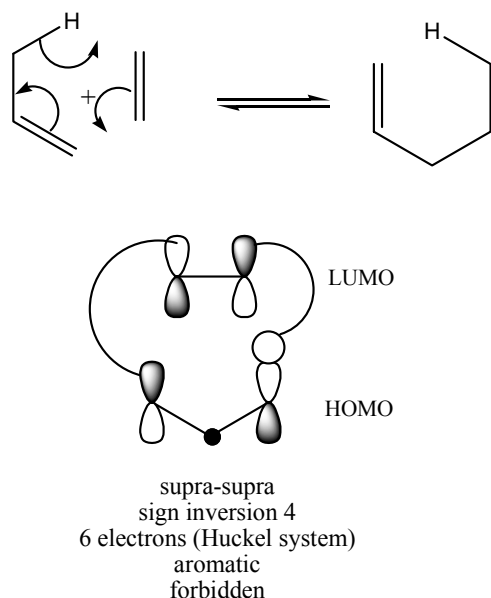


Scheme 9. Investigation of sigmatropic hydrogen, alkyl and allyl shift by the FOA approach under reaction photochemical conditions.

B-4: Cheletropic reactions



Scheme 10. Investigation of cheletropic reactions by the FOA approach under photochemical reaction conditions.

B-5: Ene reactions

Scheme 11. Investigation of ene reactions by the FOA approach under photochemical reaction conditions.

CONCLUSION

In conclusion, the simplicity and expeditiousness of predicting allowedness of pericyclic reactions by the FOA approach using interaction of HOMO and LUMO molecular orbitals based on Huckel-Mobius aromaticity concept in transition state has been amply shown. This approach seems to be more powerful than the Woodward-Hoffmann approach which appears to be limited to reactions with sufficiently high symmetry, and the Huckel-Mobius that use the non-participating lowest basis set (Ψ_1). One important impact of the current approach is its capability in addressing the photochemical concerted reactions. Since the aromaticity of HOMO and LUMO in transition state is considered in the current approach, the concerted reactions both under the thermal and photochemical conditions can be investigated. On the other hand, in this approach thermal reactions prefer aromatic transition state due to such a transition state will be less energetic and easier to attain. In contrast, photochemical reactions prefer antiaromatic or less stable transition state due

to the controlling factor in photochemical processes is conversion of excited state reactants into ground state product.

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