Conjugated Systems

1 Conjugated Systems and Resonance

Requirements for Conjugation: Same as resonance!
- Parallel array of atomic p orbitals on adjacent atoms (adjacent sp2 or sp hybridized atoms)

• The two pi-bonds in allene (the lower structure above) are NOT conjugated because the formal p atomic orbitals do not overlap across both double bonds, the 2 p A.O.s on the central carbon are at RIGHT ANGLES to each other, this situation is called cumulative.

Significance of Conjugation
- Allows reactions to be explained which cannot using simple Lewis structures, since under these conditions simple two-atom Lewis bonding does not occur, pi-bonding can occur over the entire length of the conjugated system, bonds including multiple atoms.

Conjugation & Resonance Are Different Ways of Describing the SAME Electron Delocalization in Pi-systems!

All conjugated systems involve resonance delocalization, and vice versa; you can draw resonance contributors for any conjugated system.

Examples of Conjugated Systems: the allyl radical:

- allylic, more stable than a 3° radical

• lower BDE means higher radical stability

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**Conjugated Systems**

• RESONANCE DELOCALIZATION in the CONJUGATED SYSTEM stabilizes the radical due to delocalization of electrons (the electrons “see” more nuclei)

Example: dienes

\[
\begin{align*}
\text{non-conjugated} & \quad + \quad 2 \text{H}_2 & \rightarrow & \text{conjugated} \\
\text{starts lower in energy} & \quad + \quad 2 \text{H}_2 & \rightarrow & \text{all the same - all pentane}
\end{align*}
\]

• the LESS EXOTHERMIC the reaction, the MORE STABLE the diene (since it starts lower in energy)
• the conjugated diene has overall lower energy electrons due to delocalization compared to the non-conjugated diene.

2 Reactions of Allyl Systems: Conjugated Intermediates

allylic position \( H_2C=CHCH_3 \)  allyl group = \( \text{allyl} \)

\[
\begin{align*}
\begin{array}{c}
\text{allyl chloride} \\
\text{allyl methyl ether}
\end{array}
\end{align*}
\]

• Allyl systems often react via conjugated (resonance stabilized) intermediates

**Allylic Substitution via S\(_{\text{N}2}\) (Review, seen before!)**

Recall: S\(_{\text{N}2}\) reactivity: \(_{3}^{3} < \text{ } _{2}^{2} < \text{ } _{1}^{1} < \text{ allylic} \) (fastest of all, because the transition state is conjugated!)

- conjugation (resonance) stabilizes the electrons in the transition state for SN2 reactions at an ALLYLIC carbon.

**One Consequence**

- slow reaction, Grignard not a strong enough nucleophile

**but!!**

- So this is a NEW REACTION, Grignard reagents will do SN2 reactions at allylic carbons to displace good leaving groups, often bromide, and make new C-C bonds, but ONLY at allylic carbons

Example

\[
\begin{align*}
\text{NBS} & \quad \text{hv} & \rightarrow & \text{Br} \\
\text{PhMgBr} & \rightarrow & \text{Ph}\text{-}
\end{align*}
\]
Bromination via Allyl Radicals (Mainly Review!)

- Where does this "unexpected product come from? The answer is in the mechanism, and the resonance contributors to the essential radical intermediate

Partial Mechanism: explains why TWO products are actually formed

- remember the resonance contributors are telling us what the real structure of the radical is, i.e. that the non-bonding electron is not localized on a single carbon atom, but that it is delocalized over two carbon atoms, the two atoms where the substitution takes place, which is why we get two products
- the resonance contributors are not two different things, but the same thing drawn two different ways
- the "other" product was always formed in allylic brominations, until now we have always tried to simply give examples where reaction at the two carbons with radical electron density gave the same product

Substitution via S_N1 (Mainly Review)
Recall

- substitution occurs at the PRIMARY carbon by an SN2 mechanism
However:

Mechanism:

- recall, protonation of an -OH group converts it from a poor to a good leaving group
- in this case, substitution occurs via an SN1 mechanism at the ALLYLIC carbon (bromide is a weak nucleophile and a resonance stabilized (conjugated) cation intermediate can be formed via SN1)
Another Example:

These are classic SN1 reaction conditions, an allylic bromide, a polar protic solvent, a weak nucleophile, heat

Q. Which is the MAJOR and which is the MINOR product?
A. This depends upon the conditions, i.e. whether the reaction is under kinetic or thermodynamic control

3 Reactions of Dienes : Kinetic versus Thermodynamic Control

Addition of HBr: recall

Analogously:

The charge is not evenly distributed in the resonance stabilized cation intermediate, shown above are two DIFFERENT ways of indicating the differing amounts of positive charge on the carbons, either in terms of the "actual" resonance hybrid cation structure, or as an unequal resonance mixture (both models say the same thing)

• Reaction is SLOWER at the primary carbon, there is less positive charge there, but reaction there forms the more substituted (more stable) alkene isomeric product
• Reaction is FASTER at the secondary carbon, there is more positive charge there, but reaction there forms the less substituted (less stable) alkene isomeric product
• YOU CAN MAKE GOOD ARGUMENTS FOR BOTH OF THE PRODUCTS, a KINETIC argument says that the 1,2-product is formed faster and should be the major product, a THERMODYNAMIC argument says that the 1,4-product is more stable and should be the major product
Another Example:

- NOTE, a bromonium ion intermediate is NOT formed here, as it would have been for Br2 addition to a simple alkene, a more stable, resonance stabilized allyl cation intermediate is formed instead.
- As in the previous example, the FASTER reaction at the carbon that has a larger partial positive charge forms the LESS STABLE 1,2-addition product, the KINETIC product, and the SLOWER reaction carbon that has a larger partial positive charge forms the LESS STABLE 1,2-addition product and the SLOWER reaction at the carbon that has a smaller partial positive charge forms the MORE STABLE 1,4-addition product, the THERMODYNAMIC product.

**What Determines Kinetic and Thermodynamic Control of Products?**
- This is best explained in terms of a reaction energy diagram.

- At all temperatures, the less stable 1,2-adduct is formed FASTER from the primary resonance stabilized intermediate.
- At low temperatures, the initially formed 1,2-product and 1,4-products "stay there", reverse reaction is not possible, there is not enough thermal energy to return (the reactions are IRREVERSIBLE), more 1,2-product is formed because this product is formed faster.
- At high temperatures, the 1,2-product and the 1,4-products can return to the intermediate (REVERSIBLE), although return of the 1,2-product is faster (requires less energy) and return of the 1,4-product is slower (requires more energy).
- Eventually the more stable 1,4-product accumulates and becomes the major product.
• when the reactions are IRREVERSIBLE, the entire process is under KINETIC CONTROL, i.e.

\[ \text{IRREVERSIBLE at lower temps} \]

major product formed faster

• when the reactions are REVERSIBLE, the entire process is under THERMODYNAMIC CONTROL, i.e.

\[ \text{REVERSIBLE at higher temps} \]

• MOST ORGANIC REACTIONS ARE UNDER KINETIC CONTROL, EXAMPLES OF THERMODYNAMIC CONTROL ARE RARE

An example in reactions of alkenes:

\[
\text{Br-} + \text{Br-} \quad \xrightarrow{\text{HBr}} \quad \text{Br} + \text{Br} \quad \text{thermodynamically controlled product} \]

\[
\text{Br-} + \text{Br-} \quad \xrightarrow{\text{HBr}} \quad \text{Br} + \text{Br} \quad \text{kinetically controlled product} \]

**4 Diels-Alder Reaction : Cycloaddition**

\[ D = \text{pi-donating group}; \ W = \text{pi-withdrawing group} \]

NOT

\[ \text{Lewis acid/base reaction} \]

\[ \text{4 electrons + 2 electrons cycloaddition} \]

This is an Addition reaction that makes two new C–C sigma-bonds and a ring: a cycloaddition reaction

• All bonds made and broken at the same time: A **Concerted reaction** (like SN2 and E2)

• 4 Electrons from diene and 2 electrons from dienophile, **thus 4 + 2 cycloaddition reaction**

• **THIS IS NOT A LEWIS ACID/BASE ELECTROPHILE/NUCLEOPHILE REACTION**, both reactants provide a pair of electrons to make a new bond to each other, AND, the reaction has an interesting "electrons in a loop" transitions state that is important

• The reaction goes faster (has a lower activation energy) with an electron donating group (-D) on the diene and an electron withdrawing group (-W) on the dienophile

**Exothermic Reaction**

• breaks 2 \( \pi \)-bonds

• makes 2 \( \sigma \)-bonds

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REMINDER of Electron Donating and Withdrawing Groups on pi-Systems

Recall: donating and withdrawing ability of substituents is measured relative to hydrogen

- Remember, distinguishing the donating and withdrawing groups is fairly easy - NO Memorization!
- With the exception of the simple alkyl and aryl substituents, all of the donating groups all have non-bonding electrons on the atom that is attached to the pi-system
- Just about everything else is a withdrawing substituent due to the inductive effect

Diels-Alder reactions are increasingly faster with increasingly stronger donating groups (D) on the diene
Diels-Alder reactions are increasingly faster with increasingly stronger withdrawing groups (W) on the dienophile

Some More on Donating Groups:

- Non-bonding electrons on the less electronegative element N are higher in energy and more "available" for resonance donation than those on oxygen
- Non-bonding electrons that are resonance delocalized into other pi-systems, e.g. part of an ester, above left, are lower in energy and less "available" for resonance donation into a diene

The Diene needs to be in the correct conformation to react:

- "s-cis" and "s-trans" refer to the different CONFORMERS corresponding to rotation around the CENTRAL C-C bond, they are related to cis-/trans- isomers of alkenes, but the restricted rotation is around a single bond
- the Diels-Alder reaction needs an "s-cis" conformation of the diene for reaction
- reaction is ALSO STEREOSELECTIVE, it is concerted, and generally needs (some) heat

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Explanation for the Stereochemistry:
Concerted reactions are often STEREOSPECIFIC!!
Recall: the following CONCERTED reactions (all bonds broken and made at the same time)

The stereochemistry of the Diels-Alder reaction is centered around the substituents, specifically.....

• both the "outside" substituents on the diene end on the same side in the cyclohexene product (i.e. both have wedged or dashed bonds)
• both "inside" groups on the diene end on the opposite side to the "outside" groups on the diene
• The W groups on the dienophile end on the same side as the "outside" groups on the diene, the ENDO RULE

The Concerted Reaction:
• the p A.O.s at the end of the diene and the dienophile have to transform into sp3 atomic orbitals as the new sigma-bonds are formed, the substituents on these atoms will "move" in response to the change in hybridization
• This is illustrated below for the case of dienophile addition from the "bottom"

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• both new bonds made at the same time on same side of the diene (the bottom in this example), the reaction is thus SUPRAFACIAL with respect to the diene
• both new bonds made at the same time on same side of the dieneophile (the top in this example), the reaction is ALSO SUPRAFACIAL with respect to the dieneophile
• the Diels-Alder reaction is a 4(s) + 2(s) cycloaddition, where (s) refers to suprafacial

Suprafacial Reaction: Definition
• Both bonds are made to the same "face" of the reactant, i.e. for a flat pi-system this means both bonds made to the bottom face or both bonds made to the top face

![Diagram showing suprafacial reaction on diene and dieneophile](image)

4(s) + 2(s) cycloaddition reaction

• If a reaction is SUPRAFACIAL on one of the reactants, then this is the same as SYN-ADDITION on that reactant

Origin of the Endo Rule
• ENDO means "in", as opposed to EXO which means "out"
• The dienophile can approach the diene in one of two different ways, i.e. with the withdrawing groups "in", towards the diene (ENDO), or with the withdrawing group "out", away from the diene (EXO). The ENDO reaction is shown below, you can see that this case the withdrawing group will either be below or above the diene.

![Diagram showing ENDO and EXO approaches](image)

• The ENDO approach of the dienophile usually leads to the lower energy transition state because the electronegative elements in the W-group can stabilize the relatively high energy electrons in the diene, this is called a secondary orbital interaction.
• The ENDO approach results in the -W group and the substituents in the "outside" of the diene (both -Me in the example above) being on the same side of the cyclohexene ring in the product, i.e. these bonds are both dashed (when reaction occurs from below) or they are both wedged if reaction occurs from above.
• In the alternative EXO approaches, the W-group is "out" with respect to the diene (it points "away" from the diene, and the electronegative elements in the -W group cannot stabilize the higher energy electrons in the diene. Reaction EXO would proceed via a higher energy transition state, i.e., slower.

![Diagram showing lower energy enantiomers](image)
**Visualize Stereochemical Consequences of the CONCERTED Diels-Alder Reaction**

**Examples: on dienophile**

- FOUR chiral/asymmetric centers are generated, but the structure has a mirror plane of symmetry, thus it is an achiral meso compound

- FOUR chiral/asymmetric centers are generated, the structure has NO mirror plane of symmetry, it is thus formed as a racemic mixture

**Examples: on diene**

- FOUR chiral/asymmetric centers are generated, but the structure has a mirror plane of symmetry, thus it is an achiral meso compound

- FOUR chiral/asymmetric centers are generated, the structure has NO mirror plane of symmetry, it is thus formed as a racemic mixture
Orientation of addition: the Regiochemistry
- The reaction is also REGIOSPECIFIC (one structural isomer is favored over others)

- There is only ONE chiral center formed (*), and so there is not need to draw the bond as wedged or dashed, in fact doing so would have no meaning in this case, we don’t need to specify that this bond is wedged or dashed with respect to any other bond in the product structure, therefore this bond should be drawn as PLAIN, with the racemic mixture symbol (±) to show that we made two enantiomers
- the 1,4-product is formed NOT the 1,3-product, these are structural isomers and shows that the reaction has REGIOSPECIFICITY - Remember, the way that we draw the molecules on paper isn’t necessarily the way that they are when undergoing a reaction, don’t be fooled by the way the structures are drawn on paper!

- these reactions can be explained using the following MINOR RESONANCE CONTRIBUTORS....
- Formation of the 1,3-product is always disfavored due to electron repulsion
Let's look at this for GENERIC donating (-D) and withdrawing (-W) groups

1,2-Addition: product formed faster, MAJOR organic product
**1,3-Addition**: product formed slower, minor organic product

![Chemical structure](image)

**Example**: with actual donating and withdrawing groups

![Chemical structure](image)

**Example Reactions with stereo- and regiochemistry**:

- **ONE chiral center**, no wedged/dashed bonds (only ±), wedged/dashed bonds have no meaning if a racemic mixture is specified, AND, **1,4-product is major**, not the **1,3-product**

- **TWO chiral centers**, need BOTH dashed bonds to illustrate the relative stereochemistry of the -D and the -W group, AND the racemic mixture symbol to indicate the other enantiomer, **1,2-product is major**, not **1,3-product**
• chiral centers in the product (*), but the product has a mirror plane of symmetry, it is a meso compound

• the product that has the -W group 1,2- with respect to the strongest donating group is major

5 pi-Molecular Orbitals : Pericyclic Reactions

Molecular orbitals - Where ARE the electrons in a molecule?
• build molecular orbitals by combining appropriate atomic orbitals
• build pi-molecular orbitals by combining p atomic orbitals
• the number of molecular orbitals we must make is equal to the number of p atomic orbitals that we combine

First, we are concerned with linear systems, cyclic systems come later

Need to (briefly) revisit concept of orbital wavefunction: example of a p-A.O.

• shown above is a graphical representation of waveform of an atomic p orbital
• the waveform is a mathematical function which evaluates to positive value, negative value, or zero
• only the relative sign of the waveform is important (+ or –), we distinguish using shading (black/white)

Revisit concept of bonding and making Molecular Orbitals by Combining Atomic Orbitals
For the case of two p atomic orbitals (AOs) on two adjacent carbon atoms, overlap of the orbital wavefunctions results in simultaneous constructive (in-phase) AND destructive (out of phase) interference of the wavefunctions to generate two new wavefunctions
• overlap of the wavefunctions of atomic orbitals of same sign (in-phase, constructive interference) generates a new bonding wavefunction, the new binding molecular orbital
• the new bonding wavefunction builds electron density between the nuclei, allows electrons to "see" both nuclei
• an electron in the new bonding wavefunction is lower in energy compared to being in the original atomic orbital

• the wave nature of orbital wavefunctions means that if the atomic wavefunctions can overlap in-phase (as above), then they must simultaneously overlap out of phase (whether we like it or not(!), shown below) which
results in DESTRUCTIVE interference of the atomic orbital wavefunctions between the atoms, which generates a new ANTI-bonding wavefunction
- the new anti-bonding wavefunction eliminates electron density between the nuclei
- an electron in the new anti-bonding wavefunction would be HIGHER in energy compared to being in the original atomic orbital

5.1 Rules for Constructing Molecular Orbitals
You will not memorize these rules, you will learn them very quickly by using them

1) The number of M.O.’s = the number of A.O.’s, BECAUSE, orbitals can’t “disappear”
2) 2 electrons per M.O., BECAUSE, of the Pauli principle
3) Lowest energy M.O. has 0 vertical nodes, BECAUSE, it is most “bonding”
4) Increasing vertical nodes means increasing energy, BECAUSE, they become less “bonding”
5) Symmetry of nodes determined by molecular symmetry, BECAUSE, they are standing waves

5.2 pi-Molecular Orbitals of Ethylene

1) 2 A.O.’s, therefore, 2 M.O.’s must be formed when they combine (pi 1 and pi 2)
2) 2 Electrons (max.) per M.O. – 2 electrons in bonding pi 1 M.O.
3) pi 1 has NO VERTICAL nodes
4) pi 2 has ONE VERTICAL node (wavefunction changes sign, goes through zero)
5) Node position determined by molecular symmetry (in the middle!), wavefunctions are STANDING WAVES

- the p-A.O.’s do not actually exist in the molecule, the M.O.s are drawn using a “cartoon” or “digital” approximate p A.O. method because it is too hard to draw the actual orbitals accurately
- The wavefunctions really look like waves!

5.3 pi-Molecular Orbitals of Butadiene

- here we consider the PI-MOLECULAR ORBITALS ONLY (ignore the sigma-MOs)
- there are 4 p A.O.’s, therefore 4 pi-M.O.’s must be formed when they combine, pi 1, pi 2, pi 3, pi 4
- 2 electrons in each M.O. (pi 1, pi 2)
- Lowest, pi 1, has no vertical nodes (all have one horizontal node)
- Increasing vertical nodes = Increasing energy
Nodes are symmetrical because the wavefunctions of the M.O.s describe STANDING WAVES

HOMO = Highest Occupied Molecular Orbital
LUMO = Lowest Unoccupied Molecular Orbital

The Wavefunction Squared give the probability of finding the electrons in the orbitals

ψ² for π2 M.O., gives probability of finding the electrons, hard to draw!
"representation" of Ψ for π2 M.O. using A.O.'s what WE draw
accurate computed Ψ for π2 M.O. too hard to draw!

• electrons are distributed over all 4 carbon atoms, but never found at a node (horizontal in this case).

5.4 π-Molecular Orbitals of The Allyl System
The allyl system describes the simplest resonance stabilized ion and radical intermediates in organic chemistry, shown below are the simplest allyl anion, allyl cation and allyl radical, each are conjugated systems, each have 3 carbon atoms involved in the conjugated system (resonance), but they have different numbers of electrons associated with the conjugated system (involved in resonance).
The Wavefunction Squared give the probability of finding the electrons in the HOMO of the allyl anion.

Example problem: What is the HOMO & LUMO of the pentadienyl anion?

1. How many p A.O.'s do we have to work with? Answer = five
2. How many M.O.'s will we have? Answer = five
3. How many electrons do we have? Answer = six
4. How many nodes will the HOMO have?  Answer = two
5. How many nodes will the LUMO have?  Answer = three

6  Frontier Molecular Orbital Theory : Pericyclic Reactions
• All pericyclic reactions are CONCERTED and involve cyclic transition states and we need M.O.'s to understand
• There are several kinds of pericyclic reaction, we look at only two:
  1. Cycloadditions
  
  2. Electrocyclic reactions

There are three different theories for pericyclic reactions, we will look at two of them:
1. Frontier Molecular Orbitals (Today)
2. Aromatic Transition State (Later)
The other theory is conservation of orbital symmetry, it is more complete the other two, but is beyond the scope of a General Organic Chemistry course

FMO Theory: (Approximate, but works!)
• fundamental Principle for Understanding Pericyclic Reactions...........
molecules come from the highest energy occupied orbital, i.e. HOMO
electrons are accepted into the lowest energy unoccupied orbital, i.e. LUMO

donated electrons flow from the HOMOs to the LUMOs
the smaller the HOMO/LUMO energy gap, $\Delta E$
the faster the reaction
• The smaller the energy gap between where the electrons come from (HOMO) and are going to (LUMO), the faster the reaction
• A **donating** substituent on the diene **raises** the energy of the electrons, specifically in the HOMO
• A **withdrawing** substituent on the dienophile **lowers** the energy of electrons, specifically in the LUMO

**Compare**: HOMO/LUMO Energy Gap in Diels-Alder reaction with the addition of D- and W- Substituents

- electron “flow” from HOMO to LUMO is determined by the HOMO/LUMO energy "gap", Delta E
- there is a **smaller HOMO/LUMO energy gap** with D- and W- substituents, Delta-E becomes smaller, **faster reaction**
- FMO theory explains the substituents effects on the rate of the Diels-Alder reaction

**Revisit Diels-Alder Reaction - 4 + 2 Cycloaddition Reaction**

• when **atomic** wavefunctions overlap in phase - they make a bond
• when **molecular** wavefunctions overlap in phase - they make a bond!
• we now ask the following question: can overlap the molecular orbitals of BOTH REACTANTS, SUPRAFACIAL/SUPRAFACIAL occur IN-PHASE and therefore make BOTH BONDS at the same time?
• If we can then the 4(s) + 2(s) CONCERTED REACTION is allowed

**FIRST**: consider suprafacial/suprafacial overlap of the HOMO of the diene + the LUMO of the dienophile
• Recall: SUPRAFACIAL IS THE SAME AS SYN-ADDITION

• Overlap of the HOMO of the diene **SUPRAFACIAL** and the LUMO of the dienophile **SUPRAFACIAL** results in IN-PHASE and BONDING interactions to make BOTH of the new sigma-bonds at the same time,
• Therefore, a concerted Diels-Alder reaction 4(s) + 2(s) cycloaddition IS ALLOWED, according to F.M.O. theory
NOW: Consider reaction "other way round", HOMO of dienophile & LUMO of diene

- Overlap of the LUMO of the diene SUPRAFACIAL and the HOMO of the dienophile SUPRAFACIAL ALSO results in IN-PHASE and BONDING interactions to make BOTH of the new sigma-bonds at the same time,
- Therefore, the concerted Diels-Alder reaction 4(s) + 2(s) cycloaddition IS ALLOWED according to F.M.O. theory using either analysis, i.e. HOMO/LUMO OR LUMO/HOMO
- When considering whether a concerted cycloaddition reaction is allowed or not it doesn't matter which HOMO/LUMO combination we consider

What About a 2(s) + 2(s) Cycloaddition Reaction?

- Overlap HOMO and LUMO of the two alkenes SUPRAFACIAL/SUPRAFACIAL (add to both sides of both molecules at the same time)

- This results in ONE ANTI-BONDING interactions for both HOMO/LUMO combinations
- A suprafacial/suprafacial 2(s) + 2(s) cycloaddition reaction is therefore FORBIDDEN according to F.M.O. theory

Example: a different 4 + 2 cycloaddition
• when this reaction is SUPRAFACIAL/SUPRAFACIAL, 4(s) + 2(s), then reaction is allowed
• ONLY suprafacial/suprafacial reaction is possible in this case because the cyclic system is not large enough to have bonding occurring any other way, so we find that the possible reaction is allowed

Example: 6 + 2 cycloaddition reaction

$\Delta$

$\Psi$ of HOMO for allyl anion
$\Psi$ of HOMO for alkene
suprafacial for allyl anion
suprafacial for alkene

ALLOWED!!

$\Psi$ of HOMO for triene
$\Psi$ of LUMO for alkene

2 electrons per arrow!

$\Psi$ of HOMO
$\Psi$ of LUMO

node
node

suprafacial for triene
suprafacial for alkene

$\Phi$

$\Phi$

HOMO $\pi_1$ $\pi_2$ $\pi_3$

LUMO $\pi_3$ $\pi_4$ $\pi_5$

$\Phi$

• 6(s) + 2(s) cycloaddition reaction is forbidden

$\Delta$

$\Psi$ of HOMO
$\Psi$ of LUMO

SUPRAFACIAL/ANTARAFACIAL to give the trans-product ALLOWED!!

• ANTARAFACIAL IS THE OPPOSITE OF SUPRAFACIAL - it means making the two bonds to OPPOSITE side
• 6(s) + 2(a) cycloaddition reaction is allowed (suprafacial/antarafacial)
• a (6(a) + 2(s) cycloaddition would also be allowed (antarafacial/suprafacial)
• antarafacial cycloadditions are possible when there are enough atoms involved in the cycloaddition, usually at least seven or eight atoms are required (above there were eight), and in fact, (s) + (a) cycloadditions are rare!
Electrocyclic Reactions

We need to consider TWO ways that the ring can be closed:
CONROTATORY: the sigma-bonds and orbitals rotate in the SAME direction (in CONCERT)
DISROTATORY: the sigma-bonds and orbitals rotate in OPPOSITE directions

Example:
• Show how you would determine the product of the reaction below using F.M.O. theory

• In this case the reaction is UNIMOLECULAR (not bimolecular), electron flow is not from one molecule to another, we are concerned with the highest energy (most reactive) electrons in the starting structure only, these are contained in the Highest Occupied Molecular Orbital, the HOMO

• As the ring closes, the important orbitals are those at the end of the conjugated system, they transform from formal p atomic orbitals into sp3 hybridized atomic orbitals, and at the same time they rotate 90 degrees so that they are pointing towards each other so that they can overlap and make the new sigma-bond.
• Conrotatory ring closure results in a bonding (in-phase) interaction between these orbitals, both in the transition state and in the final product, conrotatory ring closure is ALLOWED
• Disrotatory ring closure results in anti-bonding (out of phase) orbital overlap, disrotatory ring closure results in a higher energy transition state, this reaction is FORBIDDEN in the language of F.M.O. theory
Disrotatory and Conrotatory Electrocyclic Reactions using FMO Theory

Electrocyclic Reactions using FMO Theory and “Fingers and Thumbs”

Examples

\[ \Delta \]

outside

outside

\[ \text{which isomer, cis- or trans- ??} \]

\( \Psi \) for HOMO

outside

\[ \text{disrotatory closure leads to bonding interaction in the transition state} \]

outside

cis-product is ALLOWED

\( \Psi \) for HOMO same as above

inside

\[ \text{disrotatory ring closure allowed} \]

outside

\( \pm \)

trans-product is allowed

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• The enantiomer is the product that is obtained by doing disrotatory ring closure in the "other direction", which results in the product with the upper CH$_3$ wedged and the lower one dashed.

What we just did is AMAZING (you should be amazed!)

\[ \text{mind} = \text{blown} \]

• These reactions can ONLY be explained and understood by taking the WAVE PROPERTIES of the electrons in the molecular orbitals into account.
• Understanding the wave nature of electrons is difficult, but **without this there is no understanding of pericyclic reactions**.
• The wavefunctions HAVE to overlap in phase in order to get the reactions to go, at least as the concerted reactions discussed here.
• These reactions represent QUANTUM MECHANICS in ORGANIC CHEMISTRY.
• The quantum/wave nature of electrons is difficult to understand, BUT:
• Explain the presence of orbitals any other way!
• Explain pericyclic reactions any other way!
The Diels-Alder reaction is stereochemical and regiochemical controlled.