Aromaticity: Stability and Instability in Cyclic π-Systems

- The molecular orbitals of conjugated systems in which the overlap of the p atomic orbitals (and therefore the electrons) are in a LOOP and DIFFERENT from the linear conjugated systems we have discussed so far.
- This is the case BOTH for stable organic structures (e.g., benzene and other aromatic molecule), AND, transition states, such as encountered in pericyclic reactions.

1. Aromatic Transition State Theory and Pericyclic Reactions

- This is an ALTERNATE model for pericyclic reactions, it gives the same answers but in many ways is easier than F. M. O. theory.
- We still need π M.O.’s of cyclic conjugated systems ("electrons in a loop")
- However, we only need energies of cyclic M.O.’s, we do not need their symmetry/phase information.
- Here we are dealing with cyclic loop π-molecular orbitals and we will find that they have degeneracies (orbitals of equal energies).

Aromaticity Concept: applies to stable molecules (e.g., benzene) and transition states (e.g., Diels-Alder reaction).

Here we are concerned NOT so much with representations of the WAVEFUNCTIONS of the orbitals, but with their relative Energies.

To determine the relative energies of cyclic π M.O.’s: Draw a Frost energy diagram….

1) Draw a circle
2) Draw a polygon, point down
3) Put M.O.’s at the vertices

Example with Six Electrons

- 6 p A.O.’s therefore six M.O.’s
- 6 M.O.’s, therefore draw 6-membered polygon (hexagon)
- 6 electrons, therefore lowest 3 have electrons, upper 3 empty
- Cyclic orbital system results in DEGENERACIES (orbitals having the same energies)

The energy of the lowest energy fully bonding M.O. in the cyclic system is lower than the energy of the lowest energy fully bonding M.I. in the linear system simply because there is an addition binding interaction because the loop is completed.

- Two pairs of orbitals in the cyclic loop Huckel system are degenerate - they have the same energies.
- The TOTAL energy of the electrons in a cyclic Huckel pi-system is lower than in a comparable linear pi-system.

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• putting 6 electrons in a cyclic - Hückel - loop results in lower energy electrons compared to an equivalent linear system, this is the origin of aromaticity - aromatic systems are stable because they have lower energy electrons

symmetries of benzene π M.O.’s (# of vertical nodes)

• the energies of the pi-molecular orbitals increase with increasing numbers of vertical nodes, and the nodes are distributed symmetrically, just as in the linear systems we talked about previously
• BUT, in the cyclic loop orbitals, there will always be TWO ways of having a single vertical node (and two ways of having 2 vertical nodes), this is the origin of the orbital DEGENERACY
• DEGENERATE orbitals are different but they have the SAME ENERGY

Example with FOUR Electrons
• 4 p A.O.’s therefore four M.O.’s
• 4 M.O.’s, therefore draw 4-membered polygon (square)

• 4 electrons in a cyclic Hückel loop gives 2 electrons in unfilled orbitals
• 4 electrons in a cyclic Hückel loop are higher in energy compared to linear system: unstable - ANTI-Aromatic
• 4 electrons in a twisted "head-to-tail" Möbius loop, however, are lower in energy again - Aromatic
Example with Eight Electrons
- 8 p A.O.’s therefore eight M.O.’s
- 8 M.O.’s, therefore draw 8-membered polygon (octagon)

8 electrons in a cyclic Hückel loop gives 2 electrons in unfilled orbitals
- 8 electrons in a cyclic Hückel loop are higher in energy compared to linear system: unstable - ANTI-Aromatic
- 8 electrons in a twisted head-to-tail Mobius loop, however, are lower in energy again - Aromatic

The Hückel Rule:
- 2 electrons, 6 electrons, 10 electrons etc. \((4n+2)\) in a CYCLIC HUCKEL pi-LOOP are AROMATIC (and thus relatively LOW in energy)
- 4 electrons, 8 electrons, 12 electrons etc. \((4n)\) electrons in a CYCLIC HUCKEL loop are ANTI-AROMATIC (and thus relatively HIGH in energy)

\(\text{AND}....\)
- 4 electrons, 8 electrons, 12 electrons etc. \((4n)\) in a TWISTED head-to-tail MOBIUS loop are AROMATIC (and thus relatively LOW in energy)
- 2 electrons, 6 electrons, 10 electrons etc. \((4n+2)\) in a TWISTED head-to-tail MOBIUS loop are ANTI-AROMATIC (and thus relatively HIGH in energy)

There is nothing mysterious about the "n" in the Hückel rule, it is just an integer that defines series, all it means is:
- when \(n = 0\) then \((4n+2) = 2\) electrons
- when \(n = 2\) then \((4n+2) = 6\) electrons etc.

\(\text{and}...\)
- when \(n = 1\) then \((4n) = 4\) electrons
- when \(n = 2\) then \((4n) = 8\) electrons etc.

The Hückel rules applies to both stable molecules and transition states!
Application of Hückel/Mobius Rule to Cycloaddition Reactions

4(s) + 2(s) cycloaddition Diels-Alder Reaction

- 6 electrons in a HUCKEL cyclic loop transition state is AROMATIC, low in energy, the reaction IS ALLOWED!

2(s) + 2(s) cycloaddition

- 4 electrons in a HUCKEL transition state is ANTIAROMATIC, high in energy, the reaction IS FORBIDDEN!

6 + 2 cycloaddition

try suprafacial/suprafacial addition

- 6(s) + 2(s) cycloaddition occurs via a Hückel continuous loop transition state
- 8 electrons in cyclic Hückel transition state is ANTIAROMATIC, relatively high energy electrons: the reaction is FORBIDDEN

try a suprafacial/antarafacial addition

- 8 electrons in a twisted Möbius transition state is low in energy: aromatic

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• 8 electrons in a suprafacial/antarafacial reaction is ALLOWED
• 6(s) + 2(a) cycloaddition is allowed, 6(a) + 2(s) would also be allowed

Application of Hückel/Mobius Rule to Electrocyclic Reactions

2 curved arrows
4 electrons

• 2 curved arrows, therefore 4 electrons involved in the transition state

4 electrons in a cyclic Hückel transition state - FORBIDDEN!!

4 electrons in a TWISTED Möbius transition state- ALLOWED!!

• The reaction can go both ways, which is easy to explain using Aromatic Transition State Theory

Examples

4 electrons

• 4 electrons involved in the transition state

DISROTRATORY ring OPENING

CONROTRATORY ring OPENING

cyclic Hückel transition state
4 electrons: FORBIDDEN!!
twisted Möbius transition state
4 electrons: ALLOWED!!

Me
Me

H
H

Me
Me

H
H

not formed
formed!!

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**Electrocyclic Reactions Using Aromatic Transition State Theory and the "Fingers and Thumbs" Method**

**Electrocyclic Reactions Using the Aromatic Transition State Theory method and a Molecular model**

- **6 electrons**
  - Hückel transition state allowed
  - therefore, must be a disrotatory ring opening reaction

- **4 electrons**
  - Möbius transition state allowed
  - therefore, must be a conrotatory ring opening reaction

- **2 electrons**
  - Hückel transition state allowed
  - therefore, must be a disrotatory ring closure reaction

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• In THIS product, the addition was SUPRAFACIAL/SUPRAFACIAL (like the Diels-Alder), both bonds were made to the same sides of both reactants at the same time, i.e. a Hückel transition state
• 8 electrons require Möbius transition state for lowest energy electrons, this would require a suprafacial/antarafacial reaction
• Because the PROVIDED PRODUCT had to have been formed via a HUCKEL transition state (suprafacial/suprafacial), THIS PRODUCT is FORBIDDEN

2 Application to Stable Molecules

Huckel Rule Summary:
(4 n + 2) electrons in a conjugated system that is CYCLIC are more stable than a corresponding NON-Cyclic system: AROMATIC i.e., 2e, 6e, 10 electrons etc.
(4 n) electrons in a conjugated system that is CYCLIC are LESS stable than a corresponding NON-Cyclic system: ANTI-AROMATIC i.e. 4e, 8e, 12 electrons etc.

Example

• benzene is more stable than expected for cyclohexatriene by ca 37 kcal/mol, this extra stabilization is due to AROMATICITY
• this stabilization can NOT be explained merely by conjugation or resonance, because.......
3 Aromatic Ions

**Example** in a surprisingly fast SN1 reaction

- 2 electrons in a cyclic cation system, ALL carbon atoms are sp2 hybridized, cyclic conjugated system
- aromatic: **stable**!

**Examples** in Bronsted acidity
- Compare cyclopropene and cyclopentadiene as Bronsted acids

- the conjugate base anion of **cyclopropene** has 4 electrons in a conjugated **Huckel loop**, it is anti-aromatic, is very unstable, has very high energy electrons, consequently, cyclopropene is a VERY WEAK Bronsted acid

- the conjugate base anion of **cyclopentadiene** has 6 electrons in a **conjugated** **Huckel loop**, it is **AROMATIC**, is relatively stable, has much lower energy electrons than the conjugate base anion of cyclopropene
- the Bronsted acidity of cyclopentadiene is **LARGER** than even a terminal alkyne.

4 Aromatic Heterocycles

A Heterocycle: a cyclic system containing N, O, S etc. that has replaced a carbon atom in a ring structure

**Pyrrole as an example**
- the nitrogen atom in pyrrole (below) looks like it should be sp3 hybridized, **however**, it is actually sp2 hybridized

- the Nitrogen atom **changes hybridization from** sp3 to sp2 because in doing so it can become AROMATIC
- hybridization and molecular geometry are intimately connected, if the structure is planar (flat), the nitrogen must be sp2 hybridized, if the N is sp2 hybridized it must be planar
- If the N is sp3 hybridized the structure can't be planar (the nitrogen is tetrahedral), if the N has tetrahedral geometry is has to be sp3 hybridized
- let's remind ourselves what sp2 and sp3 hybridization really means for the nitrogen in pyrrole, drawing the nitrogen properly so that it shows the spatial orientation of the formal atomic orbitals around it is difficult, we need to look at it from the side, as shown below
• If the Nitrogen is sp\textsuperscript{3} hybridized the structure is NON-PLANAR and NOT AROMATIC (the sp\textsuperscript{3} hybridized atom breaks the conjugation there is no Huckel loop
• If the Nitrogen is sp\textsuperscript{2} hybridized the structure is PLANAR and AROMATIC since there are 6 electrons in a Huckel loop

\begin{equation}
\text{overlap with } \pi\text{-electrons POOR}
\end{equation}

\begin{equation}
\text{N tetrahedral and sp}\textsuperscript{3} hybridized}
\end{equation}

\begin{equation}
\text{if the N is sp}\textsuperscript{3} hybridized then there is poor overlap between the orbital with the non-bonding electrons (sp\textsuperscript{3} hybridized), the system is NOT conjugated in a HUCKEL loop, the structure is non-aromatic}
\end{equation}

\begin{equation}
\text{overlap with } \pi\text{-electrons GOOD}
\end{equation}

\begin{equation}
\text{N is planar and sp}\textsuperscript{2} hybridized}
\end{equation}

\begin{equation}
\text{N IS sp}\textsuperscript{2} hybridized and the structure is PLANAR in order to be AROMATIC}
\end{equation}

\begin{equation}
\text{because the N is sp}\textsuperscript{2} hybridized the non-bonding electrons are associated with a } p\text{ A.O., overlap with the pi-electrons is GOOD, they ARE conjugated with the pi-electrons, there are SIX electrons in a cyclic conjugated loop}
\end{equation}

\begin{equation}
\text{by having a formal sp}\textsuperscript{2} hybridization for the N atom, pyrrole becomes AROMATIC}
\end{equation}

Furan as an example

\begin{equation}
\text{the oxygen in furan O is sp}\textsuperscript{2} hybridized to allow ONE (and only one) of the electron pairs to be CONJUGATED with those in the C=C bonds, resulting in 6 electrons in a cyclic Huckel loop}
\end{equation}

\begin{equation}
\text{only ONE PAIR of non-bonding electrons on the oxygen are counted, let's remind ourselves what sp2 hybridization really means for the oxygen atom in furan, again, we must look from the side}
\end{equation}

\begin{equation}
\text{all atoms in the same plane the structure is FLAT}
\end{equation}
• because the O is sp2 hybridized the ONE PAIR of non-bonding electrons are associated with a p A.O., overlap of these electrons with the pi-electrons results in a cyclic conjugated system with SIX electrons - aromatic
• the other pair of non-bonding electrons are in an sp2 hybridized A.O., they are at RIGHT ANGLES to the conjugated pi-system, they are IRRELEVANT to aromaticity.

Heterocycle Bronsted bases as examples

**Pyridine**

- pyridine is a (relatively) strong base, gets non-bonding electrons into a bond
- protonated pyridine is a (relatively) weak acid, it is aromatic

**Pyrrole**

- pyrrole is a relatively weak base, making bonds BREAKS stable aromatic structure
- protonated pyrrole is a relatively strong acid, since deprotonation regenerates stable aromatic system

Example problem: which nitrogen protonates more easily in imidazole?

**5 Molecules Avoid Anti-Aromaticity by Becoming Non-Planar**

**Annulenes: cyclic hydrocarbons with alternating single/double bonds**

- cyclobutadiene is [4]annulene it is anti-aromatic
- benzene is [6]annulene it is aromatic
- cyclooctatetraene is [8]annulene it is NON-aromatic!!
• cyclooctatetraene is AVOIDS being non-aromatic by assuming a non-planar "tub" shape that breaks the conjugation of the p A.O.'s, all of the p AOs are NOT PARALLEL
• a pi-systems must be flat to be aromatic or antiaromatic to ensure parallel array of p A.O.'s and a HUCKEL loop
• most annulenes are in fact non-planar
• In reality, there are few examples of true anti-aromatic systems for this reason, anti-aromatic structures tend to become non-planar to avoid the high-energy situation represented by anti-aromaticity

Example problems: which of the following are aromatic when the structures are as flat (planar) as possible?

- Which electrons are counted?

Example from above:

- The electrons on nitrogen are counted because if the structure is FLAT, the N atom must be sp2 hybridized, and if it is sp2 hybridized then the non-bonding electrons must be in a p AO that is vertical to the plane of the molecule, i.e. in a p AO that is parallel to all of the other p atomic orbitals in the ring. The non-bonding electrons on the N are thus conjugated with the other electrons, thus there are 6 electrons in the cyclic loop in this structure.