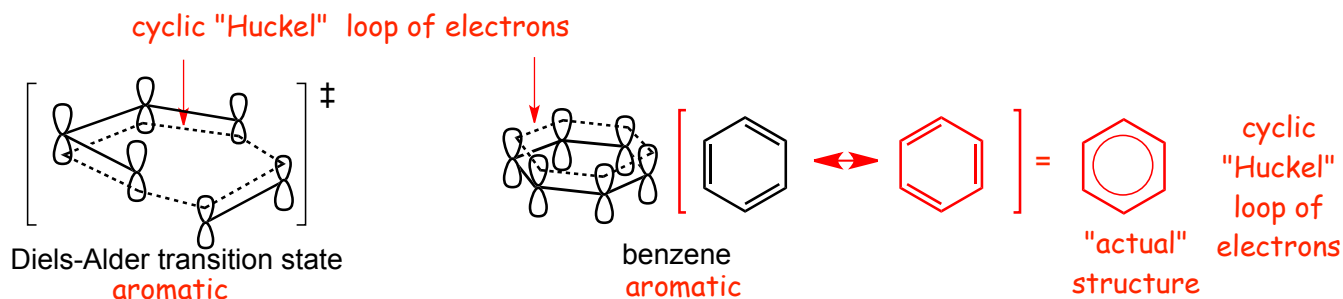


- The molecular orbitals of conjugated systems in which the overlap of the p atomic orbitals (and therefore the electrons) are in a **loop** and **different** from the linear conjugated systems we have discussed so far.
- This is the case **both** for stable organic structures (e.g. benzene and other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

1 Aromatic Transition State Theory and Pericyclic Reactions

- This is an **alternative** 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 the relative energies of the cyclic π -M.O.'s this time, we do not need their symmetry/phase wavefunction information,
- Here we are dealing with π -molecular orbitals in cyclic loops, and we will find that they have degeneracies (orbitals of equal energies).

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



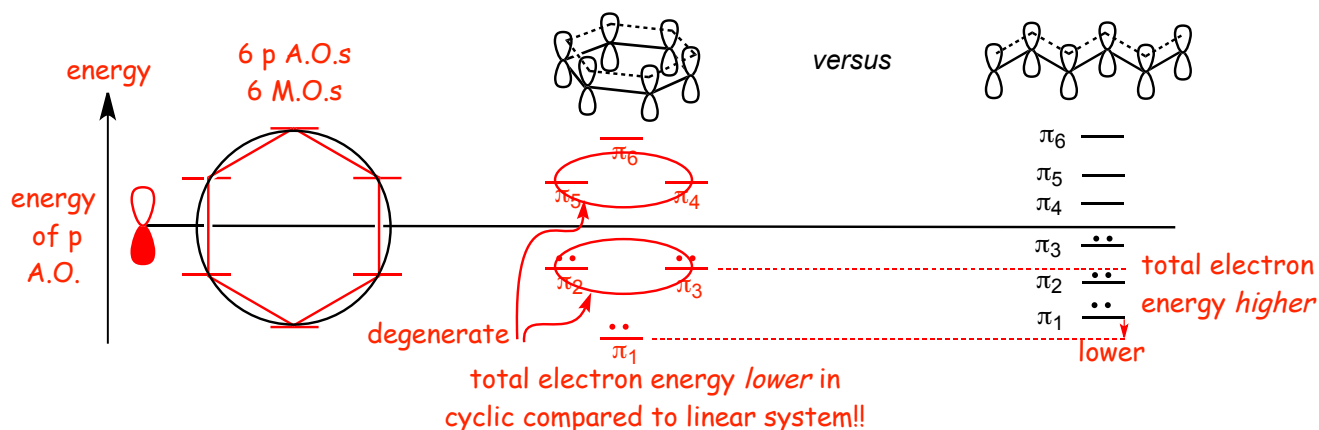
Here we are concerned **not** so much with representations of the **wavefunctions** of the orbitals, but with their **relative energies**.

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.

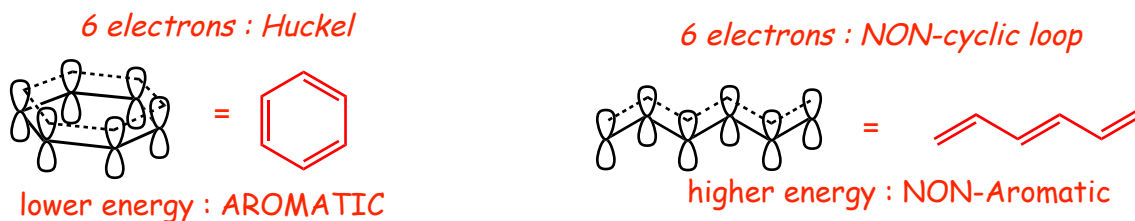
Example with Six Electrons

- 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)



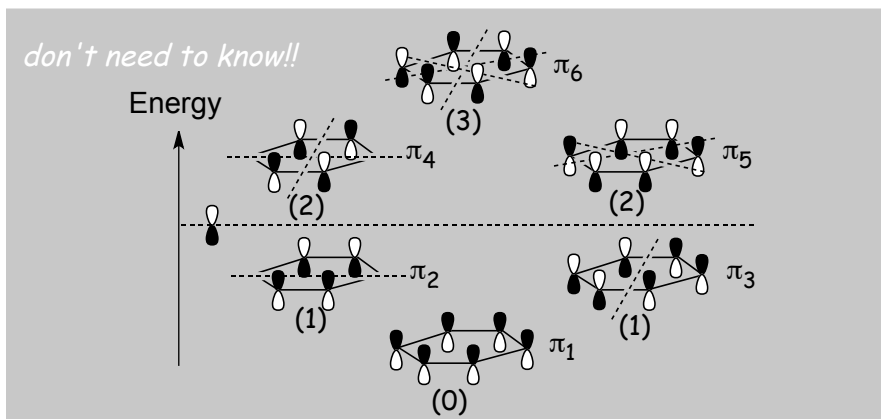
- The energy of the lowest energy fully bonding M.O. in the cyclic system is lower than the energy of the lowest energy fully bonding M.O. in the linear system simply because there is an additional bonding interaction because the loop is completed.

- 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 π -system is lower than in a comparable linear π -system.



- Putting 6 electrons in a cyclic Huckel 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.

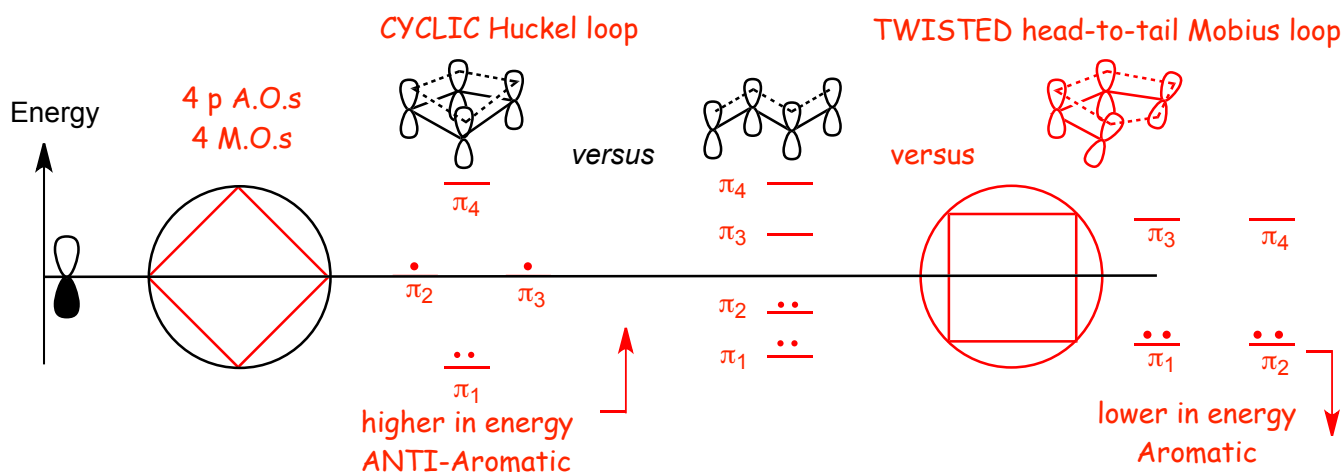
symmetries of benzene π M.O.'s (# of vertical nodes)



- The energies of the π -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**.

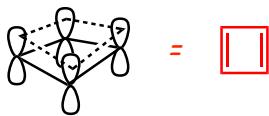
Example with Four Electrons

- 4 p A.O.'s therefore four M.O.'s
- 4 M.O.'s, therefore draw 4-membered polygon (square)

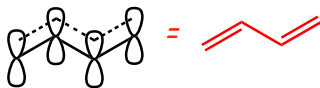


- 4 electrons in a **cyclic** Huckel loop gives 2 electrons in unfilled orbitals.
- 4 electrons in a **cyclic** Huckel loop are higher in energy compared to linear system: unstable - **antiaromatic**.
- 4 electrons in a **twisted "head-to-tail" Mobius** loop, however, are lower in energy again - aromatic.

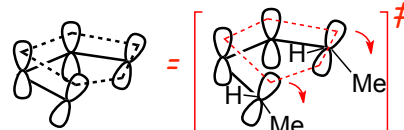
4 electrons : Huckel



higher energy : ANTI-Aromatic



4 electrons : Mobius

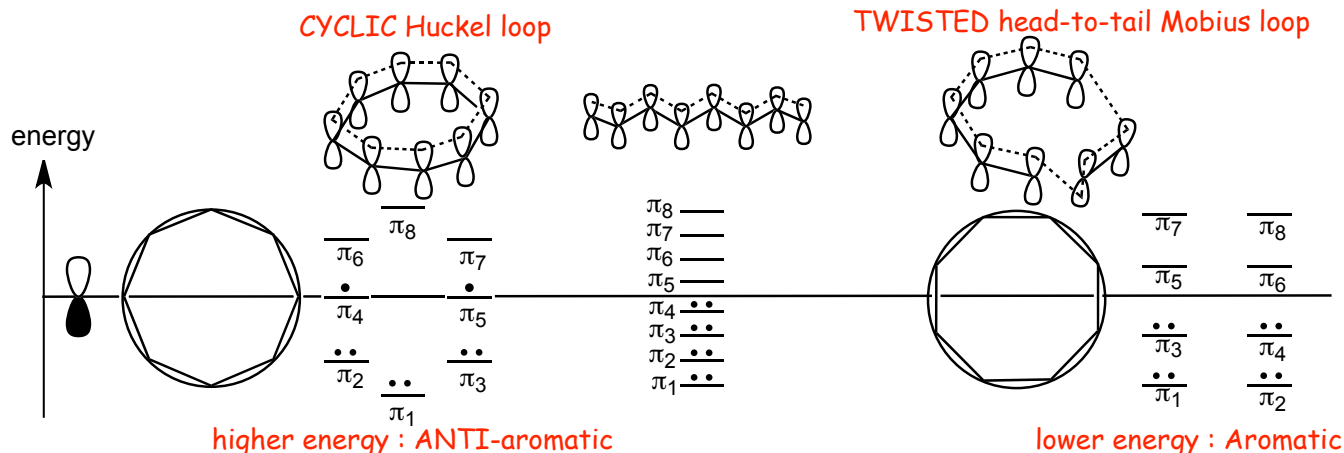


lower energy
Aromatic

electrocyclic
conrotatory

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 Huckel loop gives 2 electrons in unfilled orbitals.
- 8 electrons in a cyclic Huckel loop are higher in energy compared to linear system: unstable - **antiaromatic**.
- 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 π -loop** are **aromatic**.
- 4 electrons, 8 electrons, 12 electrons etc. $(4n)$ electrons in a **cyclic Huckel π -loop** are **antiaromatic**.

and...

- 4 electrons, 8 electrons, 12 electrons etc. $(4n)$ in a **twisted head-to-tail Mobius loop** are **aromatic**.
- 2 electrons, 6 electrons, 10 electrons etc. $(4n + 2)$ in a **twisted head-to-tail Mobius loop** are **antiaromatic**.

There is **nothing mysterious** about "n" in the Huckel rule, it is just an integer that defines series, all it means is:

when $n = 0$ then $(4n + 2) = 2$ electrons

when $n = 1$ then $(4n + 2) = 6$ electrons etc.

and...

when $n = 1$ then $(4n) = 4$ electrons

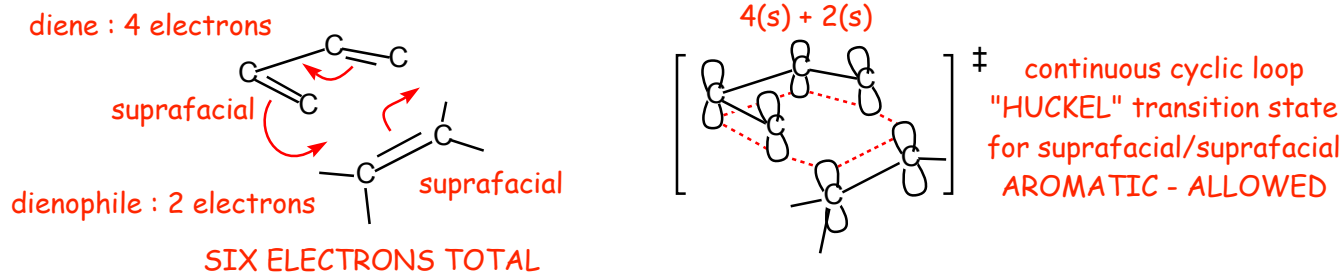
when $n = 2$ then $(4n) = 8$ electrons etc.

The Huckel rules applies to both stable molecules and transition states!

- Aromatic means lower energy electrons (more stable).
- Anti-aromatic means higher energy electrons (less stable).

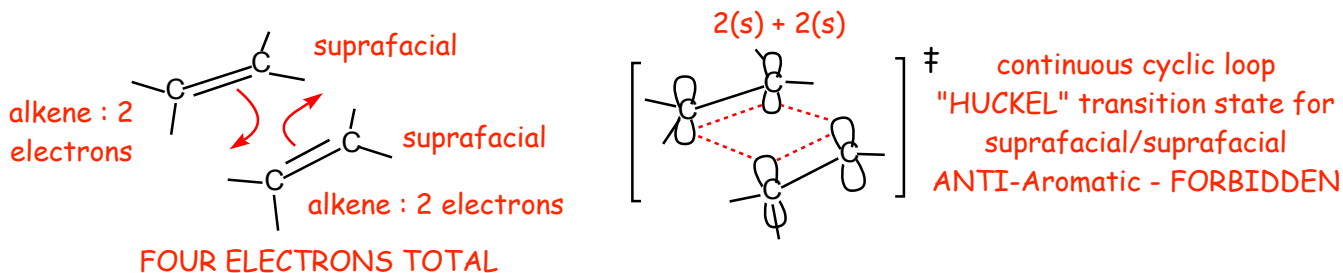
Application of Hückel/Mobius Rule to Cycloaddition Reactions

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



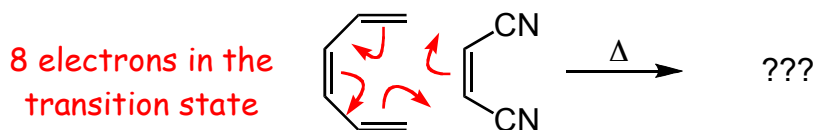
- 6 electrons in a **Huckel** cyclic loop transition state is **aromatic**, low in energy, the reaction is **allowed!**

2(s) + 2(s) cycloaddition

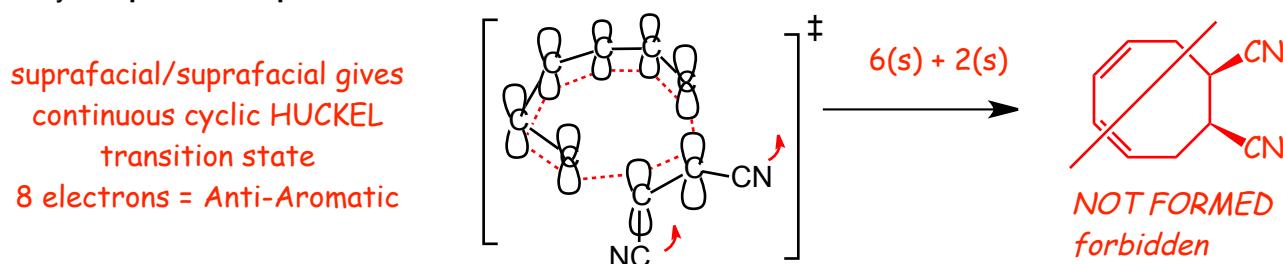


- 4 electrons in a **Huckel** transition state is **antiaromatic**, high in energy, the reaction is **forbidden!**

6 + 2 cycloaddition

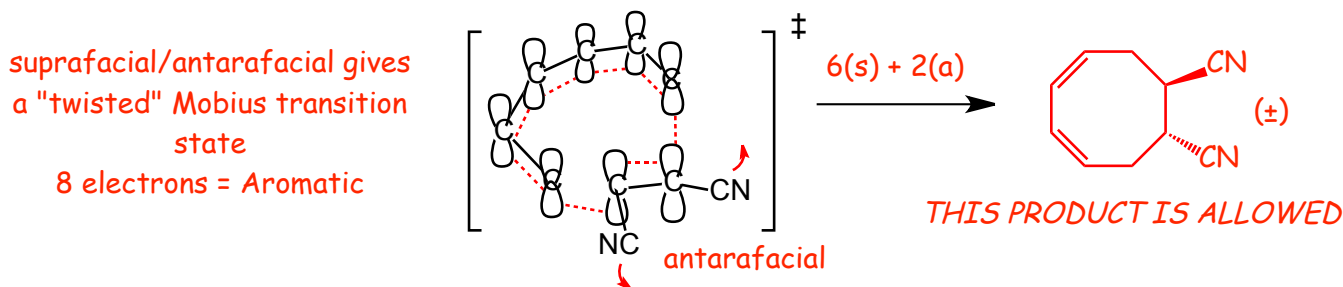


Let's try a **suprafacial/suprafacial** addition:



- $6(s) + 2(s)$ cycloaddition occurs via a Huckel continuous loop transition state.
- 8 electrons in cyclic Hückel transition state is **antiaromatic**, relatively high energy electrons : the reaction is **forbidden**.

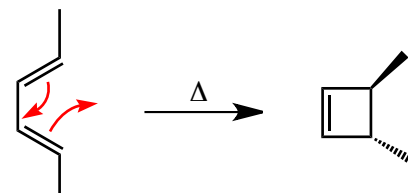
Let's try a **suprafacial/antarafacial** addition:



- 8 electrons in a **twisted Möbius** transition state is low in energy: **aromatic**.
- 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/Möbius Rule to Electrocyclic Reactions

2 curved arrows
4 electrons

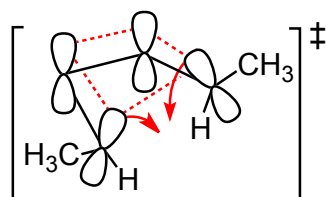


- 2 curved arrows, therefore 4 electrons involved in the transition state.

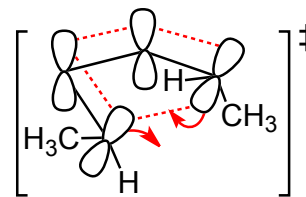
continuous Hückel transition state

TWISTED Möbius transition state

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

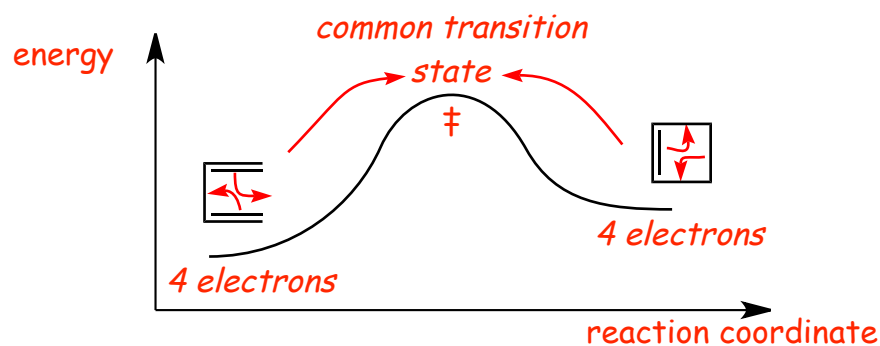


DISROTATORY



CONROTATORY

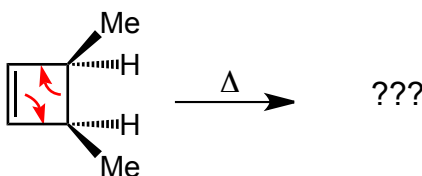
4 electrons in a TWISTED Möbius transition state - ALLOWED!!



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

Examples

4 electrons

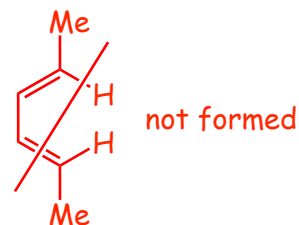
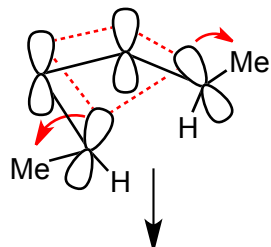


- 4 electrons involved in the transition state.

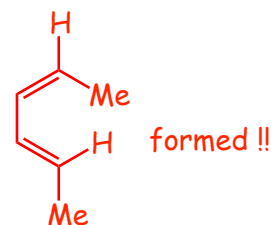
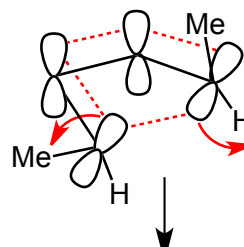
DISROTATORY ring OPENING

CONROTATORY ring OPENING

cyclic Hückel transition state
4 electrons:
FORBIDDEN!!



twisted Möbius transition state
4 electrons:
ALLOWED!!!

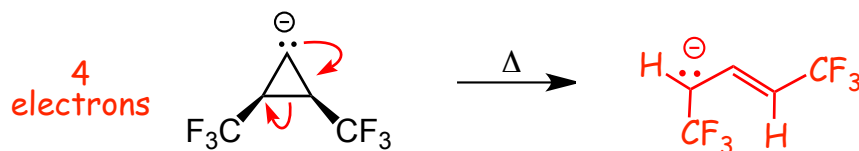


An example with 6 electrons:



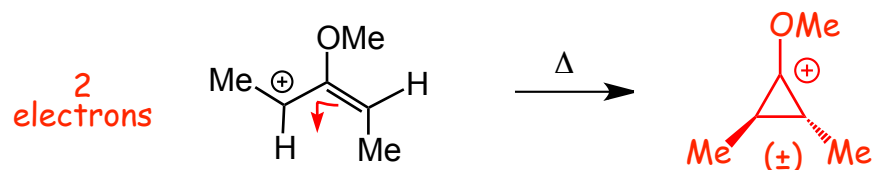
- There is a 6-electron Hückel transition state for disrotatory ring opening: allowed.

An example with 4 electrons:



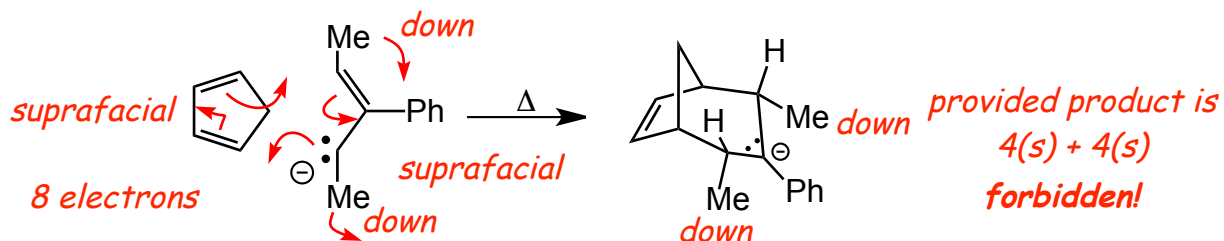
- There is a 6-electron Möbius transition state for conrotatory ring opening: allowed.

An example with 2 electrons:



- There is a 2-electron Hückel transition state for disrotatory ring opening: allowed.

Is the **Following Reaction** with a provided product **Allowed or Forbidden**?



- In **the provided** product, the addition must have been **suprafacial/suprafacial** (like the Diels-Alder).
- The provided product must have been formed in a **Hückel** transition state.
- However, the reaction involves 8 electrons, which requires a Möbius transition state for lowest energy electrons.
- A Möbius transition state would require a suprafacial/antarafacial reaction.
- Because the **provided product** was formed in a suprafacial/suprafacial reaction, **the provided product must be forbidden** (the allowed reaction would have proceeded via a Möbius transition state).

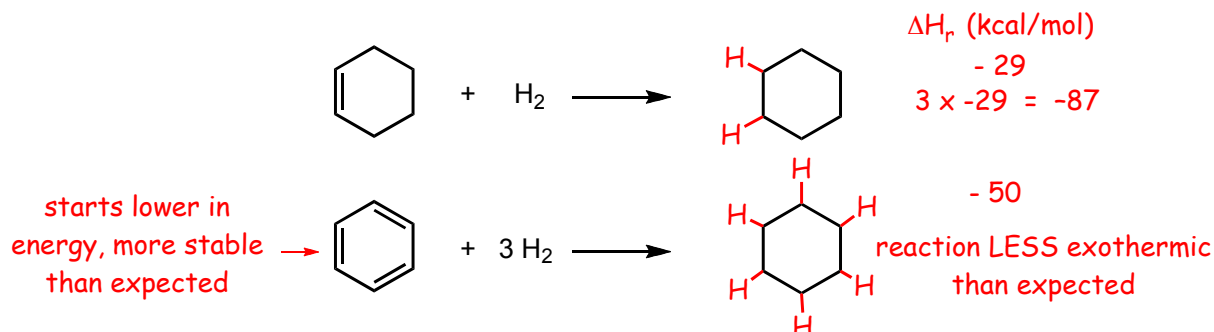
2 Application to Stable Molecules

The Huckel Rule Summary:

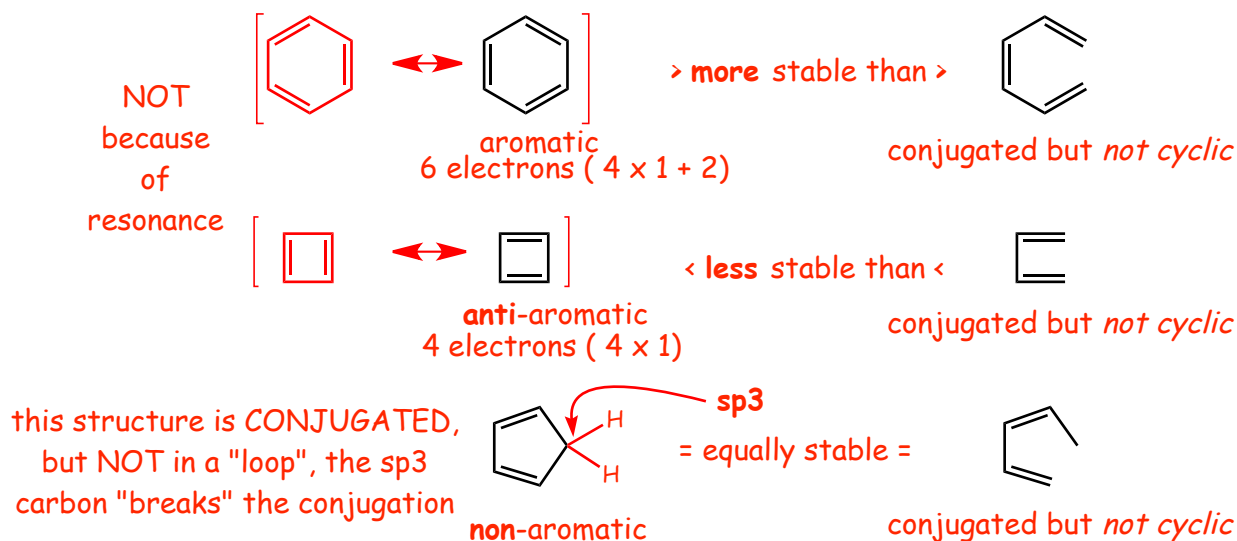
(4 n + 2) electrons in a cyclic conjugated system are **Aromatic i.e., 2e, 6e, 10 electrons etc.**

(4 n) electrons in a cyclic conjugated system are **Antiaromatic i.e. 4e, 8e, 12 electrons etc.**

Example

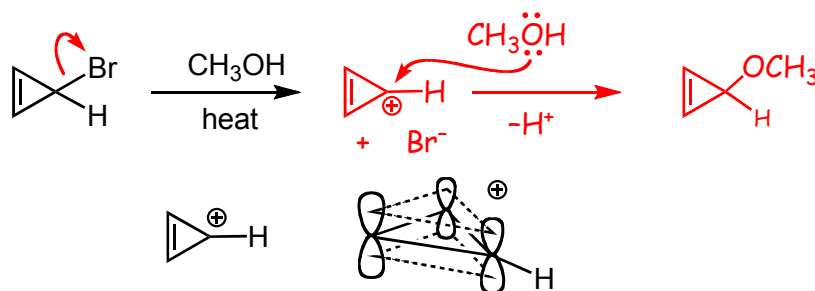


- Benzene is **more stable** than expected for cyclohexatriene by ca 37 kcal/mol, this extra stabilization is due to **aromaticity**.
- This stabilization can **not** be explained merely by conjugation or resonance, because:



3 Aromatic Ions

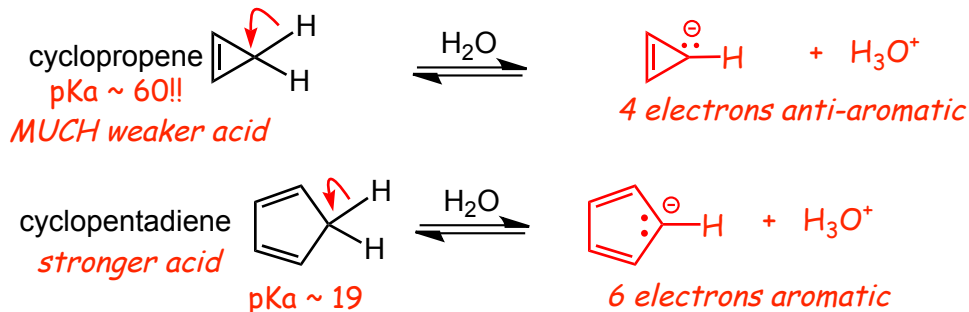
Example in a surprisingly fast S_N1 reaction:



- There are 2 electrons in a cyclic cation system, **all** carbon atoms are sp² hybridized, cyclic conjugated system
- The cation is therefore aromatic and is therefore **stabilized**.

Examples in Bronsted acidity

- Compare cyclopropene and cyclopentadiene as Bronsted acids:



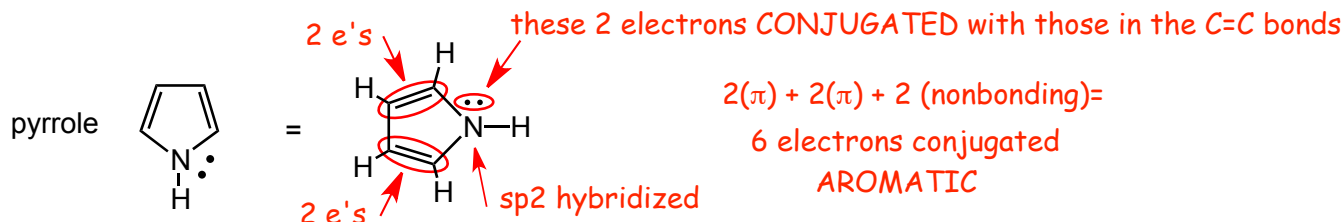
- The conjugate base anion of **cyclopropene** has **4 electrons in a conjugated Huckel loop**, it is antiaromatic, is very unstable, has very high energy electrons, consequently, cyclopropene is a **very weak** Bronsted acid.
- The conjugate base anion of **cyclopentadiene** has 6 electrons in a **conjugated 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

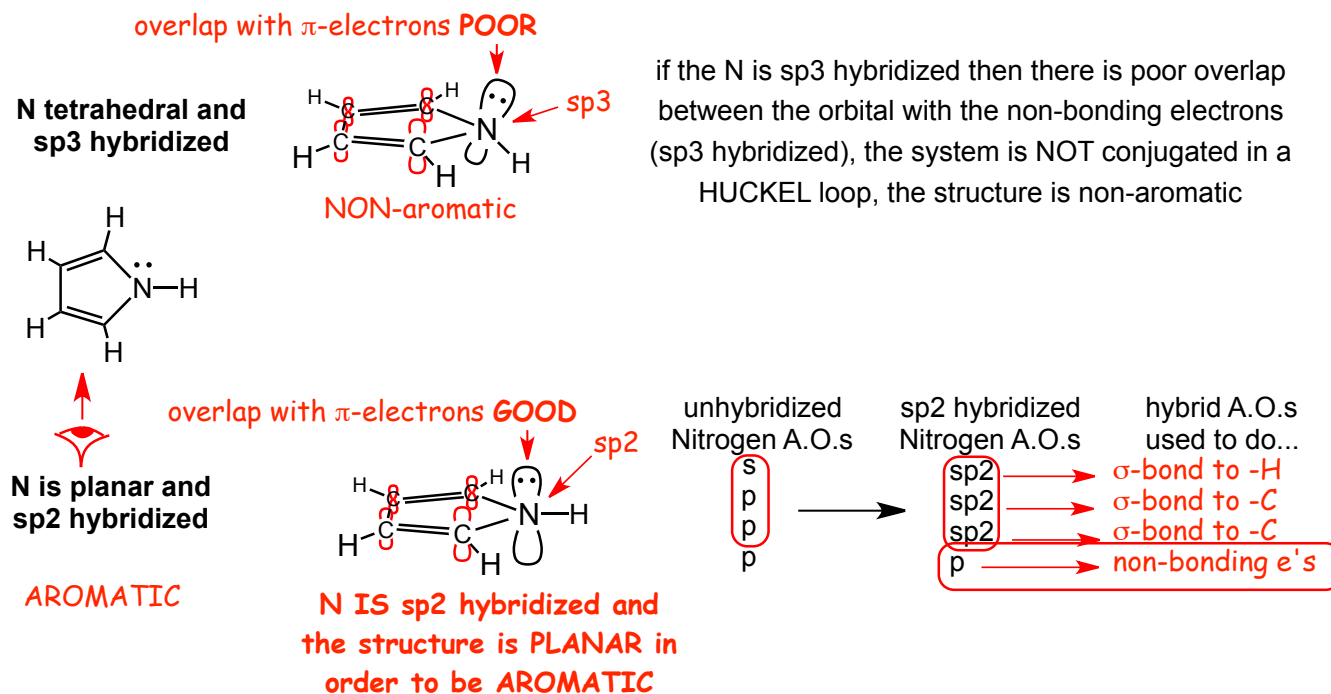
A Heterocycle is a cyclic system containing N, O, S etc. that has replaced a carbon atom in a ring structure.

Pyrrole as an example

- The nitrogen atom in pyrrole looks like it should be sp^3 hybridized, **however**, it is actually sp^2 hybridized!

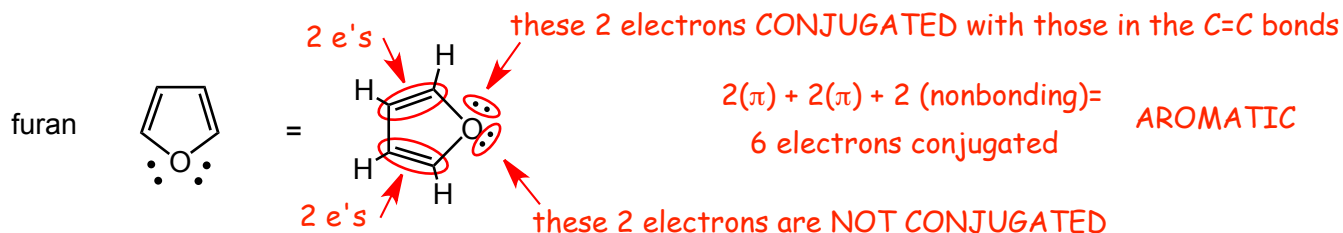


- The Nitrogen atom **changes hybridization from sp^3 to sp^2** because in doing so it can become **aromatic**.
- Hybridization and molecular geometry are intimately connected, if the structure is planar (flat), the nitrogen must be sp^2 hybridized, if the N is sp^2 hybridized it must be planar.
- If the N is sp^3 hybridized the structure can't be planar (the nitrogen is tetrahedral), if the N has tetrahedral geometry it has to be sp^3 hybridized.
- Let's remind ourselves what sp^2 and sp^3 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

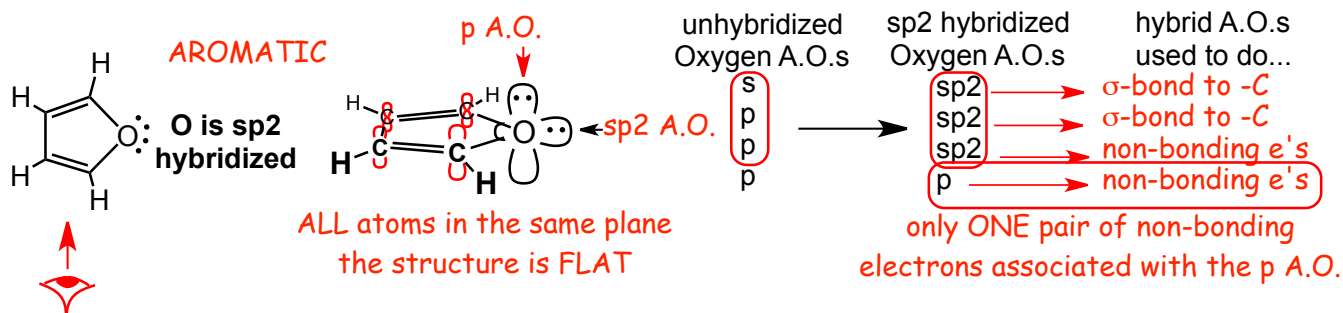


- Because the N is sp^2 hybridized the non-bonding electrons are associated with a p A.O., overlap with the pi-electrons is **good**, they **are** conjugated with the π -electrons, there are **six** electrons in a cyclic conjugated loop
- By having a formal sp^2 hybridization for the N atom, pyrrole becomes **aromatic**.

Furan as an example

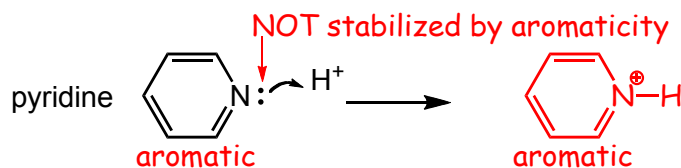


- The oxygen in furan O is **sp² hybridized** to allow **one** (and only one) of the electron pairs to be **conjugated** with the electrons in the C=C bonds, **resulting in 6 electrons in a cyclic Huckel loop**.
- Only **one pair** of non-bonding electrons on the oxygen are counted, let's remind ourselves what sp² hybridization really means for the oxygen atom in furan, again, we must look from the side:

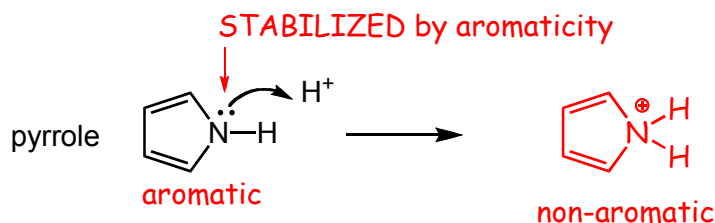


- Because the O is sp² hybridized the **one pair** of non-bonding electrons are associated with a p A.O., overlap of these electrons with the π -electrons results in a cyclic conjugated system with **six electrons - aromatic**.
- The other pair of non-bonding electrons are in an sp² hybridized A.O., they are at **right angles** (orthogonal to) to the conjugated π -system, they are **irrelevant** to aromaticity.

Heterocycle Bronsted bases as examples

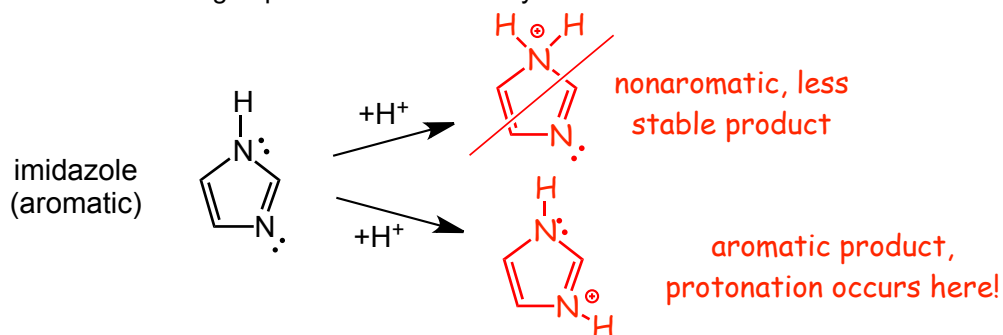


- Pyridine is a (relatively) strong base, as a base it gets a pair of non-bonding electrons into a bond.
- Protonated pyridine is a (relatively) weak acid, it is **aromatic**.



- 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?



- The protonation reaction that preserves the stable aromatic system is favored.

5 Molecules Avoid AntiAromaticity by Becoming Non-Planar

Annulenes: Are cyclic hydrocarbons with alternating single/double bonds.



4 electrons anti-aromatic

- Cyclobutadiene is [4]annulene it is **antiaromatic**.



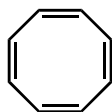
6 electrons aromatic

- Benzene is [6]annulene it is **aromatic**.

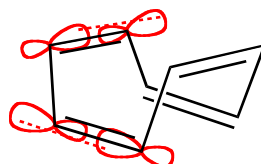


8 electrons ~~anti-aromatic nonaromatic!!~~

- Cyclooctatetraene is [8]annulene it is **nonaromatic!**
- Why is this?

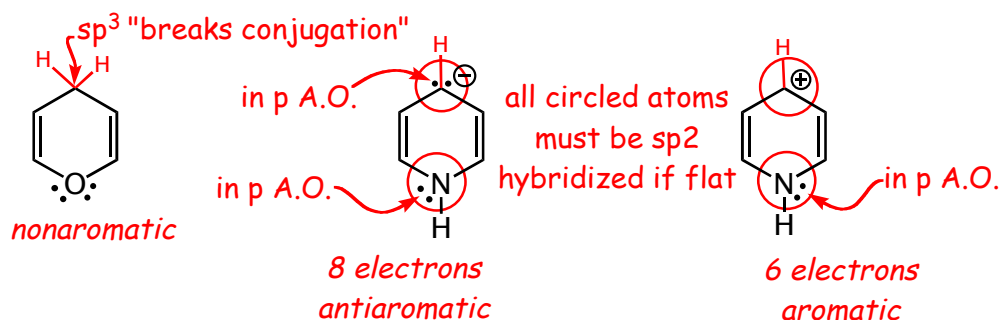


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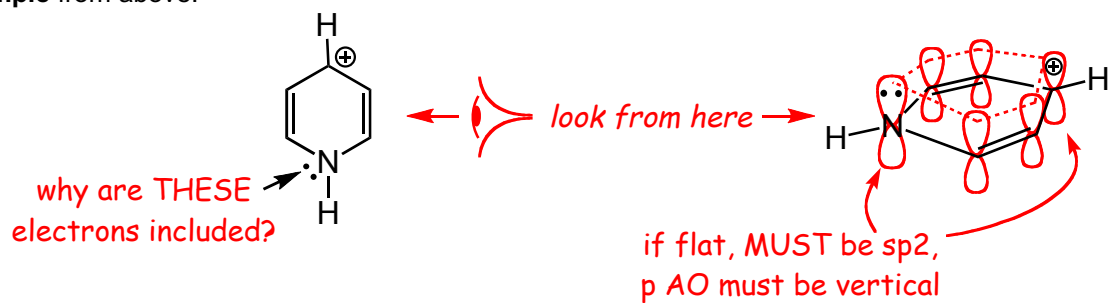
- Cyclooctatetraene avoids being antiaromatic by assuming a non-planar "tub" shape that breaks the conjugation of the p A.O.s, in this conformation all of the p AOs are **not parallel** any more.
- A π -systems must be flat to be aromatic or antiaromatic to ensure parallel array of p A.O.'s and a **Huckel** loop.
- Most annulenes are in fact non-planar.
- In reality, there are few examples of true antiaromatic systems for this reason, **antiaromatic** structures **tend to become non-planar** to avoid the high-energy situation represented by antiaromaticity.

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



- Which electrons are counted?

The example from above:



- The electrons on nitrogen are counted because if the structure is **flat (planar)**, the N atom must be sp^2 hybridized, and if it is sp^2 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.