

# Lecture 2

## A Molecular Orbital Approach to $\pi$ Bonding

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## Reference textbook

- “Organic Chemistry” by Paula Yurkanis Bruice, 8th Edn.
  - Chapter 8, sub sections concerning aromatic compounds, esp. **sections 8.8, 8.19**

**Refresher** from previous learning -

- Chapter 1, **section 1.6, Introduction to MO theory.**

This lectures assumes prior learning in **molecular orbital theory**

**REVISE YOUR 1<sup>st</sup> year notes if you need a refresher**

<https://www.masterorganicchemistry.com>

Is also a good resource, and referred to in this lecture

# Learning Objectives – Lecture 2

## *Section 1 – Valence bond and molecular orbital pictures of unsaturated hydrocarbons*

Sketch diagrams to depict how  $\pi$ -overlap of extended systems of p-orbitals can give rise to molecular orbitals of differing energy (and rank the resulting molecular orbitals in order of increasing stability)

Construct energy level diagrams for the  $\pi$ -systems of cyclic hydrocarbon molecules (and derived ions) using the “polygon drawn on its vertex” (“Frost circle”) approach, and use these diagrams to classify the system as aromatic or **not aromatic (the later being non-aromatic and/or anti-aromatic)**

# Lecture Outline: L2

## **1. Molecular Orbital diagrams (*mostly recap on previous knowledge*)**

- Hydrogen
- Ethene
- 1,3-Butadiene

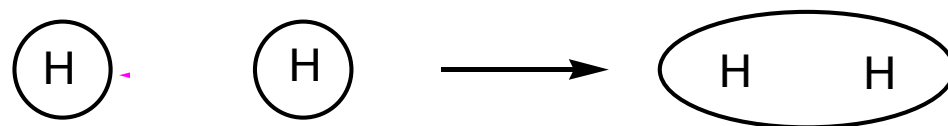
## **2. MO diagrams for cyclic $\pi$ systems**

- Stability of aromatic compounds
- Comparison to compounds that are not aromatic
- Frost circle

# 1. Molecular orbital diagrams

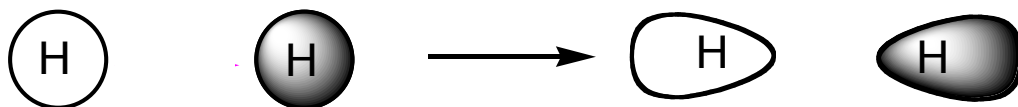
## The hydrogen molecule, $H_2$

- MO theory assumes that the valence electrons of the atoms within a molecule become the valence electrons of the entire molecule.
- Molecular orbitals are assumed to be formed by a **Linear Combination of Atomic Orbital** wave functions (LCAO).
- A combination of 'n' atomic orbitals will give rise to 'n' molecular orbitals.



$\Psi_1$   
a  $\sigma$  bond/orbital

and



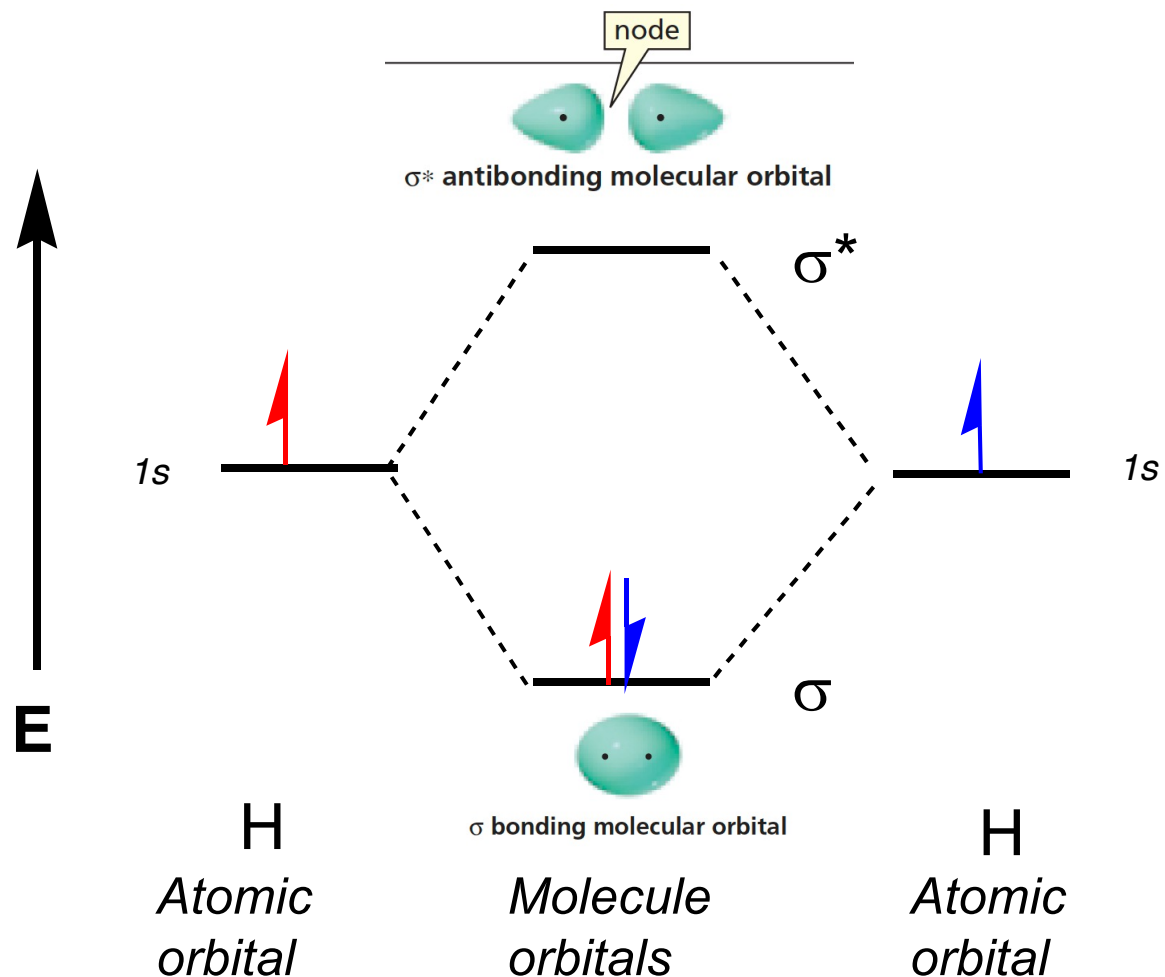
$\Psi_2$   
a  $\sigma^*$  antibonding  
orbital

# 1. Molecular orbital diagrams

## The hydrogen molecule, $\text{H}_2$

- The antibonding orbital switches phase. This is referred to as a node.
- In general MO's increase in energy with increasing numbers of nodes.

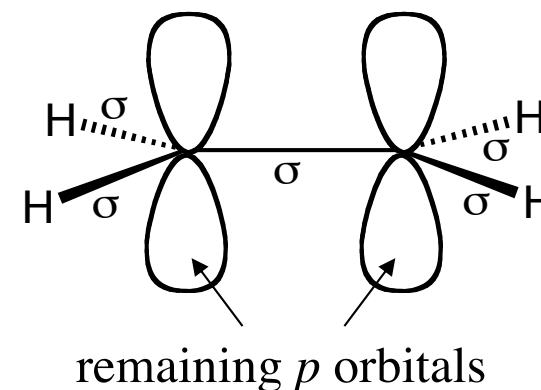
Energy level  
mixing diagram  
for  $\text{H}_2$ :



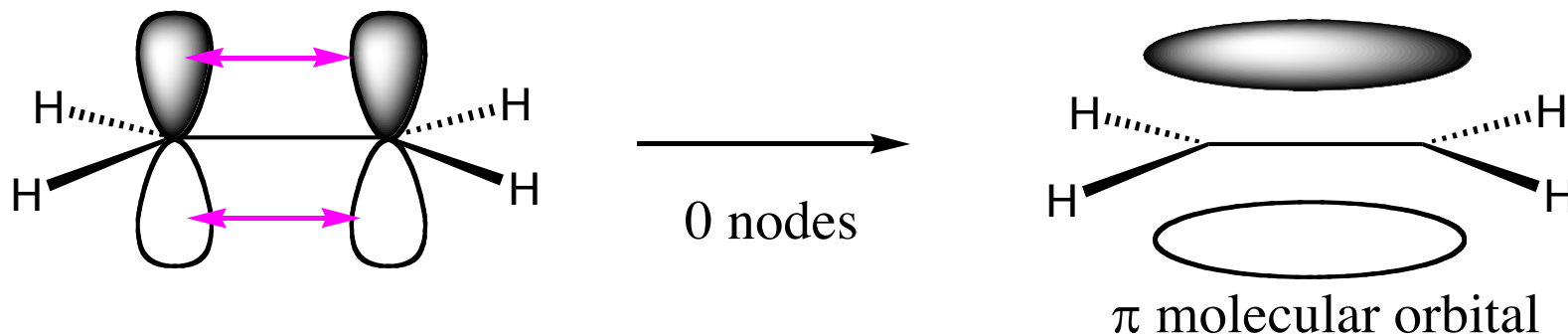
# 1. Molecular orbital diagrams

## Ethene (ethylene), $\text{H}_2\text{C}=\text{CH}_2$

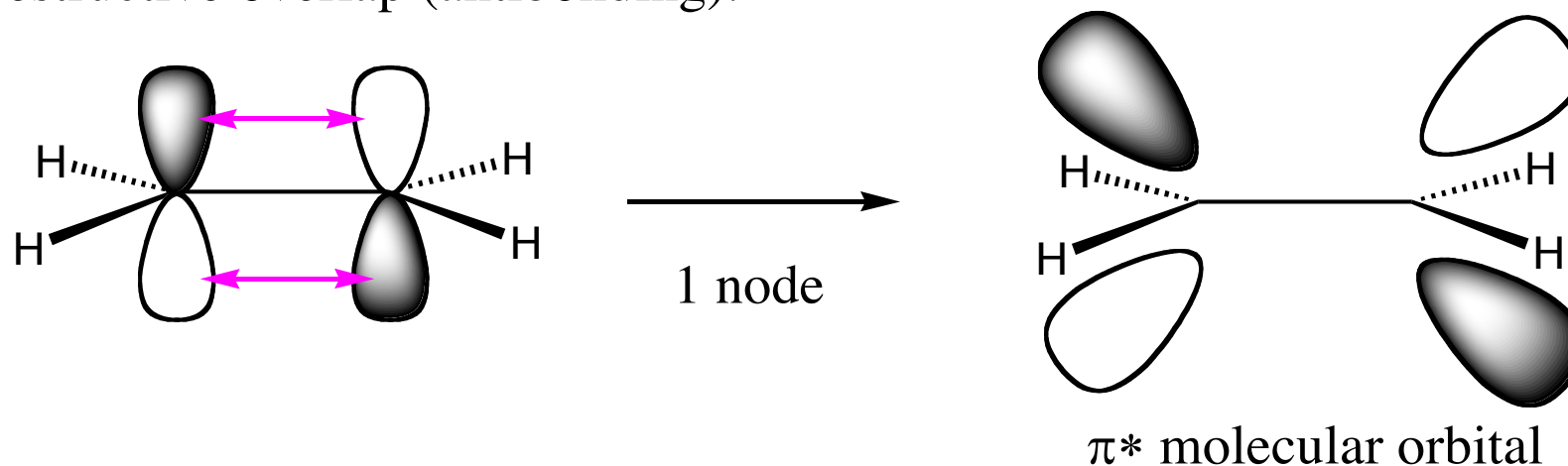
- Developing the  $\pi$  **system only**
- The two  $p$  orbital can either be in-phase or out-of-phase



Constructive overlap (bonding):



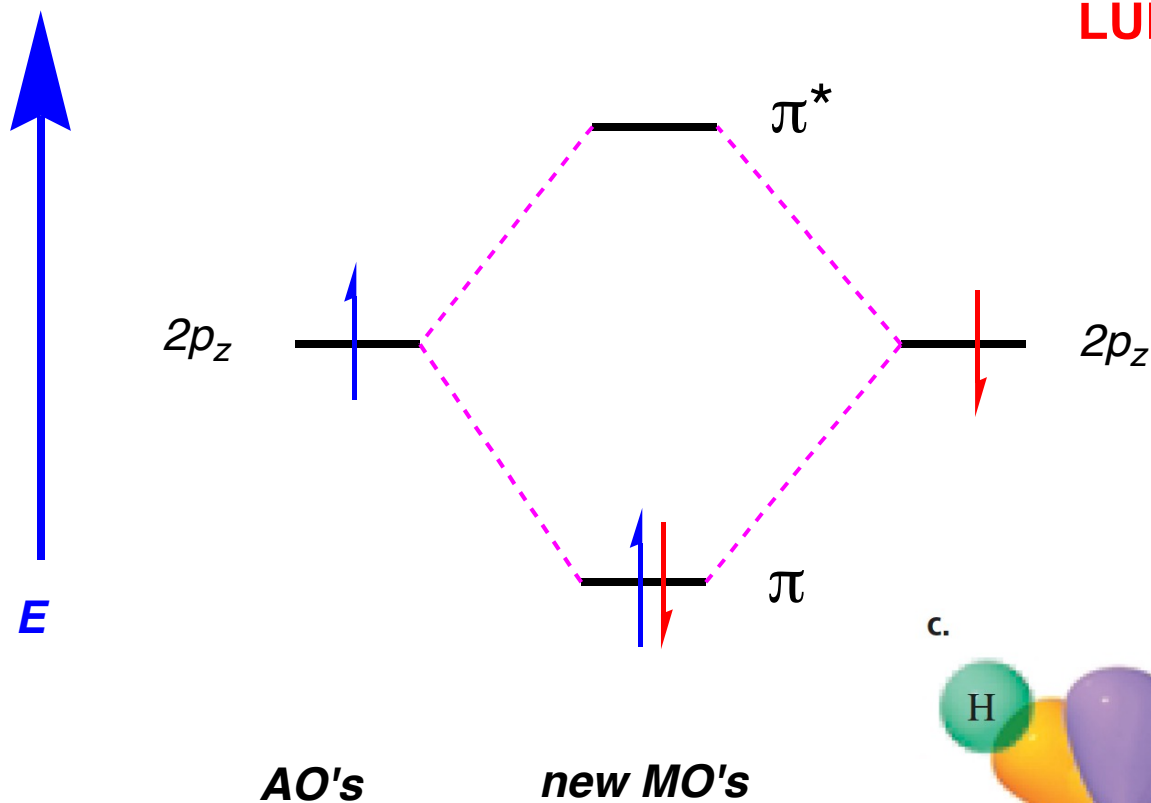
Destructive overlap (antibonding):



# 1. Molecular orbital diagrams

## Ethene (ethylene), $\text{H}_2\text{C}=\text{CH}_2$

- Mixing MO diagram for  $p$  orbitals

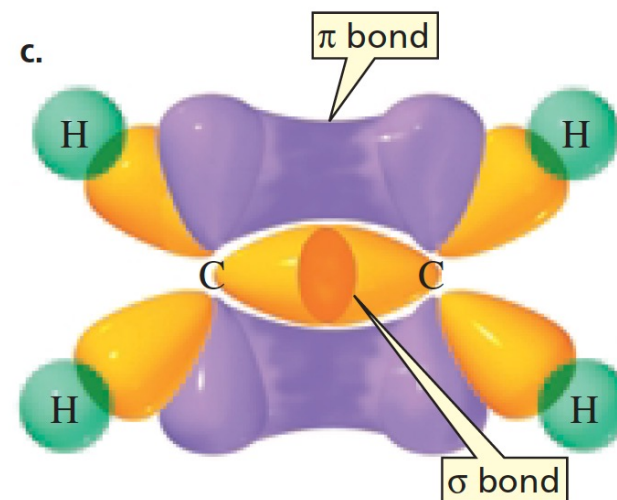


Refresher: The terms

**HOMO**

**LUMO**

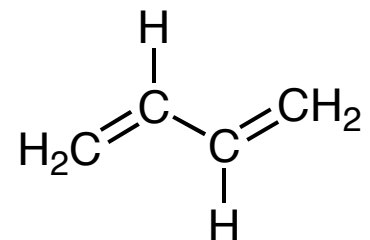
- Don't forget ethene also has 4 x C-H sigma bonds and 1 x C-C sigma bond



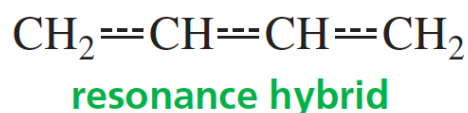
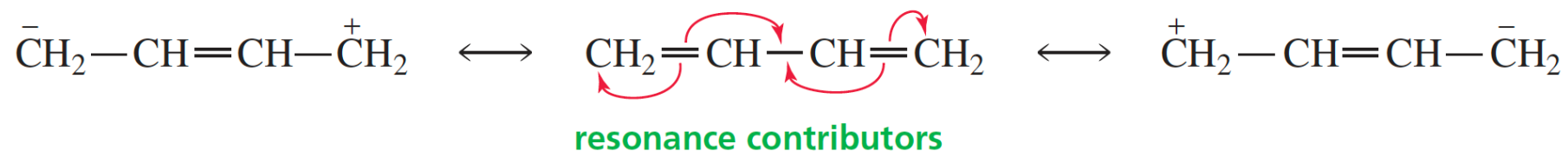


# 1. Molecular orbital diagrams

## 1,3-Butadiene

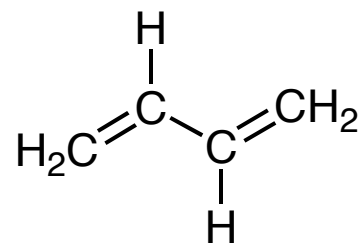


- In lecture 1 we used resonance contributors to explain why compounds are stabilised by electron delocalisation.



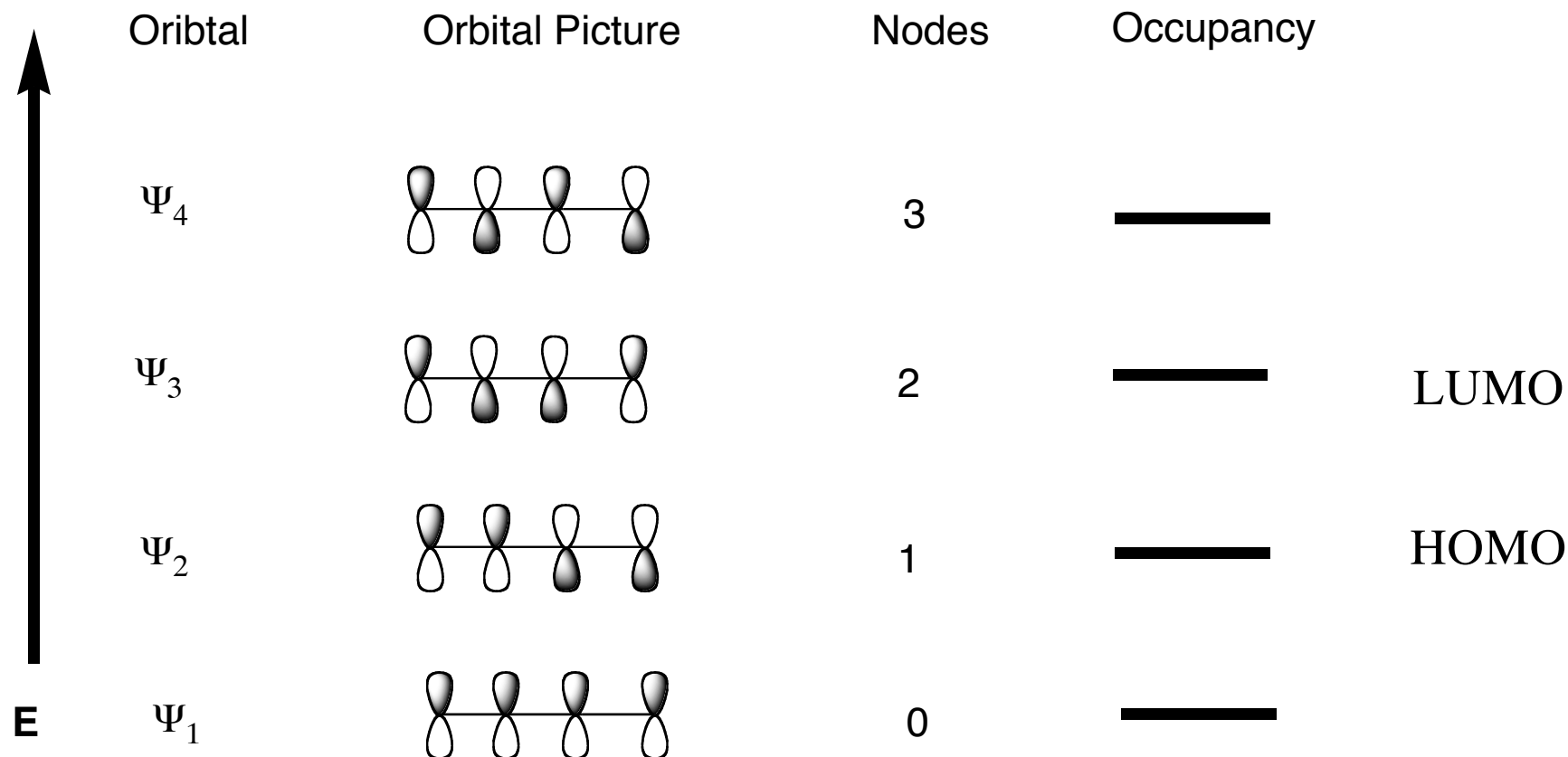
- LCAO-MO theory can also explain why electron delocalization stabilises compounds.

# 1. Molecular orbital diagrams



## 1,3-Butadiene

- The number of molecular orbitals for a  $\pi$ -system is equal to the number of contributing  $p$  orbitals.
- The 4 molecular  $p$  orbitals may be pictured (in the ground state) as:



MO calculations show that the  $\pi$  electron energy for 1,3-butadiene is lower than that for two isolated double bonds.

## 2. MO diagrams for cyclic $\pi$ systems

- A good resource is <https://www.masterorganicchemistry.com/2017/05/05/the-pi-molecular-orbitals-of-benzene/>, the following slides show some diagrams from this website.
- Also further explanation of Frost circles can be found at <https://www.masterorganicchemistry.com/2017/05/17/frost-circles/>

## 2. MO diagrams for cyclic $\pi$ systems

### Frost circle, or the 'polygon drawn on its vertex'

- To draw the molecular orbitals of a **cyclic  $\pi$  -system**, draw the appropriate polygon, vertex-down, and then fill it up with electrons (*polygon method*)
- The relative energies of the molecular orbitals correspond to the relative levels of the polygon vertices

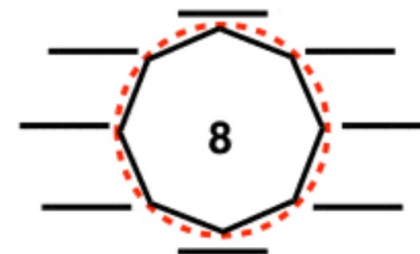
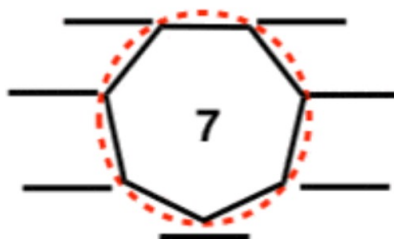
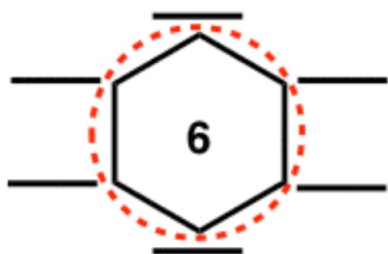
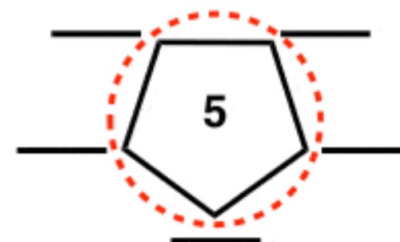
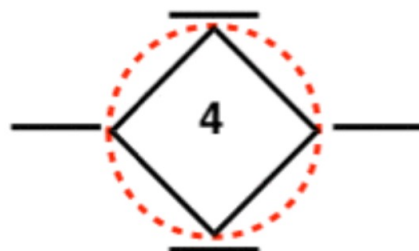
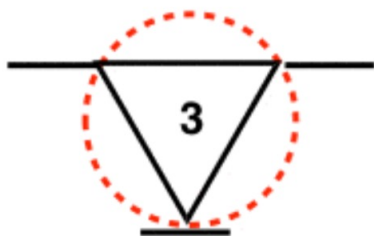


- Draw a circle around the corners of the polygon – this is a **Frost circle**
- Draw the circle halfway line – below the line = **bonding MOs**, on or above the line = **antibonding MOs**
- This applies to all **cyclic  $\pi$  -systems**, including *but not always* aromatic.

## 2. MO diagrams for cyclic $\pi$ systems

Frost circle, drawn around a 'polygon drawn on its vertex'

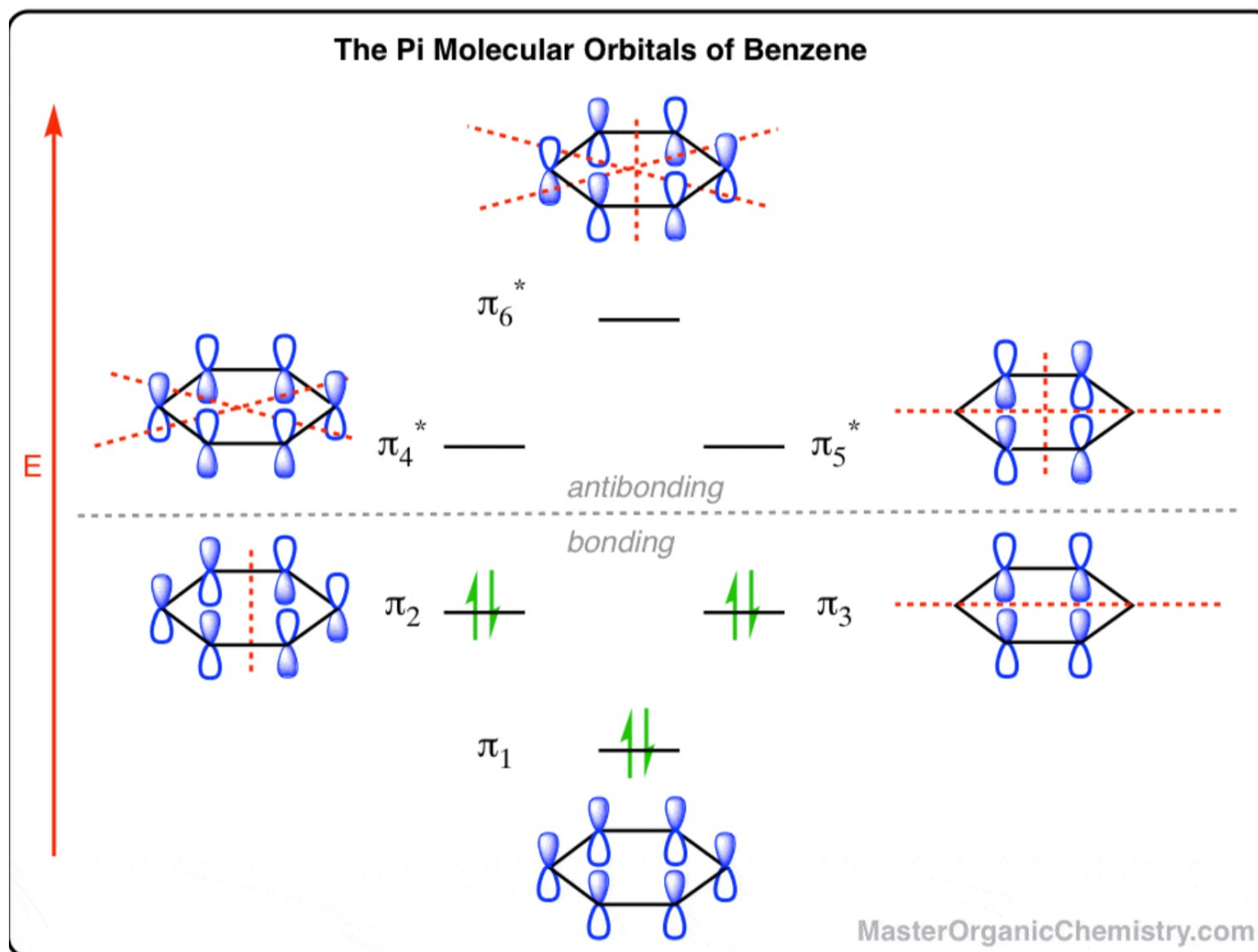
- E.g. for different ring sizes -



## 2. MO diagrams for cyclic $\pi$ systems

### Benzene

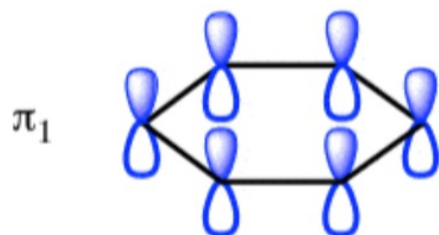
- Why are there 4 'levels' of MO energies in benzene, and not 6?
- Let's first look at benzene, then compare this to linear hexatriene



## 2. MO diagrams for cyclic $\pi$ systems

### Benzene

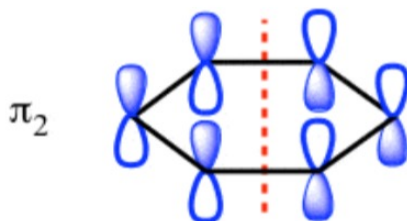
- Why are there 4 'levels' of MO energies in benzene, and not 6?  
Because of **symmetry** (i.e. the planarity of the molecule)



- Lowest energy MOs
- There are ZERO nodes **between** orbitals
- (remember there is a node in the plane but that's inherent to all p orbitals)

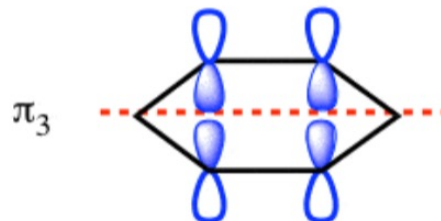
- Cyclic systems have nodal planes, rather than 'nodes'
- There are TWO ways to arrange the orbitals of benzene such that each contains ONE nodal plane
- The MO energy levels are the same "degenerate"

Benzene with one nodal plane



"through-bond"

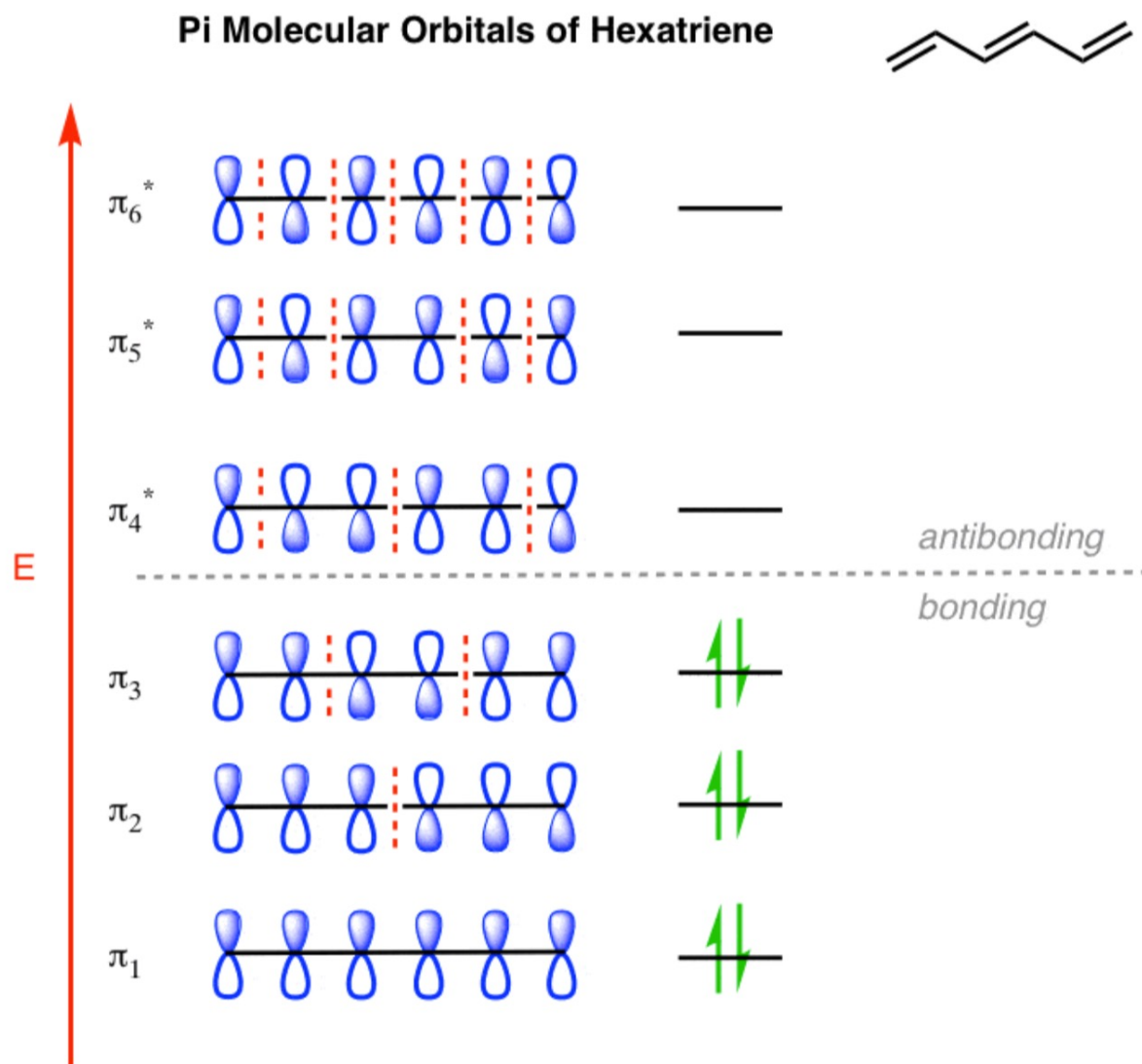
Benzene with one nodal plane (2)



"through-atom"

## 2. MO diagrams for cyclic $\pi$ systems

### Benzene compared to linear hexatriene





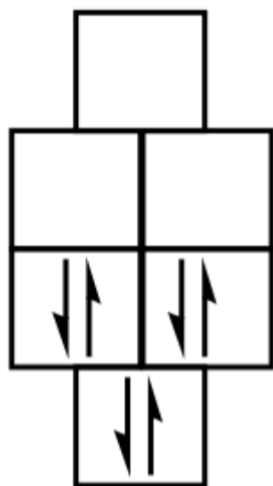
## 2. MO diagrams for cyclic $\pi$ systems

### Benzene compared to linear hexatriene

Crudely represented you can think of it as -



hexatriene



benzene

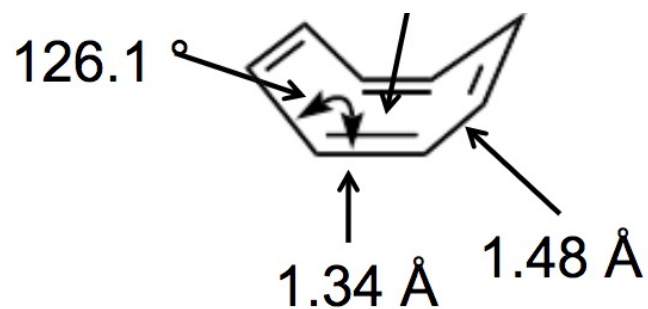
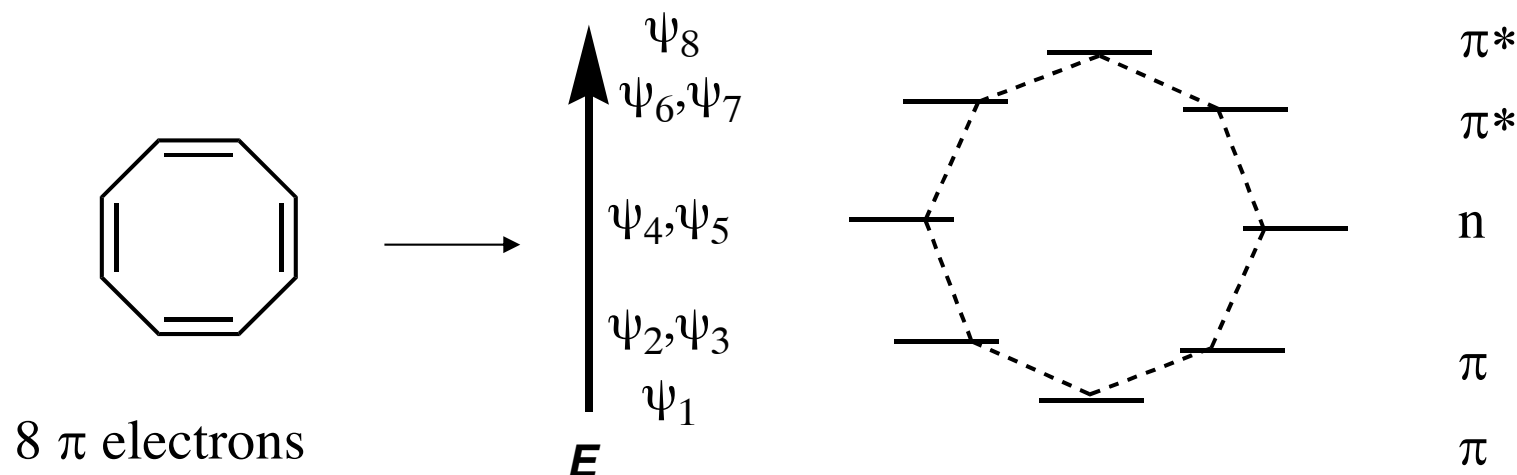
- The HOMO of benzene is lower in energy than the HOMO of hexatriene
- Lower energy = more stable, more unreactive

**BREAK**

## 2. MO diagrams for cyclic $\pi$ systems

### Cyclooctatetraene

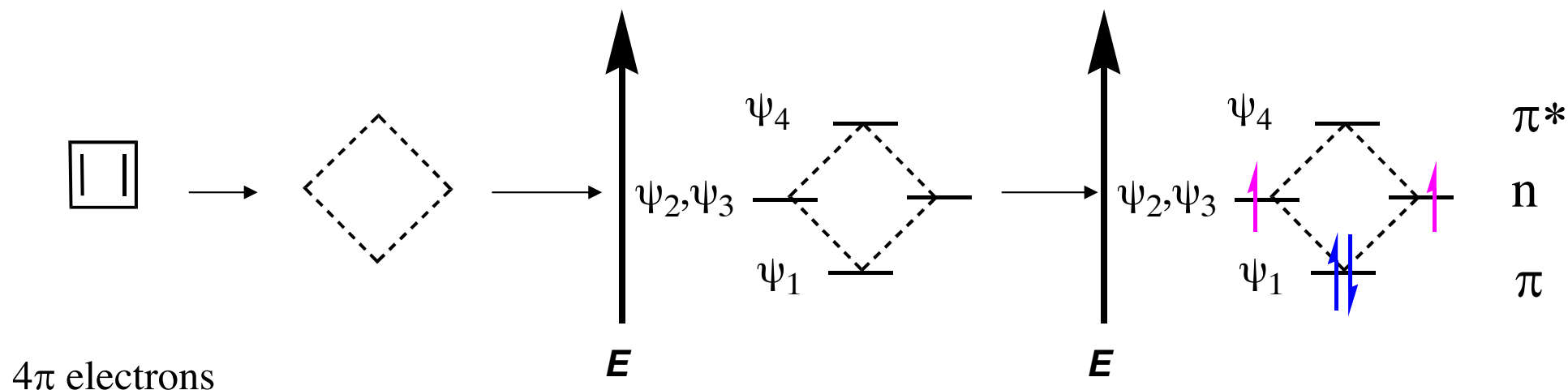
- Is this compound aromatic? We can use the MO approach to tell -



## 2. MO diagrams for cyclic $\pi$ systems

### 1,3-Cyclobutadiene

- Draw the polygon standing on one vertex.
- Draw an energy level at each vertex.
- Populate the 4  $\pi$  electrons starting from the lowest MO.





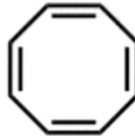
Is 1,3-cyclobutadiene aromatic?

## 2. MO diagrams for cyclic $\pi$ systems

### Summary of aromatic versus other systems

Antiaromatic Compounds Are *Unusually* Unstable

What are the key factors that determine whether a molecule is antiaromatic?

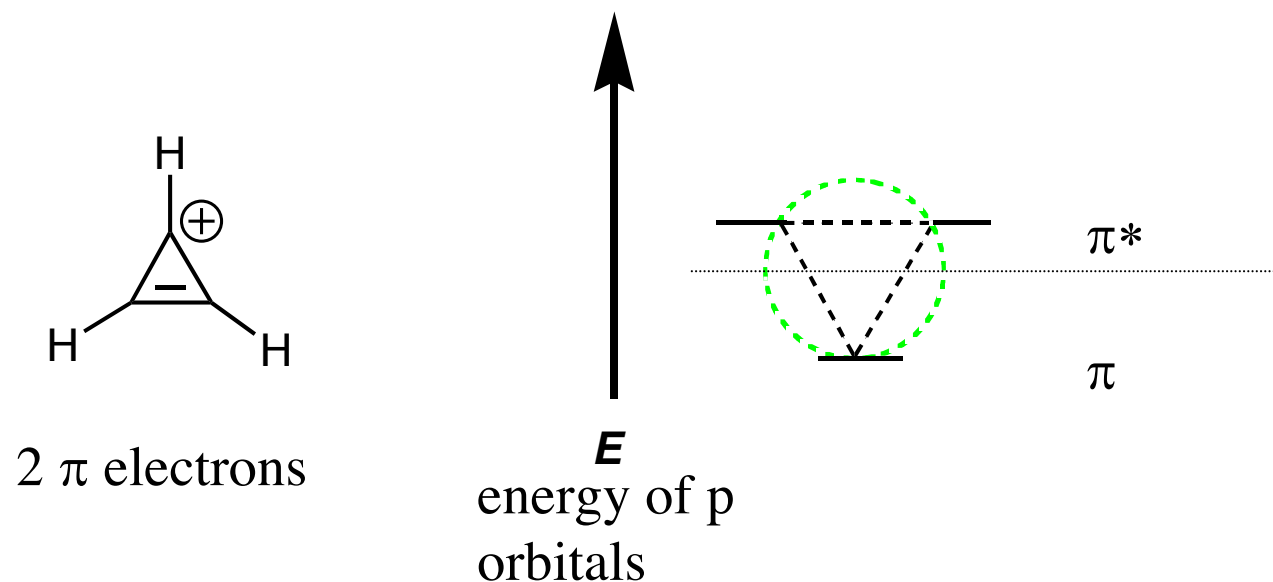
Summary: Anti-Aromaticity		
Aromatic	Anti-Aromatic	Non-Aromatic
<i>unusually stable</i>	<i>unusually unstable</i>	<i>everything else</i>
•Cyclic	•Cyclic	<i>Fails any one of the 4 criteria on the left</i>
•Conjugated	•Conjugated	
•(4n+2) Pi electrons	•(4n) Pi electrons	
•Flat	•Flat	
e.g. 	e.g. 	e.g. 
<b>benzene</b> (resonance energy of 36 kcal/mol)	<b>cyclobutadiene</b> (only stable below -100 °C )	<b>cyclooctatetraene</b> (adopts a tub-like shape to "escape" anti-aromaticity)

Read this - <https://www.masterorganicchemistry.com/2017/03/27/antiaromaticity/>

## 2. MO diagrams for cyclic $\pi$ systems

### Charged systems

- The same 'polygon' and Frost circle workflow applies.....



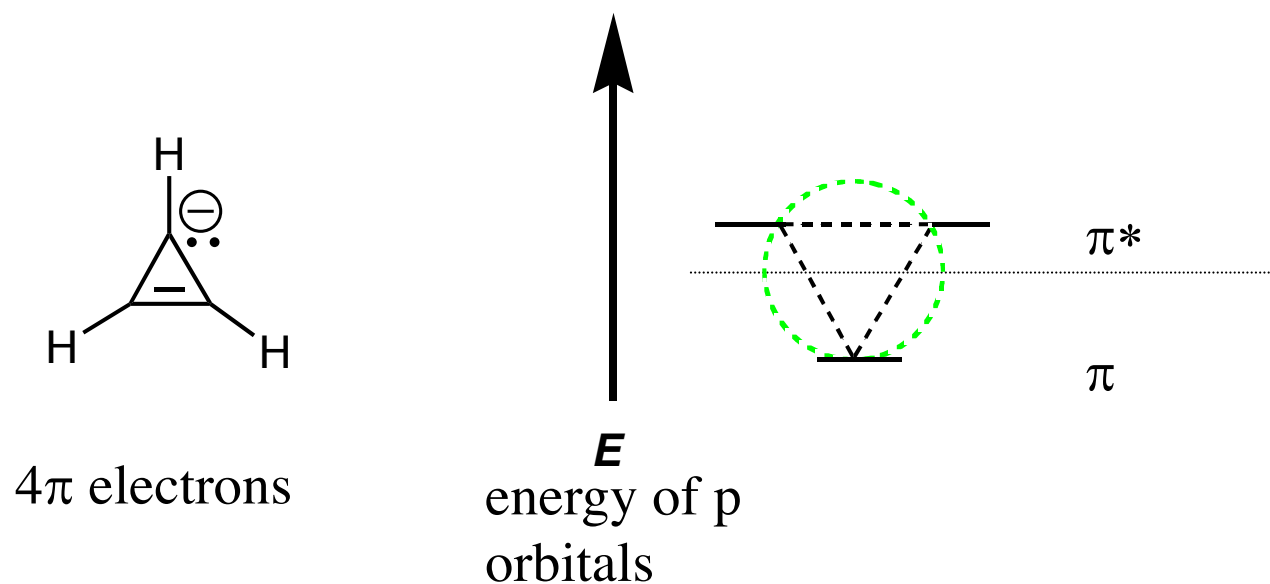
*Aromatic*

*Maximum stabilisation per electron*

## 2. MO diagrams for cyclic $\pi$ systems

### Charged systems

- The same 'polygon' and Frost circle workflow applies.....

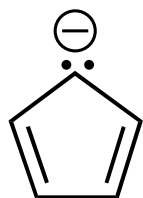


*Not aromatic*  
*Not stable*

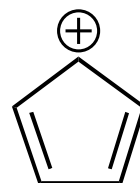
## 2. MO diagrams for cyclic $\pi$ systems

### Charged systems

- Have a go at.....



and



Comment on their relative stabilities, using MO orbital diagrams to explain your answer