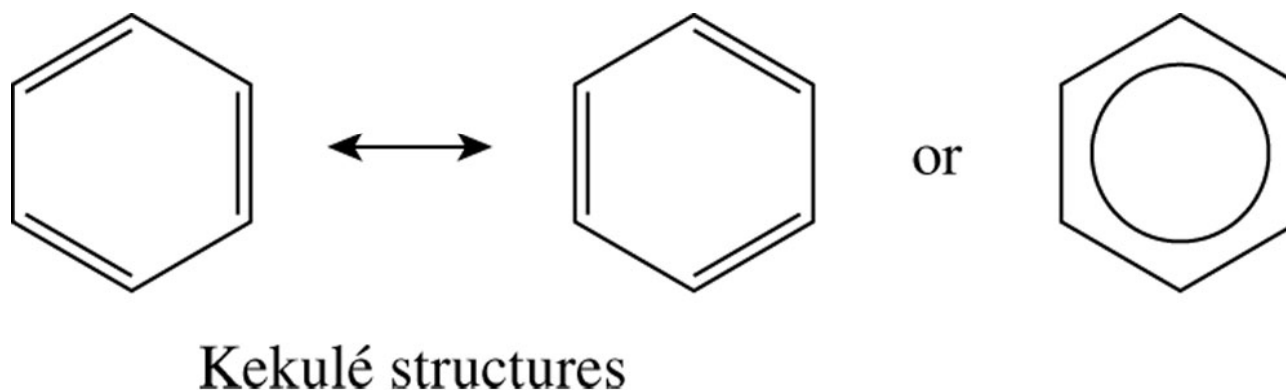


# Chapter 16 Benzene and Aromatic Compounds

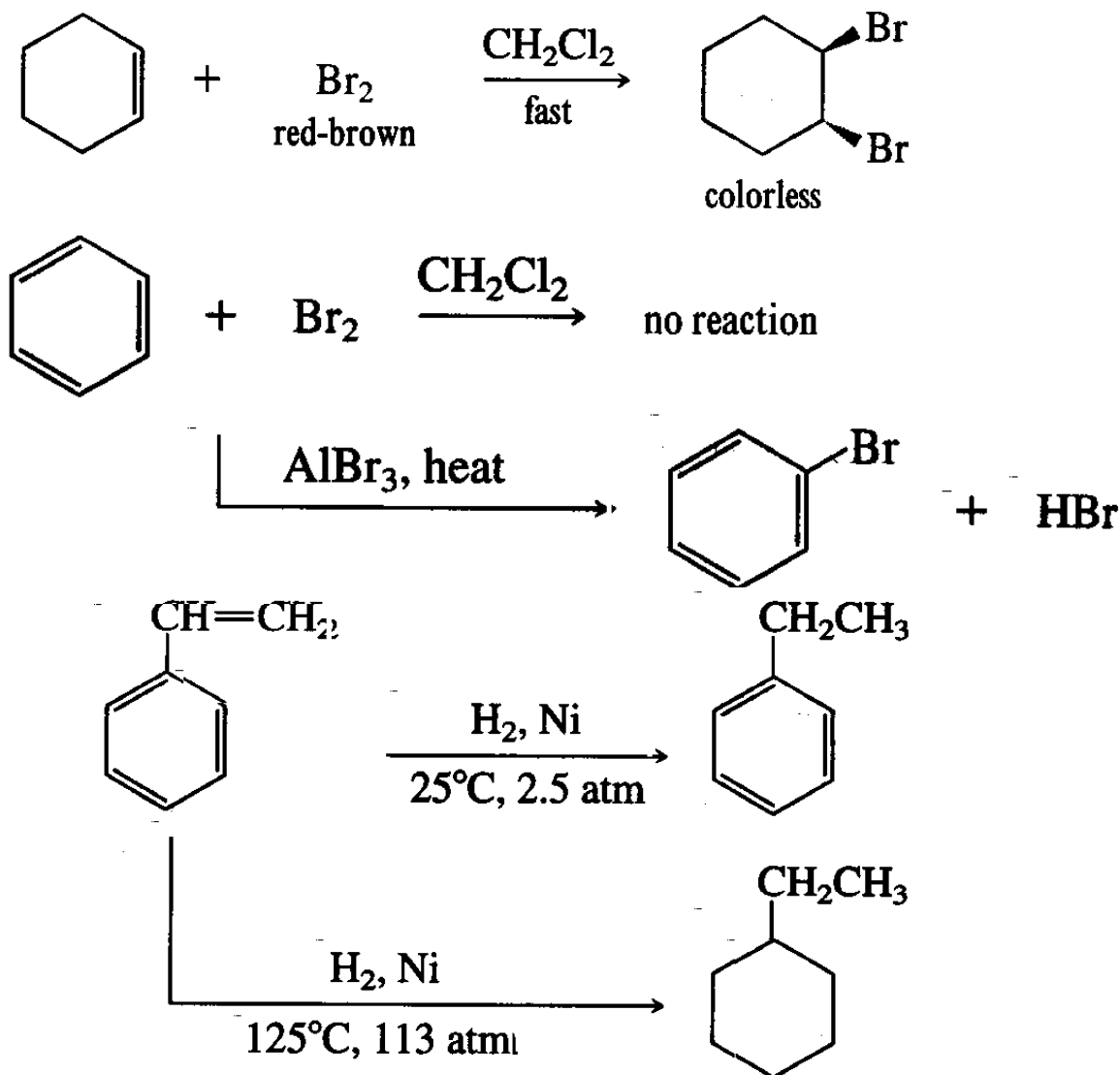
## 16.1 Benzene $C_6H_6$ (1825, M. Faraday), liquid



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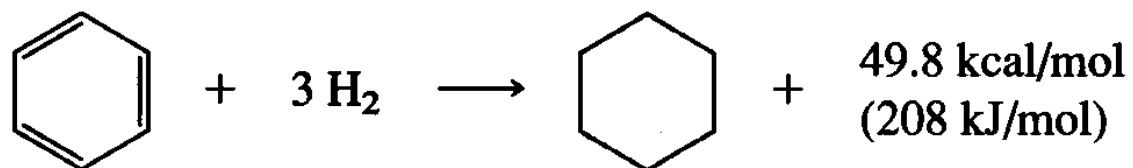
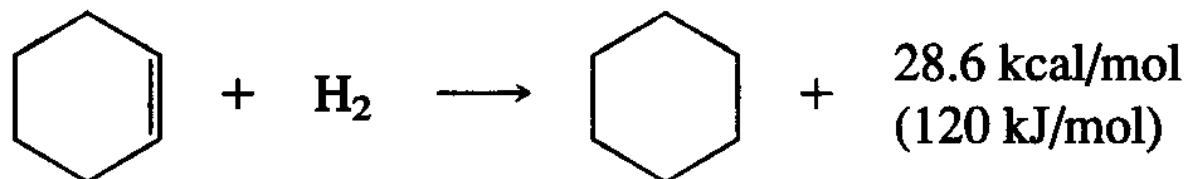
All of the carbon–carbon bonds of benzene are the same length (1.4 Å), intermediate between the length of a single bond (1.5 Å) and the length of a double bond (1.3 Å).

# The different reactivity of benzene and alkene



⇒ Benzene is much less reactive than alkene,  
due to resonance stabilization

## 16.2 Resonance Energy of benzene

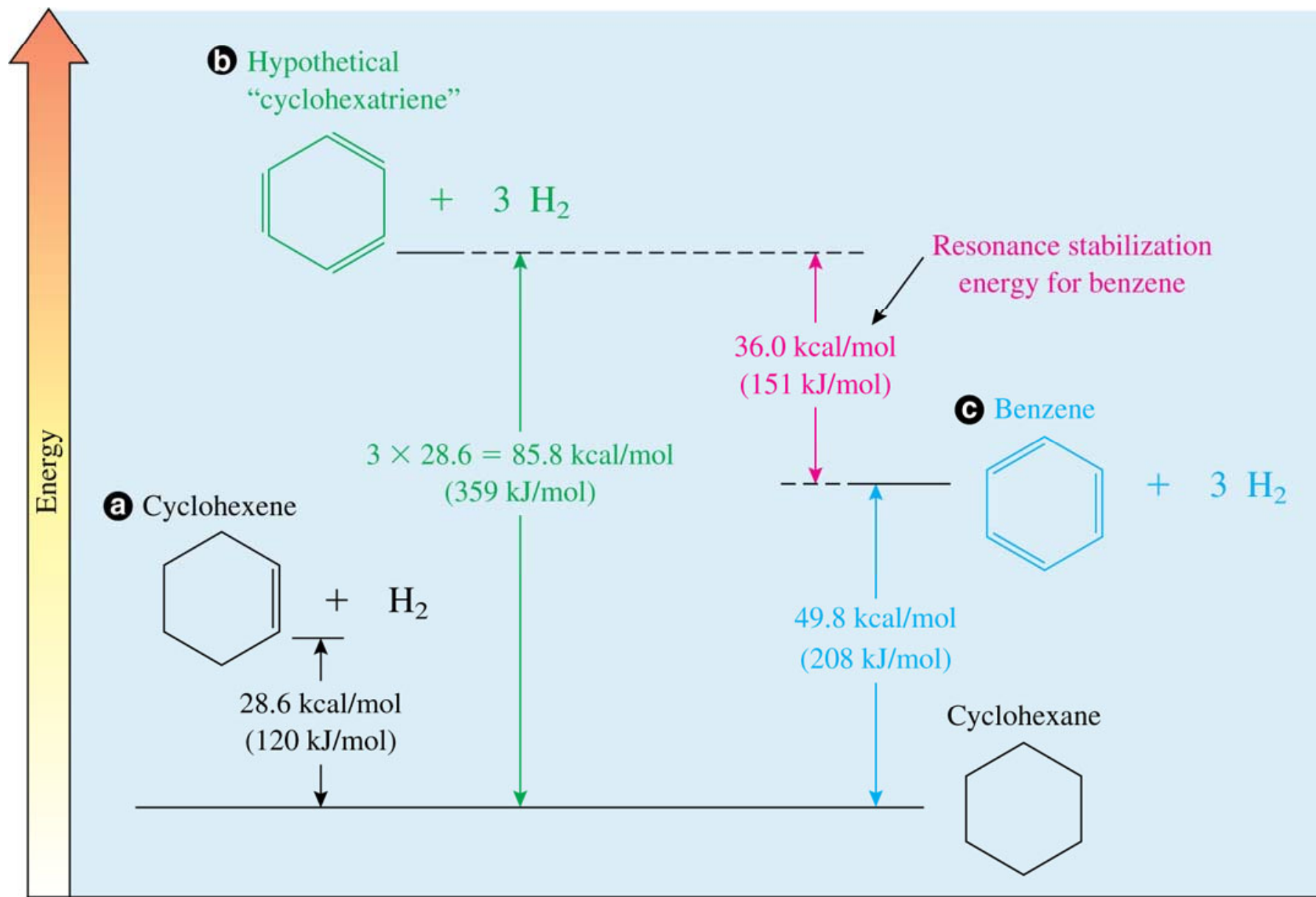


---

<b>heat evolved from the reaction of 3 C=C without resonance stabilization (3 × 28.6 kcal/mol)</b>	<b>85.8 kcal/mol (359 kJ/mol)</b>
<b>minus heat evolved from the reaction of 3 C=C of benzene</b>	<b>−49.8 kcal/mol (208 kJ/mol)</b>
<b>equals the resonance stabilization of benzene</b>	<b>36.0 kcal/mol (151 kJ/mol)</b>

---

# Resonance Energy of benzene



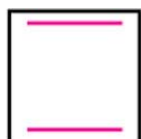
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## 16.3 Molecular Orbital Model for Cyclic Conjugated Molecules

Is the resonance structure only the explanation for the stability of benzene ?



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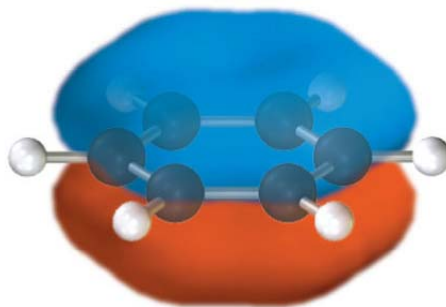
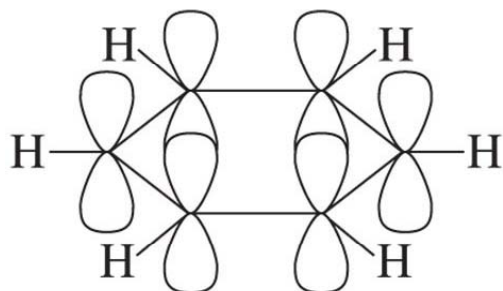


Cyclobutadiene

⇒ Unstable

⇒ React rapidly at temperatures above 35 K

Why Benzene is very stable?



Each carbon has three  $sp^2$  hybrid AOs and one  $p$  AO

All six of  $p$  AOs combine to form delocalized MOs!

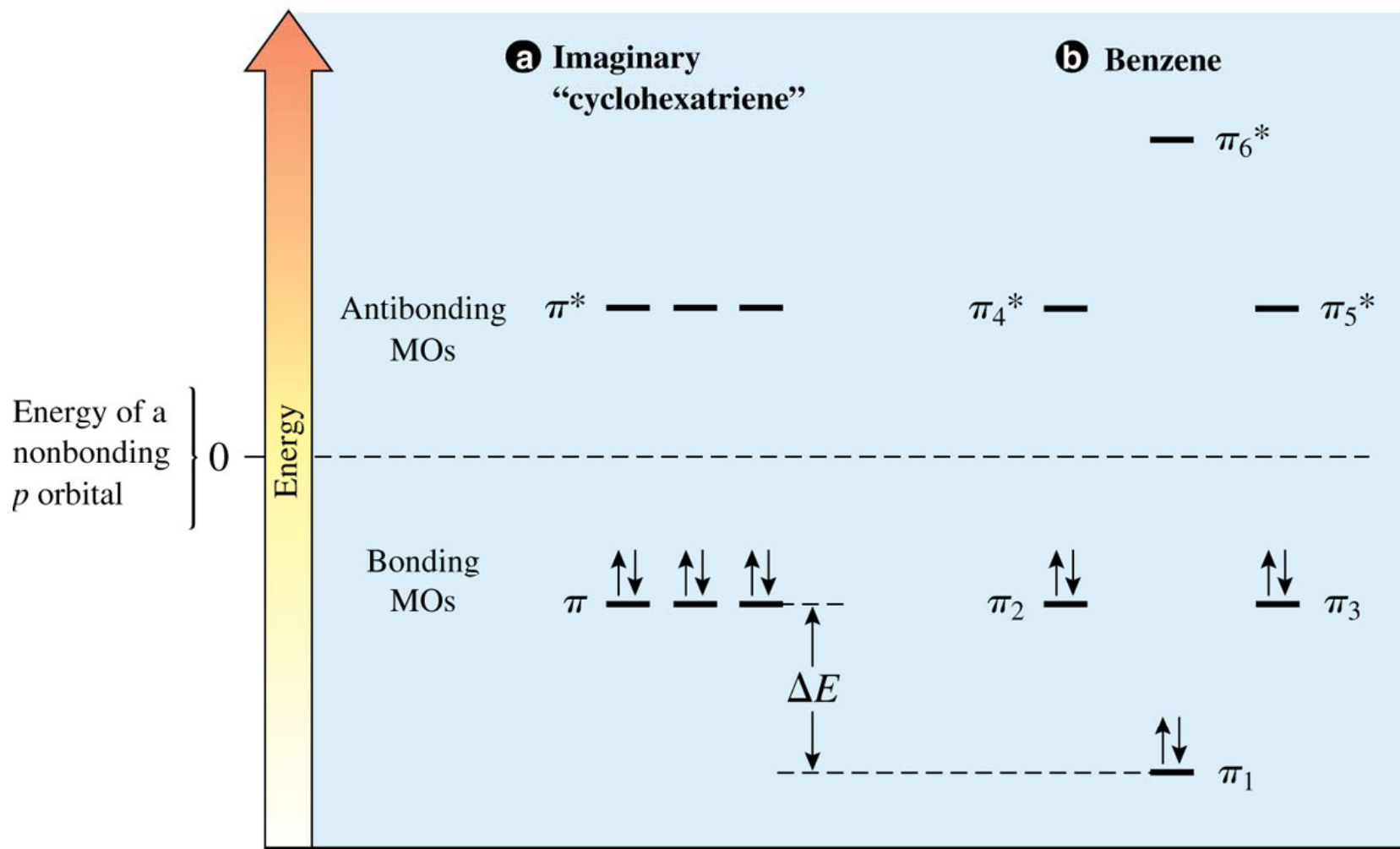
# Another explanation for the stability

## ⇒ Molecular orbital theory (Drawing the MO pictures)

### Rules to draw the MO pictures (CHAP 3 p68)

1. Two AOs on the bonding atoms overlap to produce two MOs. In more complicated situations the number of MOs produced equals the number of AOs initially involved.
2. One combination of the two AOs results in a lower-energy, bonding MO; the other combination results in a higher-energy, antibonding MO with a node between the nuclei. The math signs are a convenient way to keep track of the nodes.
3. The same rules are used to assign electrons to MOs as are used to assign electrons to AOs. Usually, there are just enough electrons to fill the bonding MOs, and the antibonding MOs remain empty.
4. The bond energy is approximately equal to the total amount of energy by which the electrons are lowered in energy in comparison to the electrons in the AOs—that is, the number of electrons times  $\Delta E$ .
5. The magnitude of  $\Delta E$  increases with increasing overlap of the AOs. However, if the atoms get too close together, repulsion between the nuclei starts to dominate, and the overall energy increases very rapidly.

By using these rules, more complex situations can also be analyzed.



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Benzene is more  
stable by  $2\Delta E$

Figure 17.2

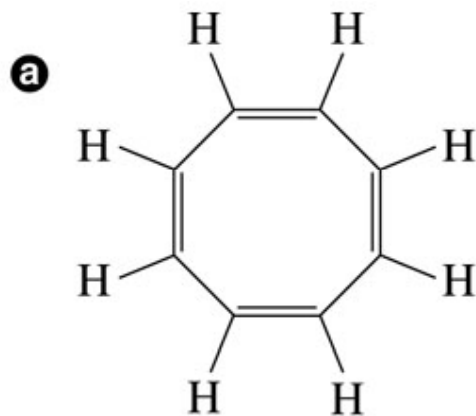
Energies of the Pi  
Molecular Orbitals of  
Imaginary  
"Cyclohexatriene"  
Compared to Those of  
Benzene.

## Additional rule to draw the MO pictures (The way to draw the MO picture of benzene)

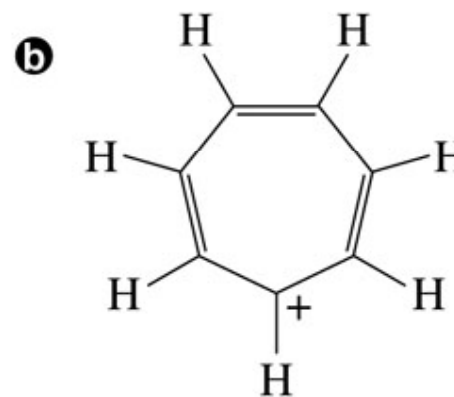
1. If the total number of MOs is even, then there is one highest energy MO and the MOs are arranged symmetrically about zero energy.
2. If the total number of MOs is odd, the pattern is the same with the exception that the highest-energy MO is absent.



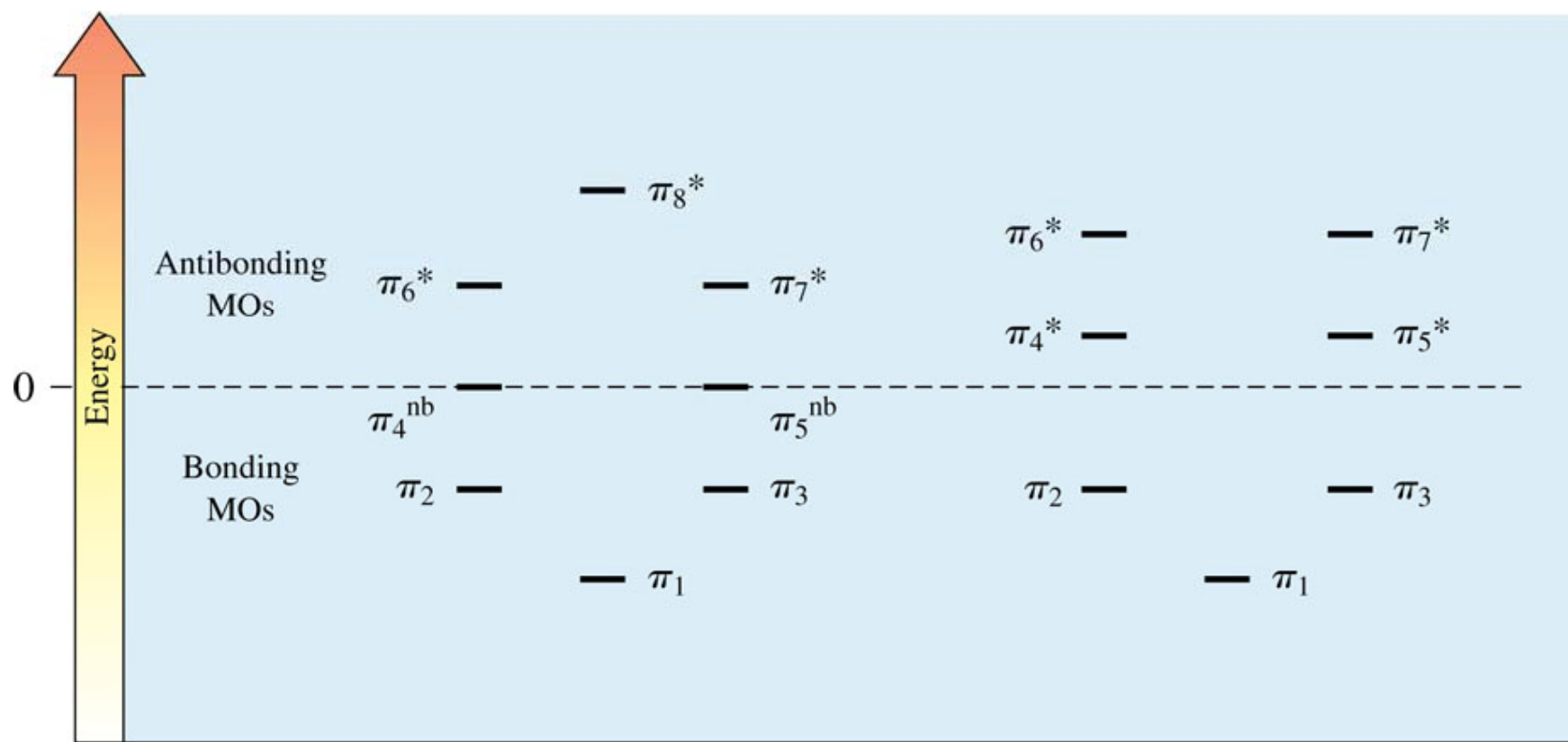
# Examples



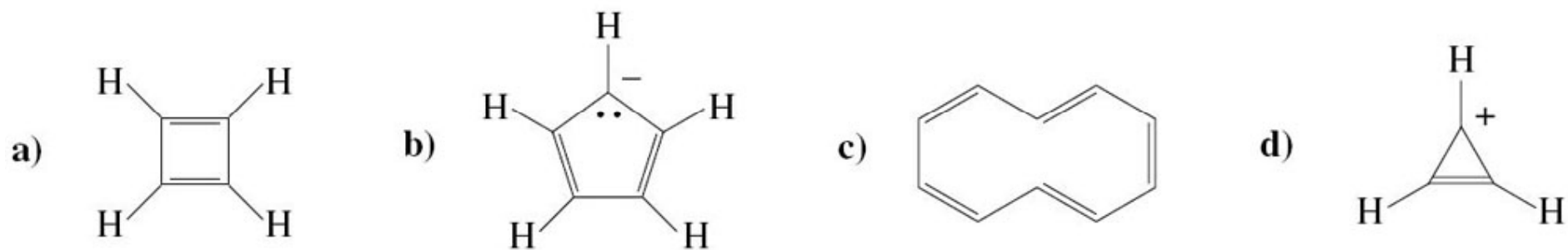
Cyclooctatetraene



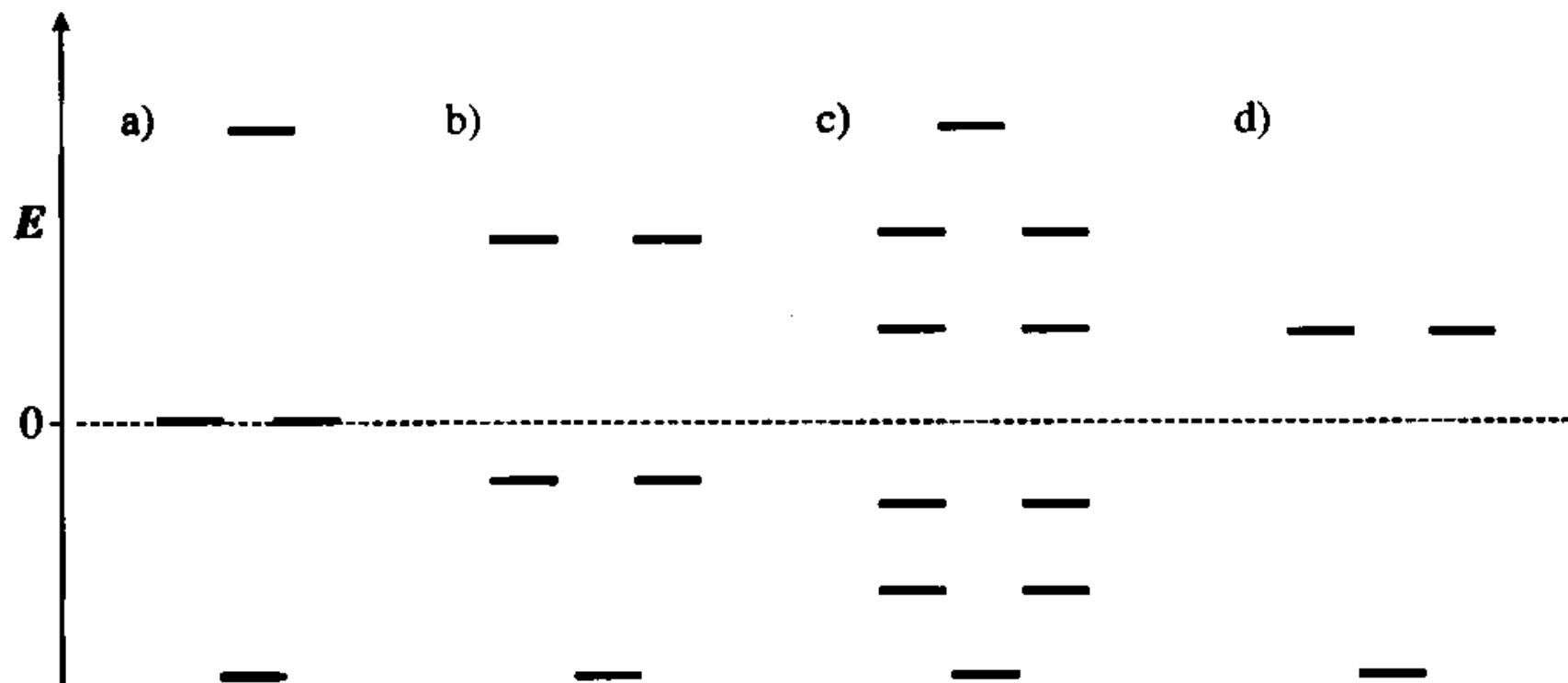
Cycloheptatrienyl carbocation



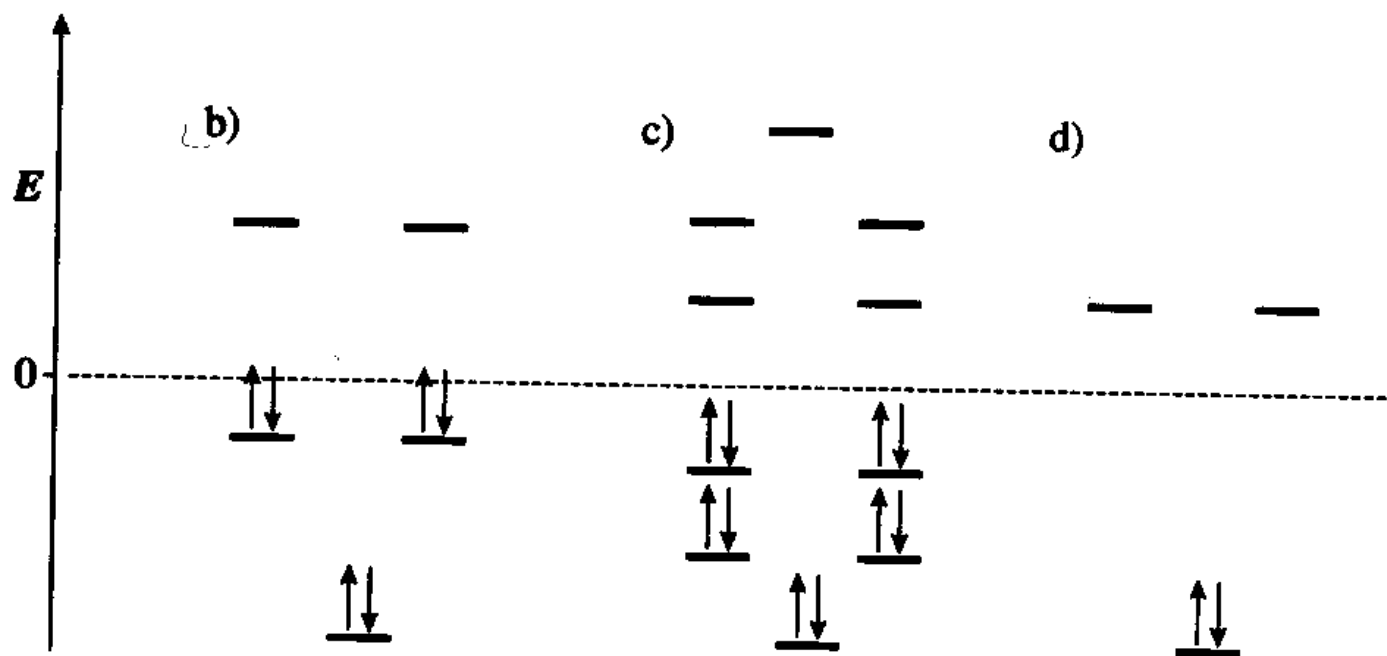
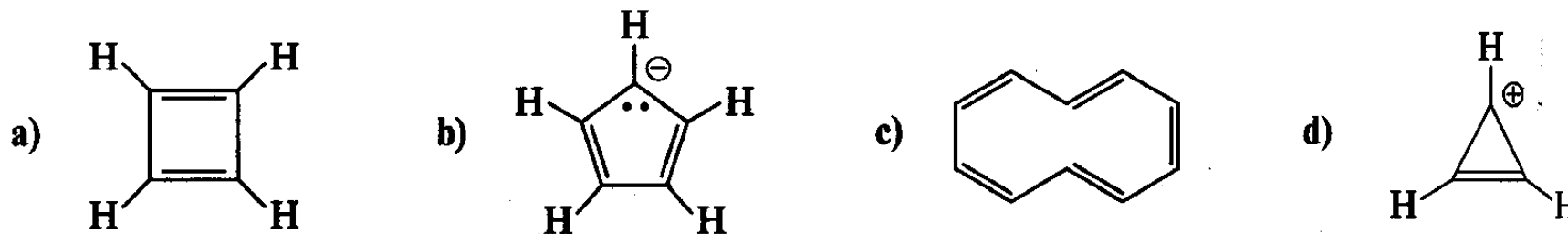
# Examples

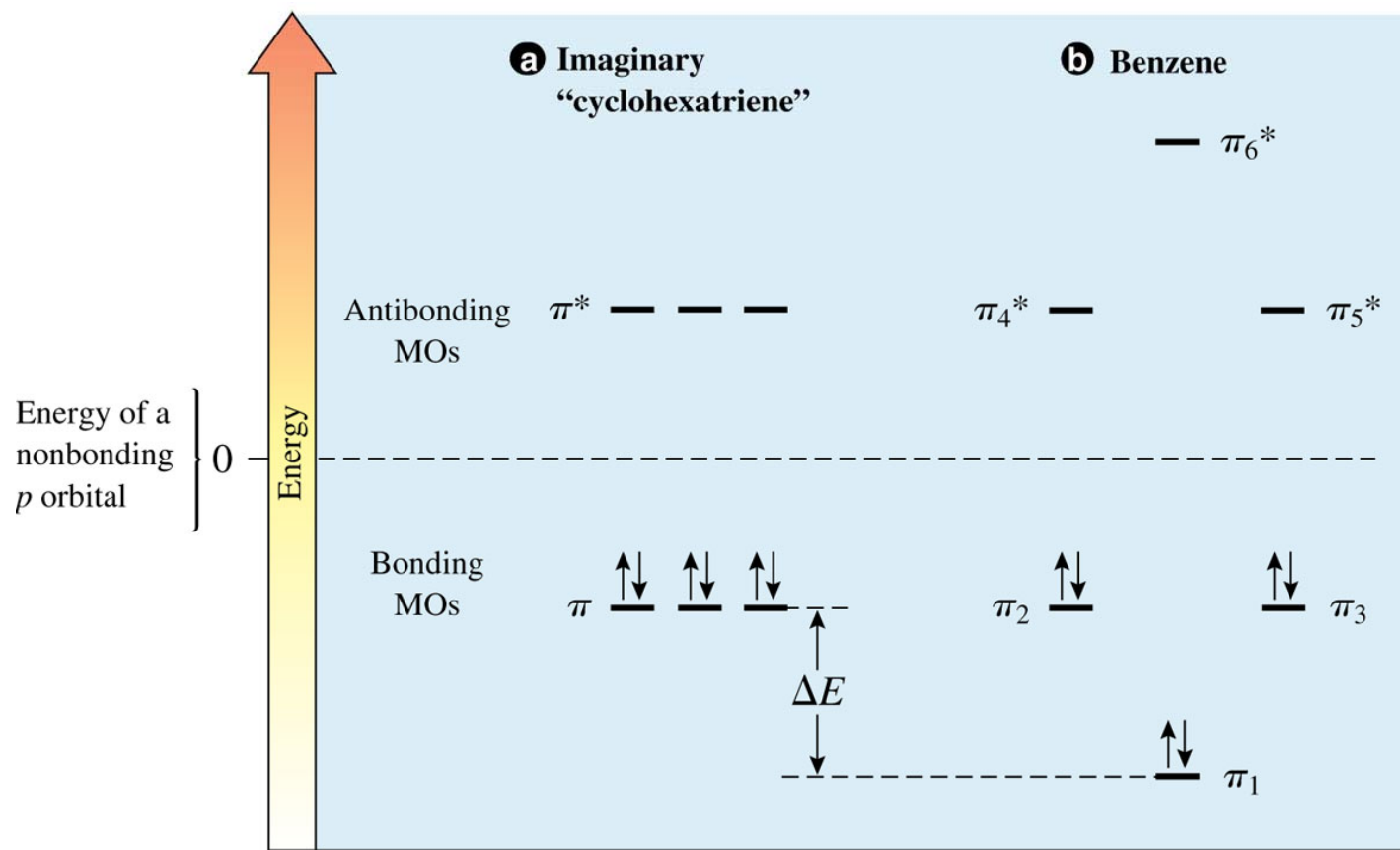


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Show the patterns for the pi MO energy levels for these compounds.



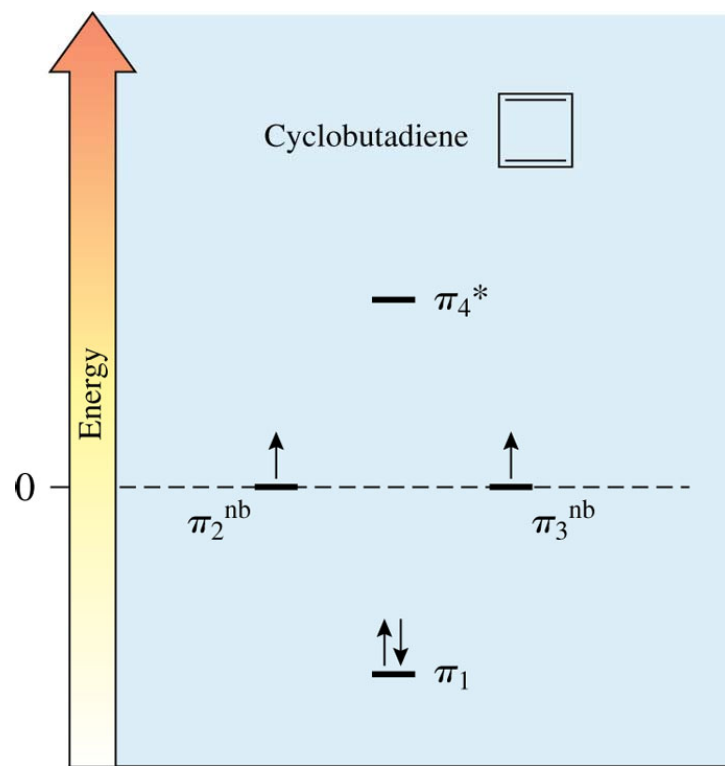


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## Benzene

- highest occupied molecular orbitals (HOMOs) completely filled with electrons
  - Cyclic compound with completely conjugated around the ring
- ⇒ Stable and called **aromatic**

# 16.4 Cyclobutadiene

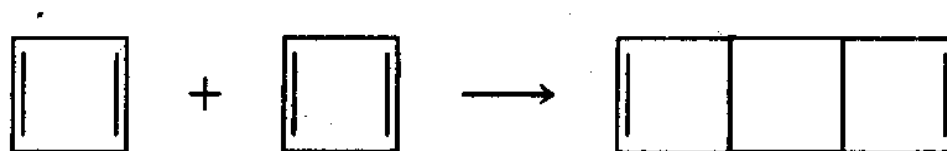


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1. **Conjugated cyclic compound.**
  2. **Half filled HOMOs**
- ⇒ **Unstable and called antiaromatic**

1. **Prepared below 35K.**
2. **Composed of shorter double bonds and longer single bonds.**

not aromatic. When a sample of cyclobutadiene is allowed to warm above 35 K; the molecules react rapidly to form dimers that are no longer conjugated and therefore are no longer antiaromatic.



## 16.5 Hückel's Rule

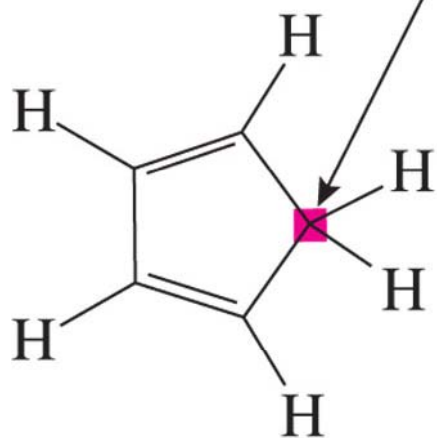
**Aromatic**  $\Rightarrow$  Cyclic, fully conjugated, planar,

and  $4n+2$  pi electrons ( $n$  is any integer)

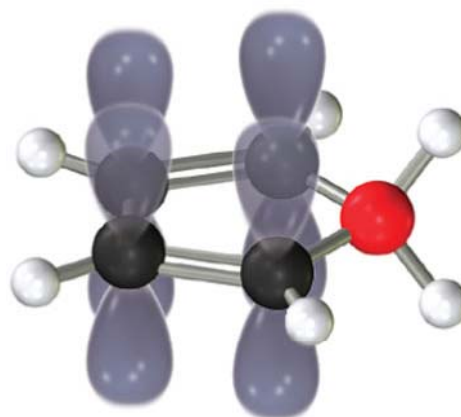
$n$	$4n + 2$	number of pairs
0	2	1
1	6	3
2	10	5
3	14	7

## Example; Cyclopentadiene is neither aromatic nor antiaromatic

This  $sp^3$ -hybridized carbon interrupts the cycle of  $p$  orbitals, so cyclopentadiene is neither aromatic nor antiaromatic.



Cyclopentadiene



→ Not fully conjugated

→ Not planar

38951-16-U23-24

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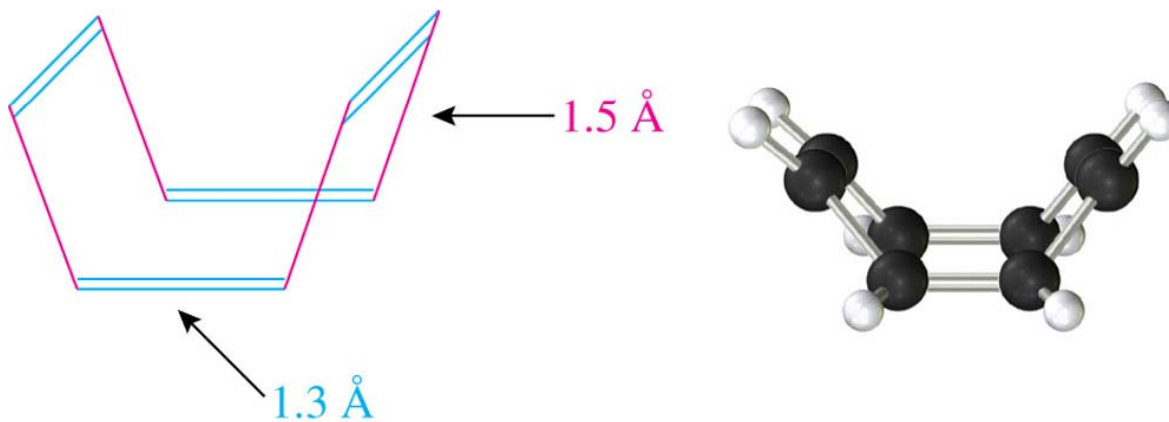
**Antiaromatic**  $\Rightarrow$  Cyclic, fully conjugated, planar,  
and  $4n$  electrons ( $n$  is any integer)

$n$	$4n$	number of pairs
1	4	2
2	8	4
3	12	6

**Example: Cyclobutadiene**



## 16.6 Cyclooctatetraene



Cyclooctatetraene

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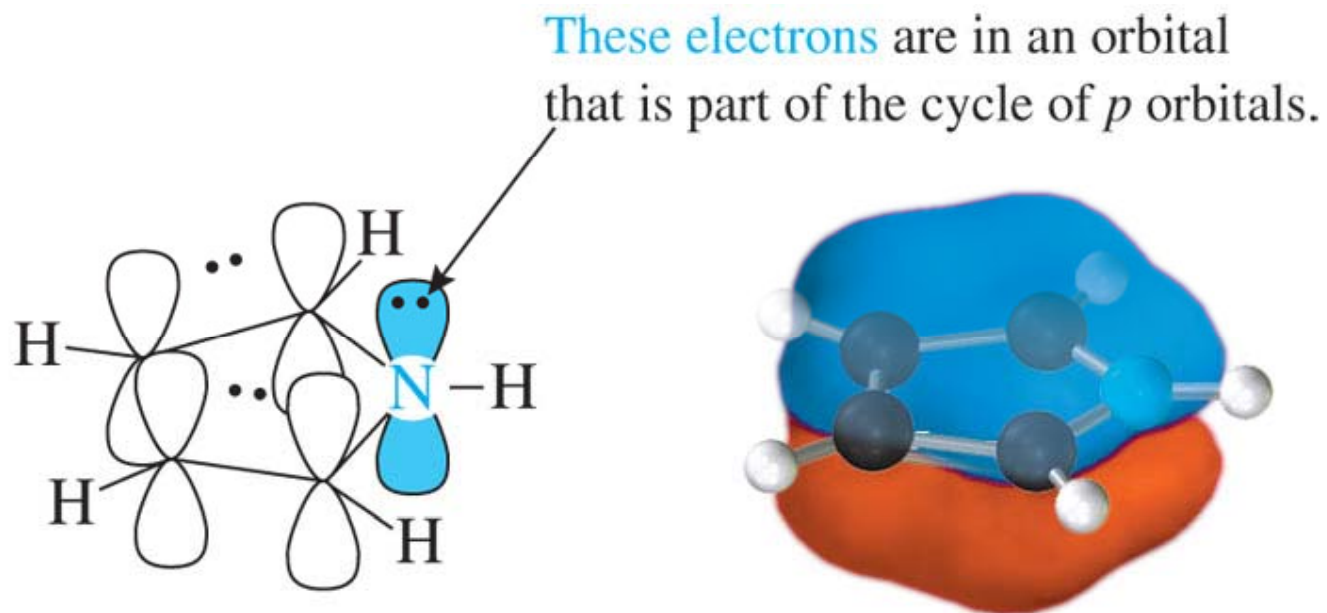
**Normal nonconjugated alkene**

⇒ **Non planar: if it is planar, antiaromatic**

⇒ **nonaromatic**

# 16.7 Heterocyclic Aromatic Compound

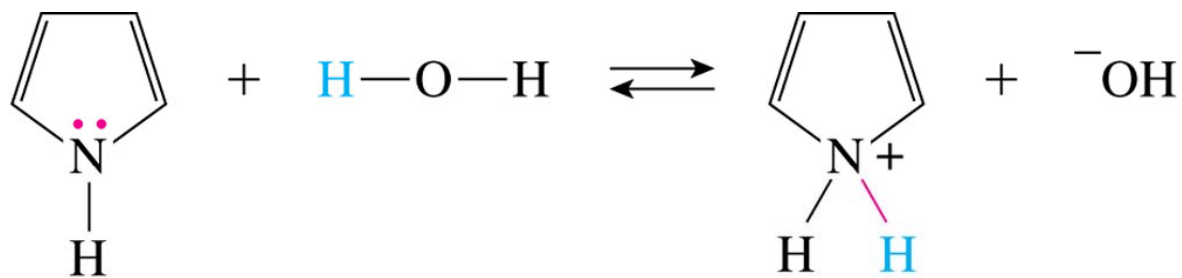
## Pyrrole



**Aromatic  $\Rightarrow$  Cyclic, fully conjugated, planar, and 6 ( $4n+2$ ) pi electrons**

38951-16-U27-29

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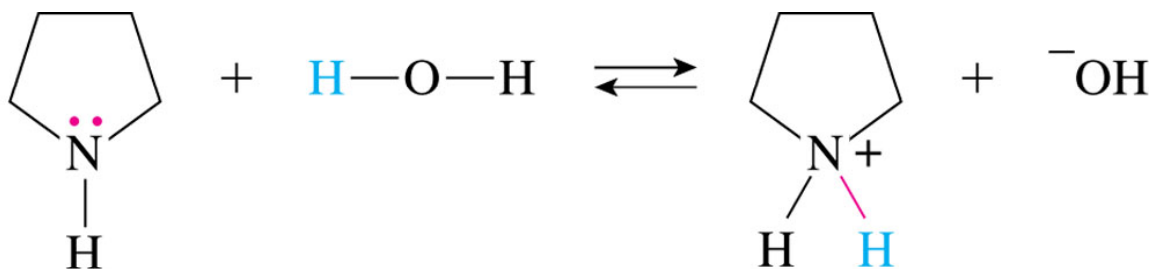


Aromatic

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Nonaromatic

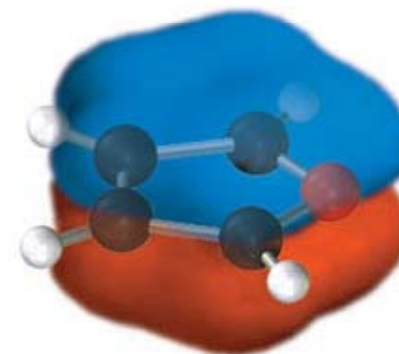
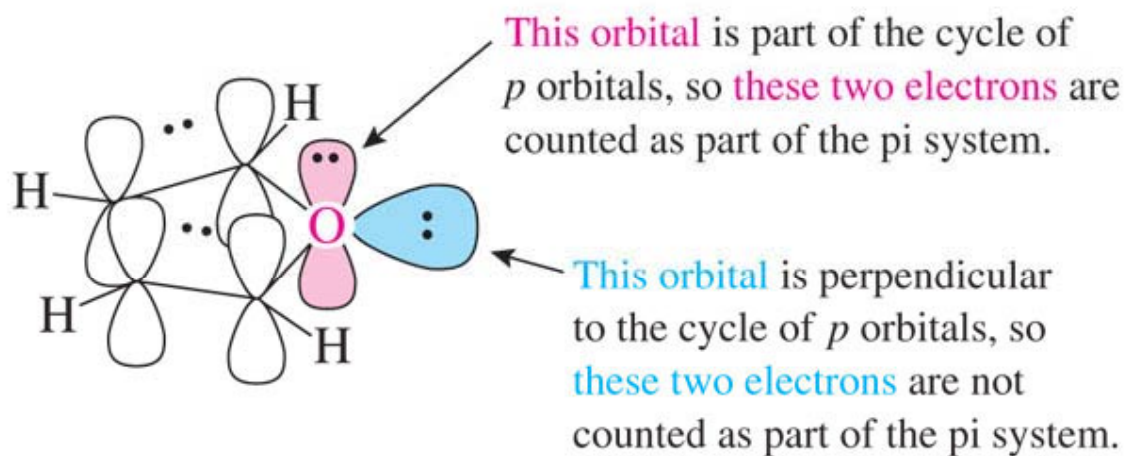
**Pyrrole is  $10^{14}$  times weaker as a base than is pyrrolidine because of the aromaticity**



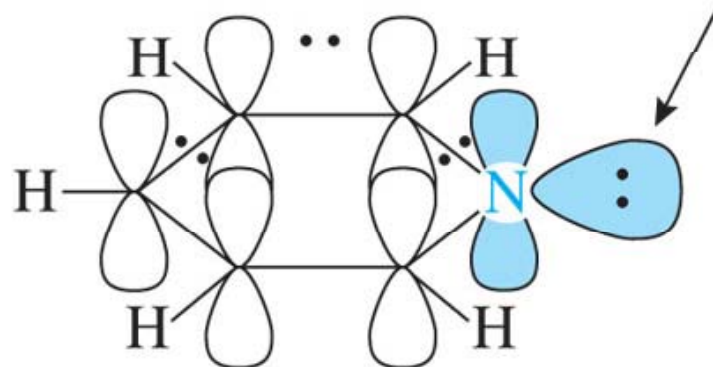
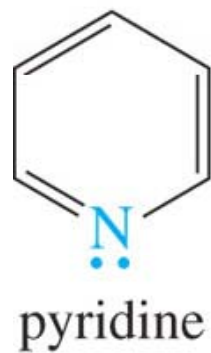
Pyrrolidine

© 2006 Brooks/Cole - Thomson

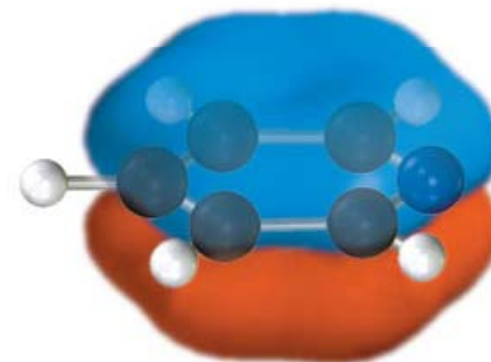
# Furan and thiophene $\Rightarrow$ Aromatic



# Pyridine $\Rightarrow$ Aromatic



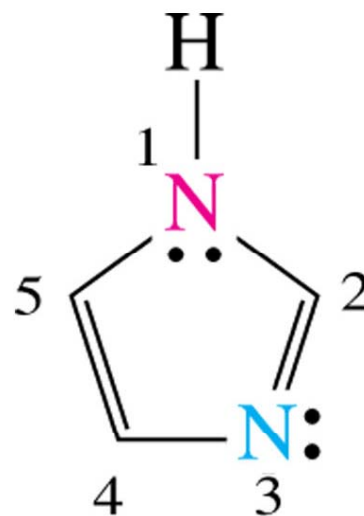
This  $sp^2$  atomic orbital is not part of the cycle of  $p$  orbitals.



38951-16-U36-38

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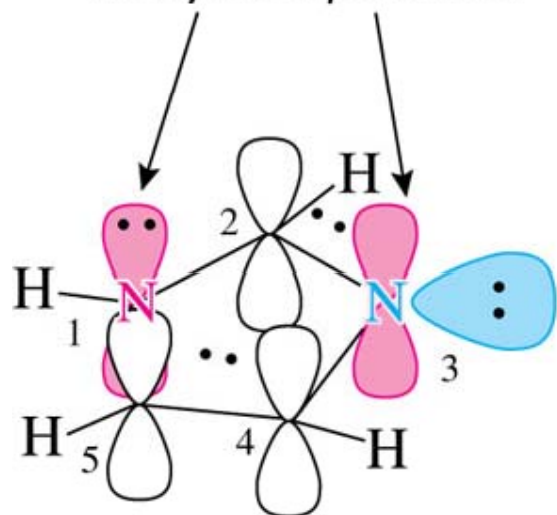
$\Rightarrow$  **Pyridine is a much stronger base than pyrrole**



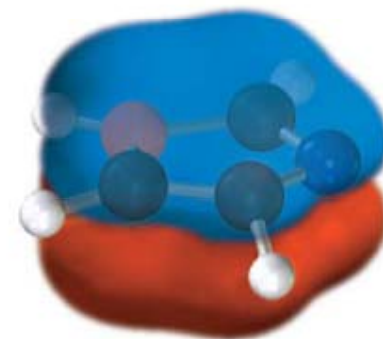
Imidazole

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These orbitals are part of the cycle of  $p$  orbitals.



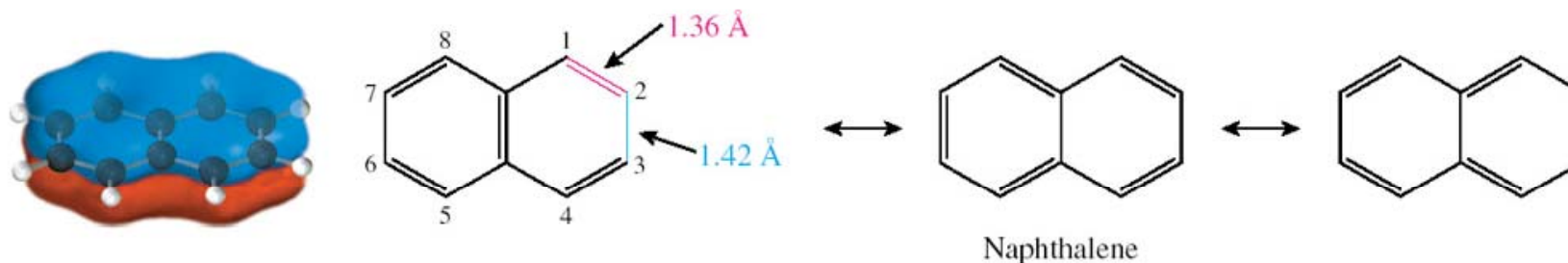
This orbital is perpendicular to the cycle of  $p$  orbitals.



# 16.8 Polycyclic Aromatic Compound

⇒ two or more benzene rings fused together

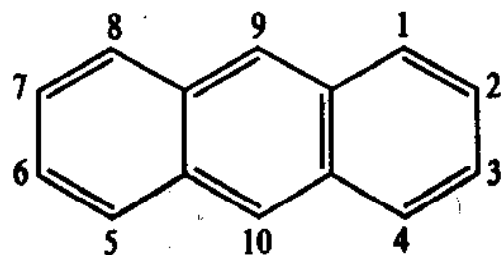
## Naphthalene



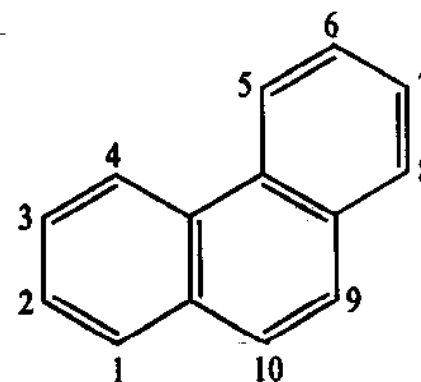
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Resonance energy: 61 kcal/mole

## Anthracene and phenanthrene

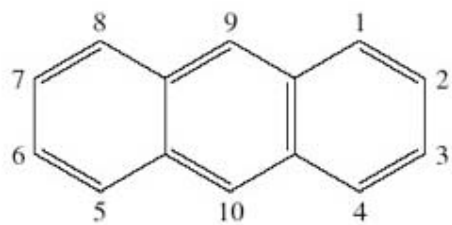
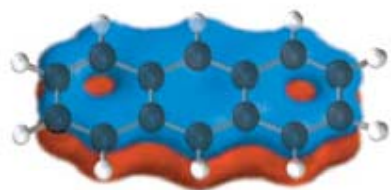


anthracene

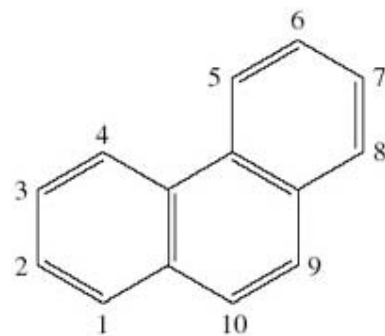


phenanthrene

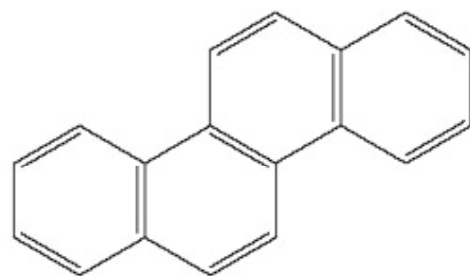
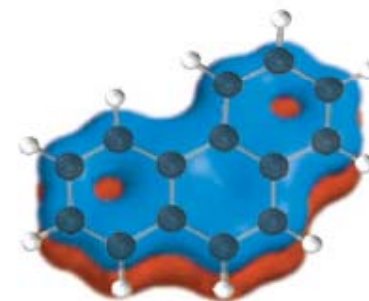
Their resonance energies are calculated to be 84 kcal/mol (352 kJ/mol) and 92 kcal/mol (385 kJ/mol), respectively.



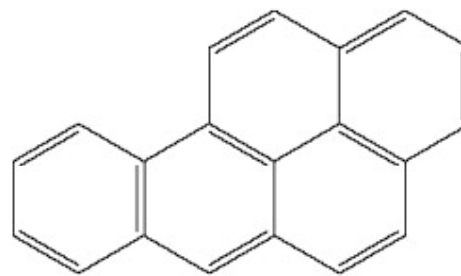
Anthracene



Phenanthrene



Chrysene

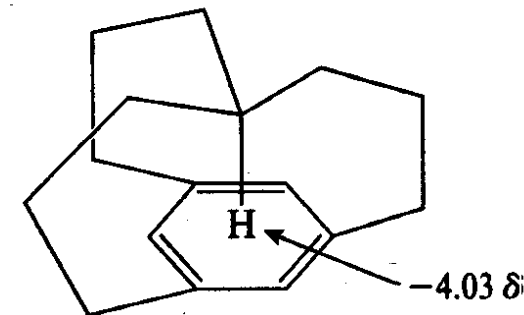
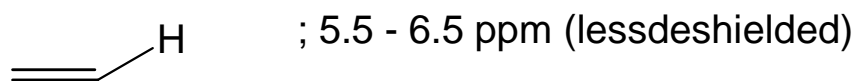
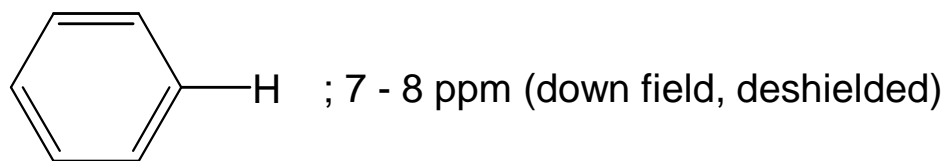


Benzo[a]pyrene

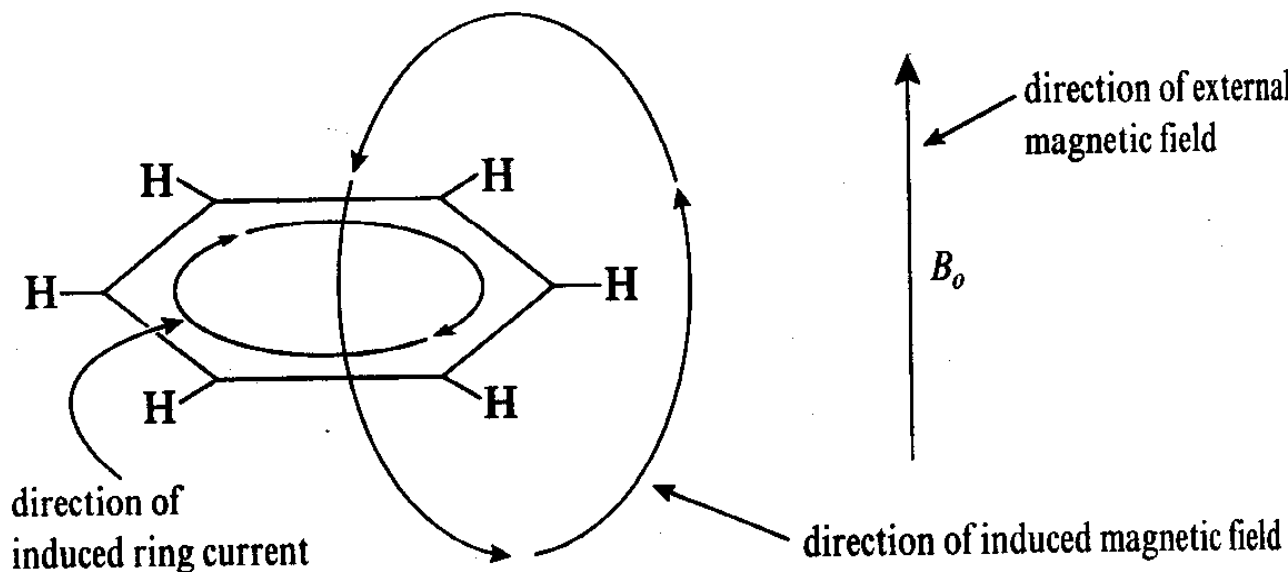
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# 16.9 NMR and Aromaticity



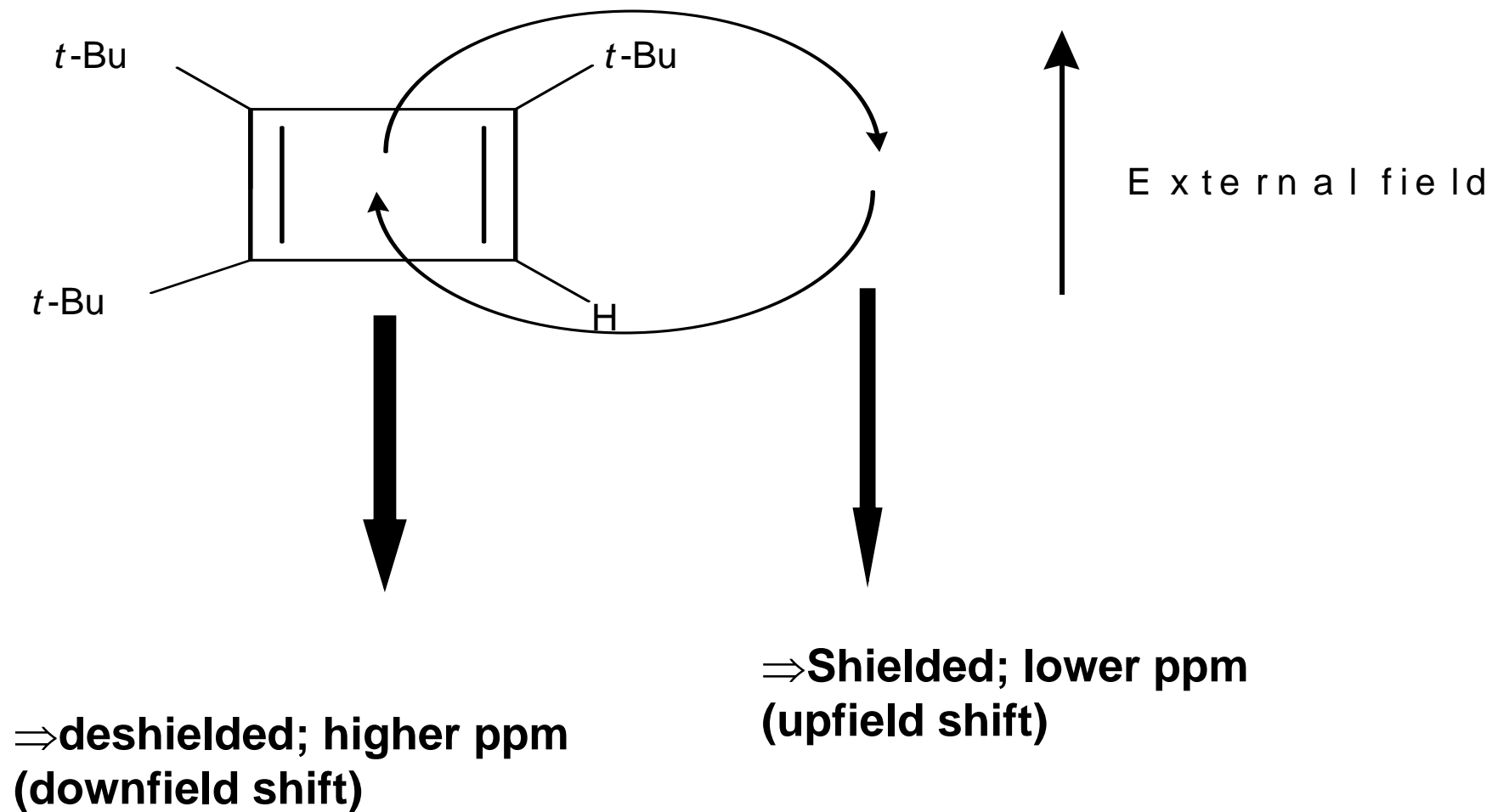
## Why? Ring current effect



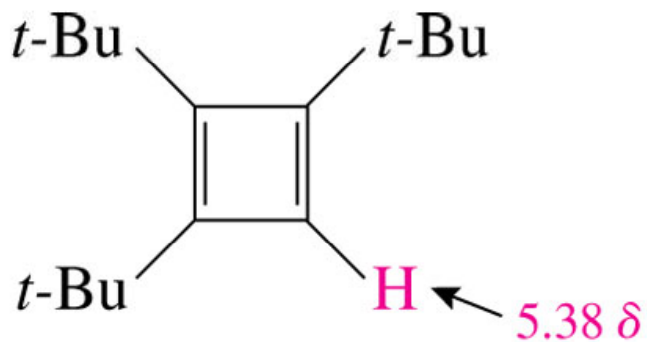
$\Rightarrow$  Shielded; lower ppm  
(upfield shift)

$\Rightarrow$  deshielded; higher ppm  
(downfield shift)

# Antiaromatic compound



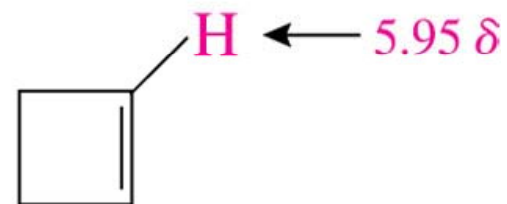
⇒ The ring current in antiaromatic compounds is termed **paramagnetic**



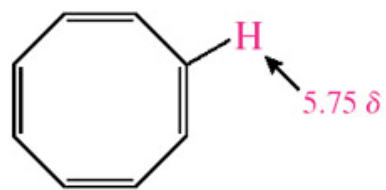
Tri-*tert*-butylcyclobutadiene

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**antiaromatic**



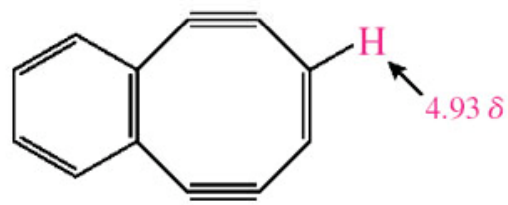
**normal alkene**



Cyclooctatetraene

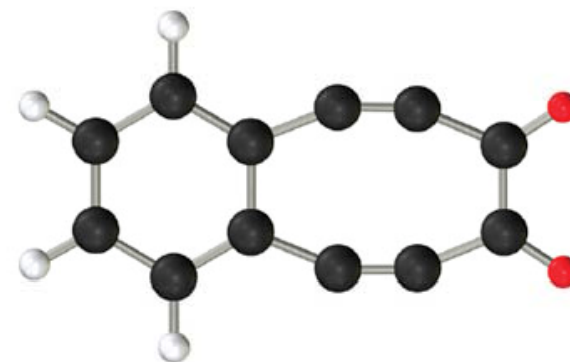
© 2006 Brooks/Cole - Thomson

**normal alkene**



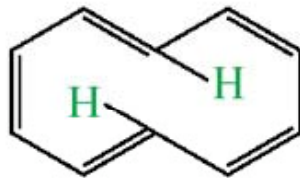
Benzo-1,5-cyclooctadiene-3,7-diyne

**antiaromatic**



# 16.10 Annulenes

1. rings that contain alternating single and double bonds
2. benzene: [6]annulene, cyclooctatetraene: [8]annulene
3. Aromatic when they have  $4n+2$  electrons in the ring



[10]Annulene (not yet prepared)

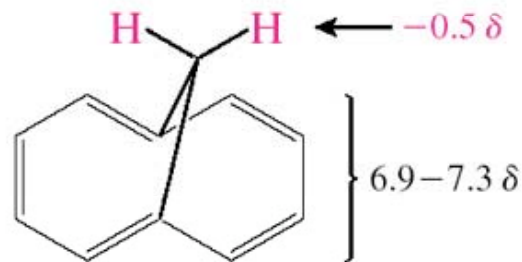
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**No ring strain**

**Two hydrogens cause  
very much steric | alkene**

**Therefore not yet  
prepared**

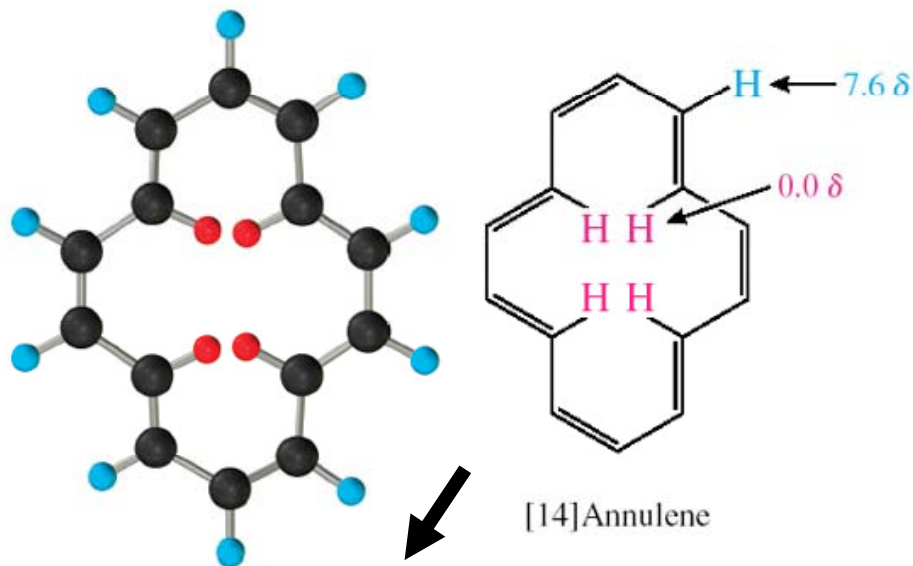


A bridged [10]annulene

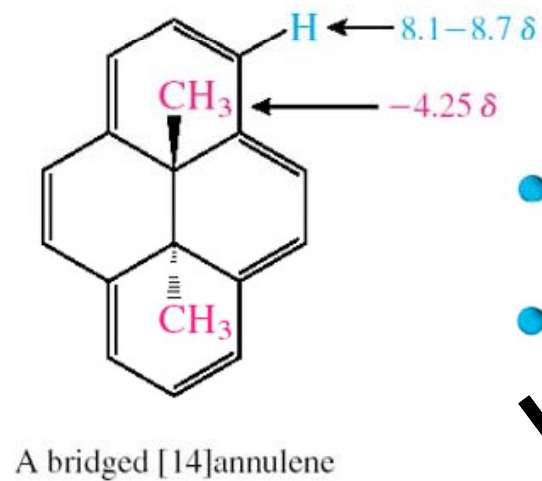


**Bridge causes the ring to  
be somewhat distorted**

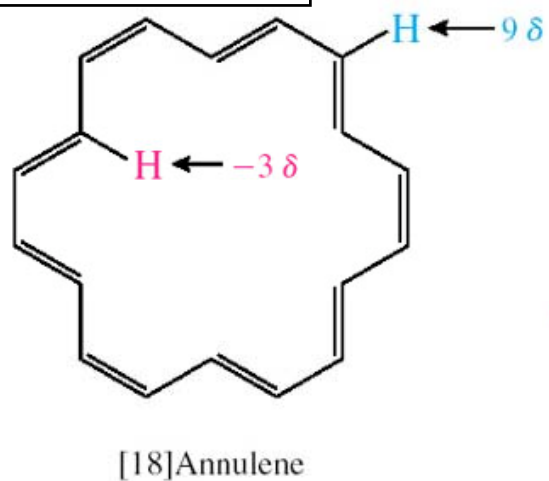
**Aromatic and  
diamagnetic ring current**



H's inside the ring are quite reactive: steric strain

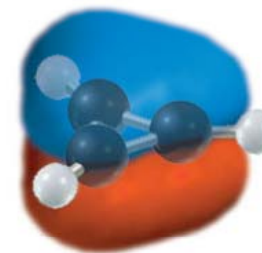
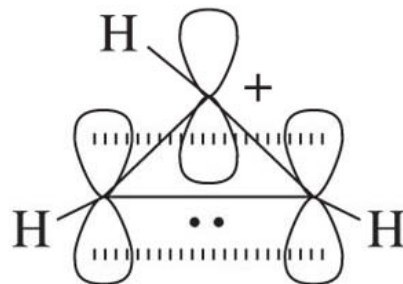
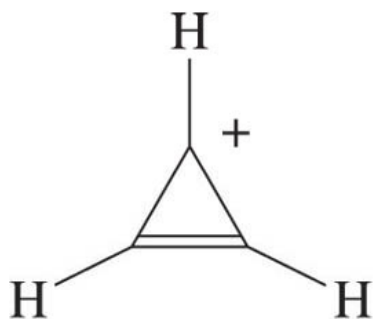


Steric intxns are absent  
Bond distances are all about 1.4 Å  
undergoes substitution rxns not addition rxns



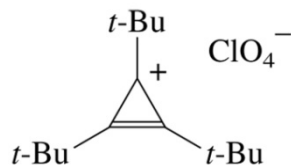
**Aromatic and diamagnetic ring current**

## 16.11 Aromatic and Aromatic Ions



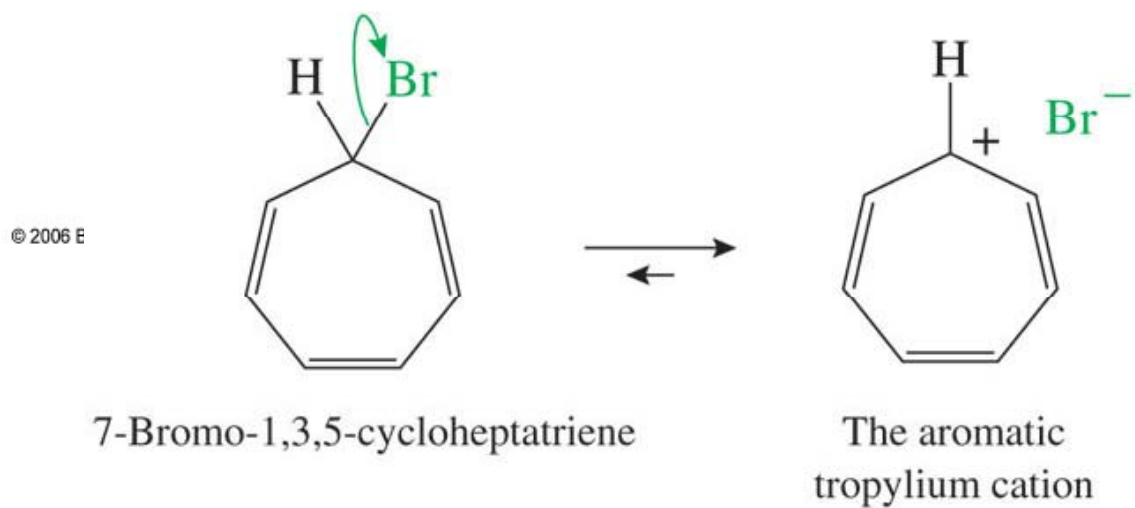
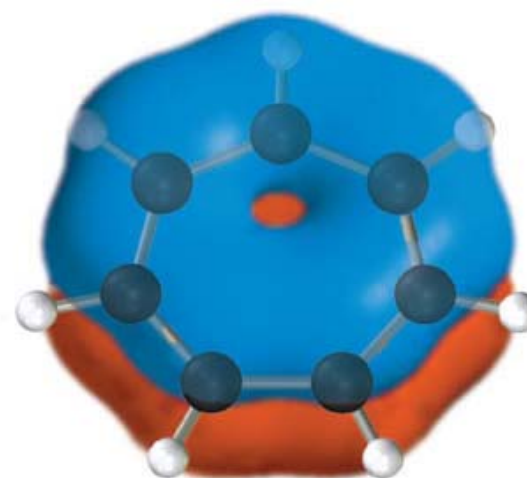
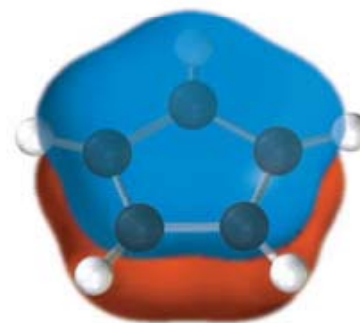
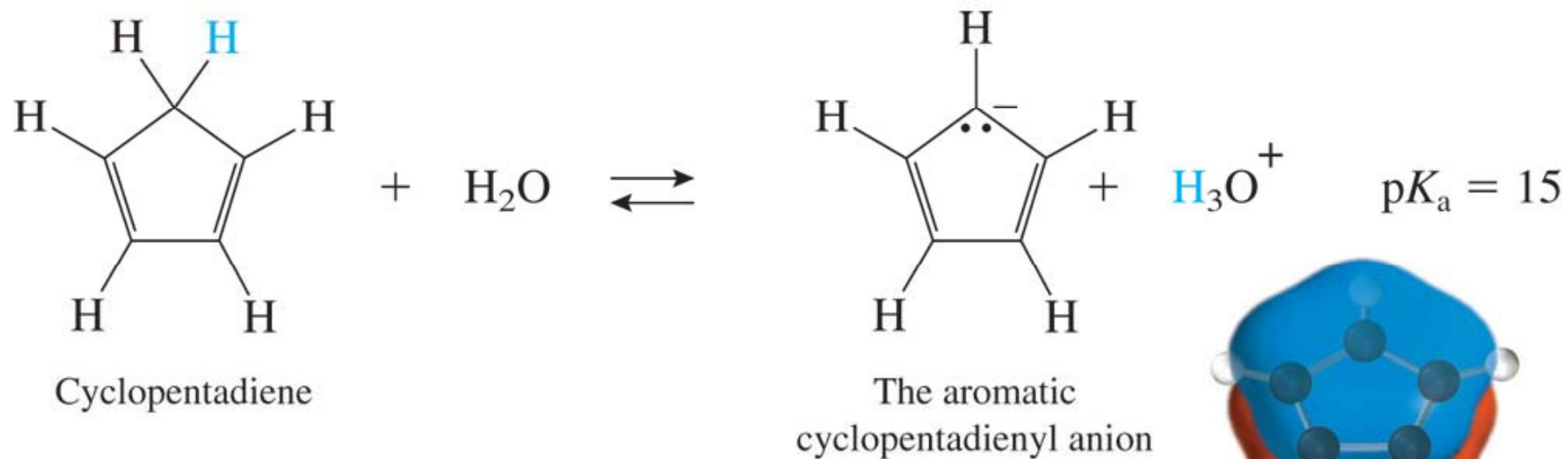
The cyclopropenyl carbocation

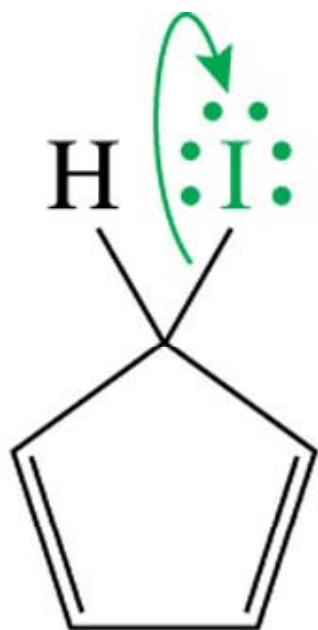
- ⇒ Trigonal planar geometry, two electrons in three pi MO's
- ⇒ Aromatic: much more stable than other carbocation, even though the ring strain



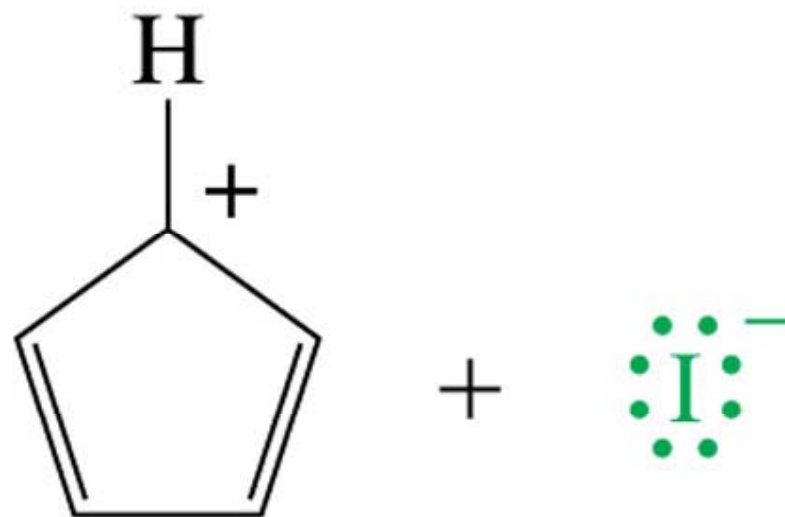
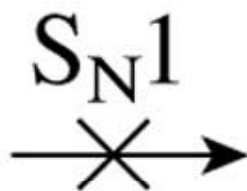
Tri-*tert*-butylcyclopropenyl perchlorate

tions, even though they have considerable angle strain. For example, most carbocations react rapidly with water, a weak nucleophile. In contrast, tri-*tert*-butylcyclopropenyl perchlorate, a carbocation salt, is stable enough to be recrystallized from water.





5-Iodo-1,3-cyclopentadiene



The antiaromatic cyclopentadienyl cation