Date:
23 /11 /2023

لجان الدُّفعات

Soul Academy

تفريغ عضويه 1

موضوع المحاضرة: Chapter (15)

رقم المحاضرة : (7)

إعداد الصيدلانيه: Gufran Khaseeb

Benzene and Aromatic Compounds

Chapter 15
Organic Chemistry, *8th Edition*
John McMurry

Background

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Four degrees of unsaturation.
- It is planar.
- All C—C bond lengths are equal.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not.

Benzene (an arene)

$C_6H_6 \xrightarrow{Br_2}$ **No reaction**

- Benzene reacts with bromine only in the presence of $FeBr_3$ (a Lewis acid), and the reaction is a substitution, not an addition.

$C_6H_6 \xrightarrow[FeBr_3]{Br_2} C_6H_5Br$

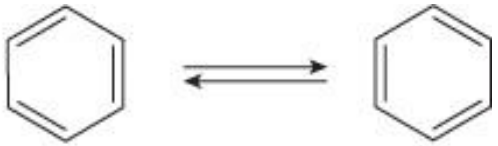
substitution
Br replaces H

→ of the alkenes (addition)
(the difference)

Background

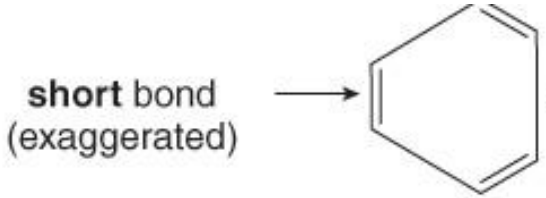
- August Kekulé (1865) proposed that benzene was a rapidly equilibrating mixture of two compounds, each containing a six-membered ring with three alternating π bonds.

Kekulé description: An equilibrium



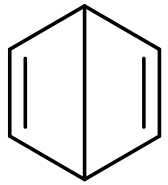
(have 2 shapes)

This structure implies that the C–C bonds should have **two different lengths**.



- three short bonds
- three long bonds

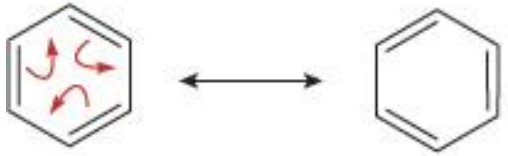
- All C—C bond lengths are equal!



James Dewar (1967) : the Dewar benzene was prepared in 1962 but it is not stable and it converts to benzene

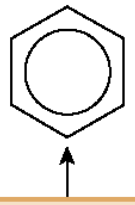
The Structure of Benzene: Resonance

- The true structure of benzene is a resonance hybrid of the two Lewis structures.



The hybrid

Some texts draw benzene as a hexagon with an inner circle:



The circle represents the **six π electrons,** distributed over the six atoms of the ring.

The electrons in the π bonds are **delocalized** around the ring.

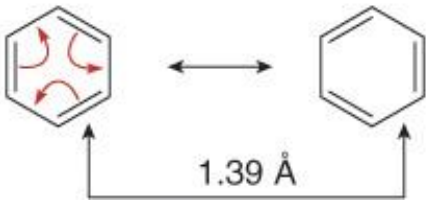
ميش ثابتة على كربون واحد (free rotation of the ring → rich in electrons

CH_3-CH_3

1.53 Å

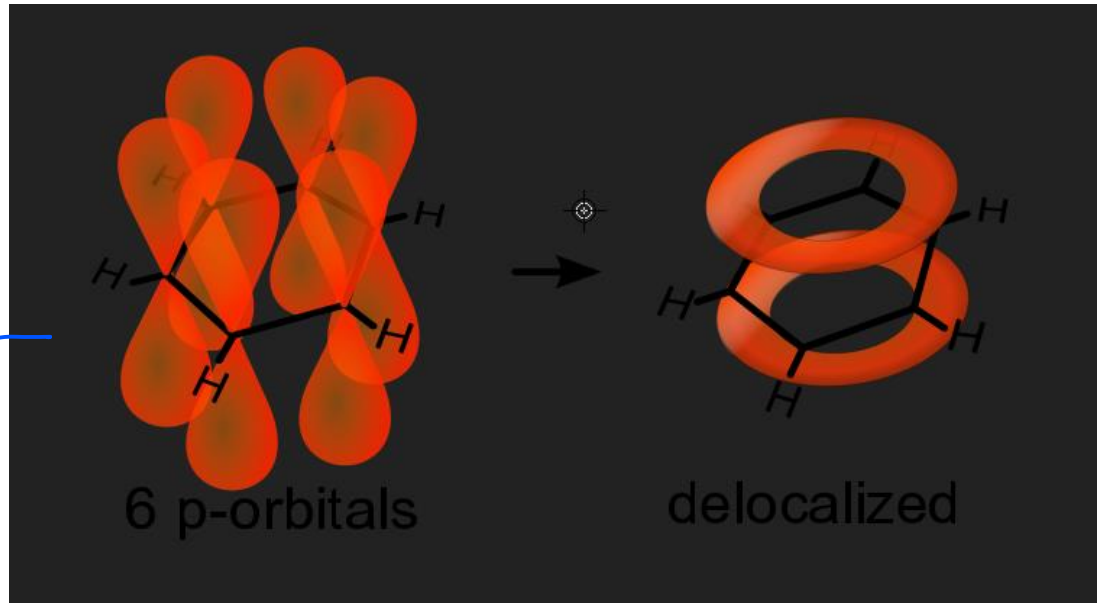
$CH_2=CH_2$

1.34 Å



The C–C bonds in benzene are equal and intermediate in length.

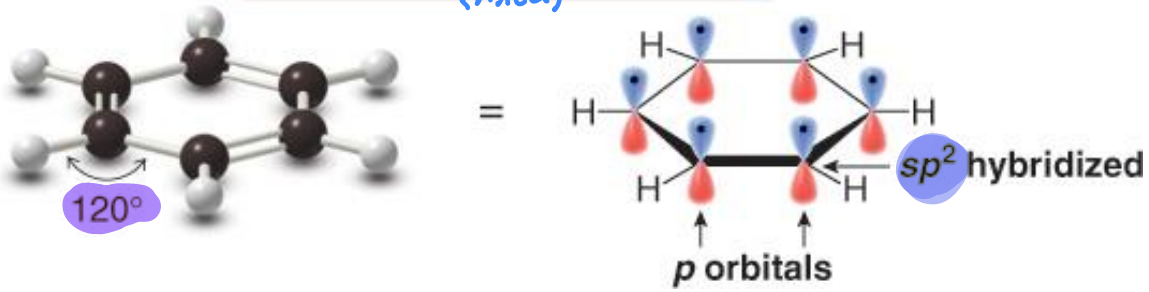
The Structure of Benzene: MO



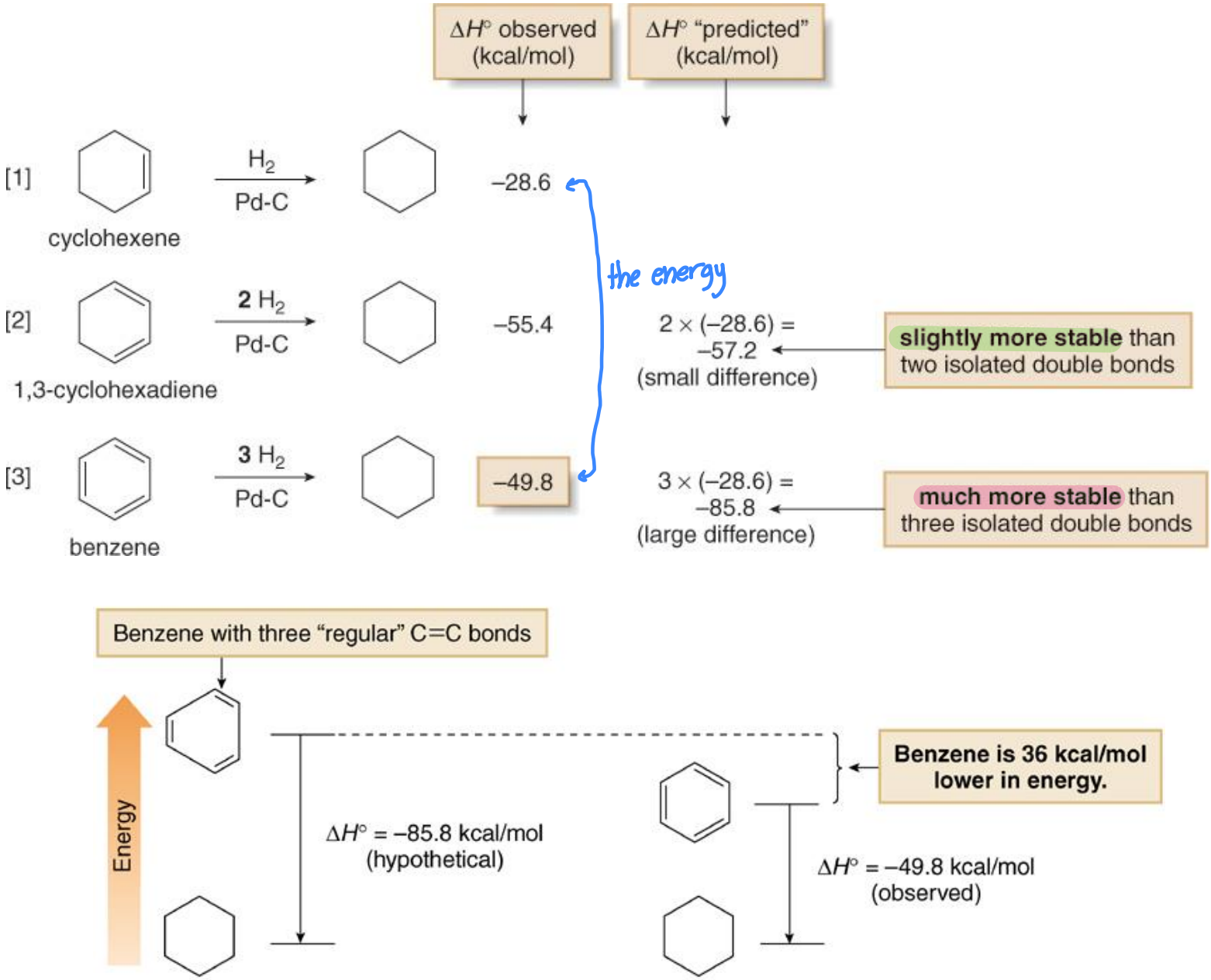
الـ orbitals قريبة ← جنب" من بعض ← result ← الـ electrons تنتقل بسهولة

Benzene—A planar molecule (fixed)

it's doesn't movment ← boat ← chair

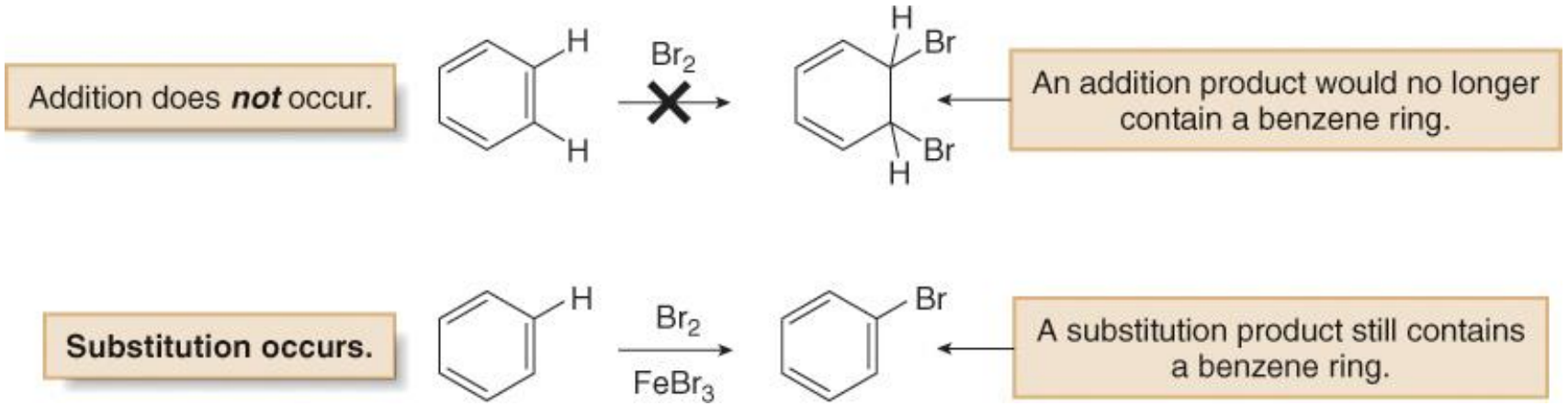


Aromaticity – Resonance Energy



Stability of Benzene - Aromaticity

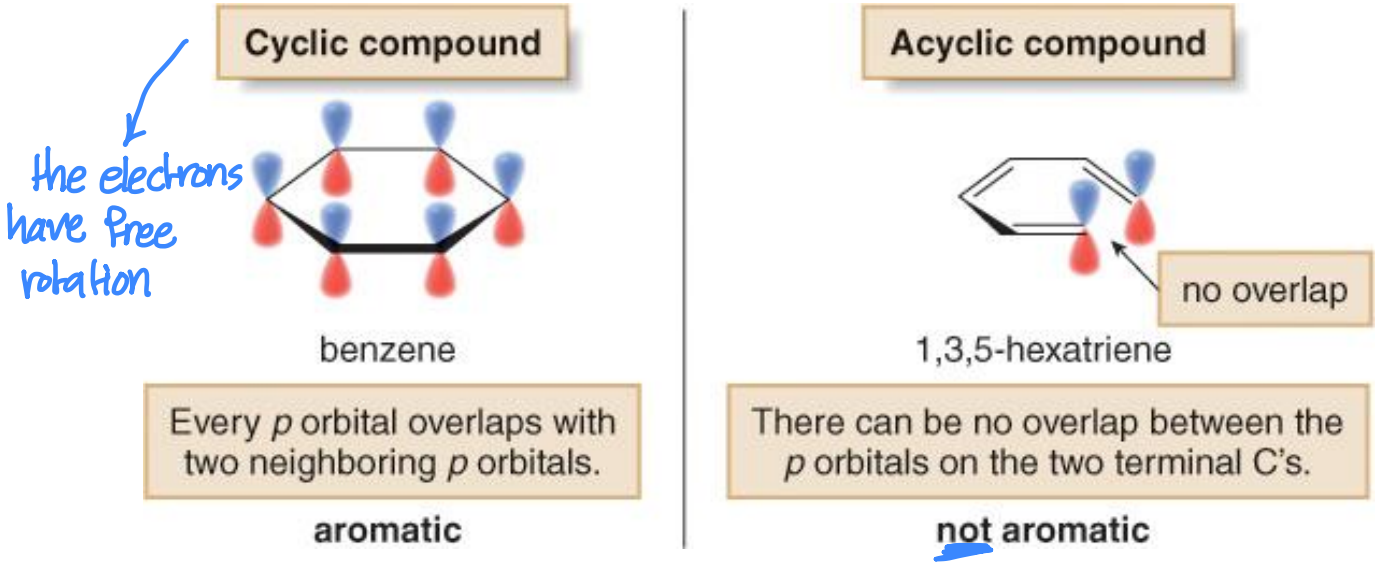
- Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.



The Criteria for Aromaticity

Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.



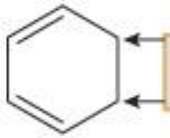
The Criteria for Aromaticity

[2] A molecule must be completely conjugated (all atoms sp^2).

A completely conjugated ring

benzene
a *p* orbital on **every** C
aromatic

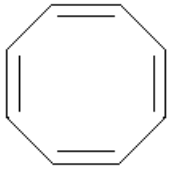
These rings are not completely conjugated.



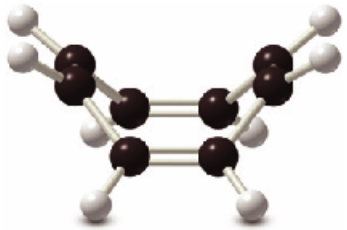
1,3-cyclohexadiene
not aromatic

1,3,5-cycloheptatriene
not aromatic

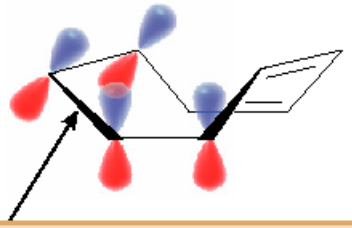
[3] A molecule must be planar.



cyclooctatetraene
not aromatic



a tub-shaped,
eight-membered ring



Adjacent *p* orbitals cannot overlap.
Electrons cannot delocalize.

The Criteria for Aromaticity—Hückel's Rule

[4] A molecule must satisfy Hückel's rule.

- An aromatic compound must contain $4n + 2\ \pi$ electrons (n = 0, 1, 2, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n\ \pi$ electrons are especially unstable, and are said to be *antiaromatic.*

Benzene
An aromatic compound

$4n + 2 = 4(1) + 2 =$
$6\ \pi$ electrons
aromatic

Cyclobutadiene
An antiaromatic compound

$4n = 4(1) =$
$4\ \pi$ electrons
antiaromatic

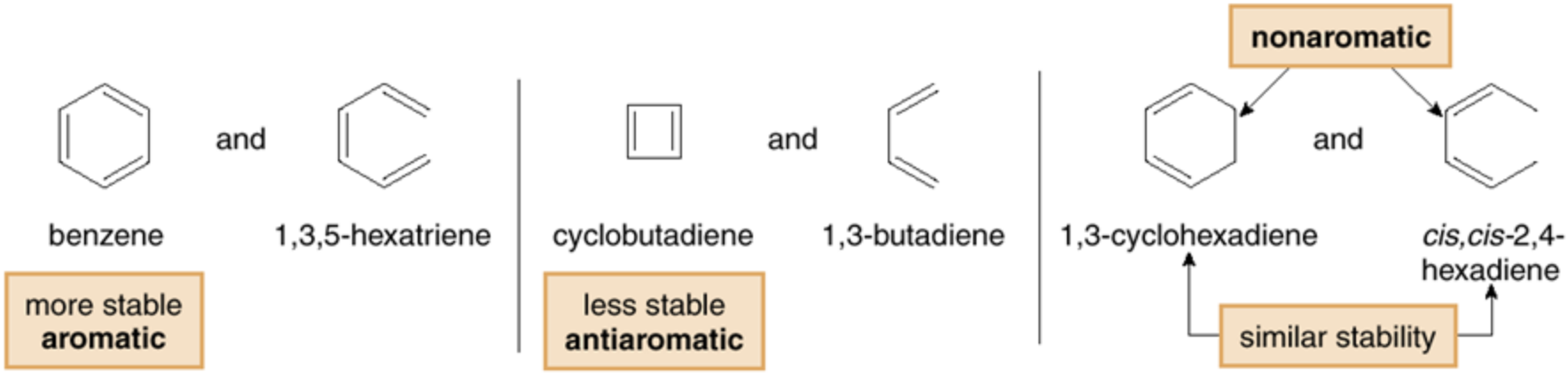
$4n + 2 = 4$
$4n = 2$
$n = \frac{1}{2}$

Table 17.2 The Number of π Electrons That Satisfy Hückel's Rule

n	$4n + 2$
0	2
1	6
2	10
3	14
4, etc.	18

The Criteria for Aromaticity—Hückel's Rule

1. Aromatic—A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.
2. Antiaromatic—A cyclic, planar, completely conjugated compound with $4n$ π electrons.
3. Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.



Examples of Aromatic Rings

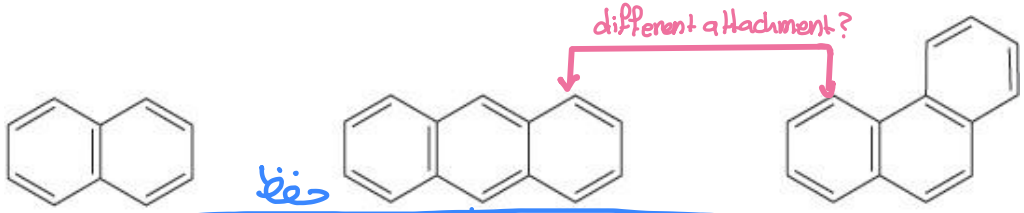
Cyclooctatetraene
8 π electrons

↳ 4n = 6
n = 4/6 (antiaromatic)

planar
antiaromatic

puckered
nonaromatic

different attachment?

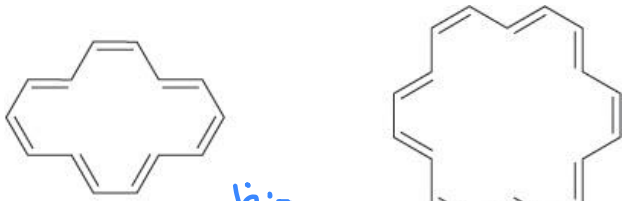


naphthalene
10 π electrons

anthracene
14 π electrons

phenanthrene
14 π electrons

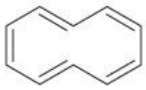
4n = 8
n = 2



[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic

[18]-annulene
$4n + 2 = 4(4) + 2 =$
18 π electrons
aromatic

[10]-Annulene fits Hückel's rule, but it's **not planar**.



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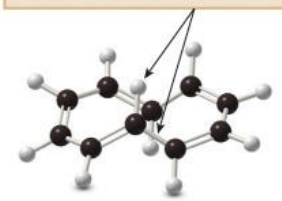


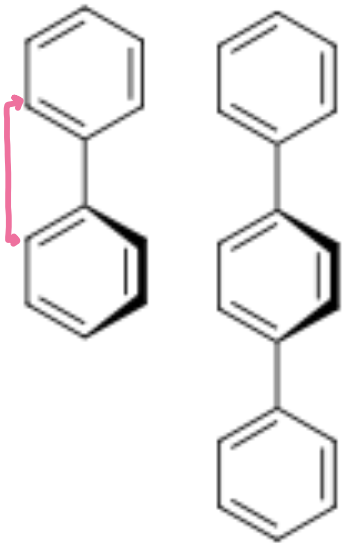
3-D representation

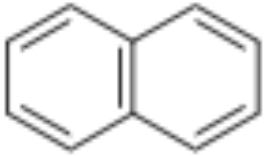
[10]-annulene
10 π electrons
not aromatic

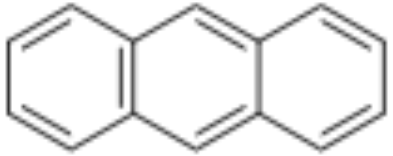
4n+2 = 10
reason → bond

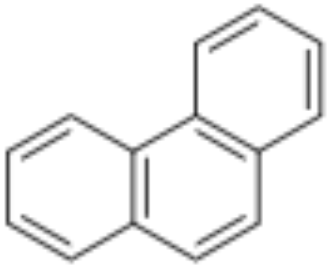
Polycyclic Aromatic Hydrocarbons

attached with one atom
(every benzene is separate system)
→ there is no overlap









biphenyl (2) terphenyl (3) naphthalene anthracene phenanthrene

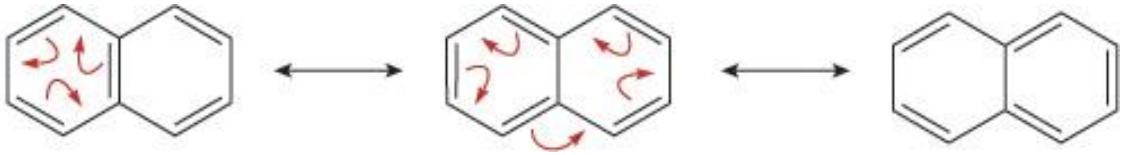
No interactions between rings

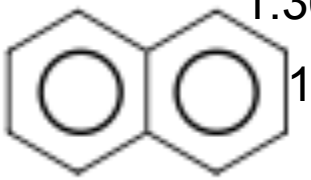
61 kcal/mol

84 kcal/mol

92 kcal/mol

Three resonance structures for naphthalene

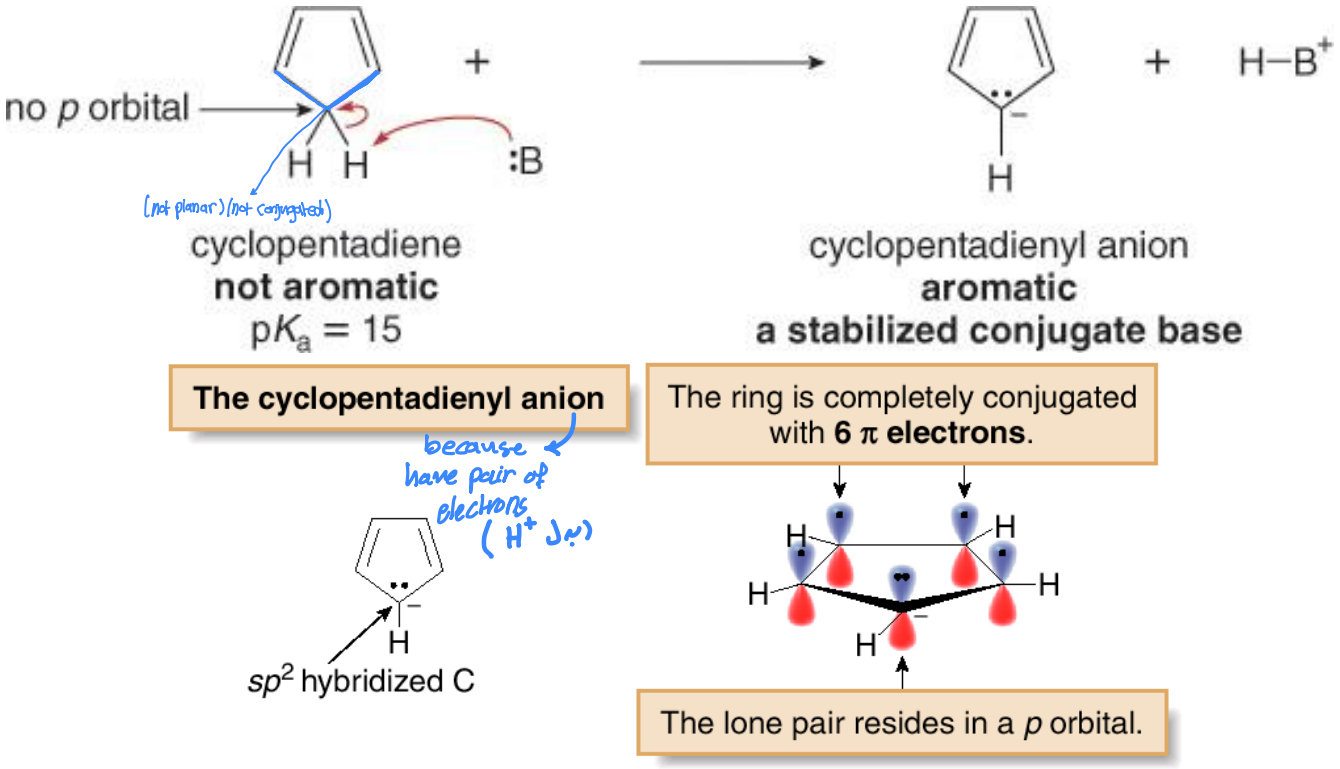




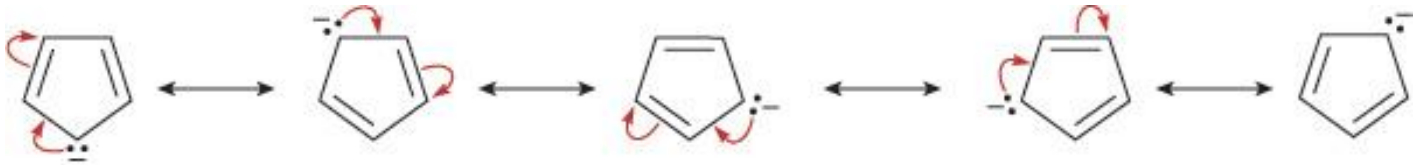
1.36 Å

1.40 Å

Other Aromatic Compounds



- The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.
  - the double bond + pair of electrons



Other Aromatic Compounds

cyclopentadienyl anion
- 6 π electrons
- contains $4n + 2$ π electrons

aromatic

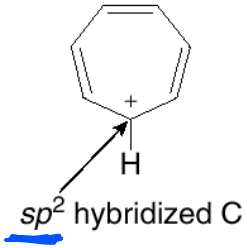
cyclopentadienyl cation (+ve charged)
- 4 π electrons
- contains $4n$ π electrons

antiaromatic

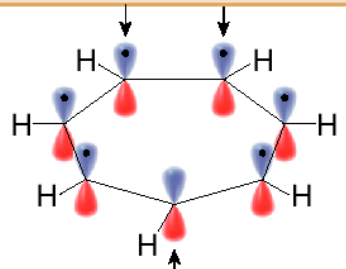
cyclopentadienyl radical
- 5 π electrons
- does not contain either $4n$ or $4n + 2$ π electrons

nonaromatic

The tropylium cation



The ring is completely conjugated with **6 π electrons**.



One *p* orbital is vacant.

- The tropylium cation is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.