Aromatics II

MO Theory

Hückel’s Rule

Spectroscopy

Ref	14: 6 – 9, 11 (both ed^{ns})
Prob	14: 23, 25 – 27, 29, 34 (8th ed)
	14: 24, 26 – 28, 30, 35 (9th ed)
Adv Rdg	15: 1 – 9 (both ed^{ns})

Review

- benzene, C_6H_6 , stable & unreactive
- explained by

1.) resonance (*last lecture*)

2.) MO Theory

good starting point:

“MO’s are formed by combination of similar AO’s; similar in *energy, size, shape*”

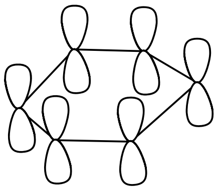
recall: # of MO’s = # of “originating” AO’s

applied to benzene:

p AO’s → π MO’s

6 p AO’s → 6 π MO’s

Illustration:



← originating p AO's

“6 p AO’s combine in various ways to form 6 π MO’s”

(*in-phase, out-of-phase, varying # of nodes ...*)

Nodes in MO’s

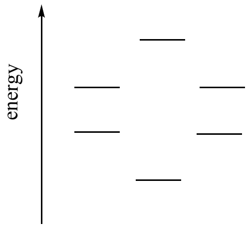
(areas w/ zero e⁻ density)

rule: “as # of nodes increases,

the energy of the MO ↑ ”

(*b/c less binding,*
it is easier for the molecule to fall apart)

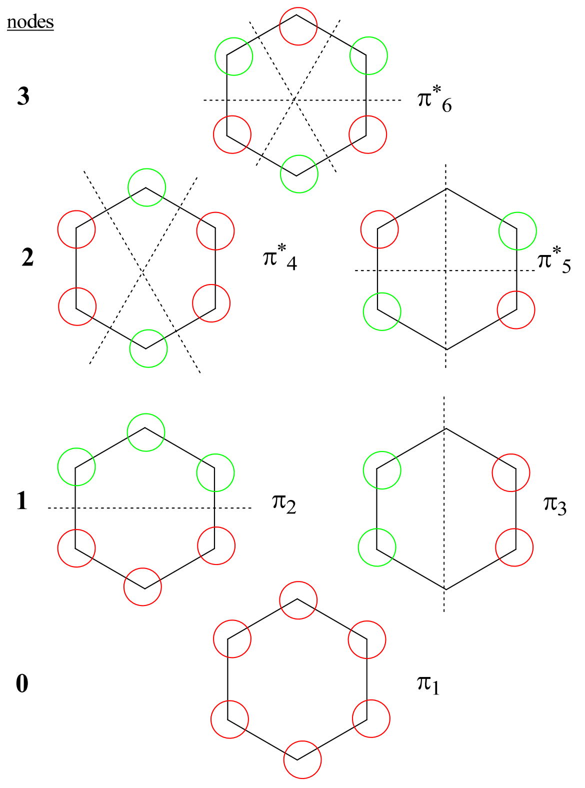
MO Energy Diagram



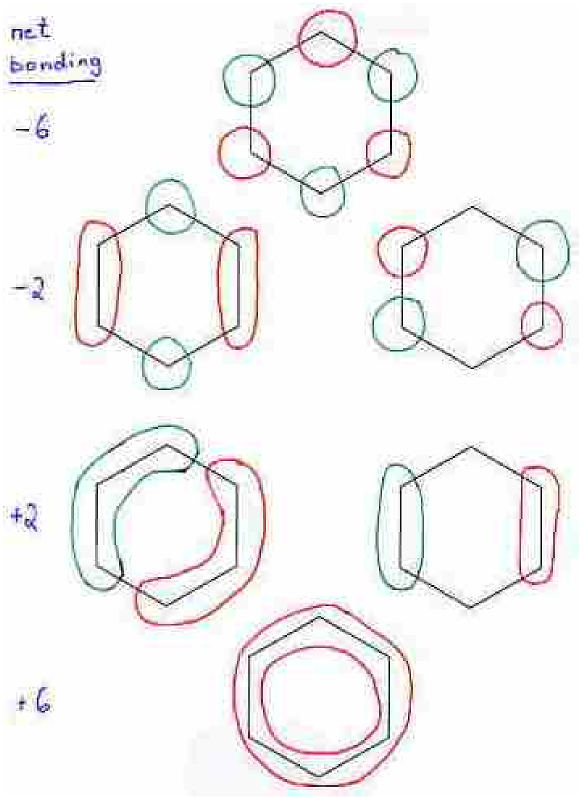
MO	# of nodes
π_6^*	3
π_5^*, π_4^*	2
π_2, π_3	1
π_1	0

comment: the # of MO’s at lvl 2 & 3 doubles up because of symmetry considerations

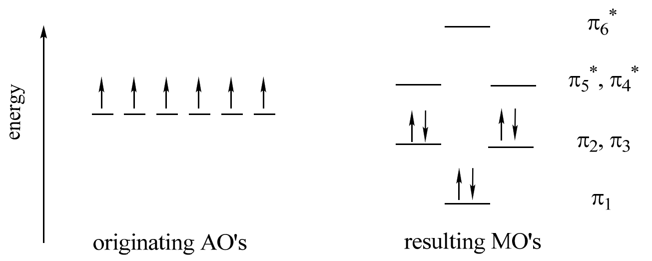
Originating/Contributing p AO's



Resulting MO's



Occupation of MO's by e⁻'s



In the ground state of the benzene molecule:

all e⁻'s are in lower energy orbitals ("bonding"),

none in higher energy orbitals ("anti-bonding)",

when compared with the originating p AO's

∴ reason for **aromatic stabilization**

(*similar MO arguments apply to all other aromatic systems*)

Hückel's Rule

predicts aromaticity of org. cmpds.

(*containg rings w/ high level of unsaturation*)

A. **Aromatic**, if

1.) monocyclic system

(*rule can be extended to polycyclic systems, such as naphthalene)*

2.) ring planar

3.) each atom in ring can be sp^2 hybridised;

p AO's form π sytem ("sideways overlap")

4.) π sytem contains

4 n + 2 e⁻'s

where n = 0, 1, 2, 3, 4, ...

\# of e⁻'s = 2, 6, 10, 14, 18, ...

B. **Anti-Aromatic** (unstable), if

1.)
2.)
3.)
} same as in A.

4.) π sytem contains

4 n e^{-}'s

C. **Non-Aromatic** (behave “normally”)

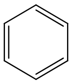
all others;

esp., non-planar systems

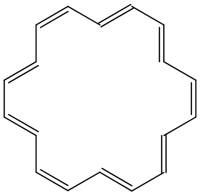
Examples

A.) Aromatic

1.) n = 1, 6 e^{-}'s

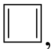


2.) n = 4, 4n + 2 = 16 + 2 = 18 e^{-}'s



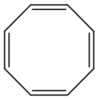
[18] annulene

B.) Anti-aromatic (*very unstable*)

, cyclobutadiene

4 e^{-}'s in π system; n =1; ∴ anti-aromatic

C.) Non-aromatic



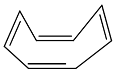
cyclooctatetraene, COT

looks anti-aromatic: 8 e^{-}'s, n = 2 , “4n rule”;

but behaves like normal alkene;

conclusion: system must be non-planar,

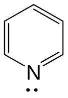
approx. “tub-like”:



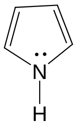
Variety of Aromatic Structures

- can contain heteroatoms (N, O S, ...)
- may be ionic

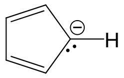
Examples:



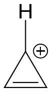
pyridine



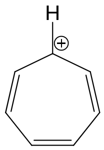
pyrrole



cyclopentadienyl anion

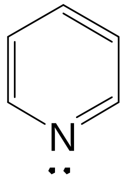


cyclopropenyl
cation,
n = 0



cycloheptatrienyl
cation,
n = 1

Pyridine



N is sp^2 hybridised;

has 3 sp^2 orbitals and 1 "pure" p orbital:

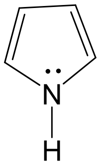
- p orbital involved in aromaticity
- 2 sp^2 orbitals form σ bonds w/ C atoms
- 1 sp^2 orbital contains lone pair of e^-'s

∴ lone pair not used in aromaticity

"remains exposed"

remains quite basic

Pyrrole



N is sp^2 hybridised;

has 3 sp^2 orbitals and 1 "pure" p orbital:

sp^2 orbitals form 3 σ bonds;

p orbital (w/ 2 e^-'s)

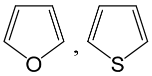
contributes to aromatic system

∴ lone pair "used up" in aromaticity

"not exposed"

pyrrole much weaker base than pyridine

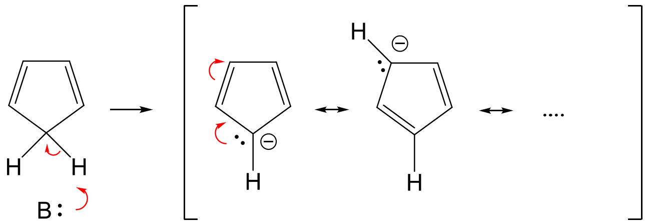
similar arguments for furan, thiophen (HMWK)



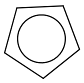
Anions

Ex. cyclopentadienyl anion, $C_5^-H_5^-$

(forms easily from cyclopentadiene with bases such as OH^-)



or



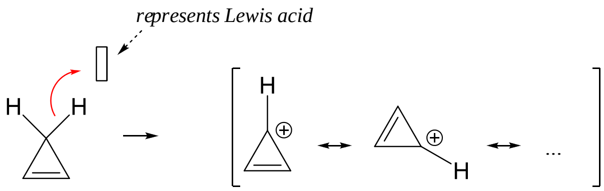
circle represents 6 e^-'s

planar, monocyclic system,
all C's sp^2 hybridised,
conjugated π system
6 e^-'s (Hückel #)

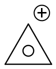
aromatic

Cations

Ex.1.: cylopropenyl cation, $C_3H_3^+$



or



circle represents 2 e^-'s

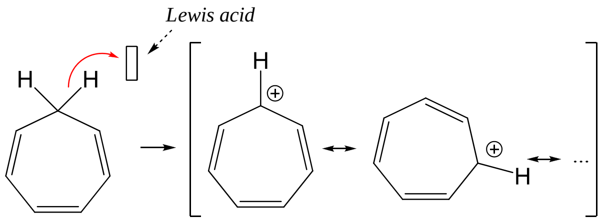
(suitable Lewis acid, trityl cation: Ph_3C^+ BF_4^-)

aromatic requirements satisfied:

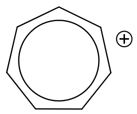
planar, monocyclic system,
all C's sp^2 hybridised,
conjugated π system
2 e^-'s (Hückel #)

aromatic

Ex.2.: cyloheptatrienyl cation, $C_7H_7^+$



or



circle represents 6 e⁻'s

aromatic requirements satisfied, as before !

Solomons Fig's: Pyridine & Pyrrole

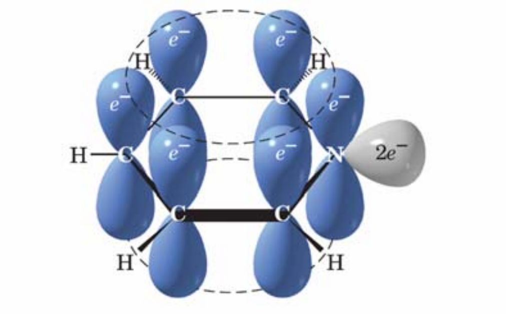


FIGURE 14.20 The stylized *p* orbital structure of pyridine.

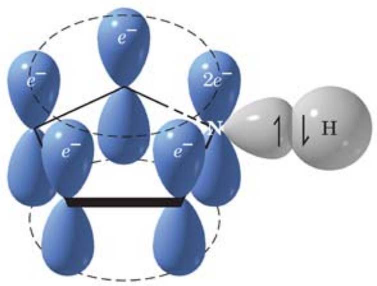
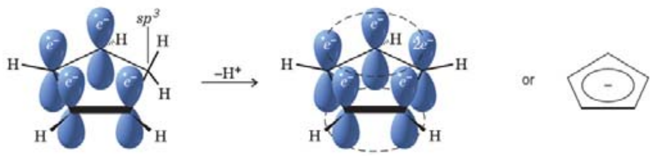


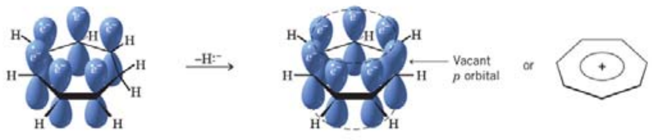
FIGURE 14.21 The stylized *p* orbital structure of pyrrole. (Compare with the orbital structure of the cyclopentadienyl anion in Fig. 14.10.)

Solomons Fig's: Cyclopentadienyl Anion & Cycloheptatrienyl Cation



Cyclopentadiene **Cyclopentadienyl anion**

FIGURE 14.10 The stylized *p* orbitals of cyclopentadiene and of the cyclopentadienyl anion.

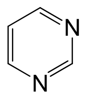


Cycloheptatriene **Cycloheptatrienyl cation**

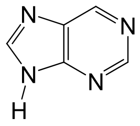
FIGURE 14.12 The stylized *p* orbitals of cycloheptatriene and of the cycloheptatrienyl (tropylium) cation.

Complex Heterocyclic Aromatics

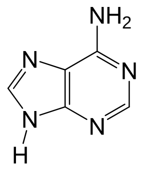
important in Biochemistry



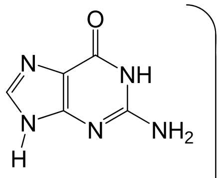
pyrimidine



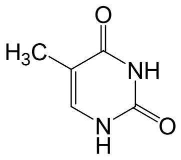
purine



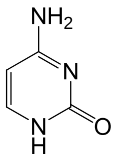
adenine



guanine



thymine



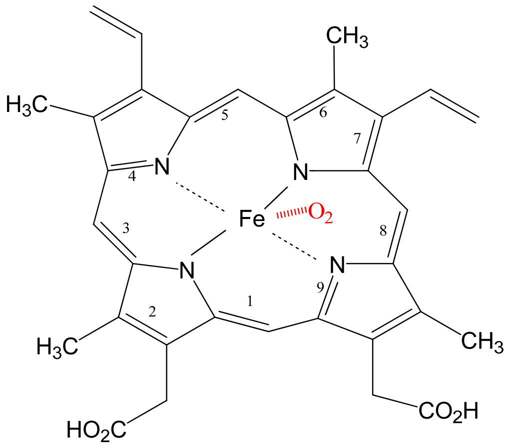
cytosine

DNA Bases

Another Aromatic System

of biological importance

Heme, part of hemoglobin,
oxygen carrier in red blood cells



numbers indicate double bonds that are part of aromatic system

n = 4, 4n + 2 =18; 18 e⁻'s = aromatic

Spectroscopy

1.) NMR

a.) δ (*aromatic*) ~ 7.0 ppm

on a 100 MHz instrument

resonates at $\nu_X \sim 100\,000\,700$ Hz

abs. shift: $\Delta\nu = \sim 700$ Hz

$$\text{chem. shift: } \delta = \frac{\Delta\nu}{\nu} \times 10^6$$

$$= \frac{700}{100 \times 10^6} \times 10^6 = 7.0 \text{ ppm}$$

HMWK:

do similar calc^{ns} for 60 and 500 MHz instruments.

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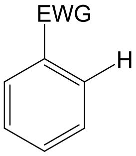
b.) J values

ortho = 9 Hz

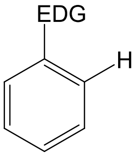
meta = 2 Hz

para ~ 0.5 Hz (negligible)

c.) effect of substituents



deshielded, high δ
"downfield"

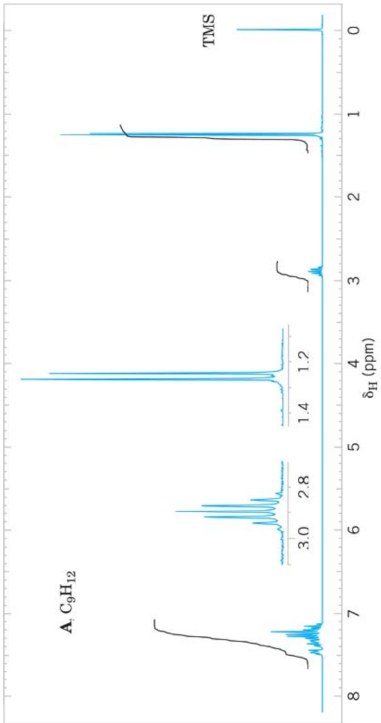


shielded, low δ
"upfield"

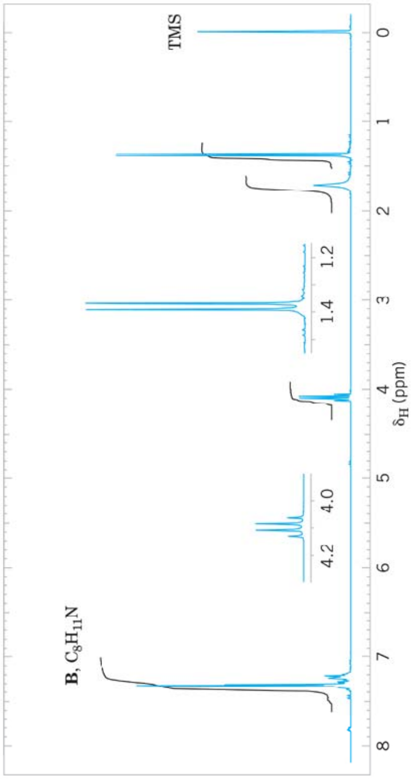
2.) IR

"aromatic bond"	type	wavenumber
= C – H	stretch	~ 3030 cm^{-1}
C = C	stretch	1600 – 1650 cm^{-1}
= C – H	bend	900 – 700 cm^{-1}

Solomons Fig. 14.27 Aromatic NMR Spectra #1



Solomons Fig. 14.27 Aromatic NMR Spectra #2



Solomons Fig. 14.27 Aromatic NMR Spectra #3